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Labile (Sulfonato)pentaamminecobalt(III) Complexes: Synthesis and Kinetics and Mechanism of Acid and Base Hydrolysis

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The syntheses of $[(NH_3)_5CoOSO_2R](ClO_4)_2$ (R = CH_3, CF_3, *p*-$NO_2C_6H_4$) are described. The extreme lability of the sulfonates is seen in the aquation (k_{H_2O}) and base hydrolysis (k_{OH}) rate data (μ = 1.0 M ($NaClO_4$), 25 °C): R = CF_3, $k_{H_2O} = 2.7 \times 10^{-2}$ s^{-1}, $k_{OH} \simeq 10^6$ M^{-1} s^{-1}; R = *p*-$NO_2C_6H_4$, $k_{H_2O} = 6.3 \times 10^{-4}$ s^{-1}, k_{OH} = 270 M^{-1} s^{-1}; R = CH_3, $k_a = 2.0 \times 10^{-4}$ s^{-1}, k_{OH} = 55 M^{-1} s^{-1}. These results extend the range of $(NH_3)_5CoX^{n+}$ reactivity $\sim\times10^5$ for base hydrolysis and $\sim\times10^2$ for aquation. ^{18}O tracer data (R = CH_3, CF_3) show that both acid and base hydrolysis proceed with essentially total ($\gtrsim$99%) Co–O (rather than S–O) cleavage. The $[Co(NH_3)_5OClO_3]^{2+}$ ion of comparable lability ($t_{1/2} \approx 7$ s, 25 °C) also hydrolyzes in acid and base with complete Co–O cleavage. Anion competition is observed in spontaneous aquation (1.0 M HCl: X = $OSO_2CF_3^-$, 3.3% $(NH_3)_5CoCl^{2+}$; X = $OSO_2CH_3^-$, 1.3%; X = $OClO_3^-$, 3.2%) and in base hydrolysis (1.0 M NaN_3: X = $OSO_2CF_3^-$, 9.8% $(NH_3)_5CoN_3^{2+}$; X = $OSO_2CH_3^-$, 10.2%; X = $OClO_3^-$, 10.3%). These data show that the competition in the acid-independent path is leaving-group dependent and significantly lower than that observed for induced aquation, while the results for base hydrolysis follow trends previously established for an S_N1CB process.

Introduction

Complexes of the type $(NH_3)_5CoX^{n+}$ have been prepared previously with a wide range of substituents (X = NO_2^-, ONO^-, N_3^-, NCO^-, OH^-, $CH_3CO_2^-$, $NH_2CO_2^-$, Cl^-, Br^-, NCS^-, SCN^-, I^-, NO_3^-, SO_4^{2-}, HSO_4^-, PO_4^{3-}, $OP(OCH_3)_3$, CH_3CN, DMF, Me_2SO, CH_3OH, OH_2, etc.). These substituents vary greatly in size, charge, bonding geometry, and electronic properties, and this is reflected in many characteristics of their acido complexes, especially in their lability toward hydrolysis.[1] Specific rate constants for aquation of the complex ions range from $\sim10^{-9}$ to 10^{-4} s^{-1}.[1] For base hydrolysis involving the metal center the range is $\sim10^{-6}$–6 M^{-1} s^{-1}.[1] It is noted that some of the complexes hydrolyze at the ligand (e.g., NCO^-,[2] CH_3CN[3]) as well as at cobalt.

In the course of our research on the acid and base hydrolysis reactions it seemed useful to prepare some complexes more labile than those previously known. An obvious route, by analogy with organic systems, was to prepare complexes containing substituted sulfonate ligands such as $CH_3SO_3^-$ or *p*-toluenesulfonate which are well-known as good leaving groups. It also seemed likely that sulfonates substituted with more electron-withdrawing groups, e.g., *p*-nitrobenzenesulfonate or $CF_3SO_3^-$, would be more labile still. Trifluoromethanesulfonic acid (triflic acid) is one of the strongest simple acids known so that its anion might be expected to be a very labile ligand.

This paper describes the synthesis of cobalt(III) pentaammine complexes of three of these sulfonate ligands. The kinetics of acid and base hydrolysis are presented, as well as ^{18}O tracer work designed to determine the relative extents of Co–O and S–O cleavage in hydrolysis. Furthermore these labile complexes as well as the recently prepared perchlorato ion,[4] $[Co(NH_3)_5OClO_3]^{2+}$, are among the few suitable for determining anion competition properties in spontaneous aquation, and this prospect was therefore pursued, as well as competition in base hydrolysis.

Experimental Section

Visible spectra (ϵ, M^{-1} cm^{-1}) were recorded with use of Cary 14 and Cary 118C spectrophotometers. ^1H NMR spectra were measured in Me_2SO-d_6 (Merck, dried over a 4-Å molecular sieve) with use of a Jeol Minimar 100-MHz instrument and an internal tetramethylsilane reference. Oxygen-18 enriched water was 1.5 atom % (Miles Laboratories) or 1.7 atom % (Bio-Rad). Mass spectral measurements on ^{18}O–CO_2 were made with a ratio-recording Altlas M86 spectrometer. The cation-exchange resin was Bio-Rad Dowex 50W × 2 (200–400 mesh, H^+ form) which was pretreated with NaOH (2 M)/H_2O_2 (2 M), HCl (3 M), NaNCS (3 M), HCl (3 M), and H_2O, respectively, to reduce the resin color and to remove iron and reducing contaminants. Sephadex SP-C25 (Na^+) cation-exchange resin was also employed. Trifluoromethanesulfonic acid (triflic acid) was "Fluorochemical acid" (MMM) and was purified by drying (H_2SO_4) and vacuum distillation. Methanesulfonic acid (Eastman) was used as received. Nitrosyl triflate was prepared by passing N_2O_3 gas (from $H_2SO_4/NaNO_2$) into purified CF_3SO_3H until crystallization was complete. Dimethyl sulfoxide and acetonitrile were dried over a 4-Å molecular sieve and distilled twice in vacuo. All other chemicals were AnalaR grade except *p*-nitrobenzenesulfonic acid (Eastman, practical grade).

The complex $[Co(NH_3)_5OH_2](ClO_4)_3$[5] was recrystallized from hot water (60 °C) by the addition of excess CF_3SO_3H, *p*-$NO_2C_6H_4SO_3^-Na^+$ or $Na^+CH_3SO_3^-$ and cooling, to give the respective sulfonate salts of the aqua complex. The $CH_3SO_3^-$ and $NO_2C_6H_4SO_3^-$ salts crystallized reproducibly as the mixed-counterion complexes $[Co(NH_3)_5OH_2](CR_3SO_3)(ClO_4)_2$, the other as the trisulfonate. Each was recrystallized twice from hot water with use of $Na^+RSO_3^-$. Alternatively $[Co(NH_3)_5OH_2]Br_3$ (1 equiv) in water containing RSO_3H (3 equiv; R = CF_3, CH_3, or *p*-$NO_2C_6H_4$) was shaken with an excess (>3 equiv) of freshly precipitated Ag_2O, and AgBr was removed by filtration. The filtrate was reduced to dryness to provide $[Co(NH_3)_5OH_2](RSO_3)_3$ complexes which were used in the solid-phase reactions described below. Anal. Calcd for $[Co(NH_3)_5OH_2](CF_3SO_3)_3$: Co, 9.68; C, 5.91; H, 2.81; N, 11.50; S, 15.79; F, 9.36. Found: Co, 9.70; C, 5.86; H, 2.95; N, 11.34; S, 15.77; F, 9.44. Calcd for $[Co(NH_3)_5OH_2](NO_2\cdot C_6H_4\cdot SO_3)_3\cdot H_2O$: C, 27.48, H, 3.97; N, 14.25; S, 12.23. Found: C, 27.48; H, 4.15; N, 14.17; S, 12.28. Calcd for $[Co(NH_3)_5OH_2](NO_2\cdot C_6H_4\cdot SO_3)(ClO_4)_2$: Co, 10.81; C, 13.22; H, 3.51; N, 15.42; S, 5.88; Cl, 13.01. Found: Co, 10.80; C, 13.32; H, 3.69; N, 14.80; S, 5.73; Cl, 12.88. Calcd for $[Co(NH_3)_5OH_2](CH_3SO_3)(ClO_4)_2$: Co, 13.45; C, 2.74; H, 4.11; N, 15.99; S, 7.32; Cl, 16.18. Found: Co, 13.34; C, 2.96; H, 4.31; N, 16.00; S, 7.33; Cl, 16.19.

