# The Stereochemistry of the Base Hydrolysis of *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{2+}$ Ions

**D. A. Buckingham, I. I. Olsen, and A. M. Sargeson**

*Contribution from the Research School of Chemistry, Australian National University, Canberra, Australia.* *Received April 25, 1967*

**Abstract:** The base hydrolysis of *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl]^{2+}$, *trans*-$[Co(NH_3)_4(^{15}NH_3)Br]^{2+}$, and *trans*-$[Co(NH_3)_4(^{15}NH_3)NO_3]^{2+}$ gives the same product ratio, 50% *cis*- and 50% *trans*-$[Co(NH_3)_4(^{15}NH_3)OH^{2}]^+$ at 25°. The ratio is independent of $[OH^-]$ and no intramolecular rearrangement of *trans*-$[Co(NH_3)_4(^{15}NH_3)OH^{2+}$ occurs in the time taken to effect hydrolysis. The common result fits the conclusion that a common intermediate is involved, and it is discussed in relation to the isotope fractionation and anion competition effects which have been observed for the same reactions.

Evidence has appeared recently to support the contention that the base hydrolysis of $[Co(NH_3)_5X]^{2+}$ ions (X = Cl, Br, I, $NO_3$) does take place by an $S_N1CB$ mechanism (eq 1–3) involving an intermediate of reduced coordination number[1,2] (2).

$$[Co(NH_3)_5X]^{2+} + OH^- \rightleftharpoons [Co(NH_3)_4NH_2X]^+ + H_2O \quad (1)$$

$$[Co(NH_3)_4NH_2X]^+ \longrightarrow [Co(NH_3)_4NH_2]^{2+} + X^- \quad (2)$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \longrightarrow [Co(NH_3)_5OH]^{2+} \quad (3)$$

$$[Co(NH_3)_4NH_2]^{2+} + Y^- + H_2O \longrightarrow [Co(NH_3)_5Y]^{2+} + OH^- \quad (4)$$

The results used to support this proposal have relied on competition between isotopic $H_2O$ (eq 3) or different species (eq 3 and 4) in aqueous solution for the supposed intermediate $[Co(NH_3)_4NH_2]^{2+}$. Probably the most conclusive of these experiments involved the competition between $^{18}OH_2$, $^{16}OH_2$, $^{18}OH^-$, and $^{16}OH^-$ for the coordination site, and it was shown[1] by using the large isotopic equilibrium constant for the equilibrium

$$^{16}OH_2 + {}^{18}OH^- \rightleftharpoons {}^{18}OH_2 + {}^{16}OH^-$$

that the complexes did not react preferentially with $^{16}OH^-$ as required by a bimolecular nucleophilic displacement mechanism. The fact that the isotopic fractionation factors were constant for the hydrolysis as required for a common intermediate also favored this interpretation.

Following this study it was shown[2] that the base hydrolysis of the above ions in the presence of anions Y ($=N_3^-$, $OAc^-$, $NO_2^-$, $NCS^-$) gave some $[Co(NH_3)_5Y]^{2+}$ as well as $[Co(NH_3)_5OH]^{2+}$. Moreover the amount was essentially constant for each anion with the series of complexes, as required for the production of a common intermediate. It should also be mentioned that neutral species such as $NH_3$ (as well as anions) compete for the supposed intermediate.[3]

The isotopic and chemical competition experiments are consistent with the conclusion that the base hydrolyses do involve intermediates having properties independent of those of the leaving group. The extent of rearrangement accompanying base hydrolysis has been used in other series of complexes[4] as evidence that for them as well a similar mechanism operates. It seemed desirable therefore to extend the isomerization studies also to the pentaammine series. The starting point of our work[5] is the demonstration by Halpern and associates[6] that the *trans*-$NH_3$ group in $Co(NH_3)_5SO_3^+$ is extremely labile. This permits the substitution of $^{15}NH_3$ stereospecifically *trans* and leads to the preparation of $[Co(NH_3)_4(^{15}NH_3)X]^{2+}$ ions and thus to the possibility of an examination of the stereochemistry of base hydrolysis in cobalt(III) pentaammine complexes.

