Anion Competition in the Hydrolysis Reactions of Pentaamminecobalt(III) Complexes

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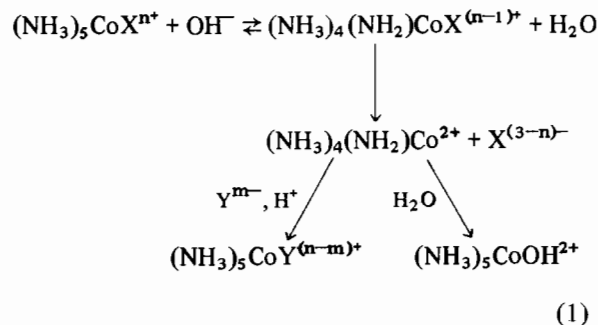
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Anion competition data are reported for the base hydrolysis (pH 8.5–9) of $[(NH_3)_5CoO_3SCF_3]^{2+}$ in 1 M NaY (Y = F^-, Cl^-, Br^-, I^- and NO_3^-). At 25 °C, $[(NH_3)_5CoY]^{2+}$ is formed along with $[(NH_3)_5CoOH]^{2+}$, as a direct product of the base catalyzed hydrolysis process (Y = F^-, <0.2; Cl^-, 7.5; Br^-, 7.1; I^-, 7.5; NO_3^-, 11.9%). Hydroxide ion as a nucleophile has also been examined, for both a 2+ and 3+ complex ion, by carrying out mixed anion (N_3^-/OH^-) competition experiments at low and high $[OH^-]$ (0.1 M and 1.1 M). It is concluded that OH^- does not compete effectively with H_2O in the attack of the reactive reduced coordination intermediate, $[(NH_3)_4(NH_2)Co]^{2+}$, formed in the base hydrolysis reaction. In this respect, the behaviour of OH^- resembles that for the isoelectronic F^- ion. Both are strongly solvated by water. The extent of competition afforded by the other anions Cl^-, Br^-, I^-, and NO_3^- is similarly accommodated, the least solvated NO_3^- ion being the best competitor. Competition by the neutral competitor NH_3 (at the 1 M level) is shown to be negligible for both a 2+ and 3+ reactant. Finally, acetate ion (1 M) competition has been determined for the base hydrolysis of $[(NH_3)_5CoX]^{n+}$, using seven different leaving groups. The results remove a previous anomaly in the literature, and show that the extent of anion competition is essentially independent of the leaving group X. Finally, this study permits a direct comparison between the acid and base hydrolysis reactions of $[(NH_3)_5CoX]^{n+}$. The relative nucleophilic effectiveness of Cl^- (and NO_3^-) towards the respective intermediates $[(NH_3)_5Co]^{3+}$ and $[(NH_3)_4(NH_2)Co]^{2+}$ believed to be involved in the two processes is evaluated. It is concluded that the different extents of anion competition reside largely in the formal charge of the intermediates. In both reactions the anion

is captured, at close to but less than a diffusion controlled rate, from an ion-atmosphere determined largely by the degree of ion-association exhibited by the intermediates.
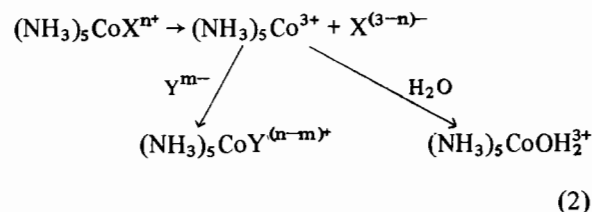
Introduction

The existence of reactive reduced coordination number intermediates in the hydrolysis reactions of $[(NH_3)_5CoX]^{n+}$ complexes has been inferred from a number of experiments [1]. One approach has been to react the complex in the presence of a competing nucleophile Y^{m-} which results in $[(NH_3)_5CoY]^{(n-m)+}$ together with $[(NH_3)_5CoOH]^{2+}$ (base hydrolysis) [2] or $[(NH_3)_5CoOH_2]^{3+}$ (acid hydrolysis) [3]:

Base Hydrolysis

$$(NH_3)_5CoX^{n+} + OH^- \rightleftarrows (NH_3)_4(NH_2)CoX^{(n-1)+} + H_2O$$

$$(NH_3)_4(NH_2)Co^{2+} + X^{(3-n)-}$$

$$Y^{m-}, H^+ \qquad H_2O$$

$$(NH_3)_5CoY^{(n-m)+} \qquad (NH_3)_5CoOH^{2+}$$

$$(1)$$

Acid Hydrolysis

$$(NH_3)_5CoX^{n+} \rightarrow (NH_3)_5Co^{3+} + X^{(3-n)-}$$

$$Y^{m-} \qquad H_2O$$

$$(NH_3)_5CoY^{(n-m)+} \qquad (NH_3)_5CoOH_2^{3+}$$

$$(2)$$

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In this type of experiment information on the existence, nature and lifetime of the respective five coordinate intermediates is derived from the dependence of the competition ratio, defined [1] as $[(NH_3)_5CoY^{(n-m)+}]/[(NH_3)_5CoOH^{2+}][Y^{m-}]$, on the nature of both the entering group Y^{m-} and leaving group $X^{(3-n)-}$ [1–3].

The mechanisms of acid and base hydrolysis have previously been considered as separate issues [1]. Partly, this is for experimental reasons; the nucleophiles Y^{m-} have been different in the two sets of competition reactions (eqns. (1), (2)). The previous limitation on the choice of Y^{m-} for the base reaction (eqn. (1)) has been the sensitivity of the product $[(NH_3)_5CoY]^{(n-m)+}$ towards OH^-. By using the especially labile $[(NH_3)_5CoO_3CF_3]^{2+}$ ion ($k_{OH} \cong 10^6$ M^{-1} s^{-1}, μ = 1.0 M, 25 °C) [4, 5] and by conducting the competition experiments at a lower pH (8.5–9), this difficulty can be overcome. Accordingly this article describes such experiments using Cl^-, Br^-, I^- and NO_3^- as competitors. Also, since most of the data on acid hydrolysis pertain to NO_3^- and Cl^- media [1, 3, 6, 7], this work permits a direct comparison of the competition properties of the two types of reduced coordination number intermediate (eqns. (1), (2)) towards common nucleophiles.

Also described are results for F^- as a competitor, completing the halide ion sequence, and mixed anion (OH^-/N_3^-) experiments which further comment [8] on the effectiveness of the isoelectronic OH^- ion as a competitor in base hydrolysis. Finally, neutral NH_3 as a nucleophile is examined, and acetate ion for a range of $[(NH_3)_5CoX]^{n+}$ (n = 2, 3) substrates which allow the resolution of anomalies [2, 8] with this anion.

Anion competition in base hydrolysis has recently been studied for Y^{m-} = NO_2^- [9], $S_2O_3^{2-}$ [10], CO_3^{2-} [11], SO_4^{2-} [11] and PO_4^{3-} [11], and the present work, which extends the range of nucleophiles to include several new non-oxygen donors, broadens considerably the basis for earlier generalizations [1, 2] on the nature of the intermediates in the hydrolysis reactions of $[(NH_3)_5CoX]^{n+}$.

Experimental

Visible spectra were recorded using Cary 118C and Cary 210 instruments. ^1H NMR spectra were obtained on a Varian T60 spectrometer using Me_2SO-d_6 solutions (internal TMS reference). Dowex 50W × 2 (200–400 mesh, H^+ or Na^+ form) and Sephadex SP C25 (Na^+ form) cation exchange resins were employed for the chromatographic experiments.

