

BASE HYDROLYSIS AND AQUATION OF *TRANS*-METHYL-SUBSTITUTED ACIDOPENTA-AMMINECOBALT(III) COMPLEXES

FABIAN BENZO, ADRIANA MASSAFERRO, MARCELO QUEIROLO and BEATRIZ SIENRA*

Química Inorgánica, Facultad de Química, C.C.1157, Montevideo, Uruguay

and

ALBERTO L. CAPPARELLI† and DANIEL O. MÁRTIRE‡

Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas (INIFTA),
Facultad de Ciencias Exactas, La Plata, Argentina

(Received 26 July 1995; accepted 27 September 1995)

Abstract—Base hydrolysis and aquation of *trans*-[Co(NH₃)₄(NH₂CH₃)X]²⁺ (where X = Cl, Br and NO₃) complexes are reported. Both types of reactions are four to eight times faster than the corresponding reactions for [Co(NH₃)₅X]²⁺ complexes. The positive activation entropies of the base hydrolysis for all the studied *trans*-[Co(NH₃)₄(NH₂CH₃)X]²⁺ ions and the stereochemistry of the hydroxo products are indicative of a dissociative conjugate base, Dcb, mechanism. The steric course of the base hydrolysis differs significantly from that of the parent penta-ammines. For the aquation reactions, the activation enthalpies of the *trans*-methylamine and penta-ammine complexes are similar, while the activation entropies are more positive (or less negative) for the former. These results are interpreted in terms of an I_d mechanism.

Although the hydrolysis of amine complexes of cobalt(III) has been extensively investigated,^{1–3} some mechanistic aspects concerning these reactions still need to be resolved. Aquation reactions of the cobalt(III) complexes appear to be largely dissociative in nature, i.e. bond breaking substantially precedes bond making. Among other evidence, the rate enhancement observed when the non-leaving groups are changed from penta-

ammine to pentakis (methylamine) (herein after called N-methylation) is consistent with the assessment above.^{4–8}

Base hydrolysis reactions of penta-ammine-cobalt(III) complexes are generally accepted to proceed according to a dissociative conjugate base Dcb mechanism in which a five-coordinated intermediate, [Co(NH₃)₄NH₂]²⁺, is formed from the conjugate base species, which rapidly reacts with water or any other competing nucleophile to produce the hydrolysis products.^{9–13} Such reactions are orders of magnitude faster than the corresponding aquation or ligand substitution processes. The rate constants for the base hydrolysis of the pentakis(methylamine) complexes are larger than those of the corresponding penta-ammine complexes. This observation has been used to support the dissociative conjugate base mechanism.^{4,7} However,

* Author to whom correspondence should be addressed.

† A. L. Capparelli is a research member of Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina).

‡ D. O. Mártire is a research member of Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (Argentina).

there is still some controversy over the questions of whether the process is entirely dissociative, D, or if it is partly concerted, I_{dc}.¹⁴⁻¹⁷

The base hydrolysis kinetics of the *trans*-[Co(NH₃)₄(NH₂CH₃)Cl]²⁺ ion has already been studied,^{5,18} but the enthalpy and entropy of activation were not determined. Here, we report the base hydrolysis and aquation of *trans*-[Co(NH₃)₄(NH₂CH₃)X]²⁺ complexes (X = Cl, Br, NO₃), which were prepared according to the recently reported syntheses.^{18,19}

Furthermore, the availability of these compounds makes it possible to study the stereochemistry of the base hydrolysis product, [Co(NH₃)₄(NH₂CH₃)OH]²⁺. Ideally, a D mechanism requires that the five-coordinate intermediate lives long enough to lose all memory of its precursor so that the stereochemistry of the products should be independent of the nature of the leaving group, i.e. if a common transition state or intermediate exists in the base hydrolysis of cobalt (III)penta-ammines complexes, the configuration of the hydroxo product should be the same for all the substrates.

