

Stereoselectivity of the Secondary Isotope Effect in the Aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

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A careful kinetic study of the acid hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and the selectively deuterated species *trans*- $[\text{Co}(\text{NH}_3)_4(\text{ND}_3)\text{Cl}]^{2+}$, *trans*- $[\text{Co}(\text{ND}_3)_4(\text{NH}_3)\text{Cl}]^{2+}$, and $[\text{Co}(\text{ND}_3)_5\text{Cl}]^{2+}$ reveals that N-deuteration reduces the hydrolysis rate at both the cis and trans sites. On a per-D basis, the rate reduction is three times more effective for trans-Cl deuteration. This result is contrary to conventional wisdom but has never been tested previously. It appears to be the first example of significant stereoselectivity for the secondary isotope effect in a substitution reaction, in either inorganic or organic systems. An explanation is offered in terms of the effect of D-substitution on zero point energies, the different extents of coupling of NH(D) and Co–Cl vibrational modes according to their stereochemical relationship, and the view that the rate of acid hydrolysis of the $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ involves an aberrant Co–Cl vibration component.

Introduction

It has been known for several decades that substitution reactions at tetrahedral carbon and octahedral cobalt(III) are normally slower in D_2O compared to H_2O .^{1–4} The rate reduction can be up to 30%. More interesting to us was the fact that N-deuterated amine Co(III) complexes are slower to hydrolyze than their undeuterated counterparts in acidified H_2O . For example, $[\text{Co}(\text{ND}_3)_5\text{Cl}]^{2+}$ is reported to aquate at close to 70% of the first-order rate constant for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$.^{2,3}

Our interest in the kinetic isotope effect for hydrolysis reactions stems from a paper by Balt and Gamelkoorn⁵ on the ammoniolysis of an elusive complex we synthesized in 1976,⁶ *trans*- $[\text{Co}(\text{en})_2(\text{N}_3)(\text{OSMe}_2)]^{2+}$. This ion has two distinct kinds of NH protons, one adjacent to the azide ligand and one remote.⁷ The two kinds of NH protons observed in the ¹H NMR spectrum were assigned by Balt et al. using the spectra for the “parent” ions, *trans*- $[\text{Co}(\text{en})_2(\text{OSMe}_2)_2]^{3+}$

and *trans*- $[\text{Co}(\text{en})_2(\text{N}_3)_2]^+$. The “confirmation” of the assignments was based on the relative hydrolysis rates of the stereoselectively deuterated complexes; the species containing ND groups adjacent to the DMSO leaving group were held to aquate some 10% more slowly than the corresponding NH species, whereas the species having ND groups exo to the leaving group was held to involve no such rate reduction. Balt and Gamelkoorn referred to Buckingham et al. for their work^{8,9} on the $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ and *trans*- $[\text{Co}(\text{NH}_3)_4(\text{ND}_3)\text{X}]^{2+}$ ions (X = Cl[−], Br[−]) as the precedent for this analysis. There are two problems here. One, these latter workers did *not* examine the effect of deuteration on the aquation *rate* but rather used the trans label to follow the *steric course* of hydrolysis. Second, the two sets of exo- and endo-NH protons in the *trans*- $[\text{Co}(\text{en})_2(\text{OSMe}_2)\text{N}_3]^{2+}$ complex are both cis to the leaving group. Thus, no one has looked at the question of the stereo- or regioselectivity of N-deuteration toward the reduction in hydrolysis rate, other than Balt and Gamelkoorn⁵ from a limited perspective.

Buckingham et al.⁸ did, however, establish site selectivity for the H–D-exchange of the cis- and trans-NH₃ groups (the trans site is about 100-fold faster to exchange), following Clifton and Pratt.¹⁰ Although an extensive set of cis and trans site exchange data have appeared in several publications,¹¹

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(1) Collins, C. J.; Bowman, N. S. *Isotope Effects in Chemical Reactions*; Van Nostrand Reinhold Co.: New York, 1970.