All the pentaamminecobalt(III) complexes were prepared by standard procedures [2, 4, 5, 12, 13] and analysed satisfactorily for C, H, and N, and where appropriate Br, Cl, F, S and I. Freshly recrystallized

perchlorate salts were routinely used except for $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ and $[(NH_3)_5CoOC(NH_2)N(CH_3)_2]^{3+}$ which where the $(S_2O_6)_{3/2} \cdot 1.5H_2O$ salts [2, 13]. Starting materials were carefully checked for trace impurities by ion-exchange chromatography (at 2 °C) on a Sephadex resin (0.1 M $NaClO_4$ (pH 3) eluent). The absence of $[(NH_3)_5CoOH_2](ClO_4)_3$ was established by ^1H NMR spectroscopy as described elsewhere [4]. $[(NH_3)_5CoI]Cl_2$, prepared as described [12], contains an appreciable $[(NH_3)_5CoCl]Cl_2$ impurity. This was established by chromatography on Dowex or Sephadex; using $NaClO_4$ eluent (1.0 or 0.1 M, respectively), the violet 2+ chloro ion elutes in front of and clearly separated from the olive green 2+ iodo-ion. The impurity was removed by conversion to the perchlorate salt and fractional recrystallization from water using cold 4 M perchloric acid as the precipitant. The first fractions were pure black-green $[(NH_3)_5CoI](ClO_4)_2$; later fractions (brown) contained $[(NH_3)_5CoCl](ClO_4)_2$ admixed with the iodo complex. No sample contained $[(NH_3)_5CoOH_2](ClO_4)_3$, although this problem was experienced by others [12].

The competition experiments in acetate ion solution were performed by directly dissolving the solid complex (0.2–0.4 g) in 1.00 M NaO_2CCH_3 (0.1 M in NaOH) at 25 °C while well stirred, and after 1 min the reaction was quenched with ammonium chloride or ammonium perchlorate (1–2 g). The mixture was diluted to 300–500 ml with water and sorbed on and eluted from Sephadex after first washing well with water (2 × 250 ml). In some experiments Dowex resin was used, and more starting complex (up to 1.0 g). The acetato and aqua ions were eluted separately and in that order using 0.5 M NaCl (pH 3, HCl) on Sephadex, and 1.0 M NaCl (pH 3, HCl) followed by 3.0 M HCl on Dowex. The [Co] in each band was determined spectrophotometrically; ϵ_{519}^{max} 77.2 for $CoOAc^{2+}$, ϵ_{490}^{max} 47.7 for $CoOH_2^{3+}$. The former value determined in this and other work [3, 5] differs considerably from the earlier result (ϵ_{519} 66.8). In all cases cobalt recoveries from the columns exceeded 98.5%.

Fluoride ion competition was determined as above using 1.00 M NaF/0.1 M NaOH, except that after sorption on the column the resin was washed with dilute (0.05 M) ammonium chloride followed by HCl (0.01 M, 200 ml). This was necessary to completely remove excess F^- and prevent the (partial) elution of $[(NH_3)_5CoOH_2]^{3+}$ as the hydroxo (2+) complex. Although the aqua and hydroxo ions are in rapid equilibrium, it should be recorded that the two complexes can be separated by ion-exchange chromatography when using neutral unbuffered eluents.

Anion competition experiments for the reaction of $[(NH_3)_5CoO_3SCF_3](ClO_4)_2$ (~200 mg) in 1.00 M NaX (X = Cl, Br, I, NO_3) containing Tris (0.1 M) or Tris/$HClO_4$ (1:0.5, 0.1 M) at 25 °C employed

TABLE I. Percent $[(NH_3)_5CoY]^{(n-m)+}$ Produced in the Base Hydrolysis of $[(NH_3)_5CoX]^{n+}$ in 1.00 M NaY (μ = 1.1 M[a]) at 25 °C.

Reactant	$CH_3CO_2^-$	F^-	Cl^-	Br^-	I^-	NO_3^-	NH_3
$[(NH_3)_5CoO_3SCF_3]^{2+}$	2.6, 2.8, 2.5, 2.0	<0.2	8.2, 7.7, 7.4, 6.9	7.0, 7.2	7.7, 6.7, 7.6, 8.1	11.7, 12.4, 11.7	<0.2
$[(NH_3)_5CoO_3SCH_3]^{2+}$	2.2, 1.8						<0.2
$[(NH_3)_5CoI]^{2+}$	2.4, 2.0						
$[(NH_3)_5CoOS(CH_3)_2]^{3+}$	2.2[b], (1.8)[c]	<0.1					<0.2
$[(NH_3)_5CoOC(NH_2)_2]^{3+}$	2.3, 2.5 (2.1, 2.3)[d]						
$[(NH_3)_5CoOC(NH_2)N(CH_3)_2]^{3+}$	2.2, 2.5 (2.1, 2.4)[d]						
$[(NH_3)_5CoOP(OCH_3)_3]^{3+}$	2.0[b]						