EXPERIMENTAL

Materials

trans-[Co(NH₃)₄(NH₂CH₃)X]X₂ complexes (X = Cl, Br, NO₃) were prepared as described previously.^{18,19} Conversions to the perchlorate salts were achieved by routine treatment with silver perchlorate for X = Cl and Br, and with cold concentrated HClO₄ for X = NO₃. The compounds were identified by chemical analysis and UV-vis spectroscopy; all spectra agreed with the literature data. The ¹H NMR spectra proved the isomeric purity of the *trans*-NH₂CH₃ complexes. [Co(NH₃)₅X](ClO₄)₂ (X = Cl, Br and NO₃) were prepared and purified as described previously.²⁰ All other reagents and solvents used were of analytical grade.

Aquation

Reaction mixtures were prepared from the appropriate quantities of the complexes (5–12 × 10⁻³ M), NaClO₄ (1 M) and aqueous HClO₄ (pH = 1). The aquation kinetics were followed spectrophotometrically at 540, 570 and 500 nm for X = Cl, Br and NO₃, respectively in the thermostated (±0.1°C) optical cell of a Spectronic 3000 diode array spectrophotometer. All reactions obeyed a first-order rate law. Variation of the complex concentration did not affect the rate constants.

The reported rate constants, which are average of 4 runs at four different concentrations, were determined using the Guggenheim method. Activation enthalpy and entropy were determined from plots of ln(*k*/T) vs 1/T.

Base hydrolysis

The kinetics of the base hydrolysis were followed spectrometrically using complex concentrations of 5–10 × 10⁻³ M and ionic strength of 0.15 M (controlled by addition of NaClO₄). A Durrum D110 stopped-flow spectrophotometer with a thermostated cell (±0.1°C) was employed. The observation wavelength was 535, 500 and 505 nm for X = Cl, Br and NO₃, respectively. Plots of ln(A_t - A_∞) vs time were linear to completion of reaction.

Due to the ionic strength effect on the rate of the base hydrolysis reaction,¹ the rate constant for the base hydrolysis of [Co(NH₃)₅X](ClO₄)₂ complexes (with X = Cl, Br and NO₃) were determined at 25°C for comparison. To this purpose, the same procedure was employed.

Stereochemistry of base hydrolysis

The product distribution on base hydrolysis was determined at 25°C by treating a solution of *trans*-[Co(NH₃)₄(NH₂CH₃)X](ClO₄)₂ (15 mg) in D₂O (0.5 cm³) with NaOD (5 × 10⁻² cm³, 1 M). After 5 min the reaction was quenched with DCl (5 × 10⁻² cm³, 1 M). The *cis/trans* ratio was determined from the ¹H NMR resonance integrals of the coordinated methyl groups. In a similar way, the *trans*-NH₂CH₃ complexes were hydrolysed in D₂O-CD₃OD and D₂O-DMSO-d₆ (dimethylsulfoxide) mixtures. In one experiment, the reaction was performed at 45°C, in order to determine whether there is a temperature effect on the steric course of the base hydrolysis.

In order to test the validity of this procedure, *trans*-[Co(NH₃)₄(NH₂CH₃)Cl](ClO₄)₂ was subjected to base hydrolysis in water. The complex (0.3 g) was dissolved in a mixture of H₂O (10 cm³) and NaOH (1 cm³, 2 M). After 5 min at 25°C the solution was acidified (HClO₄); the aqua complex crystallized on adding concentrated HClO₄. It was filtered off, washed with ethanol and diethylether, and dried *in vacuo*. The sample was dissolved in DMSO-d₆ (60 mg cm⁻³) in order to obtain the ¹H NMR spectrum. In another experiment, the chloro complex (0.3 g) was dissolved in H₂O (10 cm³) with NaOH (1 cm³, 2 M). After 5 min at 25°C the solution was acidified with HClO₄ to quench the reaction and the solution was lyophilized. The

resulting solid was dissolved in DMSO- d_6 (60 mg cm^{-3}) and the ^1H NMR spectrum was registered.