(2) Pearson, R. G.; Stellwagon, N. C.; Basolo, F. *J. Am. Chem. Soc.* **1960**, *82*, 1077.

(3) Adamson, A. W.; Basolo, F. *Acta Chem. Scand.* **1955**, *9*, 1261.

(4) Chan, S. C. *J. Chem. Soc.* **1965**, 418.

(5) Balt, S.; Gamelkoorn, H. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1495.

(6) Begbie, C. M.; Jackson, W. G. *Inorg. Chim. Acta* **1982**, *60*, 115.

(7) Balt, S.; Gamelkoorn, H. J. *Transition Met. Chem.* (Dordrecht, Neth.) **1985**, *10*, 164.

(8) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *Aust. J. Chem.* **1967**, *20*, 597.

(9) Buckingham, D. A.; Durham, L.; Sargeson, A. M. *Aust. J. Chem.* **1967**, *20*, 257.

(10) Clifton, P.; Pratt, L. *Proc. Chem. Soc.* **1963**, 339.

the original work¹² has never been published. Nonetheless, their work provides the synthetic basis for the present study in which we carefully examine the rates of acid hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$, $\text{trans}-[\text{Co}(\text{NH}_3)_4(\text{ND}_3)\text{Cl}]^{2+}$, $\text{trans}-[\text{Co}(\text{ND}_3)_4(\text{NH}_3)\text{Cl}]^{2+}$, and $[\text{Co}(\text{ND}_3)_5\text{Cl}]^{2+}$.

Experimental Section

¹H and ²H NMR spectra were measured with use of a Varian Unity Plus 400 MHz instrument at 20 °C.

Synthesis and Characterization. The salts $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ ¹³ and $[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$ ¹⁴ were synthesized and purified by the published methods. Chloro species. UV-vis (0.1 M $\text{CF}_3\text{SO}_3\text{H}$) λ , nm (ϵ_{max}): 532 (51.2); lit. 533 (50.3, 50.9).¹⁵ ¹H NMR ($\text{Me}_2\text{SO}-d_6$): δ 2.87 (3H, *trans*-NH₃); δ 3.61 (12H, *cis*-NH₃). Aqua species. UV-vis (0.1 M $\text{CF}_3\text{SO}_3\text{H}$) λ , nm (ϵ_{max}): 493 (47.5); lit. 492 (47.7).¹⁵ ¹H NMR ($\text{Me}_2\text{SO}-d_6$): δ 2.75 (3H, *trans*-NH₃); δ 3.80 (12H, *cis*-NH₃), δ 5.67 (2H, Co-OH₂).

The perdeuterated aqua complex was synthesized by dissolution of $[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$ in 0.01 M NaOD, followed by immediate reacidification (1 M DCl) to pH 1–2. Crystallization was achieved by addition of a fifth volume of 70% HClO₄. The *trans*- $[\text{Co}(\text{NH}_3)_4(\text{ND}_3)\text{OH}_2](\text{ClO}_4)_3$ salt was prepared by Hg(II) induced aquation of the *trans*- $[\text{Co}(\text{NH}_3)_4(\text{ND}_3)\text{Cl}](\text{ClO}_4)_2$ complex described in following paragraphs.

Perdeuterated $[\text{Co}(\text{ND}_3)_5\text{Cl}](\text{ClO}_4)_2$ was prepared from a saturated solution of the protic compound in D₂O at ca. 60 °C. It was cooled quickly to ca. 30 °C, a little anhydrous Na₂CO₃ was added (to pD ca. 12–13), and the supersaturated solution of the complex was immediately filtered directly into a one-fifth volume of a 1:1 mixture of ice and 70% HClO₄. The complex precipitated within seconds and was collected, washed with 2-propanol and ether, and air-dried. It was recrystallized from water (pH 3, $\text{CF}_3\text{CO}_2\text{H}$) using HClO₄ as precipitant.