[a]0.1 M NaOH except for $[(NH_3)_5CoO_3SCF_3]^{2+}$ where 0.1 M Tris and *Tris*/HClO4 (pH 8.5–9) were used as well. [b]Ref. 2. [c]Ref. 17. [d]Raw results; numbers immediately above are corrected for some C–O cleavage and intramolecular O- to N-urea isomerization (Refs. 2, 13, 14), parallel paths which cannot give rise to anion competition.

Dowex resin and 1 M NaClO4 (pH 3, HClO4) to elute the aniono product and 3 M HCl to elute the aqua ion. All reactions were quenched with 1 M HClO4 to pH ~ 2 after 30 s. Ice jacketed columns were employed for the nitrate and iodide experiments, and light was rigorously excluded for the latter because of the appreciable photosensitivity of the $[(NH_3)_5CoI]^{2+}$ ion.

The following molar extinction coefficients were used to determine the [Co] in eluates: $CoBr^{2+}$, ϵ_{550}^{max} 57.9; CoI^{2+}, ϵ_{382}^{max} 2000; $CoONO_2^{2+}$, ϵ_{500}^{max} 56.5; CoN_3^{2+}, ϵ_{515}^{max} 272; $CoCl^{2+}$, ϵ_{532}^{max} 50.9 (1.0 M NaClO4).

The competition experiments in 1 M NH3/0.1 M NaOH, 2 M NaN3/0.1 M NaOH and 1.00 M NaN3/1.1 M NaOH were performed, in the absence of light [2], as described for acetate ion media. Reaction times were 60 s, except for $[(NH_3)_5CoCl]^{2+}$ in 0.1 M OH$^-$ (5.0 min) and in 1.1 M OH$^-$ (1.0 min).

All of the O-bonded complexes react with 100% Co–O cleavage in base [4], except for $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ [2] and possibly $[(NH_3)_5CoOC(NH_2)N(CH_3)_2]^{3+}$ [13] for which some (2.5%) of the $[(NH_3)_5CoOH]^{2+}$ product arises by C–O bond cleavage. Also, the O-bonded urea complexes lead to a little O- to N-linkage isomerization in 0.1 M OH$^-$ (urea, 7%; Me2urea, 3%) [14]. The deprotonated N-isomers (pK_a ~ 3) are stable in base [13, 14], and hence to avoid elution with the identically charged (2+) competition product during the chromatography, the product mixtures were acidified and/or the pH of the eluent was controlled (≤3). Under these conditions the N-urea isomers protonate and rapidly reisomerize to the O-bonded forms (3+ ions) which elute together with $[(NH_3)_5CoOH_2]^{3+}$ [14]. Their presence in the aqua bands has been corrected for, using the known proportions [14] and the known

molar extinction coefficients [13, 14] for the O-urea complexes.

The competition data (Table I) for the O-urea complexes are corrected for these additional reaction pathways, albeit small contributions, to give the competition between solvent and added anion for the direct ligand substitution process (*i.e.*, Co–O cleavage).

Results and Discussion

The $[(NH_3)_5CoO_3SCF_3]^{2+}$ hydrolyses in base extraordinarily rapidly ($K_{OH} \cong 10^6$ M^{-1} s^{-1}; μ = 1.0 M, 25 °C) [4]. Above pH 8, hydrolysis occurs very largely (>97%) by the [OH$^-$] dependent pathway, despite the high rate of the background spontaneous aquation (k_s = 2.7 × 10^{-2} s^{-1} at 25 °C; k_{OH}[OH$^-$]/k_s = 37 (pH 8), 117 (pH 8.5)) [4, 5]. Also, it is noted that the rate of base hydrolysis of $[(NH_3)_5CoX]^{2+}$ at constant ionic strength is generally independent of the nature of the competing 1$^-$ anion [11].

