Contribution from the Chemistry Department, University of New South Wales, Faculty of Military Studies,
Royal Military College, Duntroon, Canberra, ACT, 2600, Australia

(Fluorosulfonato)pentaamminecobalt(III)

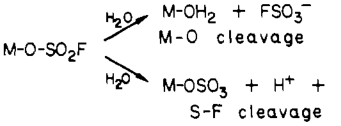
W. G. JACKSON* and C. M. BEGBIE

Received August 12, 1980

The labile complex $[Co(NH_3)_5O_3SF](ClO_4)_2$ has been synthesized and its rate of hydrolysis measured ($k = 2.2 \times 10^{-2}$ s^{-1}, 0.01 M $HClO_4$, 25 °C). It solvolyzes with Co–O cleavage to give $[Co(NH_3)_5(solvent)]^{3+}$ and concurrently with S–F cleavage to yield $[Co(NH_3)_5F]^{2+}$ and SO_3 rather than $[Co(NH_3)_5OSO_3]^+$ and F^-. The proportion of $[Co(NH_3)_5F]^{2+}$ is strongly solvent dependent (H_2O or 0.01 M $HClO_4$, 26%; Me_2SO, 44%; 0.01 M NaOH, ≤0.4%). It is proposed that the O-bonded $[Co(NH_3)_5O_3SF]^{2+}$ solvolyzes with Co–O rupture competitively with isomerization to an F-bonded form, which cleaves S–F to produce $[Co(NH_3)_5F]^{2+}$. Other plausible mechanisms are considered. Anion competition is observed by the Co–O cleavage pathway (1 M HCl, 3.3% $[Co(NH_3)_5Cl]^{2+}$; 1 M NaN_3, 0.1 M NaOH, 9.4% $[Co(NH_3)_5N_3]^{2+}$), and the amount of competition is similar to that of the analogous reactions of the labile species $[Co(NH_3)_5OClO_3]^{2+}$ and $[Co(NH_3)_5O_3SCF_3]^{2+}$. Finally, N_3^- competition (5.1%) is reported for the base hydrolysis of $[Co(NH_3)_5F]^{2+}$ in 1 M NaN_3, and the mechanistic implications of this anomalously low result are considered.

Introduction

Fluorosulfonic acid is the strongest simple acid known.[1] Its conjugate base FSO_3^- hydrolyses slowly to SO_4^{2-} and F^- in neutral to basic solution but the rate of hydrolysis of the parent acid must be extremely rapid since the hydrolysis of FSO_3^- is appreciably acid catalyzed.[2] The reactive species could be FSO_3H or $HFSO_3H$. A metal ion can mimic a proton, and if the metal ion is relatively inert to substitution, information on the mechanism of hydrolysis can be obtained by examining the rate of hydrolysis of a fluorosulfonato complex and the distribution of the complex ion products M–OSO_3 and M–OH_2 (eq 1). The extremely weak base FSO_3^- is a very poor ligand and few complexes are known.[1] However, success in the isolation of pentaamminecobalt(III) complexes of feebly basic anions derived from other strong acids, $HClO_4$[3] and CF_3SO_3H,[4,5] prompted an attack on the synthesis of $[Co(NH_3)_5O_3SF]^{2+}$. We describe here the preparation and characterization of $[Co(NH_3)_5O_3SF](ClO_4)_2$ and its rate and mode of aquation (Co–O or S–F cleavage). Also described are anion competition studies on the spontaneous aquation (1 M HCl) and base hydrolysis (1 M NaN_3) reactions, for comparison with results for other unusually labile $Co(NH_3)_5$ systems.[4-6] Moreover, fluorosulfonic acid is a known fluorinating agent,[1] and this work has uncovered analogous reactions for the FSO_3^- cobalt complex which intramolecularly transfers F^- to the metal. Likely mechanisms for F^- transfer are therefore considered. Finally, this work required the development of a procedure for separating $[Co(NH_3)_5F]^{2+}$ from similar 2+ pentaamminecobalt(III) cations, and in passing we have applied this method successfully to a study of N_3^- competition in the slow base hydrolysis reaction of $[Co(NH_3)_5F]^{2+}$. The results and their implications are reported herein.



(1)

Experimental Section

Visible spectra were recorded on a Cary 118C instrument thermostated to $25.0_0 \pm 0.0_5$ °C. ^1H NMR spectra were measured in dry Me_2SO-d_6 (99.8% D, CEA-France) with an internal $SiMe_4$ reference on a Varian T60 spectrometer at 35 °C. Dimethyl sulfoxide (BDH) was purified by drying (4-Å molecular sieves) and distillation under vacuum. Fluorosulfonic acid (Fluka) was distilled twice at 760 mm (bp 162.7 °C) with use of an all-glass apparatus protected from moisture with a SiO_2 drying tube. All other chemicals were AnalaR grade.

Crude $[Co(NH_3)_5F](NO_3)_2$ prepared as described[7] was freed of a substantial $[Co(NH_3)_5OH_2]^{3+}$ impurity by sorption on and elution (0.5 M $NaNO_3$) from Sephadex SP C25 (Na^+ form) cation-exchange resin. The fluoro complex eluted first, and long fine pink needles of pure $[Co(NH_3)_5F](NO_3)_2$ deposited from the chilled eluate (0 °C, 24 h). This was converted to the diperchlorate salt by anion exchange on Dowex 1-X8 resin (200–400 mesh, Cl^- form) and treatment of the resultant concentrated aqueous solution of the Cl^- salt with cold saturated aqueous $LiClO_4$. The crystals were collected after 12 h at 5 °C, washed with methanol and ether, and air-dried (ϵ_{515}^{max} = 46.8, H_2O). Anal. Calcd for $[Co(NH_3)_5F](ClO_4)_2$: H, 4.18; N, 19.35; F, 5.25; Cl, 19.59. Found: H, 3.99; N, 19.18; F, 5.30; Cl, 19.44. ^1H NMR spectrum (in Me_2SO-d_6): δ 3.63 (12 H, cis NH_3), 2.20 (3 H, trans NH_3). This spectrum also confirmed the absence of $[Co(NH_3)_5OH_2](ClO_4)_3$ and lattice water.[4]