The selectively deuterated *trans*- $[\text{Co}(\text{ND}_3)_4(\text{NH}_3)\text{Cl}](\text{ClO}_4)_2$ salt was obtained by rapidly extracting the perdeuterated complex on a frit using small portions of H₂O which was 0.05 M in pyridine (20 °C). The extracts were filtered directly into 5 M HClO₄ at 0 °C, which immediately yielded crystalline product, recrystallized as described.

The compound *trans*- $[\text{Co}(\text{NH}_3)_4(\text{ND}_3)\text{Cl}](\text{ClO}_4)_2$ has been described previously.⁸ We used a py/pyH⁺ buffer (total [py] = 0.05 M, py/pyD⁺ = 9:1) in D₂O (99.9% D) to follow the deuteration of a saturated solution of the fully protic compound by NMR (25 °C) and quenched the reaction (70% HClO₄) when the *trans*-NH₃ signal at δ 2.87 in the ¹H NMR spectrum had decayed essentially to zero, relative to the *cis*-NH₃ peak at δ 3.61 ppm.

In preliminary work, we used ²H NMR to follow deuteration at both sites, for the various buffer media tried and, in particular, for the reaction of $[\text{Co}(\text{ND}_3)_5\text{Cl}]^{2+}$ in H₂O/pyridine buffer.

The degree of deuterium in the two sites for the isolated salts was determined by ¹H NMR. Solutions were 50.0 mg/0.50 mL of $\text{Me}_2\text{SO}-d_6$ (99.9% D). Relative peak areas were determined by cutting of chart paper and weighing. Residual proton peaks were amplified by known amounts for this purpose including the solvent $\text{Me}_2\text{SO}-d_5$ peak which, using the areas in the spectrum of $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ of known concentration, provided absolute proton

counts. We synthesized six compounds in all, with varied D content in both *cis*- and *trans*-NH₃ sites.

Kinetics of Acid Hydrolysis. Reactions were followed spectrophotometrically using a 7-cell compartment housed in an HP8453A diode array UV-vis spectrophotometer and thermostated by water circulation from a Lauda R6 (20 L) bath. Bath (52.0 ± 0.1 °C) and cell (49.5 ± 0.1 °C) temperatures were determined using an in-house built and calibrated microthermometer.¹⁶ Cell 1 was solvent and was regularly zeroed to correct for any baseline drift over long time periods with this single beam instrument. The solvent was 0.10 M $\text{CF}_3\text{SO}_3\text{H}$ (3M company), preequilibrated in 1 cm cuvettes for 30 min prior to adding the cobalt complex. These concentrations were varied in the range (5–40) × 10⁻³ M. Five sets of runs were made on each compound such that the [Co]₀ independence of the derived rate constants could be verified; cobalt concentrations were calculated using two of the observed sharp isosbestic points, at 351 nm (ϵ 43.1) and 508 nm (ϵ 44.9). A final set of runs was made using the same compound (h_{15}) in all six cuvettes and run over the identical time period, to check for any small temperature gradients in the multicell block. The results (10⁵*k*, s⁻¹) were 3.18, 3.15, 3.21, 3.13, 3.17, and 3.19; the average *k* value ($=3.17 \times 10^{-5} \text{ s}^{-1}$) is but 1% from the extreme values, and so, temperature control within the cell block was excellent.

Reactions were followed at 300 s intervals for 60000 s (ca. 3*t*_{1/2}) in the range 340–650 nm, but for reasons that will be discussed here, only data for the first half-life were used to define isosbestic points and to determine the hydrolysis rate constant (at 560 nm). Instrument integration times were set to 1 s, with a closed shutter the default position. Several repetitive runs were made on the same complex where the spectral sampling times were varied 2-fold, to check on a possible contribution from photoaquation. None was found, as the *k*(obsd) values could be reproduced to better than ±1%. Plots of *A* versus *t* were fitted to the standard first-order rate equation $A = A_\infty + (A_0 - A_\infty)\exp(-kt)$ by nonlinear least-squares analysis and using a fixed *A*_∞ calculated from [Co]₀ and ϵ_{560} 14.6 M⁻¹ cm⁻¹ for the aqua product. This was the essential strategy employed some 45 years ago,³ and the kinetic results for the acid hydrolysis of the $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion at 49.5 °C in the present and previous works are in remarkably close agreement. For the perdeuterated complex, the results are in very close agreement for the second study² but not the first.³ Finally, we note that the previous claim² that rate constants obtained by the Guggenheim method¹⁷ for absorbance data covering just one half-life agreed with results from the *A*_∞(constant) method cannot be sustained; at least *two* half-lives of data are required for reliable rate constants by the Guggenheim method.