## Experimental Section

*trans*-$[Co(NH_3)_4(OH)(SO_3)]$. $[Co(NH_3)_5SO_3]_2SO_3$ was prepared as described previously.[7] It was dissolved in excess concentrated HCl at ~20°, and the complex chloride was precipitated immediately with ethanol. This product, recrystallized from water with HCl and LiCl at ~20°, gave principally *trans*-$[Co(NH_3)_4(H_2O)SO_3]Cl$. The aquo sulphito complex was reconverted to the pentaammine salt by crystallizing it from aqueous ammonia solution with ethanol. $[Co(NH_3)_5SO_3]Cl$ was then treated with a 3% aqueous solution of LiOH for 5 min, and *trans*-$[Co(NH_3)_4(OH)SO_3]$ crystallized out slowly as fine plates on the dropwise addition of ethanol.

*trans*-$[Co(NH_3)_4(^{15}NH_3)Cl](ClO_4)_2$. Freshly prepared *trans*-$[Co(NH_3)_4(OH)SO_3]$ (5 g) was added to a solution of $^{15}NH_4Cl$ (4 g) (96% $^{15}N$) and LiOH (2.4 g) in water (50 ml). The complex dissolved and then *trans*-$[Co(NH_3)_4(^{15}NH_3)SO_3]Cl$ commenced to crystallize. After 10 min all the complex was crystallized by adding ethanol. The isolated compound was washed with ethanol and ether, dried in air, and treated with a solution of concentrated HCl saturated with LiCl. The solution was gently warmed at first and then heated on the steam bath until all the complex was converted to *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl]Cl_2$ (3.3 g). The *trans*-chloride was collected and treated with an equivalent amount of $AgClO_4$ in dilute $HClO_4$ ($10^{-3}$ *M*). The AgCl precipitate was filtered off and the complex perchlorate precipitated by adding excess concentrated $HClO_4$. *Anal.* Calcd for $[Co(NH_3)_4(^{15}NH_3)Cl](ClO_4)_2$: N, 18.72; H, 3.98. Found: N, 18.98; H, 4.24 ($\epsilon_{532}$ 50.7 in $10^{-3}$ *M* $HClO_4$).

*trans*-$[Co(NH_3)_4(^{15}NH_3)Br](ClO_4)_2$. *trans*-$[Co(NH_3)_4(^{15}NH_3)H_2O](ClO_4)_3$ was suspended in a KBr–HBr solution and heated on a steam bath until all the aquo complex was changed to bromo bromide. This was collected and converted to the perchlorate in the same way as for the chloro complex ($\epsilon_{550}$ 54.5 in $10^{-3}$ *M* $HClO_4$).

*trans*-$[Co(NH_3)_4(^{15}NH_3)NO_3](ClO_4)_2$. *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl](ClO_4)_2$ (1.5 g) was dissolved in dilute $HClO_4$ (50 ml, $10^{-3}$ *M*) and poured into a solution (50 ml) of $Hg(NO_3)_2$ (1.0 *M*) in concentrated $HNO_3$. The nitrato complex crystallized as the nitrate which was collected and washed with dilute $HNO_3$, ethanol, and ether. The nitrate was then treated with cold concentrated $HClO_4$ to convert it to the perchlorate and finally recrystallized from water by adding concentrated $HClO_4$. *Anal.* Calcd for $[Co(NH_3)_4(^{15}NH_3)NO_3]$-

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(1) M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).

(2) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **88**, 5443 (1966).

(3) I. I. Olsen, unpublished work.

(4) R. B. Jordan and A. M. Sargeson, *Inorg. Chem.*, **4**, 1849 (1965).

(5) Professor Henry Taube has had an interest in this problem as well and has made a number of suggestions which significantly improve the analysis of the results and for which we are grateful.

(6) J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Am. Chem. Soc.*, **88**, 2877 (1966).

(7) A. Werner and H. Grüger, *Z. Anorg. Chem.*, **16**, 406 (1898).