The ^1H NMR spectra were recorded on a Varian XL-100 spectrometer with tetramethylsilane (TMS) as internal reference.

RESULTS

Aquation

The pseudo-first-order rate constants, k_{aq} , were determined in the interval 26.7–56.2°C, for X = Cl, 26.7–50.4 for X = Br and 15.3–30.3 for X = NO_3 . They were the same in 0.01 M as in 0.1 M HClO_4 and over a two-fold range of initial complex concentration. The activation parameters for the *trans*-methylamine complexes, as well as the rate constant, k_{aq} , at 25°C, obtained by interpolation, are collected in Table 1. The corresponding literature values for the pentaammine, $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}]^{2+}$ ions are included in Table 1 for comparison.²¹

The aquation reactions of the *trans*-methylamine complexes are five to six times faster than those of the parent penta-ammines, irrespective of the nature of the leaving group (Table 1). The values of k_{aq} for *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{X}]^{2+}$ (with X = Cl and Br) lie between those for the penta-ammine and the pentakis(methylamine) complexes. For X = Cl, ΔH^\ddagger is the same for the penta-ammine, the *trans*-methylamine and the pentakis(methylamine) complexes, while ΔS^\ddagger becomes less negative in that series. The same behaviour has been reported for some $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{X}]^{3+}$ complexes (with X = dimethylsulfoxide, dimethylformamide, acetonitrile).⁶ These trends indicate that the activations parameters of $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}]^{2+}$ are question-

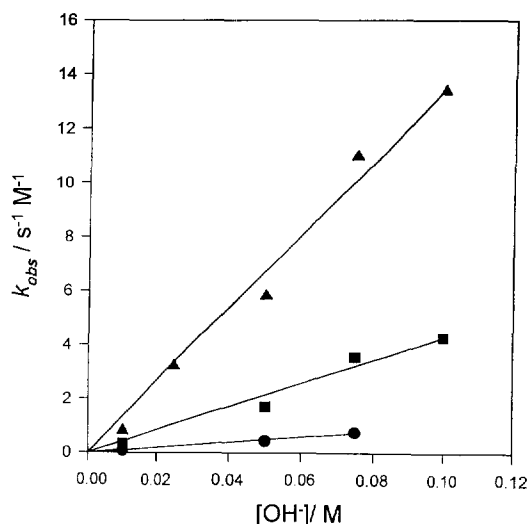


Fig. 1. Pseudo-first-order rate constant, k_{obs} , vs $[\text{OH}^-]$ for the base hydrolysis of *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{NO}_3]^{2+}$ (\blacktriangle) *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{Br}]^{2+}$ (\blacksquare) and *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{Cl}]^{2+}$ (\bullet), at 30.6°C and ionic strength 0.15 M (NaClO_4).

able. Furthermore, reported values for rate constants and ΔG^\ddagger are more reliable than values of ΔH^\ddagger and ΔS^\ddagger due to error compensation.²

Base hydrolysis

Under the conditions of these experiments, the contribution of the spontaneous aquation reactions is negligible. Plots of $\ln(A_1 - A_\infty)$ vs time were linear to completion of reaction. The corresponding pseudo-first-order rate constants (k_{obs}) was proportional to $[\text{OH}^-]$ for *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{X}]^{2+}$ (Fig. 1) and $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ ions (results

Table 1. Rate constants at 25°C and activation parameters for the aquation of acido(amine)cobalt(III) complexes

| Complex | $10^6 k_{\text{aq}}$ (s^{-1}) | ΔH^\ddagger (kJ mol^{-1}) | ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$) |
|---|--|--|---|
| $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+ a}$ | 1.77 | 94.2 | -39 |
| <i>trans</i> - $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{Cl}]^{2+ b}$ | 8.89 | 97 | -15 |
| $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}]^{2+ c}$ | 39.6 | 95 | -10 |
| $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+ a}$ | 5.97 | 97.0 | -19.6 |
| <i>trans</i> - $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{Br}]^{2+ b}$ | 31.7 | 97 | -5 |
| $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}]^{2+ d}$ | 286 | 86.1 | -23.4 |
| $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{2+ a}$ | 24.1 | 100.3 | 3.3 |
| <i>trans</i> - $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{NO}_3]^{2+ b}$ | 134 | 99 | 13 |

^a Data from ref. 1.