The triflato complex was hydrolysed in 1 M NaY (Y^{m-} = Cl$^-$, Br$^-$, I$^-$, NO3$^-$) at and above pH 8 using *Tris* (pH ~ 11) or *Tris*/ClO4 (pH ~ 8) to control the [OH$^-$]. The extent of anion competition (Table I) was found to be independent of [OH$^-$] in this range (10^3-fold variation), as expected [8] for reaction occurring exclusively *via* the base catalyzed route. Note that, except for Y^{m-} = NO3$^-$, competition is much higher by this path than by the spontaneous aquation reaction mode [15]. For most of the other nucleophiles (Y^{m-} = F$^-$, CH3CO2$^-$, NH3), the competition could be determined in the usual way ([OH$^-$], 0.1 M) because the products $[(NH_3)_5CoY]^{(n-m)+}$ are

relatively stable towards base. Moreover, we were not limited to the labile triflato complex as reactant, and a range of 2+ and 3+ substrates were examined.

Acetate ion competition was studied in detail since previous reports indicated that competition by this anion was anomalously greater for the 2+ substrate $[(NH_3)_5CoI]^{2+}$ (4.8%) [8] than for the 3+ reactants $[(NH_3)_5CoOP(OCH_3)_2]^{3+}$ (2.0%) [2] and $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ (2.2 [2], 1.8 [16]). This is the reverse of the trend found for N_3^- as a competitor [2, 17] and with a wider range of reactants (1+, 2+ and 3+) [2]. The new results (Table I) for CH_3-CO_2^- competition with a similar wide range of substrates clearly invalidates the previous [8] anomalously high result. A common product distribution (2.2 ± 0.3% $CoO_2CCH_3^{2+}$) pertains for the three 2+ and four 3+ substrates. This common result, independent of the leaving group, is expected for CH_3-CO_2^- and H_2O competing for the common intermediate $[(NH_3)_4(NH_2)Co]^{2+}$.

It is interesting to note that the anticipated slightly higher competition (by ~20%) for the 3+ compared to the 2+ substrates was not observed, although the expected difference (~0.4%, absolutely) would be difficult to distinguish from experimental error (±0.3%). Slightly different results were obtained recently [11] for SO_4^{2-} competition (5.4 ± 0.3% $CoOSO_3^+$, three 3+ reactants; 4.8 ± 0.3%, three 2+ reactants), removing an earlier anomaly [8] similar to that noted for $CH_3CO_2^-$. For systems exhibiting higher anion competition, the small differences between the results for the two sets of differently charged substrates are even clearer. With N_3^-, SCN^- and $S_2O_3^{2-}$ for example, the competition exceeds 10% and the differences are of the order of 2–3% absolutely [2, 10].

There is now a consistency in the anion competition results. Slightly higher competition is observed for more highly charged substrates, irrespective of the competing anion, and this has been interpreted [2] as anion capture by a reactive reduced coordination number intermediate. It reacts with an inherited ion-atmosphere and hence the results show a dependence on the charge of the precursor conjugate base complex $[(NH_3)_4(NH_2)CoX]^{n+}$. Relevant now and to later discussion, it is important to note that the higher anion competition does not correlate with expectations based on considerations of ion-pairing. Several other [2] lines of evidence strongly militate again *direct* anion capture from the ion-paired conjugate base $[(NH_3)_4(NH_2)CoX]^{(n-1)+}Y^{m-}$. For example, the relative magnitude of 2+/1— and 1+/1— ion-pair constants, on both theoretical and experimental grounds, suggest at least twice the abundance of ion-pairs for a 2+ as opposed to a 1+ complex (at $\mu = 1$ M), and hence about twice the extent of anion competition for a given competitor. Clearly this is not the case (Table I). The present and other

data require an intermediate $[(NH_3)_4(NH_2)Co]^{2+}$ derived from the ion-paired conjugate base which must survive for a time sufficient for *some* equilibration of its inherited ion-atmosphere with the bulk solution.