Control experiments were performed on the *d*₃- and *d*₁₅-chloro and aqua salts to see if the D remained intact on the time scale of the hydrolysis reactions (over one *t*_{1/2}; ca. 20000 s). It can be lost by exchange or redistributed through isomerization. Saturated solutions in 0.1 M $\text{CF}_3\text{SO}_3\text{H}$ were maintained at 50 °C for 5 h and then cooled and the respective perchlorate salts crystallized by addition of 70% HClO₄. The ¹H NMR spectra were measured and analyzed as for the variously deuterated reactant chloro complexes. There was no detectable loss of D-label from the *d*₁₅-Cl species, nor scrambling in the *d*₃ form, but there was a little D-loss from the aqua ion, and only from the *trans* position (as Buckingham et al. observed⁸). Loss or site scrambling of label from the product, however, has no effect on the aquation rates for the chloro species.

Finally, the intrinsic stability of the aqua product, $[\text{Co}(\text{NH}_3)_5\text{OH}_2]^{3+}$, (or its deuterated analogues) under prolonged heating

(11) Bramley, R.; Creaser, I. I.; Mackey, D. J.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 244.

(12) Nelson, P.; Sargeson, A. M. Results to be published.

(13) Schlessinger, G. G. *Inorg. Synth.* **1967**, *9*, 160.

(14) Lamb, A. B.; Mysels, K. J. *J. Am. Chem. Soc.* **1945**, *67*, 468.

(15) Jackson, W. G.; Begbie, C. M.; Randall, M. L. *Inorg. Chim. Acta* **1983**, *70*, 7.

(16) Jackson, W. G. *Aust. J. Chem.* **1981**, *34*, 215.

(17) Guggenheim, E. A. *Philos. Mag.* **1926**, *2*, 538.