$[Co(NH_3)_5O_3SF](ClO_4)_2$. Recrystallized $[Co(NH_3)_5Cl]Cl_2$ (15.0 g, 0.06 mol)[4] was added in ~1-g portions over 20 min to an excess of well-stirred redistilled FSO_3H (50 mL, 86.5 g, 0.865 mol) in a fume hood. Over this period the mixture was warmed slowly to 60–70 °C. Copious fumes of HCl were evolved, and the gas evolution was completed by heating the deep pink thin syrupy solution to 90 °C (30 min). This was cooled and added dropwise to excess well stirred dry (Na) ether (2 L) to produce a fine pink solid. This was washed by trituration with several changes of ether and then filtered to give an air-stable solid, free of FSO_3H (25.0 g, 95% yield). Crude $[Co(NH_3)_5O_3SF](FSO_3)_2$ so obtained gave a negative test for Cl^- (Ag^+). It was recrystallized by extraction with water (5 °C) on a filter into ice/$HClO_4$ (70%) at ~40 °C, which quickly produced fine pink plates of pure $[Co(NH_3)_5O_3SF](ClO_4)_2$ (21 g, 80% overall yield). Anal. Calcd for $[Co(NH_3)_5O_3SF](ClO_4)_2$: H, 3.42; N, 15.85; S, 7.25; F, 4.30; Cl, 16.04. Found: H, 3.49; N, 15.63; S, 7.40; F, 4.21; Cl, 16.10. The ^1H NMR spectrum in dry Me_2SO-d_6 confirmed the absence of bound and lattice water.[4]

The synthesis above was repeated with use of $[Co(NH_3)_5O_3SCF_3](CF_3SO_3)_2$[4,5] in place of $[Co(NH_3)_5Cl]Cl_2$, and it yielded pure $[Co(NH_3)_5O_3SF](ClO_4)_2$ in similar yield. $[Co(NH_3)_5OH_2]Cl_3$ in hot FSO_3H also gave $[Co(NH_3)_5O_3SF]^{2+}$ but contaminated with a little $[Co(NH_3)_5OSO_3H](FSO_3)_2$, which was difficult to remove completely by recrystallization (vide infra).

$[Co(NH_3)_5O_3SF](ClO_4)_2$ is stable indefinitely in the solid state in the absence of moisture.

Aquation Kinetics. The rate of disappearance of $[Co(NH_3)_5O_3SF](ClO_4)_2$ was followed spectrophotometrically at 540 nm in 0.010 M $HClO_4$ at 25.0 °C. Absorbance vs. time traces were commenced in <5 s after dissolution by using a device described elsewhere[4] whereby the solid complex was extracted by a rapid flow of preequilibrated solvent. It was passed through a frit and then mixed to avoid Schlieren

---

[1] A. W. Jache, *Adv. Inorg. Chem. Radiochem.*, **16**, 177 (1974), and references therein.

[2] M. M. Jones and W. L. Lockhart, *J. Inorg. Nucl. Chem.*, **30**, 1237 (1968), and references therein.

[3] J. MacB. Harrowfield, A. M. Sargeson, B. Singh, and J. C. Sullivan, *Inorg. Chem.*, **14**, 2864 (1975).

[4] D. A. Buckingham, P. J. Cresswell, W. G. Jackson, and A. M. Sargeson, *Inorg. Chem.*, in press.

[5] N. E. Dixon, W. G. Jackson, M. J. Lancaster, G. A. Lawrance, and A. M. Sargeson, *Inorg. Chem.*, **20**, 470 (1981).

[6] N. E. Dixon, W. G. Jackson, W. Marty, and A. M. Sargeson, submitted for publication in *Inorg. Chem.*

[7] F. Basolo and R. K. Murmann, *Inorg. Synth.*, **4**, 171 (1953).

0020-1669/81/1320-1654$01.25/0

effects and to ensure that fine particles of undissolved complex did not enter the spectrophotometer cell. First-order rate constants were calculated in the usual way; $k = (2.22 \pm 0.06) \times 10^{-2}$ s^{-1}, the mean and standard deviation of four determinations.

Competition Experiments. The usual techniques[4,6,8-10] were modified to accommodate the high reactivity of $[Co(NH_3)_5O_3SF]^{2+}$ and the need to chromatographically separate products that have the same charge and that do not separate on the Dowex 50W-X2[8,9] or Sephadex SP C25[10] cation-exchange resins usually employed. All the reactions and separations described below were routinely carried out in the dark; this was especially important where the product $[Co(NH_3)_5N_3]^{2+}$ was involved since it quickly decays photochemically, particularly in basic solution.[4]

1. Base Hydrolysis of $[Co(NH_3)_5O_3SF]^{2+}$ in 1 M NaN_3. Weighed solid complex $[Co(NH_3)_5O_3SF](ClO_4)_2$ (~0.75 g) was dissolved directly in 1.00 M NaN_3 (50 mL), which was 0.10 M in NaOH. After 3.0 min at 25 °C, NH_4ClO_4 (1 g) was added to reduce the pH and the mixture diluted to ~500 mL with ice water and then sorbed on a prewashed (H_2O, followed by 1 M NaCl) Biorex 70 (Na^+ form, 200–400 mesh) column. The column was rinsed with water and then eluted with NaCl. Four cleanly separated bands were obtained in the following order: $[Co(NH_3)_5OSO_3]^+$ (trace only; 1.0 M NaCl), $[Co(NH_3)_5N_3]^{2+}$ (1.5 M NaCl), $[Co(NH_3)_5F]^{2+}$ (trace only; 1.5 M NaCl), and $[Co(NH_3)_5OH_2]^{3+}$. The first three bands were eluted completely from the column and acidified (pH 3, $HClO_4$), and their volumes and absorption spectra recorded without delay. It proved convenient to remove $[Co(NH_3)_5OH_2]^{3+}$ by segmenting the column and extracting the resin with 1.5 M HCl. The cobalt in the four fractions was determined with use of the following extinction coefficients[8,9] measured on authentic samples in the same media: $[Co(NH_3)_5OSO_3]^+$, ϵ_{515} 61.0; $[Co(NH_3)_5N_3]^{2+}$, ϵ_{516} 272; $[Co(NH_3)_5F]^{2+}$, ϵ_{515} 46.8; $[Co(NH_3)_5OH_2]^{3+}$, ϵ_{492} 47.7. The experiment was repeated three times, and the average recovery of cobalt exceeded 98%.

2. Acid Hydrolysis of $[Co(NH_3)_5O_3SF]^{2+}$ in 1 M HCl. Weighed samples of $[Co(NH_3)_5O_3SF](ClO_4)_2$ (~0.75 g) were dissolved directly in 1.00 M HCl (30 mL, Volucon) at 25 °C. After 20 min, the solution was diluted with water (400 mL, 5 °C) containing Na_2HPO_4 (8.5 g) to buffer it to pH ~7. The mixture was sorbed on Biorex 70, washed, and eluted with NaCl as above. The four clear bands $[Co(NH_3)_5OSO_3]^+$ (trace only; 1.0 M NaCl), $[Co(NH_3)_5Cl]^{2+}$ (1.5 M NaCl), $[Co(NH_3)_5F]^{2+}$ (1.5 M NaCl), and $[Co(NH_3)_5OH_2]^{3+}$ (1.5 M HCl) were obtained, and their cobalt contents were estimated spectrophotometrically as in section 1 ($[Co(NH_3)_5Cl]^{2+}$, ϵ_{533} 50.5). In duplicate experiments the cobalt recovery exceeded 99%.