Scrutinizing now the halide ion competition data, the striking result is the remarkable similarity of the numbers (Table I) for Cl^-, Br^- and I^- and the lack of competition afforded by F^-. For the nucleophilic and classically associative reactions at square planar Pt(II) centres there is a spread in rates covering 3 to 4 orders of magnitude, $I^- \gg Br^- > Cl^- \gg F^-$, iodide ion demonstrating pronounced nucleophilicity. Given that the base catalyzed Co(III) hydrolysis reactions involve a reduced coordination number intermediate, the present data support strongly a case for the decay of this reactive $[(NH_3)_4(NH_2)Co]^{2+}$ intermediate to the $[(NH_3)_5CoY]^{(n-m)+}$ product at a rate approaching diffusion control, the major component of the activation energy arising from the process of abstraction of the competing anion Y^{m-} from the solvation sheath, with little if any contribution from bond making with Co(III) by incoming Y^{m-} or H_2O in this step [1]. The solvation (free) energies for I^-, Br^-, Cl^- in water are very similar ($Cl^- \gtrsim Br^- \gtrsim I^-$), while the much smaller anion F^- is strongly solvated, and these trends correlate nicely with the observed competition.

While F^- competition can be directly measured, competition for the isoelectronic OH^- ion cannot. This is so because OH^- and H_2O entry afford the common product $[(NH_3)_5CoOH]^{2+}$. However, Green and Taube [18] found that OH^- (0.1 M) does not compete significantly with H_2O by virtue of the pronounced equilibrium isotope effect for the $^{16}OH^- + {}^{18}OH_2 \rightleftarrows {}^{18}OH^- + {}^{16}OH_2$ reaction; $^{18}OH_2/$ $^{16}OH_2$ capture in preference to $^{18}OH^-/{}^{16}OH^-$ is effectively recorded in the $^{18}O/{}^{16}O$ ratio of the $[(NH_3)_5CoOH]^{2+}$ product which, on the time scale of the experiments, does not exchange its oxygen with the OH^-/OH_2 bulk. Subsequently, Sargeson *et al.* [8] concluded that OH^- did not compete effectively, even up to concentrations of 1 M. They noted that in concurrent N_3^-/OH_2 competition experiments for the reaction of $[(NH_3)_5CoI]^{2+}$ in $OH^-/$ OH_2/N_3^-, N_3^- competition was unaffected by the $[OH^-]$. We have conducted similar experiments for another 2+ ion and one 3+ ion (Table II) to support this important result. The sensitivity of the experiments is such that up to 3% OH^- competition in 1 M OH^- would go undetected. The result is significant since the isoelectronic and relatively small F^- and OH^- ions are both strongly H-bonded to H_2O, and therefore are not readily abstracted by the $[(NH_3)_4(NH_2)Co]^{2+}$ intermediate from its solvation sheath, strengthening the case for a strong correlation between anion competition and anion solvation.

TABLE II. Product Distributions for the Base Hydrolysis of $[(NH_3)_5CoCl]^{2+}$ and $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ in N_3^-/OH^- at 25 °C.

Reactant	Conditions	μ, M	CoN_3^{2+}		R^a, M^{-1}
$(NH_3)_5CoCl^{2+}$	$1.0\ M\ N_3^-/0.1\ M\ OH^-$	1.1	8.5,	8.5	0.093
	$2.0\ M\ N_3^-/0.1\ M\ OH^-$	2.1	14.1,	14.3	0.083
			$(14.5)^b$		$(0.085)^b$
	$1.0\ M\ N_3^-/1.1\ M\ OH^-$	2.1	8.1,	7.9	0.087
	$1.0\ M\ N_3^-/1.0\ M\ ClO_4^-/0.1\ M\ OH^-$	2.1	8.0,	8.0	0.087
			$(8.1)^b$		$(0.088)^b$
$(NH_3)_5CoOS(CH_3)_2^{3+}$	$1.0\ M\ N_3^-/0.1\ M\ OH^-$	1.1	12.5	12.3	0.142
			$(12.8)^{b,c}$		$(0.147)^{b,c}$
			$(12.3)^d$		$(0.140)^d$
	$2.0\ M\ N_3^-/0.1\ M\ OH^-$	2.1	21.1,	22.1	0.138
	$1.0\ M\ N_3^-/1.1\ M\ OH^-$	2.1	12.0,	12.2	0.138
	$1.0\ M\ N_3^-/1.0\ M\ ClO_4^-/0.1\ M\ OH^-$	2.1	11.7,	12.1	0.135