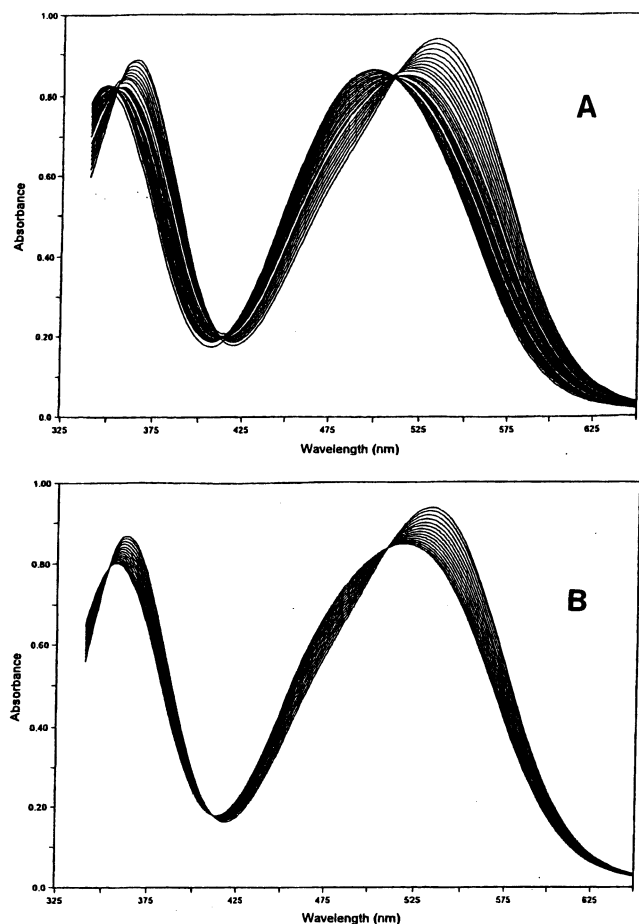


Figure 1. Changes in absorption spectra accompanying the hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in dilute triflic acid at 49.5 °C: typical runs, covering, A, about $3t_{1/2}$; B, about $1t_{1/2}$.

(50 °C) in dilute triflic acid needed to be tested. It was stable. This control followed from the observation of “steps” in absorbance versus time traces for hydrolysis of the chloro complex. Beyond times corresponding to a half-life of aquation, invariably the absorbance would suddenly change more than expected, in perceptible but small steps, and then proceed to change with time in a line parallel to that prior to the “step”. This behavior was observed for all hydrolysis reactions of the chloro complex, and this problem of “decomposition” has been commented on previously,³ although not in explicit terms. It has been labeled as NH_3 loss from the aqua complex, but it is not as simple as this, given the nonreproducible nature of the interference. However, whatever the reason, we were both aware of the problem and able to avoid it by restricting the reaction time for the acid hydrolysis reaction. Stepping led ultimately to a loss in sharpness in the isosbestic points, but it never occurred prior to one half-life of aquation of any of the chloro complexes.

Results

In Figure 1A is shown a series of spectra for the acid hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ covering a period of ca. $3t_{1/2}$. Reasonable isosbestic points were observed. Global analysis using the Specfit software yielded a first-order rate constant $k = (3.63 \pm 0.01) \times 10^{-5} \text{ s}^{-1}$, and in Figure 1S (Supporting Information), we display two traces extracted from the analysis, one for absorbance increasing and one decreasing. The fits are deceptively good, and indeed, all six runs

Table 1. First Order Rate Constants^a for Acid Hydrolysis of Partly and Selectively Deuterated $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ Ions in 0.1 M $\text{CF}_3\text{SO}_3\text{H}$ at 49.5 °C

cis-NH ^b	trans-NH ^b	% D	$10^5 k, \text{ s}^{-1}$	$10^5 k(\text{av}), \text{ s}^{-1}$
12	3	0	3.18, 3.03, 3.25, 3.10, 3.08	3.14
12	0.6	16	2.95, 2.76, 2.95, 2.74, 2.64	2.81
12	0.1	19	2.76, 2.58, 2.81, 2.68, 2.61	2.69
1.5	3	70	2.61, 2.67, 2.85, 2.64, 2.76	2.71
1	3	75	2.46, 2.59, 2.46, 2.54, 2.52	2.51
0	0	100	2.45, 2.31, 2.52, 2.39, 2.28	2.39

^a A single column of data represents specific rates determined simultaneously for six compounds in a 6-cell thermostated block. The five values in a row represent repetition of such determinations from day to day. $[\text{Co}]_0 = (5-40) \times 10^{-3} \text{ M}$. ^b There are 12 cis-NH₃ and 3 trans-NH₃ protons in the parent $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ complex; numbers in these columns which are less than 12 or 3 represent substitution by D. Thus, the notation 1.5 cis-NH and 3 trans-NH refers to a complex of stoichiometry $[\text{Co}(\text{cis}(\text{NH}_3)_{1.5}\text{cis}(\text{ND}_3)_{10.5}\text{trans}(\text{NH}_3)\text{Cl})^{2+}$.

conducted simultaneously and analyzed in this way yielded similar and reproducible results; the mean k was $(3.64 \pm 0.06) \times 10^{-5} \text{ s}^{-1}$. However, using standard single wavelength analysis at 560 nm, where the proportional absorbance change is optimal and downward, yielded $k = (3.17 \pm 0.02) \times 10^{-5} \text{ s}^{-1}$ (A_∞ was fixed at its calculated value, and only $1t_{1/2}$ of data were used). This is significantly smaller than the $3.64 \times 10^{-5} \text{ s}^{-1}$ value from the global data analysis. In the context of the present work, such a variation is unacceptable, and we sought a resolution of the problem before carrying out kinetic studies on the range of N-deuterated complexes under identical conditions.