$[Co(NH_3)_5N_3]Cl_2$[6] (50 g) was suspended in water (150 mL) and shaken with a 5-fold excess of Dowex 1 × 8 anion-exchange resin ($CH_3CO_2^-$ form, derived from the Cl^- form by treatment with CO_3^{2-}

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followed by CH_3COOH). The resin was removed from the resultant solution of $[Co(NH_3)_5N_3](CH_3CO_2)_2$, and cold CF_3SO_3H (50 mL) was added carefully to the chilled filtrate. After 12 h at 0 °C the large red-violet needles of $[Co(NH_3)_5N_3](CF_3SO_3)_2$ which had deposited were collected and washed with ether/ethanol (20:1) followed by ether. The insoluble $[Co(NH_3)_5Cl]Cl_2$ was recovered from the filtrate with use of HCl and recycled to obtain more of the triflate salt. The combined $[Co(NH_3)_5N_3](CF_3SO_3)_2$ was recrystallized from methanol by the addition of ether. $[Co(NH_3)_5N_3](ClO_4)_2$ was prepared similarly with use of $HClO_4$ in place of CF_3SO_3H and was recrystallized from water by the addition of $HClO_4$.

$[Co(NH_3)_5OClO_3](ClO_4)_2$ was synthesized by passing dry N_2O_3 gas into finely divided $[Co(NH_3)_5N_3](ClO_4)_2$ (4.0 g) suspended in $HClO_4$ (50 mL, 70%) as described previously.[4] The product was sucked dry at the filter and recrystallized once by very quickly extracting the solid with ice water (5 × 50 mL) and filtering onto an excess of an ice/70% $HClO_4$ (2:1) mixture at approximately −40 °C. The fine pink platelets were collected, were washed with ethanol followed by ether, and were kept over P_2O_5 under vacuum. Anal. Calcd for $[Co(NH_3)_5OClO_3](ClO_4)_2$: H, 3.42, N, 15.83; Cl, 24.04. Found: H, 3.48; N, 15.90; Cl, 24.14.

$[Co(NH_3)_5OSO_2CF_3](ClO_4)_2$ and $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$. $[Co(NH_3)_5N_3](CF_3SO_3)_2$ (14.5 g, 0.03 mol) was dissolved in freshly distilled CF_3SO_3H (60 mL) under dry nitrogen. The slow addition of $NO{\cdot}OSO_2CF_3$ (5.4 g, 0.09 mol; excess) to the well-stirred solution effected complete dissolution of the azido complex and destruction of the azide. The then pink-red solution was added dropwise to ether (1 L) at 5 °C. The gelatinous precipitate was triturated with dry ether (Na) several times to yield a fine pink solid which was collected and washed generously with more ether. The product, dried under vacuum, was moderately air stable and analytically pure. It can be recrystallized quickly from cold dry acetone by the addition of ether. Anal. Calcd for $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$: Co, 9.97; C, 6.09; N, 11.84; H, 2.56; S, 16.27; F, 9.64. Found: Co, 9.90; C, 5.95; N, 11.74; H, 2.70; S, 16.25; F, 9.54.

The triflate salt was converted to crystalline pink platelets of the perchlorate salt with good recovery with use of ice/$HClO_4$, as described for $[Co(NH_3)_5OClO_3]ClO_4$ above. The triflate salt was also recrystallized from water with use of cold aqueous CF_3SO_3H, but the recovery was low (~40%). Anal. Calcd for $[Co(NH_3)_5OSO_2CF_3](ClO_4)_2$: Co, 11.98; C, 2.44; H, 3.07; N, 14.24; S, 6.52; Cl, 14.41; F, 11.58. Found: Co, 11.99; C, 2.47; H, 3.32; N, 14.11; S, 6.46; Cl, 14.65; F, 11.34.

$[Co(NH_3)_5OSO_2CH_3](ClO_4)_2$ was prepared by an analogous method to the triflato complex with use of CH_3SO_3H in place of CF_3SO_3H. Two other methods produced the methanesulfonato complex in good yield, but they are generally less convenient: $[Co(NH_3)_5OH_2](CH_3SO_3)_3$ heated in vacuo (~5 mmHg) over P_2O_5 for 5 h at 100 °C; $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ warmed in CH_3SO_3H solution (50 °C, 20 min). The crude products were recrystallized from cold water (5 °C) with use of $HClO_4$ (70%) or aqueous $NaClO_4$ and afforded fine pink needles. The products were washed with ethanol and ether and dried in vacuo. ϵ_{518}^{max} 52.5, ϵ_{350}^{max} 42.5 (0.01 M $HClO_4$). ^{1}NMR spectrum (Me_2SO-d_6): δ 4.00 (12 H, cis NH_3), 2.53 (3 H, trans NH_3), 2.62 (3 H, CH_3). Anal. Calcd for $[Co(NH_3)_5OSO_2CH_3](ClO_4)_2$: C, 2.74; H, 4.11; N, 15.99; S, 7.32; Cl, 16.18. Found: C, 2.96; H, 4.31; N, 16.00; S, 7.33; Cl, 16.29.

$[Co(NH_3)_5OSO_2C_6H_4NO_2$-*p*$](ClO_4)_2$. Method 1. $[Co(NH_3)_5OH_2](p\text{-}NO_2C_6H_4SO_3)_3$ was heated at 100 °C for 8 h over P_2O_5 in vacuo (~1 mmHg). The cooled purple-pink solid was extracted with dry sulfolane and the chloride salt obtained by the addition of LiCl and ethanol. This solid was recrystallized quickly from water (5 °C) with use of saturated aqueous $NaClO_4$ and afforded pink-orange plates of the perchlorate salt. Anal. Calcd for $CoN_6H_{19}C_6SCl_2O_{13}$: N, 15.42; H, 3.51; C, 13.22; S, 5.88; Cl, 1301. Found: N, 14.95; H, 3.59; C, 13.32; S, 5.73; Cl, 12.98.

Method 2. $[Co(NH_3)_5OH](ClO_4)_2$ was obtained from $[Co(NH_3)_5OH_2](ClO_4)_3$ triturated with an aqueous $NaClO_4$/Tris mixture and was recrystallized from water (pH 8, tris) with use of $NaClO_4$. The hydroxo complex (5.0 g, 0.014 mol) in dry *N,N*-dimethylformamide (20 mL) containing triethylamine (1.6 g, 0.016 mol) was treated dropwise over 5 min with excess p-$NO_2C_6H_4SO_2Cl$ (6.7 g, 0.03 mol), while the solution was cooled (~5 °C) and well stirred. The product which formed immediately was precipitated as the Cl^- salt with use of excess acetone and was recrystallized twice from water as the perchlorate salt, as described above.

$[Co(NH_3)_5Cl]Cl_2$[7] was recrystallized twice from hot (80 °C) water by the addition of HCl (11 M) and converted to the perchlorate salt by grinding to a thin paste with $HClO_4$. This process was repeated, and the product was finally recrystallized twice from water/$HClO_4$.