3. $[Co(NH_3)_5O_3SF]^{2+}$ in H_2O, 0.01 M $HClO_4$, 0.01 M NaOH, or Me_2SO. Weighed complex samples (0.5–1.0 g) were dissolved in solvent (35–50 mL) at 25 °C and allowed to react for 2–3 min (0.01 M NaOH) or 20 min (H_2O, 0.01 M $HClO_4$, Me_2SO) before dilution (H_2O, 5 °C, 300–500 mL) and sorption on Sephadex SP C25 (Na^+ form) cation-exchange resin. For the experiment in 0.01 M NaOH, $HClO_4$ (5 M, 5 °C) was added to pH ~1 before the dilution step. Elution with $NaClO_4$ or NaCl gave first $[Co(NH_3)_5OSO_3]^+$ (0.1 M) followed by $[Co(NH_3)_5F]^{2+}$ (0.2 M) and finally orange $[Co(NH_3)_5OH_2]^{3+}$ or pink $[Co(NH_3)_5(OSMe_2)]^{3+}$ (0.4 M). The cobalt in the eluates was determined spectrophotometrically as above. Some aquation of $[Co(NH_3)_5(OSMe_2)]^{3+}$ to give $[Co(NH_3)_5OH_2]^{3+}$ occurred in the time of elution and although these complexes can be separated on Sephadex and the Me_2SO complex eluted intact by lowering the temperature, it was convenient to elute them together and determine the cobalt as total $[Co(NH_3)_5OH_2]^{3+}$. This was achieved by adding NaOH (1 M) to the combined band such that $[OH^-] = 0.1$ M, allowing 5 min (25 °C) for complete base hydrolysis[6] to $[Co(NH_3)_5OH]^{2+}$, and finally reacidifying to pH 1 with HCl or $HClO_4$. The three experiments were each performed in triplicate; the cobalt recovery generally exceeded 98%.

In other experiments samples of crude $[Co(NH_3)_5O_3SF](FSO_3)_2$ and $[Co(NH_3)_5O_3SF](ClO_4)_2$ repeatedly recrystallized from water/$HClO_4$ were reacted in 0.01 M NaOH and the products separated and estimated as above. Also two more competition experiments on pure $[Co(NH_3)_5O_3SF](ClO_4)_2$ in 1.00 M NaN_3/0.10 M NaOH were carried out as described in secion 1, but the products were separated on Sephadex as above.

The rapid reaction (<2 min, 35 °C) of $[Co(NH_3)_5O_3SF](ClO_4)_2$ in Me_2SO-d_6 was followed also by ^1H NMR spectroscopy. The trans NH_3 signals of the products $[Co(NH_3)_5F]^{2+}$ (δ 2.20) and $[Co(NH_3)_5OS(CD_3)_2]^{3+}$ (δ 2.56) are distinct, and proton integration indicated ~45% fluoro complex and ~55% Me_2SO complex. The H_2O signal (δ 3.40) of added water (trace) was shifted downfield 3–4 ppm depending upon [Co], indicative of the reaction with the $(CD_3)_2SO(SO_3)$ product to give HSO_4^-.

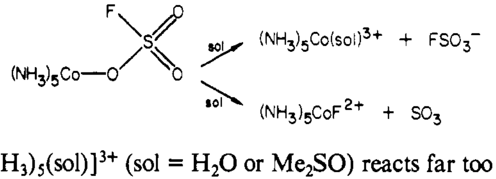
4. Base Hydrolysis of $[Co(NH_3)_5F](ClO_4)_2$ in 1 M NaN_3. Weighed complex samples (~0.5 g) were allowed to react 25–35 min in 1.00 M NaN_3/0.10 M NaOH (~50 mL) at 25 °C. The mixture was quenched with water (400 mL) containing NH_4ClO_4 or NH_4Cl (1 g), and the components $[Co(NH_3)_5N_3]^{2+}$, unreacted $[Co(NH_3)_5F]^{2+}$, and $[Co(NH_3)_5OH_2]^{3+}$ were separated on Biorex 70 and their cobalt contents determined as described in section 1. The cobalt recovery in four experiments ranged from $98^1/_2$ to $101^1/_2$%.

5. Other Separations. Mixtures of authentic samples of the complex 2+ ions $[Co(NH_3)_5Br]^{2+}$, $[Co(NH_3)_5Cl]^{2+}$ or $[Co(NH_3)_5N_3]^{2+}$, and $[Co(NH_3)_5F]^{2+}$ or $[Co(NH_3)_5ONO_2]^{2+}$ were found to separate readily on a 8 × 3 cm Biorex 70 (Na^+ form, 200–400 mesh) column with 1.0–1.5 M NaCl eluant (pH ~6). Only on longer columns could the azido be separated from either of the halo complexes, while the nitrato and fluoro complexes still eluted together. The bromo could be separated from the chloro ion.

Results

Reaction of $[Co(NH_3)_5O_3SF]^{2+}$ in H_2O and Me_2SO. The rate of disappearance of the FSO_3^- complex in 0.01 M $HClO_4$ at 25 °C was followed spectrophotometrically at 540 nm, and the value $k = (2.22 \pm 0.06)\ 10^{-2}$ s^{-1} was obtained ($t_{1/2} = 31$ s). In Me_2SO the reaction was found to be essentially complete ($>4t_{1/2}$) after 2 min (^1H NMR spectrum), which indicates that the reaction is at least as rapid in Me_2SO.

Chromatography of aged H_2O or Me_2SO solutions of $[Co(NH_3)_5O_3SF]^{2+}$ revealed considerable (25–45%) and apparently variable amounts of $[Co(NH_3)_5F]^{2+}$, which was believed at first to be an impurity in the isolated $[Co(NH_3)_5O_3SF](ClO_4)_2$. Considerable amounts (40–50%) of $[Co(NH_3)_5F]^{2+}$ were apparent also from the ^1H NMR spectrum of the FSO_3^- complex in Me_2SO-d_6. However, in quantitative experiments, different but reproducible proportions of $[Co(NH_3)_5F]^{2+}$ were found in the H_2O (26.2 ± 0.5 (3)%) and Me_2SO (44.0 ± 1.3 (3)%) reactions. The amount of fluoro product found in water is similar to the amounts found in 0.01 M $HClO_4$ (25.8 ± 0.4 (2)%) and 1 M HCl (24.3 ± 0.1 (2)%) (Table I). The calculated cobalt recoveries in these and other experiments based on the molecular weight for the pure FSO_3^- complex (442.1) were close to the expected 100% in all cases ($\sum$Co, Table I), but this is not an especially sensitive criterion of purity; the calculated cobalt recoveries are about 90% for a FSO_3^- complex containing a 40% F^- complex impurity. However, the elemental analyses, particularly for sulfur, indicated that the FSO_3^- complex contained little if any $[Co(NH_3)_5F](ClO_4)_2$ (calculated for F^- complex 0%; calculated for FSO_3^- complex 7.25%; found 7.40%). The results therefore indicate that all the $[Co(NH_3)_5F]^{2+}$ arises *during* the reaction in H_2O, aqueous acid, or Me_2SO. $[Co(NH_3)_5OH_2]^{3+}$ or $[Co(NH_3)_5OSMe_2]^{3+}$ is produced along with $[Co(NH_3)_5F]^{2+}$, and this other reaction path corresponds to Co–O cleavage in $[Co(NH_3)_5OS_3F]^{2+}$ (eq 2). It is important to note that



(2)

$[Co(NH_3)_5(sol)]^{3+}$ (sol = H_2O or Me_2SO) reacts far too slowly with F^- or FSO_3^- to account for the production of the $[Co(NH_3)_5F]^{2+}$ by fast anation subsequent to a solvolysis step.