We carried out a similar comparison for data on the base catalyzed hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$ where absorbance changes are large at some λ and smaller at others, but where k calculated by global data analysis gives a result within 0.5% of single wavelength calculations, for several selected λ values. This is in sharp contrast to the present $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ system. The problem for the $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ acid hydrolysis reaction therefore does not lie with the instrument, nor with the analytical method. The clue to the difficulty can be seen by very closely scrutinizing the data set shown in Figure 1A. One can see the irregular gaps in absorbance appearing beyond the period shown in Figure 1B where the changes are smooth and the isosbestic points sharp. The effect is subtle but real, and these irregular small gaps can be seen in a duplicate data set shown in Figure 2S (Supporting Information), but at more frequent and regular intervals, and they are therefore even less obvious.

The resolution to the problem was to use no more than $1t_{1/2}$ of data, and this approach necessarily required the use of a calculated rather than fitted final spectrum. The success of this approach had already been demonstrated for the $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$ system where such “stepping” problems are absent even to periods of $5t_{1/2}$.

The results so obtained were reproducible to the desired level ($\pm 1\%$) and are given in Table 1 for the six sets of runs on each of six compounds ranging in composition from h_{15} to d_{15} . It has already been noted that the data for the six simultaneous runs on the h_{15} complex show no significant rate variation with cell position. Second, and a key point, the results show no systematic dependence upon $[\text{Co}]_0$ over

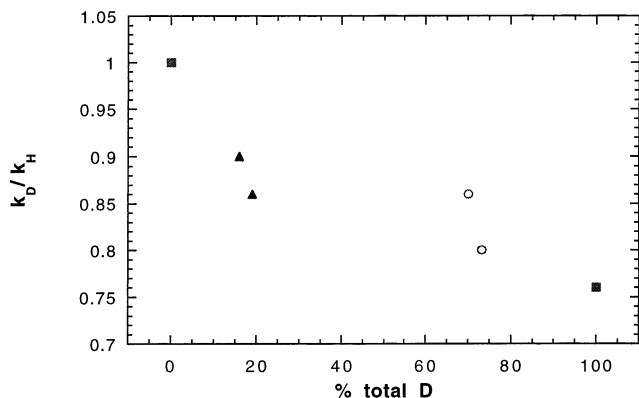


Figure 2. Plot of k_D/k_H vs % total deuterium incorporation into $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ for its acid hydrolysis in 0.1 M triflic acid at 49.5°C; %D = $100 \times (\text{no. of cis-ND} + \text{trans-ND})/15$. Refer to Table 1 for the isotopic compositions and rate data. Triangles are for substrates mostly deuterated at the trans- NH_3 , circles for substrates mostly deuterated at the cis- NH_3 .

a wide range for any of the complexes studied, confirming the first-order assumption for data analyzed for only $1t_{1/2}$ of data but with a fixed, known A_∞ value. Third, it is apparent that the small rate variations upon repetitive measurement from day to day are not significantly greater than the spread for those determined simultaneously. This can be gauged from the data normalized to the first-order rate constant for the h_{15} complex (arbitrarily set to 1.00).

A plot of k_D/k_H (Figure 2) shows that the rate is not reduced linearly in % D incorporation in the bound amines. While a linear relationship may be true for the cis or trans amines individually (we do not yet have enough data to support this possibility), it is clear that deuteration of the amines either cis or trans to the leaving group Cl^- brings about a rate reduction, and to different extents.