Characterization. All the complexes, except those noted below, eluted as single bands from Dowex cation-exchange resin, and the elution behavior was characteristic of the formal charge carried by the cation (2+, 1.0 M $NaClO_4$; 3+, 2–3 M $NaClO_4$ or HCl). Similar behavior was observed on Sephadex resin although lower electrolyte concentrations (pH >2) are required here (1+, 0.1 M $NaClO_4$; 3+, 0.3 M $NaClO_4$) to elute the cations. Ice-jacketed columns were employed to minimize aquation reactions. For the $[Co(NH_3)_5OClO_3]^{2+}$ and $[Co(NH_3)_5OSO_2CF_3]^{2+}$ complexes, hydrolysis was too rapid for direct chromatography to be a useful guide to purity (in particular, this method could not ascertain the absence of $[Co(NH_3)_5OH_2]^{3+}$). However, no significant amounts (<1%) of the potential impurities $[Co(NH_3)_5Cl]^{2+}$, $[Co(NH_3)_5N_3]^{2+}$, or $[Co(NH_3)_5NO_2]^{2+}$ were established in this way. The perchlorato and triflato complexes were solvolyzed in dried Me_2SO and CH_3CN ($10t_{1/2}$, ≤60 min) and then chromatographed on Sephadex or Dowex. Under the conditions, 0.7 M $NaClO_4$, 1.0 M $NaClO_4$, or 0.1 M Tris/$HClO_4$ (pH 7.2) as eluants, $[Co(NH_3)_5OH_2]^{3+}$ separates cleanly from $[Co(NH_3)_5OSMe_2]^{3+}$ (ϵ_{517}^{max} 62) or $[Co(NH_3)_5NCMe]^{3+}$ (ϵ_{465}^{max} 63), and none (<1%) of the aqua complex was detected in these experiments.

The ^{1}H NMR spectra confirmed the absence of $[Co(NH_3)_5OH_2]^{3+}$ and other cobalt(III) pentaammine species in the isolated sulfonato complexes. The aqua complex displays a $Co{-}OH_2$ signal at δ 5.62 in dry Me_2SO-d_6, a region clear of other signals for all the spectra. The dried cobalt complexes as their perchlorates salts (200 mg) were dissolved in dried Me_2SO-d_6 (0.5 mL) and their spectra recorded. The region δ 5–6 was scanned several times with a 100-fold amplitude increase, and the noise level was such that the H_2O signal of 0.5% $[Co(NH_3)_5OH_2]^{3+}$ could be readily detected. For the $[Co(NH_3)_5OSO_2CF_3]^{2+}$ and $[Co(NH_3)_5OClO_3]^{2+}$ complexes, solvolysis was complete within 5 min and hence the cis and trans NH_3 signals in these spectra correspond to those of $[Co(NH_3)_5OSMe_2]^{3+}$. No $[Co(NH_3)_5OH_2]^{3+}$ arises by competition during solvolyses in the NMR tube because [Co] >> free $[H_2O]$ in the Me_2SO-d_6, as shown by a blank spectrum on the solvent.

Competition Experiments. Base Hydrolysis. The usual procedure[8] was modified to accommodate the very labile $[Co(NH_3)_5OSO_2CF_3]^{2+}$ and $[Co(NH_3)_5OClO_3]^{2+}$ ions which react appreciably in the time of mixing. Moreover, their rapid rate of background aquation ($t_{1/2} \approx 7$ and 26 s, respectively; 25 °C) precluded the usual procedure of predissolution in 1 M NaN_3 before the addition of base. In these cases therefore the solid complex (~1.0 g) was dissolved directly in 1.00 M NaN_3 (~80 mL) containing NaOH (0.125 M) (Volucon reagent) at 25 °C. The solution, ~0.025 M Co, was quenched after 30 s with cold 5 M $HClO_4$ to give a pH of ~2 (HN_3 evolved *is very toxic*). Similar experiments were performed with quench times ranging from 10 s to 5 min. For the less reactive $[Co(NH_3)_5OSO_2CH_3]^{2+}$ complex, the salt was dissolved in water, and then NaN_3 was quickly added to give $[N_3^-] = 1.00$ M. A solution of NaOH 1 M in NaN_3 was then rapidly mixed in, so that the final $[OH^-] = 0.125$ M. (It was important to have $[N_3^-]$ constant and independent of mixing time, since the competition results depend critically on $[N_3^-]$ (but not $[OH^-]$).) The background aquation of this sulfonato complex ($t_{1/2} \approx 58$ min, 25 °C) was not a serious problem in the time scale of these experiments (<2 min). The base hydrolysis reaction was quenched at 1 min in one of the experiments and at 5–10 min in the others. Longer reaction (>30 min) led to detectable decomposition of the azido and particularly the hydroxo product, as shown in blank experiments.

Some competition experiments on the methanesulfonato complex ion were performed with use of the method described for the perchlorato and triflato complexes.

The acid-quenched product solutions were diluted at least 10-fold with water and sorbed, washed, and eluted from Dowex resin as previously described.[8] The azido complex eluted first (1 M $NaClO_4$; pH 3, $HClO_4$), followed by the aqua ion (3 M HCl). The molar absorptivities[8] used to derive the [Co] in these eluates were for $[Co(NH_3)_5N_3]^{2+}$ ϵ_{515}^{max} 272 and for $[Co(NH_3)_5OH_2]^{3+}$ ϵ_{492}^{max} 47.7.

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All experiments were conducted at 25 °C in the dark. It was found in separate experiments that the azido complex was photolyzed appreciably under normal laboratory lighting. This was important since as much as a 15% loss through photolysis was not immediately evident from the criteria of "good" experiments—reproducibility and a >98.5% recovery of cobalt from the column (e.g., a loss of 15% of the azido complex results in only 0.15 × 10 = 1.5% loss of total cobalt).

Acid Hydrolysis. The solid complexes $[Co(NH_3)_5OSO_2CF_3](ClO_4)_2$ and $[Co(NH_3)_5OClO_3](ClO_4)_2$ (~1.0 g) were dissolved in 1.00 M HCl (Volucon; ~80 mL at ~25 °C). The insoluble perchlorato complex did not all dissolve immediately but reacted completely within 60 s. After 5 min, the then clear pink-orange solutions were diluted to 500 mL (H_2O) and quickly sorbed on and eluted from Dowex resin as described for the base hydrolysis competition experiments. Violet $[Co(NH_3)_5Cl]^{2+}$ eluted first (1 M $NaClO_4$, pH 3, $HClO_4$; $\epsilon_{532}{}^{max}$ 50.5),[8] followed by pink-orange $[Co(NH_3)_5OH_2]^{3+}$ (3 M HCl; $\epsilon_{492}{}^{max}$ 47.7); [Co] were determined spectrophotometrically as before. For more slowly aquating $[Co(NH_3)_5OSO_2CH_3](ClO_4)_2$ ($t_{1/2} \approx 58$ min, 25 °C), the reaction in 1.00 M HCl was allowed 6.0 h before quenching. Duplicate "blank" experiments to determine precisely the extent of Cl^- anation of $[Co(NH_3)_5OH_2]^{3+}$ over 6.0 h at 25 °C were made on $[Co(NH_3)_5OH_2](ClO_4)_3$ (1 g) in 1.00 M HCl (60 mL).

Oxygen-18 Experiments. Base Hydrolysis. $[Co(NH_3)_5OSO_2CF_3](ClO_4)_2$, $[Co(NH_3)_5OSO_2CH_3](ClO_4)_2$, and $[Co(NH_3)_5OClO_3](ClO_4)_2$ (~700-mg samples) were dissolved directly in $H_2{}^{18}O$ (~10 mL, 1.71 g atom %) containing normal NaOH (0.1 M) at ~25 °C. After 60 s ($>>10t_{1/2}$), samples (1.0 mL) were taken, and the remainder of the solutions were quickly cooled, and iced HBr (60% w/v) was added cautiously until crystallization commenced. A further addition of HBr provided granular $[Co(NH_3)_5{}^{18}OH_2]Br_3$ in essentially quantitative yield within 3 min. This was collected, washed with methanol (AnalaR), and dried over 2 h in vacuo. Dehydration at 70 °C provided $H_2{}^{18}O$ which was converted to $C^{18}O_2$ with $Hg(CN)_2/HgCl_2$ at 400 °C and purified by gas chromatography.[9] Reference $C^{18}O_2$ was obtained from the solvent samples above (1.0 mL) by distilling off the $H_2{}^{18}O$ on a vacuum line and equilibrating with normal CO_2.[10] Blank base hydrolysis experiments were performed on $[Co(NH_3)_5Cl](ClO_4)_2$, which had been carefully purified and dried and established to be H_2O free, to test the accuracy of the procedure for determining the degree of Co–ligand bond rupture.