^{a}R = $[CoN_3^{2+}]/[CoOH^{2+}][N_3^-]$, M^{-1}. ^{b}Ref. 17. ^{c}Ref. 14. ^{d}Ref. 2.

Ammonia, extremely soluble in water, is well solvated (H-bonded) and hence unlikely to be a good competitor. The results (Table I) confirm this; there is no detectable competition ($\leqslant 0.2\%$). On a statistical basis alone, 1.8% competition would be expected in $1\ M$ aqueous NH_3. Even in the base hydrolysis reaction of *cis*-$[Co(en)Cl(NH_2(CH_2)_2NH_2)]^{2+}$, the dangling amine does not compete with water when one would expect a considerably enhanced prospect [19].

Finally, it is especially interesting to note the competition results for Cl^- and NO_3^-. Nitrate ion, a very weak base and poorly solvated by water, is captured effectively (12.1% $CoNO_3^{2+}$, for $1\ M\ NO_3^-$). Indeed, on a mole for mole basis, it is the best competitor observed to date, SCN^- excepted, and it is especially informative to compare the capacity of these two ions Cl^- and NO_3^- to capture the supposed $[(NH_3)_5Co]^{3+}$ intermediate formed in acid hydrolysis (induced aquation). Their *relative* effectiveness ($NO_3^- > Cl^-$) in both kinds of hydrolysis reaction is worthy of note; R values indicate a ratio of ~1.9:1 in acid hydrolysis [3, 6, 7] remarkably similar to that found here for base hydrolysis, 1.8:1. Furthermore, their absolute effectiveness, approximately 3.5 times better in acid hydrolysis as opposed to base hydrolysis, very nicely correlates with the formal charge of the respective intermediates 3+ and 2+ respectively. The relative extents of competition correspond to those anticipated for the ionic atmospheres appropriate to 3+ and 2+ reactants. The former should be approximately 2–3 fold richer in anion than the latter on a statistical basis, as estimated from known ion-pair constants for typical 3+ and 2+ complex cations.

This simple rationalization of the competition results for two quite different hydrolysis processes, acid and base hydrolysis, obviously requires testing for a wider range of competing anions.

A particularly interesting question is the relative effectiveness of each 'end' of ambidentate nucleophiles such as SCN^- (S or N capture), NO_2^- (N, O) and $S_2O_3^{2-}$ (S, O) in capturing the $[(NH_3)_5Co]^{3+}$ and $[(NH_3)_4(NH_2)Co]^{2+}$ intermediates, a problem free of the complication of the extent of ion-pairing which clearly is related to the formal charge, and reports on some of these studies should appear shortly [9, 10].

One outstanding difference between acid and base hydrolysis is the stereochemistry of substitution [1, 15]; $[(NH_3)_5Co]^{3+}$ reacts with retention (specific ND_3 labelling experiments) while *trans*-^{15}N labelled $[(NH_3)_4(NH_2)Co]^{2+}$ adds nucleophiles Y^{m-} to give a mixture of *cis*- and *trans*-$[(NH_3)_4(^{15}NH_3)CoY]^{(n-m)+}$. The fact that this difference does not appear to be reflected in the extent of anion competition suggests that the respective intermediates, although both short lived, survive at least for a time sufficient for their rotation with respect to the solvation sheath, such that the anion (or solvent) can enter adjacent to or remote from the leaving group. As we have argued, they appear to survive even for a time sufficient for *some* equilibration of their ionic atmosphere with the bulk solution.

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