This is a previously unrecognized and important result. Before speculating on the ramifications, let us quantify the effect. The rate reduction for ammine deuteration trans to the leaving group Cl^- is 12.9%, and 19.2% for the cis site. Without regard to the number of deuterons in each site, these rate reductions are 1 (trans):1.5 (cis), which could nearly be regarded as essentially equal within experimental error. However, on a per deuteron basis, they are $4.3 \pm 1.0\%$ for trans, and $1.6 \pm 0.5\%$ for cis deuteration. Thus, in terms of the numerical extent of deuteration, incorporation at the trans site is nearly three times more effective.

The acid hydrolysis reaction of $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ is believed to involve a transition state having leaving Cl^- and incoming H_2O both weakly bonded (I_d). There is no 5-coordinate intermediate of any significant lifetime, and further, the hydrolysis is known to proceed via a process in which water enters largely adjacent to the leaving group.^{8,18} For this reaction, early on Adamson and Basolo³ discussed the possibility of a H-bonding arrangement of the kind shown, partly on the basis that the rate reduction for the protic amine complex in D_2O was comparable to the effect for the ND_3 complex in H_2O (Figure 3). Later, they dismissed this idea because the complexes α - and β -trans- $[\text{Co}(\text{pic})_4\text{Cl}_2]^+$, which

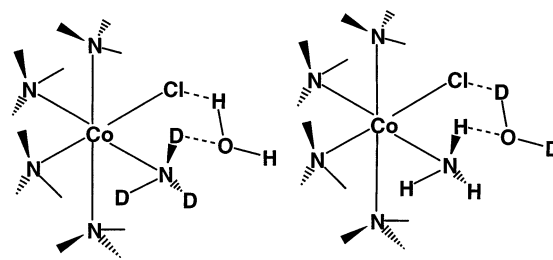


Figure 3. Possible modes of H-/D-bonding between the cis-ammine and the leaving group.

lack amine protons, also showed the effect in D_2O .² However, we believe the solvent isotope effect may have quite different origins, and that H-bonding (vs D-bonding) may play some role. The particular role is clearly not related to the cooperative effect of ammine–solvent–leaving group, because the trans ammine remote from departing Cl^- is three times more effective than the cis, rather than ineffective.

We looked for examples in organic chemistry where a significant stereoselectivity has been observed for the secondary isotope effect (α or β). There have been several studies, especially in connection with the intensely investigated nonclassical ion problem.¹ The relative k_H/k_D rates shown in Figure 3S (Supporting Information) refer to the effect of mono-D incorporation relative to the $-\text{CH}_2-$ species, on the rate of acetolysis of the brosylate derivatives.^{19,20} The secondary isotope effects range from zero ($k_H/k_D = 1$) to substantial ($k_H/k_D = 1.18$), but in no case is there a difference in the stereoselectivity due to H replacement by D.

The stereochemical role of the deuterated site may be rationalized in terms of vibrational zero-point energies for N–H (N–D) weakly coupled to Co–Cl vibrations to different extents, according to their relative stereochemical positions (90° or 180°). Such a view is consistent with the idea that hydrolysis is largely the result of an aberrant Co–Cl vibration for a dissociative reaction.

The results of the present work suggest a useful extension to different inorganic reaction types such as solvolysis, solvent exchange, and geometric and linkage isomerization, and such studies should include a variation in solvent. Linkage isomerization in particular lends itself well to a study of solvent effects,²¹ because the entering and leaving groups remain constant.

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Supporting Information Available: Additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18) Brasch, N. E.; Buckingham, D. A.; Clark, C. R.; Finnie, K. S. *Inorg. Chem.* **1989**, *28*, 3386.

(19) Jerkunica, J. M.; Borcic, S.; Sunko, D. E. *J. Am. Chem. Soc.* **1967**, *89*, 1732.

(20) Murr, B. L.; Nickon, A.; Swartz, T. D.; Werstik, N. H. *J. Am. Chem. Soc.* **1967**, *89*, 1730.

(21) Jackson, W. G.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Aust. J. Chem.* **1982**, *35*, 1561.