^b This work. Estimated errors: in $k_{\text{aq}} \pm 2\%$; in ΔH^\ddagger , $\pm 2 \text{ kJ mol}^{-1}$; in ΔS^\ddagger , $\pm 4 \text{ J K}^{-1} \text{mol}^{-1}$.

^c Data from ref. 5.

^d Data from ref. 22.

not shown). The slopes of the straight lines yield the bimolecular rate constant, k_{OH} . Values of k_{OH} for the *trans*-methylamine complexes were determined in the intervals 16.0–40.0°C for X = Cl, 19.2–40.0°C for X = Br and 21.3–34.5°C for X = NO₃. The activation enthalpy and entropy along with the bimolecular rate constant, k_{OH} , interpolated at 25°C, for the *trans*-methylamine and penta-ammine complexes, are listed in Table 2. The literature values for the [Co(NH₂CH₃)₅Cl]²⁺ ion are also shown for comparison (to our knowledge kinetics studies of the base hydrolysis of [Co(NH₂CH₃)₅Br]²⁺ and [Co(NH₂CH₃)₅NO₃]²⁺ ions have not been reported thus far).

As for the aquation reactions, the base hydrolysis reactions of the *trans*-methylamine complexes are faster than those of the parent penta-ammines. The rate of enhancement is originated in ΔH^\ddagger .

Stereochemistry of base hydrolysis

For aqueous solutions and the solvent mixtures entered in Table 3, the products of the base hydrolysis reactions after acidification are *cis*- and *trans*-[Co(NH₃)₄(NH₂CH₃)H₂O]³⁺ ions.

The good resolution of the methyl signals in the ¹H NMR spectra of the *cis* and *trans* aqua products makes possible a quantitative evaluation, without isolation of the products. The spectra of the *cis* and *trans*-[Co(NH₃)₄(NH₂CH₃)H₂O]³⁺ ions in D₂O only showed the methyl ¹H resonances, due to complete exchange of amine and water protons.^{18,19} A representative spectrum is given in Fig. 2. The product distributions, calculated from the resonance integrals, are listed in Table 3. The reported values

Table 3. Steric course of the base hydrolysis of *trans*-[Co(NH₃)₄(NH₂CH₃)X]²⁺ ions in aqueous (D₂O) mixtures at 25°C

| Cosolvent | (%) ^a | <i>cis</i> (%) ^b | | |
|----------------------------------|------------------|-----------------------------|--------|---------------------|
| | | X = Cl | X = Br | X = NO ₃ |
| — | — | 11 | 13 | 17 |
| MeOD ^c | 20 | 12 | 12 | 17 |
| MeOD | 40 | 12 | 12 | 18 |
| DMSO-d ₆ ^d | 20 | 12 | 14 | 18 |
| DMSO-d ₆ | 40 | 12 | 14 | 18 |

^a % (v : v) of the cosolvent.

^b % *cis*-[Co(NH₃)₄(NH₂CH₃)D₂O]³⁺ in the products of the base hydrolysis. Estimated error in the percentage of *cis*-product is 2%. The entries are averages over at least three independent measurements.

^c MeOD = deuterated methanol.