Acid Hydrolysis. Similar experiments to those described above were carried out on the same complexes (~300 mg) in $H_2{}^{18}O$ (~10 mL) acidified with a drop of normal HCl (11 M). The solutions were stirred and the reactions quenched 5 min ($\geq 10t_{1/2}$) after the last of the complex had dissolved. For the methanesulfonato complex, a total of 6 h was allowed for aquation. The known[11] rate of water exchange in $[Co(NH_3)_5OH_2]^{3+}$ was used to correct for the small loss of the ^{18}O label by this route.

Kinetics. Most kinetic measurements were performed on a Cary 16K spectrophotometer with the cell chamber thermostated to ±0.05 °C (water circulation). A Cary 118C spectrophotometer was used for some measurements. For stopped-flow kinetics, complex solutions ((2–5) × 10^{-3} M) were made up in 1.00 M $NaClO_4$ and mixed, after thermal equilibration, with buffer solutions (0.2 M, adjusted to give $\mu = 1.00$ M with use of $NaClO_4 \cdot H_2O$). A Durrum stopped-flow apparatus was used for the fast reactions. Rate data were treated routinely by nonlinear least-squares analyses[12] of the first-order equation: $(A - A_\infty) = (A_0 - A_\infty)e^{-kt}$.

Results and Discussion

Syntheses. Three new pentaamminecobalt(III) complexes have been prepared with use of the sulfonate ligands $CF_3SO_3^-$, p-$NO_2C_6H_4SO_3^-$, and $CH_3SO_3^-$.

The $CH_3SO_3^-$ and p-$NO_2C_6H_4SO_3^-$ complexes were prepared by solid-phase dehydration of $[Co(NH_3)_5OH_2]X_3$ (where X = $CH_3SO_3^-$ or p-$NO_2C_6H_4SO_3^-$) in vacuo at ~100 °C (eq 1). This is a well-known strategy,[13] but it is noted that neither $[Co(NH_3)_5OH_2](CF_3SO)_3$ nor $[Co(NH_3)_5OH_2](ClO_4)_3$ (*hazard*!) lose water under these conditions.

$$[Co(NH_3)_5OH_2]X_3 \xrightarrow[\sim 1\ torr]{\Delta} [Co(NH_3)_5X]X_2 + H_2O\uparrow \quad (1)$$

The complex ion $[Co(NH_3)_5OSO_2CF_3]^{2+}$ was synthesized by solvolysis of $[Co(NH_3)_5N_3]^{2+}$ in the concentrated sulfonic acid at 25 °C (eq 2). The reaction may occur both by NO^+ reacting with the coordinated N_3^- ion and by solvolysis of the complex and release of HN_3 which then reacts rapidly with $ONOSO_2CF_3$. The use of the triflate salt in triflic acid ensures the absence of undesired anions which could coordinate. Even ClO_4^- is in this category; the $[Co(NH_3)_5OClO_3]^{2+}$ ion is surprisingly long lived in dilute aqueous acid ($t_{1/2} \approx 7$ s at 25 °C).[4] The methanesulfonato complex was prepared analogously, and this method of preparation is superior to the aqua complex dehydration synthesis. The $CH_3SO_3^-$ complex was formed also from $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ in CH_3SO_3H, and it is of interest that the "reverse" reaction, $[Co(NH_3)_5OSO_2CH_3]^{2+}$ in CF_3SO_3H, gave the triflato complex.

$$[Co(NH_3)_5N_3]^{2+} + CF_3SO_3H \xrightarrow{NOOSO_2CF_3} [Co(NH_3)_5OSO_2CF_3]^{2+} + N_2 + N_2O \quad (2)$$

The isolation and purification of the sulfonato complexes presented difficulties because of their lability toward solvolysis, in water in particular, and the relative insolubility of the solvolysis product, e.g., $[Co(NH_3)_5OH_2](ClO_4)_3$. However the least labile sulfonato complex $[Co(NH_3)_5OSO_2CH_3]^{2+}$ ($t_{1/2} \approx 58$ min, 25 °C) was purified satisfactorily by recrystallization from cold water/$HClO_4$. The triflato complex ($t_{1/2} \approx 26$ s, 25 °C) was recrystallized by extraction of the crude material ($CF_3SO_3^-$ salt) with ice water (pH 3, HCl) directly into an ice/$HClO_4$ mixture at −40 °C, in a manner similar to that described for obtaining pure $[Co(NH_3)_5OClO_3](ClO_4)_2$.[4]

$[Co(NH_3)_5OSO_2C_6H_4NO_2$-$p](p$-$NO_2C_6H_4SO_3)_2$, prepared by the solid-phase dehydration of the aqua complex, proved insoluble in water and most other solvents. However, extraction into dry sulfolane and precipitation with LiCl yielded the water-soluble chloride suitable for conversion to the perchlorate salt with use of ice water/$HClO_4$. Later in this work a better synthesis, from $[Co(NH_3)_5OH](ClO_4)_2$ and p-$NO_2C_6H_4SO_2Cl$ in *N*,*N*-dimethylformamide (DMF) in the presence of $N(C_2H_5)_3$, was developed to give the desired complex in high yield and purity. Since $[(NH_3)_5CoOH_2]^{3+}$ does not react with p-$NO_2C_6H_4SO_2Cl$ in DMF, triethylamine was used to consume the liberated HCl and hence retain the nucleophilic $[(NH_3)_5CoOH]^{2+}$ moiety (eq 3). This is one of a variety of reactions using the nucleophilic capacity of coordinated HO^- in $[Co(NH_3)_5OH]^{2+}$ to capture organic electrophiles in nonaqueous media. The reactions are usually rapid and almost certainly do not involve Co–O rupture.[14] In some instances the appropriate labeling experiments have been done to show that the bound HO^- is the nucleophile.[14]

$$[(NH_3)_5CoOH]^{2+} \xrightarrow[DMF]{NO_2C_6H_4SO_2Cl} [(NH_3)_5CoOSO_2C_6H_4NO_2]^{2+} + HCl \quad (3)$$

Properties. The sulfonato complexes were all pink crystalline solids, solvolyzed by water, DMF, Me_2SO, methanol, ethanol, acetonitrile, and other solvents. The triflato and perchlorato complexes in particular solvolyze rapidly in water and in sharp contrast to complexes with poorer leaving groups (e.g., Cl^- or Br^-), solvolyze even more rapidly in dipolar aprotic media such as Me_2SO and DMF. In the latter solvents, solvolysis of Cl^- or Br^- is slower usually by 1–2 orders of magnitude compared to water.[15]

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Despite their sensitivity to water, the solid sulfonato and perchlorato complexes do not decay rapidly in moist air and can be stored over P_2O_5 without change for months.