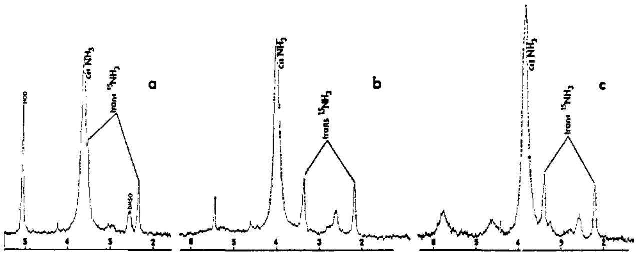

Figure 1. The 60-Mc pmr spectra of *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl](ClO_4)_2$ (a), *trans*-$[Co(NH_3)_4(^{15}NH_3)NO_3](ClO_4)_2$ (b), and *trans*-$[Co(NH_3)_4(^{15}NH_3)OH_2](ClO_4)_3$ (c) in $d_6$-dimethyl sulfoxide (reference sodium trimethylsilylpropanesulfonate 0.0 ppm).

$(ClO_4)_2$: N, 20.95; H, 3.72. Found: N, 21.00; H, 3.74 ($\epsilon_{500}$ 56.4 in $10^{-3}$ *M* $HClO_4$). The chloro, bromo, and nitrato complexes were found to be free of aquopentaamminecobalt(III) ion by means of the cation-exchange method. Bio-Rad Analytical Resin Dowex ($H^+$) 50W-X2, 200–400 mesh, was used. Some $[Co(NH_3)_5OH_2](NO_3)_3$ was found in the initial nitrato nitrate, but this was removed during the recrystallizations.

*trans*-$[Co(NH_3)_4(^{15}NH_3)(OH_2)](ClO_4)_3$. *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl](ClO_4)_2$ (0.4 g) was dissolved in 25 ml of 0.3 *M* $Hg(ClO_4)_2$ in 0.05 *M* $HClO_4$. After 5 min the aquo complex which formed was precipitated by adding concentrated $HClO_4$ and cooling ($\epsilon_{490}$ 47.3 in $H_2O$).

**Base Hydrolysis.** *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl](ClO_4)_2$, *trans*-$[Co(NH_3)_4(^{15}NH_3)Br](ClO_4)_2$, and *trans*-$[Co(NH_3)_4(^{15}NH_3)NO_3](ClO_4)_2$ were hydrolyzed at 25° by dissolving the complex (0.3 g) in water (10 ml) and adding NaOH (1.0 ml, 2 *N*). After 5 min the solutions were acidified; the aquo complex crystallized on adding concentrated $HClO_4$ and was collected immediately. In two experiments with the chloro complex 10 ml of 2.0 *N* NaOH and 100 ml of 0.02 *N* NaOH were added to the complex solutions, 0.3 g/10 ml and 0.3 g/100 ml, respectively.

**Base Hydrolysis in the Presence of Azide Ions.** *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl](ClO_4)_2$ (1 g) was dissolved in 15 ml of dilute $HClO_4$ ($10^{-3}$ *M*) and added to a solution of NaOH (50 ml, 0.1 *N*) saturated with $NaN_3$ at 25°. After 5 min the solution was cooled in an ice bath, and excess LiCl was added to precipitate the formed azido complex (yield 0.2 g). The chloride was converted to the perchlorate as described for the chloro complex. The cold filtrate was treated with cold concentrated HBr; the aquo bromide salt crystallized and was then converted to the perchlorate in the usual way.

The **pmr spectra** of the complexes were obtained using a Perkin-Elmer R10 60-Mc spectrometer. The samples were dissolved in $d_6$-dimethyl sulfoxide acidified with a trace of $D_2SO_4$ (98%) (concentration ~200 mg/ml) or in dilute $D_2SO_4$ solutions (concentration ~100 mg/ml). The reference used in $d_6$-DMSO was sodium trimethylsilylpropanesulfonate.