^d DMSO-d₆ = deuterated dimethylsulphoxide.

are averages over at least three independent measurements. No significant differences were found for solvent mixtures listed in Table 3 for each anionic ligand. The values for X = Cl and Br are significantly lower than those for X = NO₃ (Table 3). This trend has also been observed for the *trans*-[Co(NH₃)₄(¹⁵NH₃)X]²⁺ ions, although the *cis/trans* ratios are higher.¹⁷ The same stereochemical result was obtained in experiments performed at 45°C.

In the experiments in which the aqua product was isolated (precipitated with concentrated HClO₄ or lyophilized), the results were the same. These last procedures are more time consuming and a larger sample is needed.

Table 2. Rate constants at 25°C and activation parameters for the base hydrolysis of acido (amine)cobalt(III) complexes

| Complex | k_{OH} (s ⁻¹ M ⁻¹) | ΔH^\ddagger (kJ mol ⁻¹) | ΔS^\ddagger (J K ⁻¹ mol ⁻¹) |
|--|---|---|--|
| [Co(NH ₃) ₅ Cl] ²⁺ | 0.60 ^a | 120 ^b | 154 ^b |
| <i>trans</i> -[Co(NH ₃) ₄ (NH ₂ CH ₃)Cl] ²⁺ | 4.8 ^a | 105 ^c | 121 ^d |
| [Co(NH ₂ CH ₃) ₅ Cl] ²⁺ | 800 ^e | 75.2 ^e | 71.5 ^e |
| [Co(NH ₃) ₅ Br] ²⁺ | 3.3 ^a | 124 ^f | 187 ^f |
| <i>trans</i> -[Co(NH ₃) ₄ (NH ₂ CH ₃)Br] ²⁺ | 14 ^a | 105 ^c | 129 ^d |
| [Co(NH ₃) ₅ NO ₃] ²⁺ | 9.2 ^a | 118 ^f | 180 ^f |
| <i>trans</i> -[Co(NH ₃) ₄ (NH ₂ CH ₃)NO ₃] ²⁺ | 59 ^a | 91.2 ^e | 95 ^d |

^a ± 10% (this work).

^b Data from ref. 23.

^c ± 4 kJ mol⁻¹ (this work).

^d ± 8 J K⁻¹ ml⁻¹ (this work).

^e Data from ref. 24.

^f Data from ref. 1.

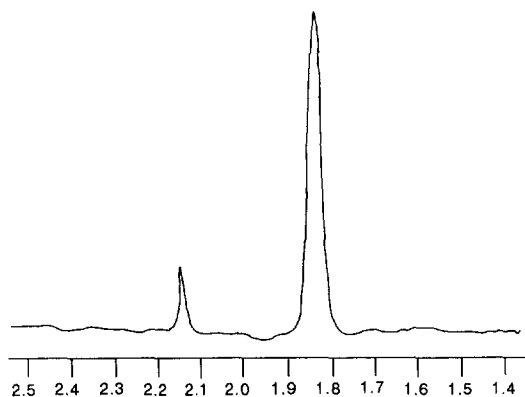
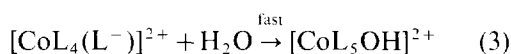
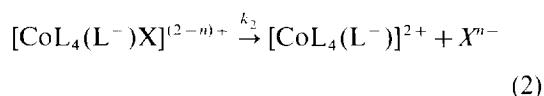
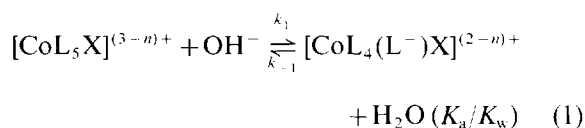


Fig. 2. 100 MHz ^1H NMR spectrum of the products of base hydrolysis at 25°C of the *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{Br}]^{2+}$ ion in D_2O . Chemical shifts in ppm relative to TMS.

DISCUSSION

In the last decades much evidence has appeared supporting the dissociative mechanism [eqs (1)–(3)] for the base hydrolysis of amine complexes of cobalt(III).



L = amine and L^- = deprotonated amine.