All complexes used in this work were tested for the presence of the likely impurities $[Co(NH_3)_5X]^{2+}$ ($X = NO_2^-, N_3^-, Cl^-$, and/or NH_3) and, in particular, $[Co(NH_3)_5OH_2]^{3+}$. Synthetic mixtures of the above ions separated readily on Sephadex SPC25 (Na^+ form) cation-exchange resin on elution with 0.2–0.5 M $NaClO_4$ (pH 3, $HClO_4$) or NaH_2PO_4 (0.2 M). Thus the absence of $[Co(NH_3)_5X]^{n+}$ ($X = Cl^-, NO_2^-, N_3^-, NH_3$) was established by selectively aquating the sulfonates $[Co(NH_3)_5OSO_2R]^{2+}$ ($R = CF_3, CH_3$, and p-$NO_2C_6H_4SO_3$) to $[Co(NH_3)_5OH_2]^{3+}$ and chromatographing the resultant mixture on Sephadex. Synthetic mixtures of $[Co(NH_3)_5X](ClO_4)_n$ and $[Co(NH_3)_5OH_2](ClO_4)_3$ in dry Me_2SO-d_6 revealed the farily sharp $Co-OH_2$ resonance in a region (δ 5.60) free of other signals, and this method for detecting aqua complex impurity can be made rather sensitive (to $\lesssim 0.5\%$ of the total cobalt) by using high [Co]; the perchlorate salts provide the desired solubility (see Experimental Section). The ^1H NMR spectra of the sulfonato and chloro complexes were recorded directly as such, but those of the labile triflato and perchlorato complexes were necessarily recorded as their common solvolysis product, $[Co(NH_3)_5OS(CD_3)_2]^{3+}$. In blank experiments it was shown that solvolysis did not lead to incorporation of water as $CoOH_2^{3+}$ in Me_2SO-d_6 containing H_2O at levels comparable to the [Co]. In addition to demonstrating the absence of aqua complex, the NMR spectra also confirmed the absence of lattice water.

The triflato and perchlorato complexes, after solvolysis ($>10t_{1/2}$) in dry Me_2SO and CH_3CN, were also examined by chromatography. Pink-violet $[Co(NH_3)_5OSMe_2]^{3+}$ and the inert yellow $[Co(NH_3)NCMe]^{3+}$ each separate from $[Co(NH_3)_5OH_2]^{3+}$ on the Sephadex or Dowex ion-exchange resins with the appropriate eluants.[16]

Finally, the ^{18}O results (ahead) established unequivocally the absence of free or bound water in the perchlorato and in two of the three sulfonato complexes.

Aquation Kinetics. The reactions were followed spectrophotometrically in aqueous perchloric acid at 25 °C and at unit ionic strength ($NaClO_4$). With the exception of $[Co(NH_3)_5OSO_2CF_3]^{2+}$, the complexes were dissolved directly in the acid solution. For measurement of the rapid solvolysis of the triflato complex ion a modified stopped-flow apparatus[17] was used. The complex ($\sim 5 \times 10^{-2}$ M) dissolved in well-dried methanol (Mg or a 3 Å molecular sieve) was contained in one syringe of the apparatus, with the aqueous acid medium in the other. The ratio of the volumes of the two drive syringes was 1:17.5 so that dilution of the aqueous acid was only slight and the effect of the ~5% CH_3OH could be neglected. The half-life of $[Co(NH_3)_5OSO_2CF_3]^{2+}$ in CH_3OH was ~10 min so that solutions were prepared immediately before a reaction run. After most of this work was completed, the hydrolysis rate was measured in aqueous $HClO_4$ in the absence of methanol with use of the method described for the perchlorato complex[4] and, later, with use of a device[18] which allowed the monitoring of reactions within 1 s of dissolution. The former method permitted a study of 60% of the aquation process and the latter method essentially all of it. Duplicate runs using all techniques gave identical results (Table I). The hydrolysis product was identified in all cases by its visible spectrum (ϵ_{max}^{492} 47.2, dilute $HClO_4$) and chromatographic behavior (3+ ion) as 100% $[Co(NH_3)_5OH_2]^{3+}$.

Table I. Rate Constants (k_{H_2O}, s^{-1}) for the Spontaneous Aquation of $[Co(NH_3)_5OSO_2R]^{2+}$ Complexes in Aqueous $HClO_4$ at 25 (± 0.05) °C and $\mu = 1.0$ M ($NaClO_4$)

	$[HClO_4]$, M			
	1.0	0.1	0.01	0.001
$[Co(NH_3)_5OSO_2CH_3]^{2+}$ [a]		2.0×10^{-4}		2.0×10^{-4}
$[Co(NH_3)_5OSO_2C_6H_4NO_2$-$p]^{2+}$ [b]	7.2×10^{-4}	6.3×10^{-4}	6.3×10^{-4}	6.7×10^{-4}
$[Co(NH_3)_5OSO_2CF_3]^{2+}$ [b,c]		2.7×10^{-2}	2.7×10^{-2}	

[a] Measured at 550 nm; [Co] typically 10^{-3}–10^{-2} M. [b] Measured at 530 nm; [Co] 10^{-3}–10^{-2} M. [c] [Complex] $\simeq 5 \times 10^{-2}$ M in methanol, mixed with 0.101 or 0.010 M $HClO_4$ in the ratio 1:17.5, giving a mixture 9.54×10^{-2} or 9.54×10^{-3} M $[HClO_4]$ and $\sim 3 \times 10^{-3}$ M [Co].

Table II. Rate Constants for Base Hydrolysis at 25.0 °C and $\mu = 1.0$ M ($NaClO_4$)[a]

$[Co(NH_3)_5OSO_2CH_3](ClO_4)_2$

pH	$10^2 k_0$, s^{-1}	k_{OH},[b] $M^{-1}\,s^{-1}$
10.21	1.51	55
10.56	3.22	52
11.07	10.9	54
11.40	26.0	60

$[Co(NH_3)_5OSO_2C_6H_4NO_2$-$p](ClO_4)_2$

pH	$10^3 k_0$, s^{-1}	$10^{-2} k_{OH}$,[d] $M^{-1}\,s^{-1}$
8.67[c]	2.83	2.7
8.99[c]	5.55	2.9
9.22[c]	7.30	2.4
9.44[c]	13.2	2.7
10.49[e]	180	2.9

[a] [Co] $\approx 5 \times 10^{-3}$ M; followed spectrophotometrically at 380 nm in 0.1 M triethylamine/$HClO_4$ buffers. [b] $k_{OH} = k_0/[OH^-]$, with $pK_{H_2O} = 13.77$ ($\mu = 1.0$ M, 25 °C). [c] 0.1 M diethanolamine buffer solution. [d] $k_{OH} = (k_0 - k_{H_2O})/[OH^-]$, $k_{H_2O} = 6.6 \times 10^{-4}\ s^{-1}$; k_{OH} was calculated with $pK_{H_2O} = 13.77$ ($\mu = 1.0$ M, 25 °C). [e] 0.1 M triethylamine buffer.

First-order reactions were observed in all instances for at least 3 half-lives of the reaction. The rate constants were essentially independent of $[H^+]$ in the range 1.0–10^{-3} M and independent of [Co] in the range 10^{-3}–10^{-2} M.

Base Hydrolysis. Hydrolysis of $[Co(NH_3)_5OSO_2CH_3]^{2+}$ and $[Co(NH_3)_5OSO_2C_6H_4NO_2$-$p]^{2+}$ in aqueous buffer solutions ($\mu = 1.0$ M, adjusted with $NaClO_4$, 25 °C) was observed spectrophotometrically with use of stopped-flow techniques. In both cases pseudo-first-order kinetics were observed. Plots of ln $|A - A_\infty|$ against time were linear for at least 3 half-lives, and the product was identified as $[Co(NH_3)_5OH]^{2+}$ by its visible spectrum and ion-exchange characteristics in acid and base. The data are consistent with rate law 4. The results are presented in Table II.

$$-d[(NH_3)_5CoOSO_2R^{2+}]/dt = k_0[(NH_3)_5CoOSO_2R^{2+}] = \{k_{H_2O} + k_{OH}[OH^-]\}[(NH_3)_5CoOSO_2R^{2+}] \quad (4)$$

Observations of the rate of base hydrolysis of the $[(NH_3)_5CoOSO_2CF_3]^{2+}$ ion were hampered by the high background aquation rate for this ion ($t_{1/2} = 26$ s, 25 °C). To satisfactorily separate the base catalyzed and spontaneous hydrolysis paths, it was necessary therefore to use a pH at which the $t_{1/2}$ for hydrolysis was $\lesssim 3$ s. Clearly a detailed study was not feasible with the apparatus used both because of the instability of solutions of this complex and because of Schlieren effects following mixing of the methanol and water solution.