---

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

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

[10] D. A. Buckingham, W. Marty, and A. M. Sargeson, *Inorg. Chem.*, **13**, 2165 (1974).

Table I. Product Distribution Data for $[Co(NH_3)_5O_3SF]^{2+}$ at 25 °C

H_2O

product	% Co			av % Co[c]
	1[a]	2	3	
$CoOSO_3^+$	1.3	0.7	2.2	1.4 ± 0.7
CoF^{2+}	26.1	25.2	25.4	26.2 ± 0.5
$CoOH_2^{3+}$	70.3	72.0	70.3	72.4 ± 0.9
ΣCo[b]	97.6	97.9	97.9	

0.01 M $HClO_4$

product	% Co		av % Co[c]
	1	2	
$CoOSO_3^+$	1.0	1.5	$1.3 \pm 0.2_5$
CoF^{2+}	25.8	24.8	25.8 ± 0.4
$CoOH_2^{3+}$	71.7	71.5	73.0 ± 0.2
ΣCo[b]	98.5	97.8	

1.00 M HCl

product	% Co		av % Co[c]
	1	2	
$CoOSO_3^+$	1.0	1.2	1.1 ± 0.1
$CoCl^{2+}$	2.5	2.2	$2.4 \pm 0.1_5$
CoF^{2+}	24.3	24.1	24.3 ± 0.1
$CoOH_2^{3+}$	71.4	72.0	72.2 ± 0.2
ΣCo[b]	99.2	99.5	

1.00 M NaN_3, 0.10 M NaOH

product	% Co				av % Co[c]
	1	2	3	4	
$CoOSO_3^+$	1.5	0.6	1.5	1.2	1.2 ± 0.4
CoN_3^{2+}	9.1	9.3	9.2	9.5	9.4 ± 0.2
CoF^{2+}	0.5	0.5			0.5 ± 0.1
$CoOH_2^{3+}$	87.9	88.1	86.8	87.1	89.1 ± 0.3
ΣCo[b]	99.0	98.5	97.5	97.8	

0.10 M NaOH

product	% Co		av % Co[c]
	1	2	
$CoOSO_3^+$	0.8	0.5	0.7 ± 0.2
CoF^{2+}	0.5	0.3	0.4 ± 0.1
$CoOH_2^{3+}$	96.8	96.2	99.0 ± 0.2
ΣCo[b]	98.0	97.0	

Me_2SO

product	% Co			av % Co[c]
	1	2	3	
$CoOSO_3^+$	1.9	1.2	3.3	2.2 ± 1.1
CoF^{2+}	41.9	43.8	44.3	44.0 ± 1.3
$CoOSMe_2^{3+}$	54.4	53.0	51.1	53.7 ± 1.8
ΣCo[b]	98.3	98.0	98.7	

[a] Experiment number (1–4). [b] Cobalt recovery. [c] Calculated by normalizing ΣCo to 100%.

The SO_3 eliminated in these reactions is consumed by solvent to give HSO_4^- in water and the known[11] $Me_2S^+OSO_3^-$ in Me_2SO.

Base Hydrolysis of $[Co(NH_3)_5O_3SF]^{2+}$. Strikingly different results to aqueous acid or Me_2SO were found for 0.1 M OH^-. The product is very largely $[Co(NH_3)_5OH_2]^{3+}$, 99% (Table I). A trace of $[Co(NH_3)_5OSO_3]^+$ was found in this as well as in the H_2O and Me_2SO experiments above (Table I). It is difficult to see how $[Co(NH_3)_5OSO_3]^+$ can arise in the Me_2SO reaction, and it therefore seems likely that the sulfato complex is a low-level impurity in the recrystallized FSO_3^- complex, particularly since we have shown that crude samples contain up to 5% $[Co(NH_3)_5OSO_3H](FSO_3)_2$. Both $[Co(NH_3)_5OSO_3]^+$ and $[Co(NH_3)_5F]^{2+}$ are essentially unreactive to 0.1 M OH^- in the time scale of the present base hydrolysis experiments (~2 min, 25 °C).[12,13] Therefore no more than the observed 0.7% $[Co(NH_3)_5OSO_3]^+$ or 0.4% $[Co(NH_3)_5F]^{2+}$ is produced in 0.1 M OH^-. This result establishes clearly that the isolated $[Co(NH_3)_5O_3SF](ClO_4)_2$ contains negligible amounts of fluoro or sulfato complex in accord with the conclusion reached in the previous section.

Table II. Azide Competition Data for the Base Hydrolysis of $[Co(NH_3)_5F]^{2+}$ at 25 °C, in 1.00 M NaN_3 and 0.1 M NaOH

expt no.	% CoF^{2+}	% CoN_3^{2+}	% $CoOH_2^{3+}$	% ΣCo[a]	$10^2 \times [CoN_3^{2+}]/([CoN_3^{2+}] + [CoOH_2^{3+}])$[b]
1	78.8	1.1_2	21.7	101.6	4.9_1
2	75.3	1.2_6	21.8	98.4	5.3_6
3	77.1	1.1_7	21.4	99.7	5.1_5
4	77.4	1.2_0	23.2	101.8	5.0
average	76.9 ± 0.7	$1.1_9 \pm 0.0_6$	22.7 ± 0.7		5.1 ± 0.2

[a] Cobalt recovery. [b] Calculated by normalizing ΣCo to 100%.

The background aquation rate ($k = 2.2_2 \times 10^{-2}$ s^{-1}) of $[Co(NH_3)_5O_3SF]^{2+}$ was too fast for a kinetic study of the base hydrolysis reaction with the equipment available, but by analogy with $[Co(NH_3)_5O_3SCF_3]^{2+}$ ($k_{OH} \approx 10^6$ M^{-1} s^{-1}), of comparable lability in acid solution,[4] it seemed certain that in 0.1 M OH^- base hydrolysis would be the dominant reaction pathway (>99%). This conclusion is reinforced by the product distribution results; some 26% $[Co(NH_3)_5F]^{2+}$ is produced in H_2O yet ≤0.4% in 0.1 M NaOH.