## Results

The pmr spectra of *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl](ClO_4)_2$, *trans*-$[Co(NH_3)_4(^{15}NH_3)NO_3](ClO_4)_2$, and *trans*-$[Co(NH_3)_4(^{15}NH_3)H_2O](ClO_4)_3$ measured in $d_6$-dimethyl sulfoxide are given in Figure 1. Figure 2 shows the pmr spectra of the same complexes and also of *trans*-$[Co(NH_3)_4(^{15}NH_3)Br](ClO_4)_2$ measured in dilute $D_2SO_4$ solution ($4 \times 10^{-3}$ *M*). In all instances the $^{14}NH_3$ groups give rise to a single broad absorption which is much sharper in the DMSO solutions than in the dilute $D_2SO_4$. The $^{15}NH_3$ group, however, produces a sharp doublet with a constant coupling constant of 72 cps for the *trans* species in both solvents. The doublet arises from the coupling of the three equivalent proton spins with the single spin on the $^{15}N$ nucleus. Integration of the spectra showed a ratio of 4:1 for the broad singlet: doublet. These absorptions were equated to the twelve *cis* $^{14}N$ protons and three $^{15}N$ protons *trans* for all four molecular ions.

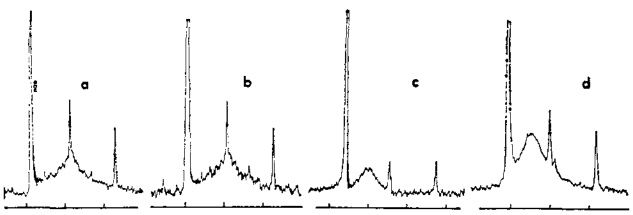

Figure 2. The 60-Mc pmr spectra of *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{n+}$ complexes in dilute $D_2SO_4$ ($4.0 \times 10^{-3}$ *N*): (a) chloro, (b) bromo, (c) nitrato, (d) aquo (arbitrary scale in ppm – HOD signal ~4.9 ppm).

In the parent chloro complex the *trans*-$^{15}NH_3$ doublet signals occur at 3.55 and 2.35 ppm in $d_6$-DMSO, Figure 1a, which are equidistant from the remnant of the *trans*-$^{14}NH_3$ signal at 2.95 ppm. One-half of the doublet almost coincides with the *cis*-$^{14}NH_3$ absorption at 3.65 ppm. It is also apparent that a trace of the *cis*-$^{15}NH_3$ doublet is present at 4.25 and 3.05 ppm ($J_{^{15}NH}$ = 72 cps). These assignments can be made with confidence since it has been shown elsewhere[8] that the *trans*-$^{14}NH_3$ and *cis*-$^{14}NH_3$ signals are separated by ~43 cps and that the signal at high field (*trans*) collapses during deuteration of the complex much faster than that due to the twelve equivalent protons at lower field. It is clear from the spectra that the initial formation of the chloro complex from *trans*-$[Co(NH_3)_4(^{15}NH_3)SO_3]Cl$ takes place substantially with retention of the original isotopic distribution. The *trans*-aquopentaammine complex was prepared by the $Hg^{2+}$-induced aquation of the corresponding chloro complex, a reaction which is known to occur without rearrangement of the ammonia groups.[8] It is also apparent from the spectra of the nitrato and aquo complexes (Figure 1b,c) that they have the *trans* configuration and within the instrumental error contain the same amount of the *cis* isomer as the parent chloro complex.

In the *trans*-aquo spectrum (Figure 1c), two broad absorptions occur at low fields, ~4.7 and 5.8 ppm. These signals arise from $H_2O$ in the solvent and $H_2O$ on the complex, respectively, and the broadening arises from proton exchange between the two species catalyzed by adding $D^+$. In "neutral" $d_6$-DMSO these signals were sharp, and that due to $H_2O$ in the solvent occurred at higher field ~3.7 ppm.

Similar observations apply to the spectra of the complex ions in the dilute $D_2SO_4$ solutions (Figure 2). The $^{15}NH_3$ doublet is sharp with $J_{^{15}NH}$ = 72 cps, but the $^{14}NH_3$ protons produce a very broad absorption band which obscures the traces of *trans*-$^{14}NH_3$ present. However, the traces of *cis*-$^{15}NH_3$ can still be observed also with a coupling constant of 72 cps. It is also apparent from Figure 2b that the bromopentaammine complex has the *trans* configuration.