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Table III. Rates of Aquation and Base Hydrolysis for Some $[Co(NH_3)_5X]^{n+}$ Complexes at 25 °C and $\mu = 1$ M

X	k_{H_2O}, s^{-1}	ref	k_{OH}, M^{-1} s^{-1}	ref
NO_2^{-} [b]	1.2×10^{-8}	*e*	4.2×10^{-6} [c]	*l*
N_3^{-}	2.1×10^{-9}	*f*	3.0×10^{-4}	*f*
$CH_3CO_2^{-}$	2.7×10^{-8}	*g*	7.0×10^{-4}	*m*
Cl^{-}	1.7×10^{-6}	*h*	0.25	*n*
ONO_2^{-}	2.4×10^{-5}	*i*	5.7	*o*
$CH_3SO_3^{-}$	2.0×10^{-4}	*d*	55	*d*
$(CH_3O)_3PO$	2.0×10^{-4} [a]	*j*	85[a]	*j*
p-$NO_2C_6H_4SO_3^{-}$	6.6×10^{-4}	*d*	270	*d*
$CF_3SO_3^{-}$	2.7×10^{-2}	*d*	$>1 \times 10^{6}$	*d*
ClO_4^{-}	0.10	*k*		

[a] For Co–O cleavage pathway. [b] N-bound isomer. [c] $\mu \approx 0$ M. [d] This work. [e] G. C. Lalor, *J. Chem. Soc. A*, 1 (1966). [f] G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1560 (1963). [g] F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, 24, 1241 (1962). [h] S. C. Chan, *J. Chem. Soc. A*, 291 (1967). [i] W. E. Jones, R. B. Jordan, and T. W. Swaddle, *Inorg. Chem.*, 8, 2504 (1969). [j] W. Schmidt and H. Taube, *Inorg. Chem.*, 2, 698 (1963). [k] J. MacB. Harrowfield, A. M. Sargeson, B. Singh, and J. C. Sullivan, *Inorg. Chem.*, 14, 2864 (1975). [l] G. C. Lalor and J. Lange, *J. Chem. Soc.*, 5620 (1963). [m] F. Basolo, J. G. Bergmann, and R. G. Pearson, *J. Phys. Chem.*, 56, 22 (1952). [n] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, 7, 174 (1968). [o] W. E. Jones, R. B. Jordan, and T. W. Swaddle, *Inorg. Chem.*, 8, 2504 (1969).

However some data were collected, and a derived rate constant was calculated on the assumption of a second-order rate law. The results were obtained with use of 0.1 M Tris/$HClO_4$ buffer (pH 7.20, $[OH^-] = 2.69 \times 10^{-7}$ M, $pK_w = 13.77$ at 25 °C, $\mu = 1$ M) as solvent. This gave a $t_{1/2}$ for hydrolysis of 2.7 and 2.3 s in duplicate experiments, $k_{obsd} = 0.3$ s^{-1}, and hence $k_{OH} \gtrsim 1 \times 10^6$ M^{-1} s^{-1}.

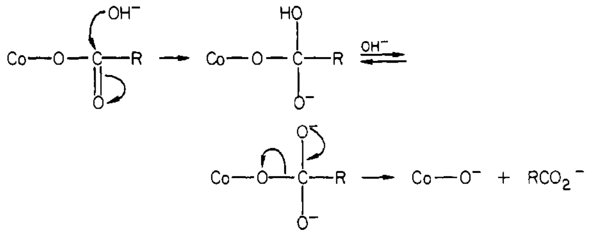
Similarly, the high rate of background aquation ($t_{1/2} \approx 7$ s, 25 °C) of the $[Co(NH_3)_5OClO_3]^{2+}$ ion prevented a detailed study of the base hydrolysis kinetics. However our interest here lay primarily in the anion competition (ahead), and it was necessary only to be confident that, under the conditions (pH ~13), the background aquation was negligible. A base hydrolysis rate constant $k_{OH} > 10^6$ M^{-1} s^{-1} seems likely by analogy with $[Co(NH_3)_5OSO_2CF_3]^{2+}$; for $[Co(NH_3)_5X]^{n+}$ in general the dominant mode of hydrolysis above pH ~10 is the base-catalyzed pathway;[1] at pH 13, >99% base hydrolysis of $[Co(NH_3)_5OClO_3]^{2+}$ would seem secure ($t_{1/2} \lesssim 10$ μs, 25 °C, $\mu = 1$ M).

The aquation and base hydrolysis rate data for the present pentaammine complexes are combined in Table III with data for analogous complexes. It is immediately clear that the sulfonato (and perchlorato) complexes greatly extend the range of hydrolysis rates known for this type of complex, and to a degree the ability of the substituent to leave the metal ion correlates with the acidity of the parent acid.

Oxygen-18 Tracer Experiments. Hydrolysis of cobalt(III) acidopentaammine complexes in which the acido substituent is the conjugate base of an oxyacid may proceed by cleavage at the Co–O bond or at the adjoining O–X bond. For the sulfonate complexes therefore cleavage could occur at the Co–O or O–S bonds and for the perchlorato complex, at the Co–O or Cl–O bonds. For $[Co(NH_3)_5O_2CCH_3]^{2+}$ it has been shown that cleavage is almost entirely at the Co–O bond[19] but that for C-halogenated acetato complexes the amount of O–C cleavage increases with the acidity of the parent acid.[19,20] These results have been correlated with kinetic evidence for two pathways in the hydrolysis reaction which has rate law 5. The term in k_1 corresponds to the normal conjugate base path with Co–O cleavage, while the term in k_2 is identified

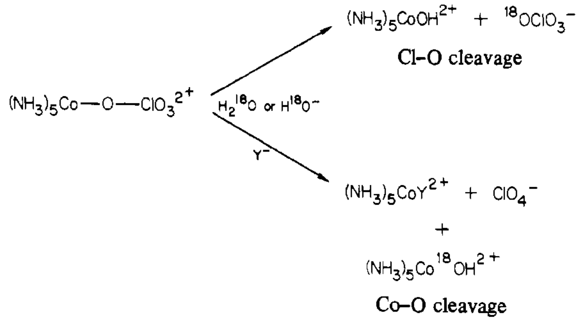
$$k_{obsd} = k_1[OH^-] + k_2[OH^-]^2 \qquad (5)$$

with a bimolecular path involving nucleophilic attack at the substituent in the complex deprotonated at the ligand, which leads to C–O cleavage (eq 6).[20] It was therefore of interest



(6)

to examine, using the usual ^{18}O-tracer methods, the relative importance of the two possible hydrolysis pathways for the corresponding complexes of the $CH_3SO_3^-$ and the fluorine-substituted derivative $CF_3SO_3^-$. The perchlorato complex has the prospect of either Co–O or Cl–O cleavage, and this was investigated also. Sulfur–oxygen or chlorine–oxygen cleavage leads to a reduction in the available path to anion competition, and since we have examined anion competition in both acid and base hydrolysis, we carried out the tracer experiments under both conditions (see eq 7).



(7)

The results (Table IV) reveal no significant S–O or Cl–O cleavage in either acid or base hydrolysis. This is the same pattern found for $[Co(NH_3)_5ONO_2]^{2+}$[21] and $[Co(NH_3)_5OSO_3]^{+}$[22] which can react by either hydrolysis route, and it may be contrasted with other reactions where Co–O cleavage is not exclusive. Recent ^{18}O-tracer work on these reactions has highlighted an important problem. In some of our early experiments, suspiciously low ^{18}O enrichments (by ~10%) were observed for $[Co(NH_3)_5{}^{18}OH_2]^{3+}$ derived from hydrolysis of the sulfonato and perchlorato complexes. To check on isotopic dilution from extraneous sources, we performed blank experiments on carefully purified $[Co(NH_3)_5Cl](ClO_4)_2$ in $^{18}OH^-$ which should give $[Co(NH_3)_5{}^{18}OH_2]^{3+}$ of identical enrichment to the solvent. We found only 90% of the expected figure, and the problem was traced to the $Hg(CN)_2/HgCl_2$ reagent used to convert $H_2{}^{18}O$ to $C^{18}O_2$, which gave rise to $C^{16}O_2$ derived either from $H_2{}^{16}O$ or from another (as yet unidentified) impurity of the same mass (44). The corrected figures for the sulfonato and perchlorato complexes were raised from a spurious ~90% to 100%. We suggest the blank experiments described here as a routine check on the validity of ^{18}O-tracer results.