It is usually assumed that the formation of the conjugate base species occurs in the fast pre-equilibrium (1), followed by the rate-determining step (2). Under such conditions and in the presence of excess of OH^- , the pseudo-first-order rate constant, k_{obs} , can be expressed as in eq. (4).

$$k_{\text{obs}} = k_{\text{OH}}[\text{OH}^-] \quad (4)$$

with

$$k_{\text{OH}} = k_2 K_a/K_w \quad (5)$$

In this process numerous factors can intervene to give variation in rate and the interpretation of comparative studies is complicated by the fact that, in aqueous solutions, it is not possible to separate

stages 1 and 2: the measurement of K_a for the coordinated amines is precluded in water by the low dissociation constants ($\text{p}K_a > 15$).

The effects of N-methylation on base hydrolysis is drastic, i.e. rate increases greater than 10^3 were observed.^{7,11} The rate enhancement for the pentakis(methylamine) ions compared with the corresponding penta-ammine ions was explained by steric crowding in the ground state of the pentakis(methylamine) ions, which is relieved in the transition state by substantially stretching the $\text{Co}-\text{X}$ bond. On N-methylation the aquation rate constants also increase, but less markedly^{7,11} (20–70 times), probably because the transition state for the base hydrolysis is more open (i.e. dissociated) than that for aquation.

For the present series of *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{X}]^{2+}$ ions there is only a modest rate enhancement of both, aquation and base hydrolysis, when one NH_3 is substituted by a NH_2CH_3 ligand (*trans* position), as shown in Tables 1 and 2. This result means that for these complexes the steric crowding effect is not relevant: a single methyl group remote to the leaving group should not involve substantial steric effects at the site.^{5,18}

The following factors could be responsible for the rate enhancement observed for the base hydrolysis of *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{X}]^{2+}$ ions: (i) variations in proton acidities of the coordinated amines (K_a) and (ii) inductive effect of the methyl substituent.* Only the second factor can also account for the rate enhancement on the aquation reactions.

The ratios $k_{\text{OH}}/k_{\text{aq}}$ (Tables 1 and 2) are 5.4×10^5 , 4.4×10^5 and 4.4×10^5 for *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{X}]^{2+}$, with X = Cl, Br and NO_3 , respectively. Comparable ratios are found for the parent penta-ammine complexes ($k_{\text{OH}}/k_{\text{aq}} = 3.8 \times 10^5$, 5.5×10^5 and 3.8×10^5 for X = Cl, Br and NO_3 respectively). It appears, therefore, that the *trans*-methylamine complexes have the same acidity as the parent penta-ammine ions (i.e. k_1/k_{-1} is the same) and consequently, the rate enhancement observed in the base hydrolysis is originated in the k_2 step, i.e. the presence of a methyl substituent produces a parallel increase on k_{aq} and k_2 . Although k_1 can be very sensitive to the nature of the other ligands in the complex (i.e. the nature of the other ligands affects amine proton lability), if there is a parallel and cancelling effect on k_{-1} , then k_1/k_{-1} will be constant and the rate increase in base hydrolysis will not be originated on changes in the acidity of the complexes.

We assert, therefore, that for the compounds studied here the rate enhancements informed on both reactions are mainly due to inductive effect of

*We are assuming here that solvational factors are similar, because we are comparing ions of the same charge and size.

the methyl substituent. It is conceivable that the methyl group influences the release of the leaving group X, donating negative charge to the cobalt. This supposition is presently being investigated by ESCA spectroscopy and some preliminary results on the *trans*-[Co(NH₃)₄(NH₂CH₃)Cl](ClO₄)₂ complex²⁵ have shown a decrease of the actual cobalt charge relative to the [Co(NH₃)₅Cl](ClO₄)₂ complex.