The pmr spectra in $d_6$-DMSO of the aquo complexes derived from the base hydrolysis of the chloro, bromo, and nitrato complexes at 25° (Figure 3a–c) indicate that substantial rearrangement has occurred. Two sets of doublets appear for the *cis*- and *trans*-$^{15}NH_3$ groups of equal intensity within the experimental error. The *cis* doublet coincides with the trace of impurity doublet (3.25 and 4.45 ppm) found in the spectrum of *trans*-

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[8] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Australian J. Chem.*, 20, 597 (1967).

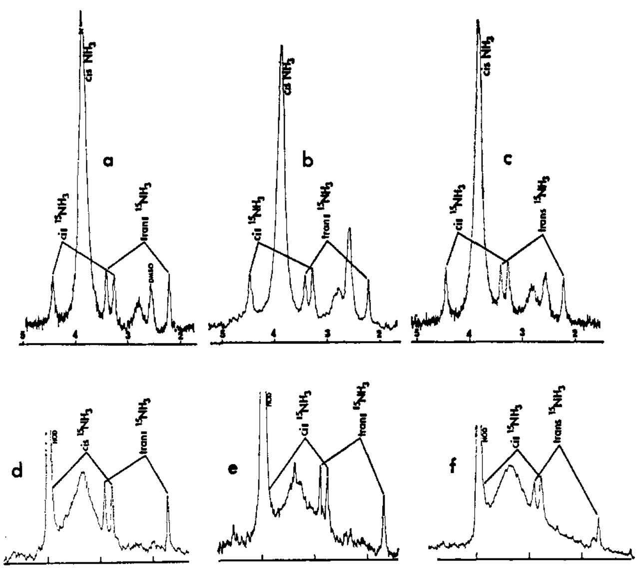

Figure 3. The 60-Mc pmr spectra of $[Co(NH_3)_4(^{15}NH_3)OH_2](ClO_4)_3$ obtained from the base hydrolysis of the *trans*-chloro (a, d), bromo (b, e), and nitrato (c, f) complexes (a–c: DMSO solutions; d–f: $D_2SO_4$, $4 \times 10^{-3}$ *N*).

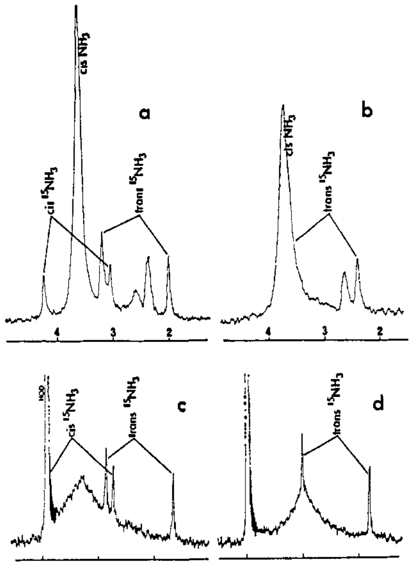

Figure 4. The 60-Mc pmr spectra of $[Co(NH_3)_4(^{15}NH_3)OH_2](ClO_4)_3$ (a, c) and $[Co(NH_3)_4(^{15}NH_3)N_3](ClO_4)_2$ (b, d) obtained from the base hydrolysis of the *trans*-chloro complex in the presence of $NaN_3$.

$[Co(NH_3)_4(^{15}NH_3)OH_2](ClO_4)_3$ (Figure 1c.) Also the absorption at 2.8 ppm due to some *trans*-$^{14}NH_3$ has increased substantially in the products. Both the $^{15}NH_3$ doublets and the *cis*- and *trans*-$^{14}NH_3$ absorptions were integrated for a series of spectra from several experiments and showed that the amounts of *cis*- and *trans*-$[Co(NH_3)_4(^{15}NH_3)OH_2]^{3+}$ were equal (±5%).

Similar conclusions arise from the analysis of the spectra of the aquo products in $D_2SO_4$ ($4 \times 10^{-3}$ *N*) (Figure 3d–f), although one branch of the *cis* doublet is obscured by the HOD signal. An attempt to separate these signals by moving the HOD absorption downfield by addition of more $D_2SO_4$ led to precipitation of the complex in the nmr tube.