Anion Competition. When $[Co(NH_3)_5O_3SF]^{2+}$ is hydrolyzed in 1.00 M HCl at 25 °C, $[Co(NH_3)_5Cl]^{2+}$ (2.4%, Table I) is directly formed along with aqua (72%) and fluoro (24%) complexes. When we correct for the pathway which produces $[Co(NH_3)_5F]^{2+}$ and the trace amount of sulfato complex found (~1%), these figures adjust to 3.3% $[Co(NH_3)_5Cl]^{2+}$ and 96.7% $[Co(NH_3)_5OH_2]^{3+}$ for the cobalt–oxygen cleavage path.

Similarly, base hydrolysis of $[Co(NH_3)_5O_3SF]^{2+}$ in 1 M N_3^- at 25 °C leads to anion competition by the Co–O cleavage pathway (9.4%, Table I).

Base Hydrolysis of $[Co(NH_3)_5F]^{2+}$ in 1 M N_3^-. The rate of base hydrolysis ($k_{OH} = 0.013$ M^{-1} s^{-1}, $t_{1/2} \approx 9$ min in 0.1 M OH^- at $\mu = 0.1$, 25 °C)[12] was too slow to permit the usual competition experiments. However it is possible to measure the anion competition, provided unreacted $[Co(NH_3)_5F]^{2+}$ can be separated from the small amount of acido product and provided the latter can be determined accurately.[14] Azide ion was a particularly suitable competitor because it is intensely absorbing (ϵ_{515} 272) and hence easily estimated at low levels and because it is relatively stable in base, provided it is kept in the dark.[4] We carried out these experiments using Biorex 70 cation-exchange resin to achieve the desired $[Co(NH_3)_5N_3]^{2+}$ and $[Co(NH_3)_5F]^{2+}$ separation. $[Co(NH_3)_5F]^{2+}$ was allowed to react in 0.1 M OH^- for as long as possible (~30 min),[15] and then, after acid quenching, the azido and aqua products were separated from a substantial amount of

---

[11] T. E. Varkey, G. F. Whitfield, and D. Swern, *J. Org. Chem.*, **39**, 3365 (1974).

[12] M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).

[13] L. L. Po and R. B. Jordan, *Inorg. Chem.*, **7**, 526 (1968).

[14] The experiments can be done by the usual procedure by first separating $[Co(NH_3)_5OH_2]^{3+}$ from a $[Co(NH_3)_5F]^{2+}$ and $[Co(NH_3)_5N_3]^{2+}$ mixture and then selectively nitrosating the azido complex component to give $[Co(NH_3)_5OH_2]^{3+}$ and repeating the chromatography. The direct separation described here is obviously advantageous since there is only ~1% azido complex.

[15] Decomposition of $[Co(NH_3)_5OH]^{2+}$ occurs in 0.1 M OH^- at 25 °C at times longer than 30 min (see ref 6).

unreacted fluoro complex (~75%). When we correct for the incomplete reaction, the competition figure for the base hydrolysis of $[Co(NH_3)_5F]^{2+}$ in 1.00 M N_3^- is 5.1 ± 0.2% (Table II).

Discussion

Synthesis and Properties of $[Co(NH_3)_5O_3SF](ClO_4)_2$. This complex was easily prepared by acid-catalyzed solvolysis of $[Co(NH_3)_5X]^{n+}$ ($X = Br^-, Cl^-, OH_2, N_3^-, OSO_2CF_3^-$) in neat FSO_3H. The chloro complex route was the most convenient since gaseous HCl was readily removed:

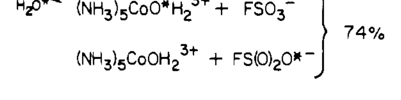
$$[(NH_3)_5CoCl]Cl_2 \xrightarrow[\Delta]{FSO_3H} [(NH_3)_5CoO_3SF](FSO_3)_2 + 3HCl\uparrow$$

The method is similar to that employed[5] for the synthesis of $[Co(NH_3)_5O_3SCF_3](CF_3SO_3)_2$, where the acid CF_3SO_3H is sufficiently strong to protonate Cl^-. Note that the method fails for the synthesis of $[Co(NH_3)_5OClO_3]^+$ from $[Co(NH_3)_5Cl]Cl_2$ in $HClO_4$ (70%) presumably because the first formed $[Co(NH_3)_5Cl](ClO_4)_2$ is insoluble in the cold; *heating is hazardous*. By a generally less convenient method, utilizing a similar principle, $[Co(NH_3)_5Br]Br_2$ can be prepared from $[Co(NH_3)_5Cl]Cl_2$ by rotary evaporation of aqueous HBr solutions; HCl is more volatile than HBr.

Crude $[CoNH_3)_5O_3SF](FSO_3)_2$ from preparation to preparation was shown to contain up to 5% $[Co(NH_3)_5OSO_3H](FSO_3)_2$. The sulfato complex impurity was reduced to an insignificant amount (<1%) by recrystallization from $H_2O/HClO_4$ at low temperature. The method was that described for recrystallization of other water-labile complexes $[Co(NH_3)_5OClO_3]^{2+}$ ($t_{1/2}$ = 7 s) and $[Co(NH_3)_5O_3SCF_3]^{2+}$ ($t_{1/2}$ = 26 s, 25 °C), and in all cases the products can be obtained free of hydrolysis product $[Co(NH_3)_5OH_2](ClO_4)_3$.[3,4] No $[Co(NH_3)_5F]^{2+}$ (<1%) was found in both the crude and the recrystallized fluorosulfonato complexes.

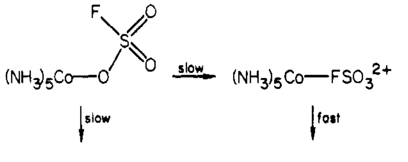
The $[Co(NH_3)_5O_3SF]^{2+}$ ion reacts rapidly in water, Me_2SO, or dimethylformamide. Both the ClO_4^- and FSO_3^- salts are insoluble in alcohols and MeCN where a similar rapid solvolysis would be expected.[5] The half-life of aquation was measured as 31 s in 0.01 M $HClO_4$ at 25 °C. Together with $[Co(NH_3)_5OClO_3]^{2+}$ ($t_{1/2} \approx 7$ s),[3] $[Co(NH_3)_5OCMe_2]^{3+}$ ($t_{1/2} \approx 17$ s),[5] and $[Co(NH_3)_5O_3SCF_3]^{2+}$ ($t_{1/2} \approx 26$ s),[4] these ions aquate $10-10^8$ times more rapidly than other isolable $[Co(NH_3)_5X]^{n+}$ species known. The properties and synthetic utility of the triflato ($CF_3SO_3^-$) complex are described elsewhere.[5] Although $[Co(NH_3)_5O_3SF]^{2+}$ is cheaper and somewhat easier to prepare than the triflato complex, it undergoes side reaction (see below) and it is generally less soluble, and so it is unlikely to rival $[Co(NH_3)_5O_3SCF_3](CF_3SO_3)_2$ as a key synthetic precursor[5] to $[Co(NH_3)_5X]^{n+}$ complexes.