Competition Experiments. Base Hydrolysis. The early competition experiments were used to show that the base hydrolysis of a variety of $[Co(NH_3)_5X]^{n+}$ complexes is consistent with the presence of a common short-lived intermediate. When the complex ions were hydrolyzed in the presence of

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Table IV. Oxygen-18 Tracer Results for the Acid and Base Hydrolysis of $[Co(NH_3)_5X]^{2+}$ ($X = CH_3SO_3^-$, $CF_3SO_3^-$, and ClO_4^-) at 25 °C

complex	conditions	*R*(solvent)[a]	*R*(product)[a]	% solvent O in product[b,f]
$[Co(NH_3)_5OSO_2CF_3]^{2+}$	acid[c]	0.02636	0.02655	101
	base[d]	0.02635	0.02623	99.5
$[Co(NH_3)_5OSO_2CH_3]^{2+}$	acid[e]	0.02648	0.02522	95.5 (101[e])
	base[d]	0.02640	0.02621	99
$[Co(NH_3)_5OClO_3]^{2+}$	acid[c]	0.02693	0.02680	99.5
	base[d]	0.02637	0.02655	101

[a] $R = m/e\ 46/(44 + 45)$. [b] Calculated as $10^2 \times$ (% ^{18}O enrichment in $[Co(NH_3)_5OH_2]Br_3$/% ^{18}O enrichment in solvent), where % enrichment = $10^2R/(2 + R) - 10^2R_{CO_2}/(2 + R_{CO_2})$; $R_{CO_2} = m/e\ 46/(44 + 45)$ for CO_2 of natural abundance (0.003 13 on our instrument). [c] ~10^{-3} M HCl in ~1.5 atom % $H_2{}^{18}O$. [d] ~0.1 M NaOH in ~1.5 atom % $H_2{}^{18}O$. [e] Corrected for subsequent H_2O exchange in aqua product (5.5%; 2.5-h aquation at 25 °C and with use of $t_{1/2}$ = 30 h). [f] Duplicate experiments, ±(0.5–1)%.

Table V. Competition Data for the Base Hydrolysis of $[Co(NH_3)_5X]^{n+}$ in NaN_3 at 25 °C and $\mu = 1.1$ M

X	$[N_3^-]$, M	% azido product (±0.5%)	ref
$CH_3OSO_2^-$	0.5 (μ = 0.75 M)	5.2	*f*
	1.0	9.4,[e] 10.1,[c] 10.2[c]	*f*
$CF_3OSO_2^-$	1.0	8.1[d]	*f*
		8.6,[e] 8.8,[e] 8.7[e]	*f*
		9.7,[c] 9.8[c]	*f*
ClO_4^-	1.0	10.1, 10.3, 10.5	*f*
Cl^-	1.0	8.5	*g*
Br^-	1.0	8.7	*g*
I^-	0.5 (μ = 0.75 M)	5.9	*g*
	1.0	9.9	*g*
ONO_2^-	1.0	10.4	*g*
SCN[a]	1.0	9.5[b]	*h*

[a] S-bound isomer. [b] Corrected for other reaction pathways. [c] In dark. [d] In sunlight. [e] Under normal laboratory lighting. [f] This work. [g] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, 88, 5443 (1966). [h] D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, 9, 655 (1970).

competing nucleophiles such as H_2O and N_3^-, the reaction yielded a mixture of hydroxo and azido species, and the product ratios were found to be very largely independent of the leaving group. The results implied that the hydrolysis was dissociative and led to a common intermediate and thence to common products.

Competition results for the base hydrolysis of $[Co(NH_3)_5OSO_2CF_3]^{2+}$, $[Co(NH_3)_5OSO_2CH_3]^{2+}$, and $[Co(NH_3)_5OClO_3]^{2+}$ ions in 1.00 M N_3^-/0.125 M OH^- ($\mu \approx 1.1$ M, 25 °C) are listed in Table V together with data for analogous complexes. The experiments were performed homogeneously in the usual way for the $CH_3SO_3^-$ complex, but a heterogeneous method was required for the labile $CF_3SO_3^-$ and ClO_4^- complexes. The experiments were performed in both ways for the $CH_3SO_3^-$ complex. The results were not significantly different, and therefore there is no reason to expect anomalous answers from the heterogeneous method.

The pattern for the three new very labile complex ions is clearly consistent with that established for other $[Co(NH_3)_5X]^{2+}$ ions (Table V). It is especially significant that the same result obtains for complexes which are up to 10^5-fold more reactive than any reported previously. Further discussion of the base hydrolysis mechanism is postponed until the publication of our competition results for the $[Co(NH_3)_5OSO_3]^+$, $[Co(NH_3)_5O_3SSO_3]^+$, $[Co(NH_3)_5OSO_2F]^{2+}$, $[Co(NH_3)_5OSMe_2]^{3+}$, $[Co(NH_3)_5(OC(NH_2)_2)]^{3+}$, and $[Co(NH_3)_5OP(OMe)_3]^{3+}$ systems. This and other work has made it clear that the competition is dependent upon the formal charge of the complex before the substituent has left. It suffices to note here that the present data support the case made previously for the S_N1CB base hydrolysis mechanism in which a common short-lived reduced coordination number amido intermediate $[Co(NH_3)_4(NH_2)]^{2+}$ is implicated.

Acid Hydrolysis. There have been just a few reports on competition in spontaneous aquation and only one since the use of the ion-exchange chromatography technique for accurately analyzing for the proportions of the competition products. The problems have been the very small amount of anion competition, just a few percent, and the lack of compounds of sufficient lability to permit experiments which can be unequivocally analyzed. Anion is incorporated also in the subsequent anation reaction of $[Co(NH_3)_5OH_2]^{3+}$, and it can be difficult sometimes to separate the two anion-entry processes.

The present results however (Table VI) demonstrate clearly that, in 1.00 M HCl, some $[Co(NH_3)_5Cl]^{2+}$ is formed concurrently with $[Co(NH_3)_5OH_2]^{3+}$ during the spontaneous aquation of the $CH_3SO_3^-$, $CF_3SO_3^-$, and ClO_4^- complexes. For the triflato and perchlorato ions, less than 0.1% $[Co(NH_3)_5Cl]^{2+}$ is formed by Cl^- anation of $[Co(NH_3)_5OH_2]^{3+}$ in the time required for complete hydrolysis ($10t_{1/2} \lesssim 5$ min,

Table VI. Chloride Ion Competition Results for the Spontaneous and Induced Aquation of Some $[Co(NH_3)_5X]^{n+}$ Complexes in 1.00 HCl at 25 °C

complex	hydrolysis time[a]	% $[Co(NH_3)_5Cl]^{2+}$ [b]	av % $[Co(NH_3)_5Cl]^{2+}$	*R*[e]
$[Co(NH_3)_5OSO_2CF_3]^{2+}$	5 min	3.4, 3.2	3.3 ± 0.2	0.034
$[Co(NH_3)_5OClO_3]^{2+}$	5 min	3.2, 3.2 (3.0, 3.4)[c]	3.2 ± 0.2	0.033
$[Co(NH_3)_5OSO_2CH_3]^{2+}$	6 h	4.0, 3.7	1.25 ± 0.2[d]	0.013
$[Co(NH_3)_5NCO]^{2+} + NO^+$ [f]	5 min		21 ± 2[g]	0.26
$[Co(NH_3)_5N_3]^{2+} + NO^+$	1–5 min		23.0 ± 0.5[h]	0.30
			24.5 ± 0.5[i]	0.32
$[Co(NH_3)_5O_2CNH_2]^{3+} + NO^+$ [f]	1–5 min		23 ± 0.5[h]	0.30
$[Co(NH_3)_5OH_2]^{3+}$	6 h	2.6, 2.6	2.6 (±0.1)	