Although the $^{18}O$ exchange in $[Co(NH_3)_5OH]^{2+}$ is known to be slow in dilute alkali,[9] the possibility of an intramolecular rearrangement in basic solution has to be considered. To check this possibility *trans*-$[Co(NH_3)_4(^{15}NH_3)OH_2](ClO_4)_3$ was dissolved in 0.2 *N* NaOH for the time required for base hydrolysis and then recovered. The pmr spectra before and after this treatment were identical, and, since we know the rate of water exchange with $[Co(NH_3)_5OH_2]^{3+}$ is also slow in acid solution,[9] the stereochemical rearrangements observed here must have taken place during the base hydrolysis reactions. Also the base hydrolysis was carried out at three $[OH^-]$ concentrations, 1.0, 0.2, and 0.01 *M*, without any change in the concentration of the *cis* and *trans* products.

The competition of species other than water for the intermediate was also examined. *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl](ClO_4)_2$ was hydrolyzed in the presence of ~4 *N* $NaN_3$ in 0.1 *N* NaOH, and both the azido and aquo products were recovered. The pmr spectra of these species are given in Figure 4 measured in both $d_6$-DMSO and dilute $D_2SO_4$. The azido complex clearly has the *trans* configuration. One-half of the *trans*-$^{15}NH_3$ doublet is obscured by the *cis*-$^{14}NH_3$ signal in the $d_6$-DMSO solution but both signals appear for the $D_2SO_4$ solutions. It is also clear that this product contains very little *cis* isomer. The aquo product contains more *trans* than *cis* isomer in contrast to the earlier results, but the experimental conditions have also been altered markedly.

## Discussion

The most significant result of this investigation is that the amount of *cis*- and *trans*-aquo products arising from the base hydrolysis is the same for the chloro, bromo, and nitrato complexes. This is required if a common intermediate is involved. The result is consistent with the common $O^{18}/O^{16}$ fractionation factors and with the common competition ratios observed for anionic species and water molecules reacting with the supposed intermediate.

While the interpretation of the isotope fractionation experiments seems unequivocal, it has been suggested that the competition experiments might also be interpreted by an SN2CB mechanism where the entering anion is insensitive to the leaving group.[10] The present results would also require the stereochemistry of the course of the SN2CB reaction to be independent of the leaving group. To rationalize the three sets of data in terms of an SN2CB mechanism requires a set of multiple coincidences which seems to us improbable. The more obvious and satisfying explanation for the common results from the different sources is that the experiments embody a common intermediate.

There has been considerable speculation about the stereochemistry of the supposed intermediate in the base hydrolysis either as a square pyramid or a trigonal bipyramid (Figure 5). The latter has been favored[11] because of its ability to be stabilized through a $p\pi$–$d\pi$ bond formed between the lone electron pair on the amido group and the vacated d orbital on the metal ion in the trigonal plane. For the square pyramid (Figure 4), the opportunity for the $\pi$ stabilization does not arise since the metal ion orbitals with the correct symmetry to

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[9] H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958).

[10] Referee for ref 2.

[11] R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

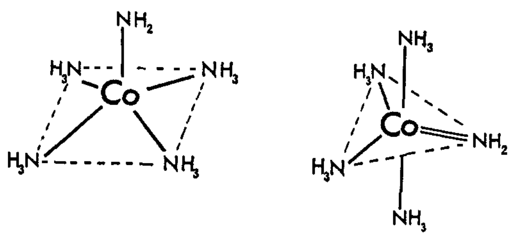
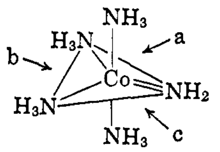


Figure 5. Possible five-coordinated intermediates in the base hydrolysis of $[Co(NH_3)_5X]^{2+}$ complex ions.

overlap with the p orbital on the amido group are filled. It would be expected that the square pyramid would lead largely to retention of the original isotopic distribution by attack of the incoming group at the vacated coordination site, although some attack of the nucleophilic reagent might occur at the "collar" of the $d_{z^2}$ orbital above the square plane leading to some rearrangement.