Reactions of $[Co(NH_3)_5O_3SF]^{2+}$ in Solution. Fluorosulfonic acid (but not FSO_3^-) hydrolyzes extremely rapidly to HF and HSO_4^-.[1,2] Since a cationic Co^{3+} center can mimic a proton, there was this expectation for the $[Co(NH_3)_5O_3SF]^{2+}$ complex. Indeed it hydrolyzes rapidly ($t_{1/2}$ = 31 s, 25 °C), but quite remarkably the products of S–F cleavage are $[Co(NH_3)_5F]^{2+}$ and HSO_4^-, rather than $[Co(NH_3)_5OSO_3]^+$ and HF. Also some $[Co(NH_3)_5OH_2]^{3+}$ arises in a competitive reaction pathway, either by substitution at the cobalt center or by S–O cleavage (eq 3). A similar reaction occurs in Me_2SO to give $[Co(NH_3)_5F]^{2+}$ (44%) and $[Co(NH_3)_5OSMe_2]^{3+}$ (56%). Note that the Me_2SO complex must arise by Co–O bond rupture, a result which suggests that Co–O cleavage occurs also in water. This conclusion is supported by the Cl^- competition results and ^{18}O-tracer work on other $[Co(NH_3)_5O_3SR]^{2+}$ complexes.[4] The $[Co(NH_3)_5O_3SF]^{2+}$ ion aquates in 1.0 M HCl to give the same amount of $[Co(NH_3)_5Cl]^{2+}$ (3.3%) as that produced in analogous reactions of $[Co(NH_3)_5O_3SR]^{2+}$, which are known to occur with exclusive Co–O bond rupture.[4] Note that anion competition is not possible by a S–O cleavage pathway.



(3)

A mechanism which accommodates the observations is (4).



(4)

The path leading to the aqua complex is the normal aquation reaction, and its rate ($k = 1.6 \times 10^{-2}\ s^{-1}$) is comparable to those[3,4] of $[Co(NH_3)_5O_3SCF_3]^{2+}$ and $[Co(NH_3)_5OClO_3]^{2+}$. All these complexes are derived from extremely poor basic ligands, and their lability toward hydrolysis is not surprising. However the other reaction pathway is unique to the FSO_3^- ligand. We propose a rate-determining linkage isomerization from the oxygen- to a fluorine-bonded form, which then eliminates SO_3 rapidly to give the observed $[Co(NH_3)_5F]^{2+}$. There is precedence for both steps of this pathway. The first, a linkage isomerization step, has been observed for O- to N-bonded NO_2^-,[16,17] N- to O-bonded $NH_2SO_3^-$,[18] S- to N-bonded SCN^-,[19] N-to O-bonded NH_2COO^- [20] and more recently N- to O-bonded $OC(NH_2)N(CH_3)_2$[21] and N- to O-bonded amide complexes[22] of the pentaamminecobalt(III) species. These rearrangements vary considerably in rate, but among the fastest is the urea complex with a remarkably short half-life of ~40 s at 25 °C.[21] The present proposal of an O- to F-bonded FSO_3^- rearrangement with a half-life of ~120 s at 25 °C is therefore not unreasonable, particularly since the FSO_3^- complex can exist in a conformation where the fluorine is sterically well disposed for attack at the cobalt center (eq 4). The second step in this pathway to $[Co(NH_3)_5F]^{2+}$ is the rapid elimination of SO_3 from the proposed $[Co(NH_3)_5FSO_3]^{2+}$ intermediate. Similar intermediates are indicated in the Cl_2-induced hydrolysis of $[Co(NH_3)_5OSMe_2]^{3+}$ in the presence of BF_4^- and PF_6^-.[3] In both these instances considerable $[Co(NH_3)_5F]^{2+}$ is produced, which cannot be accommodated by capture of the free F^- in solution. It has been proposed[3] that the $[Co(NH_3)_5]^{3+}$ intermediate captures BF_4^- or PF_6^- to give first the unstable fluorine-bridged complexes $[Co(NH_3)_5FBF_3]^{2+}$ or $[Co(NH_3)_5FPF_5]^{2+}$, which then rapidly eliminate BF_3 or PF_5.

The solvent dependence of the relevant importance of the two reaction paths (eq 4) is consistent with these proposals. In Me_2SO significantly more (44%) $[Co(NH_3)_5F]^{2+}$ is pro-

---

(16) W. G. Jackson, G. A. Lawrance, P. A. Lay, and A. M. Sargeson, *Inorg. Chem.*, **19**, 904 (1980).

(17) The oxygen-scrambling reactions $Co^{18}ONO \rightleftarrows CoON^{18}O$ (ref 16) and $Co^{17}ONO \rightleftarrows CoON^{17}O$ (W. G. Jackson, P. A. Lay, G. A. Lawrance, and A. M. Sargeson, unpublished data) have been observed also.

(18) E. Sushynski, A. Van Roodselaar, and R. B. Jordan, *Inorg. Chem.*, **11**, 1887 (1972).

(19) D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, **9**, 655 (1970).

(20) D. A. Buckingham, D. J. Francis, and A. M. Sargeson, *Inorg. Chem.*, **13**, 2630 (1974).

(21) N. E. Dixon, D. P. Fairlie, W. G. Jackson, and A. M. Sargeson, results to be submitted for publication.

(22) D. P. Fairlie and W. G. Jackson, results to be submitted for publication.

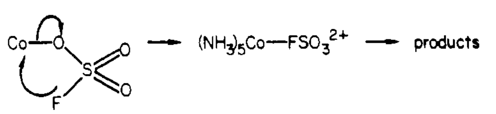
duced than in water (26%). Water is a much stronger H donor than Me_2SO, while F^- is a strong H-bond acceptor.[23] Therefore the enhancement in the F^--transfer process relative to the solvolysis step can be understood if water preferentially solvates the incipient fluoride. Preferential solvation of fluorine by H_2O should reduce its availability relative to Me_2SO.