The base hydrolysis reaction of the *trans*-[Co(NH₃)₄(NH₂CH₃)X]²⁺ ions, with X = Cl, Br, NO₃, is faster than that for the corresponding penta-ammines and slower than the base hydrolysis for the pentakis(methylamine) complexes. This effect is originated in ΔH^\ddagger rather than in ΔS^\ddagger . The large and positive ΔS^\ddagger values observed for all the penta-ammine complexes studied are consistent with the conjugate base mechanism, irrespective of whether the bulk of the positive ΔS^\ddagger for the overall hydrolysis arises from dissociation of the leaving group (reaction 2),⁷ or from the deprotonation of starting complex (reaction 1).²

The existence of a penta-coordinated intermediate, [Co(L)₄(L⁻)]²⁺, of the base hydrolysis of penta-ammine cobalt(III) complexes is still being discussed.^{17,26} One way to probe the existence of energy minima (i.e. genuine intermediates) *en route* to products is the demonstration of stereochemical properties independent of the source of the intermediate. The product distribution of the base hydrolysis of the *trans*-[Co(NH₃)₄(NH₂CH₃)X]²⁺ (X = Cl, Br, NO₃) ions in various aqueous mixtures is independent of the nature of the solvent, but there is a small leaving group effect (see Table 3). The same behaviour was observed for the parent penta-ammines.¹⁷ In this case the percentage of *cis*-[Co(NH₃)₄(¹⁵NH₃)H₂O]³⁺ product of the base hydrolysis of *trans*-[Co(NH₃)₄(¹⁵NH₃)X]²⁺ ions was 46 for X = Cl and Br, and 49 for X = NO₃.¹⁷ We conclude after Buckingham¹⁷ that the results do not prohibit the formation of a penta-coordinated cobalt(III) species for all substrates, but they require its lifetime to be so short that it captures a solvent molecule before bond angles can equilibrate,^{27,28} i.e. before a relative stable configuration is reached.

It is interesting to note the drastic effect of the methyl group on the steric course of the base hydrolysis. In order to account for the almost equal *cis/trans* product distribution of the base hydrolysis of *trans*-[Co(NH₃)₄(¹⁵NH₃)X]²⁺ (X = Cl, Br, NO₃) ions, Nordmeyer¹⁰ proposed a trigonal bipyramidal structure for the five-coordinate intermediate, formed from a conjugate base with the amido group *cis* to the leaving group. On the other hand, more retentive steric courses, like those observed in the present work, can be explained in terms of a penta-coor-

ordinated intermediate, formed from a conjugate base with the amido group *trans* to the leaving group.¹⁸ The assumption of a reaction route via *trans* deprotonation has some experimental support.^{18,29}

The faster aquation reactions for the *trans*-[Co(NH₃)₄(NH₂CH₃)X]²⁺ ions compared with those for the parent penta-ammines is originated in ΔS^\ddagger . A good correlation between ΔS^\ddagger and ΔV^\ddagger has been reported⁶ for some penta-ammine and pentakis(methylamine) complexes, where the leaving group was dimethylsulfoxide, dimethylformamide, acetonitrile or chloride. The ΔH^\ddagger values for the penta-ammines and the pentakis(methylamine) complexes were found to be very similar and both ΔS^\ddagger and ΔV^\ddagger values were more positive (or less negative) for the latter. Accordingly, the authors⁶ suggested a more dissociated activated state for the pentakis(methylamine) complexes, i.e. less participation of the incoming water molecule in the transition state for those complexes. In this line, the trend in activation parameters for aquation from [Co(NH₃)₅X]²⁺, to *trans*-[Co(NH₃)₄(NH₂CH₃)X]²⁺ and to [Co(NH₂CH₃)₅X]²⁺ indicates no mechanistic disparity, but merely a trend towards less participation of the incoming water molecule. Variation of the non-leaving groups does not seem to require relevant changes in the aquation mechanism.

Acknowledgements—We thank the financial assistance from CONICYT, Uruguay and Bach, and Jorge Cernadas for recording ¹H NMR spectra.