[a] $>10\,t_{1/2}$, except for the $[Co(NH_3)_5OH_2]^{3+}$ control. [b] The multiple entries indicate the number of separate determinations. [c] Previous values (J. MacB. Harrowfield, A. M. Sargeson, B. Singh, and J. C. Sullivan, *Inorg. Chem.*, 14, 2864 (1975)). [d] Corrected for subsequent Cl^- anation of $[Co(NH_3)_5OH_2]^{3+}$ (2.6%, last entry in table). [e] $R = [Co(NH_3)_5Cl^{2+}]/[Co(NH_3)_5OH_2{}^{3+}][Cl^-]$. [f] Corrected for other reaction pathways not involving Co–X cleavage. [g] D. A. Buckingham, D. J. Francis, and A. M. Sargeson, *Inorg. Chem.*, 13, 2630 (1974). [h] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, 6, 1027 (1967). [i] W. L. Reynolds, S. Hafezi, A. Kessler, and S. Holly, *Inorg. Chem.*, 18, 2860 (1979).

25 °C). The figures of 3.3% and 3.2% Cl^- capture, respectively, therefore do not need correction for this path. For the methanesulfonato complex, aquation was also much faster (~50-fold) than subsequent anation. However a small but significant correction (2.6%) was necessary for some chloro complex arising by this route. This value was accurately defined by running blanks ($[Co(NH_3)_5OH_2]^{3+}$ in 1.00 M HCl) over the same period (6.0 h) required for complete aquation of the $CH_3SO_3^-$ complex ($10t_{1/2}$) and separating the small amount of chloro from the aqua complex by chromatography, as in the other experiments. Thus the corrected figure[23] for direct Cl^- incorporation for $[Co(NH_3)_5OSO_2CH_3]^{2+}$ aquating in 1 M HCl is (3.9% − 2.6%) = 1.3%, and again this is real, albeit small.

The calculated competition factors R for these reactions (eq 8) are 0.034, 0.033, and 0.013 for the $CF_3SO_3^-$, ClO_4^-, and

$$R = [Co(NH_3)_5Cl^{2+}]/[Co(NH_3)_5OH_2^{3+}][Cl^-] \qquad (8)$$

$CH_3SO_3^-$ complexes, respectively. The R value can be interpreted as an indication of how much bond making to water and anion is involved in the course of dissociation of the leaving group.[24,25] If the entering group gets to exert its nucleophilicity, it should be reflected in higher R values and a spread in values for different nucleophiles. Moreover R should be leaving group dependent. While we have examined only Cl^- competing against H_2O for three good leaving groups in this work, two features of the results (Table VI) are nonetheless striking. First, the competition is low and the R values are similar in magnitude for the three 2+ ions which range in reactivity from $t_{1/2} \approx 7$ s to $t_{1/2} \approx 58$ min at 25 °C. Second, none of the ions capture Cl^- anywhere near as effectively as the presumed $[Co(NH_3)_5]^{3+}$ intermediate generated, for example, in the NO^+-induced aquation of $[Co(NH_3)_5N_3]^{2+}$ where $R = 0.30$ for Cl^- ($\mu = 1$ M, 25 °C).[26] Since several other induced aquations yield $R \simeq 0.30$[25,26] and are presumed different sources of a common five-coordinate $[Co(NH_3)_5]^{3+}$ intermediate, it is tempting to reinforce the conclusion that the spontaneous aquations do not involve such an intermediate. At the very least, they cannot involve the same intermediate. At present it remains unclear why induced aquation leads to high and spontaneous aquation low-anion competition. If a $[Co(NH_3)_5]^{3+}$ intermediate is formed and is necessary to give both a relatively high competition and a result independent of the leaving group, the obvious question is how good a leaving group is required to produce this intermediate? Perchlorate and triflate are the best leaving groups to date among the many isolable complexes, and although their rates are closer to the S_N1 dissociative limit, this is clearly not reflected in the anion competition results. Recently it has been suggested that five-coordinate intermediates of any chemically significant lifetime are not involved even in induced-aquation reactions.[27,28] Rather the anion competition results have been interpreted in terms of dissociative interchange (S_N1) reactions whereby anion entry results from a preassembled ion-paired complex. Then leaving-group independence of the competition is not required. Furthermore, complexes which form the stronger ion pairs, the more highly charged species in particular, lead to higher anion competition. It need be pointed out that this alone cannot accommodate all the facts. For example, there is the glaring anomaly of the aquation of $[Co(NH_3)_5OP(OMe)_3]^{3+}$ in 1 M HCl which yields 4.5% Cl^- competition,[21,29] while the nitrosation of $[Co(NH_3)_5N_3]^{2+}$, presumed to generate the reactive $[Co(NH_3)_5(N_4O)]^{3+}$ species, which also carries a 3+ formal charge, leads to 22% Cl^- competition.[26] Moreover, anions which are the best competitors appear to have, for a given formal charge of the substrate, the lowest ion-association constants. Furthermore, we have recently found examples of anion competition in spontaneous aquation, fast and slow, which give low up to quite high R values, comparable to those observed in induced aquation, and the results have no obvious correlation with reactivity, size, bonding geometry, or charge of the leaving group. We will be reporting on these elsewhere, but we should also comment here that the analysis of the induced-aquation results is also a matter of controversy in its own right.[30] In summary, the spontaneous aquation competition results to date are inconclusive, and although they do at least preclude a discrete common five-coordinate intermediate, the reactions fit the pattern of other $[Co(NH_3)_5X]^{n+}$ auations where there is general agreement that they are essentially dissociative.

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Registry No. $[Co(NH_3)_5OSO_2CF_3](ClO_4)_2$, 76024-69-6; $[Co(NH_3)_5OSO_2CH_3](ClO_4)_2$, 76024-71-0; $[Co(NH_3)_5OSO_2C_6H_4NO_2\text{-}p](ClO_4)_2$, 76024-73-2; $[Co(NH_3)_5OClO_3](ClO_4)_2$, 18042-14-3; $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$, 75522-50-8; $[Co(NH_3)_5OH_2](CF_3SO_3)_3$, 69897-22-9; $[Co(NH_3)_5OH_2](NO_2C_6H_4SO_3)_3$, 76024-74-3; $[Co(NH_3)_5OH_2](NO_2C_6H_4SO_3)(ClO_4)_2$, 76024-75-4; $[Co(NH_3)_5OH_2](CH_3SO_3)(ClO_4)_2$, 76024-76-5; $[Co(NH_3)_5N_3](CF_3SO_3)_2$, 76024-77-6; $[Co(NH_3)_5N_3](ClO_4)_2$, 14283-04-6; $[Co(NH_3)_5OH_2](CH_3SO_3)_3$, 76024-78-7; $[Co(NH_3)_5OH_2](ClO_4)_3$, 13820-81-0; $[Co(NH_3)_5OH_2]Br_3$, 14404-37-6; $[Co(NH_3)_5N_3]Cl_2$, 14916-48-4; $[Co(NH_3)_5OH](ClO_4)_2$, 18885-27-3; N_3^-, 14343-69-2; Cl^-, 16887-00-6.

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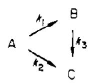
[23] It is readily shown that for a consecutive reaction scheme



where $(k_1 + k_2) > 10k_3$ and where $k_1 >> k_2$, the "extra" C produced via B → C at $10t_{1/2}$ of the $(k_1 + k_2)$ reaction is closely approximated by that produced in the same time commencing with pure B.

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