The hydrolysis of $[Co(NH_3)_5O_3SF]^{2+}$ in 0.01 M OH^- affords a striking contrast. No $[Co(NH_3)_5F]^{2+}$ is produced. The reaction is base catalyzed and undoubtedly proceeds via the well-established[24] S_N1cB process (eq 5). The short-lived

$$(NH_3)_5CoO_3SF^{2+} \rightleftharpoons (NH_3)_4(NH_2)CoO_3SF^{+} \longrightarrow$$
$$(NH_3)_4(NH_2)Co^{2+} + FSO_3^- \xrightarrow{H_2O} (NH_3)_5CoOH_2^{3+} \quad (5)$$

intermediate $[Co(NH_3)_4(NH_2)]^{2+}$ scavenges nucleophiles in solution, and water always wins handsomely over competing anions even at concentrations of 1 M.[8,24] The lack of competition by FSO_3^-, at much lower concentrations, is therefore not surprising.

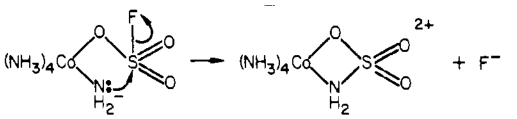
There is precedence for another possibility that warrants consideration. Fluoride can be captured by cobalt in the base-catalyzed process in a similar way to which it is captured in water or Me_2SO, i.e., by virtue of its proximity to the cobalt center (eq 6). This amounts to a base-catalyzed linkage



(6)

isomerization process, and this has been observed for the O to N rearrangement of $[Co(NH_3)_5ONO]^{2+}$[16] and S to N rearrangement of $[Co(NH_3)_5SCN]^{2+}$.[19] If this is accepted, then the immediate product $[Co(NH_3)_5FSO_3]^{2+}$ must cleave subsequently at the Co–F rather than at the S–F bond since no $[Co(NH_3)_5F]^{2+}$ is formed. In the conjugate base mechanism the amide group is generally believed to strongly labilize the metal–leaving group bond in a dissociative process. Therefore the very rapid loss of FSO_3^- rather than SO_3 is a reasonable consequence since it involves metal–X cleavage whereas the elimination of SO_3 (S–F cleavage) does not.

The linkage isomerization of $[Co(NH_3)_5SCN]^{2+}$[19] is relevant in the context of the $[Co(NH_3)_5O_3SF]^{2+}$ chemistry. It isomerizes completely to $[Co(NH_3)_5NCS]^{2+}$ in H_2O and Me_2SO without competitive solvolysis. In OH^-, the S to N rearrangement is faster than in water but there is also a significant base hydrolysis path (74%) to $[Co(NH_3)_5OH]^{2+}$. As for the FSO_3^- complex, the hydrolysis path is enhanced relative to the intramolecular path. For the S to N isomerization a unique mechanistic possibility was raised,[25] viz., attack by *cis*-NH_2^- at the electrophilic carbon of $CoSCN^{2+}$ in the $[(NH_3)_4(NH_2)CoSCN]^{2+}$ intermediate followed by rearrangement. It raises the question as to why a similar mechanism, with a difference consequence, does not operate for $[Co(NH_3)_5O_3SF]^{2+}$ (see eq 7). Chelated sulfamato product[26]



(7)

was sought but not found (<1%). Intramolecular aminations of this type are not uncommon, and there is an obvious steric requirement, cis NH_3 deprotonation. For example, complexes of the type $[Co(NH_3)_5OP(O)_2(OR)]^+$ undergo attack by cis NH_2^- to form chelated phosphoramides $[Co(NH_3)_4(OP(O)_2NH_2)]^+$, provided OR^- is a good leaving group.[27] Since sulfur is generally less electrophilic than phosphorus and F^- is a poor leaving group, the failure to observe this reaction in the present work is not especially surprising. Alternatively the negative result could suggest that it is deprotonation of the trans NH_3 which is effective in the base hydrolysis of $[Co(NH_3)_5O_3SF]^{2+}$. This suggestion is consistent with the greater acidity of the trans NH_3 (~30-fold) in complexes of the type $[Co(NH_3)_5(O)]^{n+}$ where (O) is an O-donor ligand, as assessed from H–D exchange rates.[28] The proposed base-catalyzed S to N rearrangement mechanism for $[Co(NH_3)_5SCN]^{2+}$ which requires cis NH_3 deprotonation could be in trouble on this point since the trans NH_3 is also more acidic than the cis but experiments are under way to settle this question.

Hydrolysis of FSO_3H and FSO_3^-. The fluorosulfonate ion hydrolyzes very slowly in water ($k = 2.1_5 \times 10^{-7}$ s^{-1}, 25 °C).[2] Surprisingly the rate of S–F cleavage of FSO_3^- in water is catalyzed by $H^+(aq)$, which implies an enormous hydrolysis rate for the fully protonated form HSO_3H since it is an extremely strong acid. These more recent kinetic studies explain the earlier curious observation[29] that the extent of FSO_3H hydrolysis depends upon its rate of addition to water. Clearly the rate of the hydrolysis of FSO_3H must be comparable with its rate of mixing with water or, less likely, the rate of dissociation of the proton.

The hydrolysis of $[Co(NH_3)_5O_3SF]^{2+}$ yields $[Co(NH_3)_5F]^{2+}$ and HSO_4^- via the $[Co(NH_3)_5FSO_3]^{2+}$ intermediate, and by analogy the reactive species in the hydrolysis of the FSO_3H is undoubtedly $HF(SO_3)$. Like the case for the proton, coordination of FSO_3^- to cobalt(III) greatly enhances the rate of hydrolysis (by a factor of 2.6×10^4), but the metal ion is much less efficient. This conforms to the usual pattern found for the relative effectiveness of metal ions and the proton in hydrolyzing organic substrates such as esters. However the comparison we make is not srictly valid since we should be comparing $[(NH_3)_5CoFSO_3]^{2+}$ with $HFSO_3$. The measured S–F hydrolysis rate for the $[(NH_3)_5CoO_3SF]^{2+}$ complex is the rate of linkage isomerization to $[(NH_3)_5CoFSO_3]^{2+}$ which is the rate-determining step. The subsequent hydrolysis of $[(NH_3)_5CoFSO_3]^{2+}$ must be faster. Therefore the metal ion is actually much more efficient in promoting the hydrolysis of FSO_3^- than the measured rates indicate. It remains doubtful that it is as efficient as H^+.

In base, the hydrolysis of FSO_3^- is accelerated but not appreciably (~2-fold faster in 0.1 M OH^- compared to water).[2] In the base hydrolysis of $[Co(NH_3)_5O_3SF]^{2+}$ S–F cleavage was not observed, and hence no comparison is possible.

Anion Competition. Base Hydrolysis. In recent years many experiments have been carried out on the base hydrolysis reactions of $[Co(NH_3)_5X]^{n+}$ complexes with a view to characterizing the supposed five-coordinate intermediate $[Co(NH_3)_4(NH_2)]^{2+}$ arising from dissociation of the conjugate base.[24] One approach has been to determine the proportion of products arising from competing nucleophiles and to demonstrate the independence of the leaving group X. A similar approach has been made in the search for the intermediate $[Co(NH_3)_5]^{3+}$.[24]

The base hydrolysis of $[Co(NH_3)_5O_3SF]^{2+}$ in 1 M N_3^- leads to anion competition by the Co–O cleavage pathway. This figure for N_3^- competition in 1 M N_3^- at 25 °C (9.4%) may

---

(23) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(24) A. M. Sargeson, *Pure Appl. Chem.*, **33**, 527 (1973).