In the trigonal bipyramid, substantial rearrangement would be expected from attack at the three sides of the trigonal plane. The attack need not be statistically disposed since the bipyramid is not symmetrical unless the amido group rearranges rapidly compared with the coordination of $H_2O$. Such a rearrangement of the amido group must be governed by the rate of proton release from the other ammonia groups coordinated if the amido group is stabilized only in the trigonal plane. It is difficult to assess this rate for the intermediate but the $[Co(NH_3)_5X]^{2+}$ complexes of the same charge have rates of proton exchange[12] in the vicinity of $10^7$ $M^{-1}$ $sec^{-1}$. If this value is assumed to be not greatly different from that for the intermediate and the rate of reaction of the intermediate is largely diffusion controlled, $\sim 10^{10}$ $sec^{-1}$, it would seem that the amido group would not have time to rearrange before the intermediate reacted. Some support for this possibility might be adduced from the fact that there is no change in stereochemistry for the hydrolysis in the range 0.01–1.0 $M$ $OH^-$ which extends the rate constant differences quoted above from $10^{10}$ to $10^5$ $sec^{-1}$.

It has been observed[8,13] furthermore that the *trans*-ammonia group exchanges its protons faster than the *cis* groups in $[Co(NH_3)_5X]^{2+}$ complexes, and it seems likely that this rate difference also reflects the acidity of the *trans* over the *cis* $NH_3$ groups. We suggest therefore that the amido group is formed *trans* to the leaving groups and that this arrangement is preserved for the short lifetime of the intermediate. If the argument relating to H–D exchange and the absence of amido group rearrangement is accepted, and if the $-NH_2$ group is in the trigonal plane, then proton loss from an $NH_3$ group which was *cis* to the original substituent is eliminated by the results. A trigonal bipyramid of the form



would give equal amounts of *cis* and *trans* products by the equivalent paths a and b, and the additional product by path c must add to the *cis* form.

If the argument relating to H–D exchange and amido group rearrangement is not accepted, then the $^{15}N$ atom is disposed about all five positions equivalently, and the statistical distribution of the entering group is 4:1, *cis*:*trans*. Clearly the results do not support this proposal either.

The equal amounts of *cis* and *trans* products formed show that the addition of water in the trigonal plane is not statistical and that attack at the site *trans* to the isotope is slightly preferred. Attack by nucleophilic reagents at Co is less likely in the positions *cis* to the double bond than in the *trans* position, since the double bond efficiently concentrates electronic charge between the Co and amido N centers. The striking result that the azido product is largely *trans* while the concomitant aquo product contains both *cis* and *trans* isomers might be rationalized by assigning $N_3^-$ a marked preference for attack *trans* to the amido group in contrast to the less selective attack by the $H_2O$ molecule. However, this experiment alone does not appear to advance our knowledge of the structure of the intermediate, although the stereochemistry in general suggests a preference for the trigonal bipyramidal intermediate over the square-pyramidal form.

One interesting result which is not related to base hydrolysis but which has some bearing on the mechanism of the induced aquation reactions is the formation of *trans*-$[Co(NH_3)_4(^{15}NH_3)NO_3]^{2+}$ from *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl]^{2+}$ + $Hg^{2+}$ with retention of configuration. It has been contended previously[14,15] that these reactions give rise to a square-pyramidal intermediate $[Co(NH_3)_5{}^{3+}]$ which then competes for both $H_2O$ and other anions in solution. Also for a series of such induced aquations full retention of configuration is observed[8] for the entry of $H_2O$. It has now been shown that if $NO_3^-$ also competes for the coordination site the same stereochemical course is observed for the formation of the nitrato ion, a result which is consistent with the previous evidence for the presence of the five-coordinate intermediate in these induced aquations.

**Acknowledgment.** The authors thank the Microanalytical Unit of the John Curtin School of Medical Research for the N and H analyses and Mr. S. Brown for the pmr spectra.

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[12] J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960).

[13] P. Clifton and L. Pratt, *Proc. Chem. Soc.*, 339 (1963).

[14] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

[15] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967).