REFERENCES

1. D. A. House, *Coord. Chem. Rev.* 1977, **23**, 223.
2. J. O. Edwards, F. Monacelli and G. Ortaggi, *Inorg. Chim. Acta* 1974, **11**, 47.
3. M. L. Tobe, *Advances in Inorganic and Bioinorganic Mechanisms* (Edited by A. G. Sykes), Vol. 2, P.I. Academic Press, London (1983).
4. D. A. Buckingham, B. M. Foxman and A. M. Sargeson, *Inorg. Chem.* 1970, **9**, 1790.
5. G. A. Lawrence, K. Schneider and R. van Eldik, *Inorg. Chem.* 1984, **23**, 3922.
6. N. J. Curtis and G. A. Lawrence, *Inorg. Chem.* 1986, **25**, 1033.
7. N. J. Curtis, G. A. Lawrence, P. A. Lay and A. M. Sargeson, *Inorg. Chem.* 1986, **25**, 484.
8. P. A. Lay, *Inorg. Chem.* 1987, **26**, 2144.
9. D. A. Buckingham, I. I. Olsen and A. M. Sargeson, *J. Am. Chem. Soc.* 1967, **89**, 5129.
10. F. R. Nordmeyer, *Inorg. Chem.* 1969, **8**, 2780.
11. D. A. Buckingham, I. I. Creaser and A. M. Sargeson, *Inorg. Chem.* 1970, **9**, 655.
12. E. Ahmed, M. L. Tucker and M. L. Tobe, *Inorg. Chem.* 1975, **14**, 1.

13. N. E. Dixon, W. G. Jackson, W. Marty and A. M. Sargeson, *Inorg. Chem.* 1982, **21**, 688.
14. F. P. Rotzinger, *Inorg. Chem.* 1988, **27**, 772.
15. F. P. Rotzinger, *Inorg. Chem.* 1988, **27**, 768.
16. W. G. Jackson, C. N. Hookey, M. L. Randall, P. Comba and A. M. Sargeson, *Inorg. Chem.* 1984, **23**, 2473.
17. N. E. Brasch, D. A. Buckingham, C. R. Clark and K. S. Finnie, *Inorg. Chem.* 1989, **28**, 4567.
18. S. Balt, H. J. Gamelkoorn, C. R. Piriz Mac-Coll and W. E. Rankema, *Trans. Met. Chem.* 1984, **9**, 224.
19. B. Sienna, A. Massaferrero and C. R. Piriz Mac-Coll, *Z. Anorg. Allg. Chem.* 1990, **590**, 222.
20. G. G. Schlessinger, *Inorganic Laboratory Preparations*. Chem. Publishing Co., New York, (1962).
21. To our knowledge no kinetics study on $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{NO}_3]^{2+}$ ion has been reported thus far.
22. L. F. Book, K. Y. Hui, O. W. Lau and W. K. Li, *Z. Anorg. Allg. Chem.* 1976, **426**, 215.
23. A. W. Adamson and F. Basolo, *Acta Chim. Scand.* 1955, **9**, 1261.
24. R. Mitzner and W. Depkat, *Z. Phys. Chem. (Leipzig)* 1973, **254**, 189.
25. L. Beyer, K. H. Hallmeier and B. Sienna, work in progress.
26. R. van Eldik, Y. Kitamura and C. R. Piriz Mac-Coll, *Inorg. Chem.* 1986, **25**, 4252, and refs therein.
27. S. Balt, H. J. Gamelkoorn and W. E. Rankema, *J. Chem. Soc., Dalton Trans.* 1983, 2415.
28. S. Balt and H. J. Gamelkoorn, *J. Chem. Soc., Dalton Trans.* 1985, 659.
29. R. J. Geue, T. W. Hambley, J. Mac B. Harrowfield, A. M. Sargeson and M. R. Snow, *J. Am. Chem. Soc.* 1984, **106**, 5478.