(25) D. A. Buckingham, I. I. Creaser, W. Marty, and A. M. Sargeson, *Inorg. Chem.*, **11**, 2738 (1972).

(26) N-Bound unidentate sulfamate is known and is stable as the $NHSO_3^{2-}$ ligand in base.[13,18]

(27) D. R. Jones and A. M. Sargeson, unpublished results.

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

(29) A. A. Woolf, *J. Chem. Soc.*, 2840 (1954).

be compared with those for the ClO_4^- (10.3%),[4] SCN^- (10.0%),[19] NO_3^- (10.4%),[8] $CF_3SO_3^-$ (9.8%)[4], and I^- (10.0%)[8] complexes. Clearly the result does not depend on the leaving group, and it would seem to support the case for a common intermediate. However, to hold this case requires some faith in the accuracy of the competition figures. A long-lived common intermediate requires the competition to be strictly independent of the leaving group. The slightly lower results[8] for the base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ (8.5%) and $[Co(NH_3)_5Br]^{2+}$ (8.8%) complexes in 1 M N_3^- therefore raise a problem. It has been noted that the competition figures, although precise (reproducible to ±0.5%), could be inaccurate to up to ±1.5% in an absolute sense because the cobalt recovery in the ion-exchange separation experiments is not 100% (but ≥98%), and conceivably the loss (1–2%) could be entirely in the $[Co(NH_3)_5N_3]^{2+}$ component of the products. This is fair comment, but despite this the competition figures have been reproduced since[30] to remarkable concordance (±0.5%) in different laboratories using different techniques, and therefore we believe the differences of 1.0–2.0% to be real.

Recent studies have revealed several more prominent examples of leaving-group dependencies in competition in base hydrolysis which, although small, are well outside experimental error.[6,30] These were not the first examples, however. Such an anomaly was observed in the very early competition studies on $[Co(NH_3)_5X]^{n+}$ ($X = Br^-, Cl^-, F^-, NO_3^-$).[12] Oxygen-18-enriched H_2O and OH^- were competed, and from accurate $^{18}O/^{16}O$ measurements it was shown that H_2O rather than HO^- was the entering group in base hydrolysis. Equally important was the observation[12] that the $H_2{}^{18}O/H_2{}^{16}O$ competition was independent of the leaving group for Cl^-, Br^-, and NO_3^- but not for F^-. $[Co(NH_3)_5F]^{2+}$ was therefore an obvious candidate for the later anion competition experiments to confirm this anomaly, but its rate of base hydrolysis was considered[8] too slow to permit the experiments. We have circumvented the problem by separating unreacted $[Co(NH_3)_5F]^{2+}$ from the 2+ acido product using a different chromatographic method.[14] The amount of azido complex formed was small (~1%) as expected, but despite this the reproducibility of the results and cobalt recoveries were excellent (Table II). The competition figure for the base hydrolysis of $[Co(NH_3)_5F]^{2+}$ in 1.00 M N_3^- is 5.1 ± 0.2%, and although the precision is good, the accuracy (±0.6%) is likely to be lower than that indicated by the reproducibility for the reasons given above. However the important point is that the competition is about half the amount formed for all the other 2+ ions,[4,8] and there can be little doubt this difference is real.

The mechanistic implications of the leaving group dependence of the competition are discussed in detail elsewhere,[6] and it suffices to note here that the fluoro result supports the case[12] that the mechanism of base hydrolysis of $[Co(NH_3)_5F]^{2+}$ is in some way different from the others.

Aquation. In 1.00 M HCl at 25 °C, $[Co(NH_3)_5Cl]^{2+}$ (2.4%, Table I) is directly formed along with aqua (24%) and fluoro (72%) complexes. These figures correspond to 3.3% $[Co(NH_3)_5Cl]^{2+}$ and 96.7% $[Co(NH_3)_5OH_2]^{3+}$ for the cobalt–oxygen cleavage path. This may be compared with the competition figures[4] under identical conditions for $[Co(NH_3)_5OClO_3]^{2+}$ (3.2%) and $[Co(NH_3)_5O_3SCF_3]^{2+}$ (3.3%), which carry the same 2+ formal charge and which are of comparable lability to $[Co(NH_3)_5O_3SF]^{2+}$. Although a common $[Co(NH_3)_5]^{3+}$ intermediate nicely accommodates this agreement, the Cl^- competition for the aquation of $[Co(NH_3)_5X]^{n+}$ for a wider range of leaving groups is markedly leaving-group dependent (1.3–40% Cl^- competition in 1 M HCl).[9,10,31] This dependence will be discussed in detail elsewhere, but we have noted the coincidence of a common Cl^- competition result for $[Co(NH_3)_5OClO_3]^+$, $[Co(NH_3)_5O_3SCF_3]^{2+}$, and $[Co(NH_3)_5O_3SF]^{2+}$ to draw attention to the danger of drawing mechanistic conclusions from results for a limited range of leaving groups. We have also highlighted the results of anion competition in the base hydrolysis reaction discussed in the previous section where the spread of competition results for a similar range of leaving groups is quite small by comparison and where a common but short-lived intermediate does seem to be involved.

Acknowledgment. The authors thank the ARGC for financial support for this work and Dr. G. A. Lawrance (ANU) for the use of his fast-reaction device. We wish to thank Professor A. M. Sargeson and Drs. G. A. Lawrance and N. E. Dixon for helpful discussions.

Registry No. $[Co(NH_3)_5O_3SF](ClO_4)_2$, 76822-78-1; $[Co(NH_3)_5O_3SF](FSO_3)_2$, 76822-79-2; $[Co(NH_3)_5F](ClO_4)_2$, 36126-23-5; $[Co(NH_3)_5Cl]Cl_2$, 13859-51-3; $[Co(NH_3)_5OH_2]^{3+}$, 14403-82-8; $[Co(NH_3)_5N_3]^{2+}$, 14403-83-9; $[Co(NH_3)_5OSO_3]^+$, 18661-07-9; $[Co(NH_3)_5(OSMe_2)]^{3+}$, 44915-85-7; $[Co(NH_3)_5O_3SCF_3](CF_3SO_3)_2$, 75522-50-8; $[Co(NH_3)_5Br]^{2+}$, 14970-15-1; $[Co(NH_3)_5ONO_2]^{2+}$, 15077-47-1.

---

(30) W. L. Reynolds and S. Hafezi, *Inorg. Chem.*, **17**, 1819 (1978).

(31) W. G. Jackson and A. M. Sargeson, unpublished results.