are available for the trien, dien, and en ligands. These are reproduced in Table V. The k_1's at ~60 °C reported here for the dien and trien 3-isomer complexes are close to the rate constants determined by Garner et al. for the intermediate aquation steps of the related inorganic complexes. It therefore appears that, whether or not the Cr is bonded to carbon, the rate constants for the aquation steps do not differ very much. It may be expected that the Cr–C cleavage in the 3-isomers (average $k \sim 5 \times 10^{-4}$ s^{-1} at 60 °C) occurs before the loss of all amine ligands because the rate constants for the final aquation steps are at least 1 order of magnitude slower than that of the Cr–C cleavage. Conversely, as is seen from Table II, in the case of the 2-isomers, complete aquation precedes the Cr–C bond cleavage, which is 2–3 times slower than the aquation steps. By comparison, the complexes containing macrocyclic ligands are considerably more stable than those containing straight-chain amine ligands—the macrocyclic effect.[29,30] Therefore, by analogy, the macrocyclic complex would be expected to undergo Cr–C cleavage with the Cr–N linkages in the complex remaining intact, and this was indeed observed. However, the ultimate reason for the faster cleavage of the Cr–C bond in the 3-isomer as compared to the 2-isomer is still unclear and is under continuing investigation.

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Registry No. **1a**, 99725-95-8; **1b**, 99725-96-9; **2a**, 99708-64-2; **2b**, 99708-65-3; **3a**, 99708-66-4; **3b**, 99708-67-5; **4a**, 99708-68-6; **4b**, 99708-69-7; 3-$HpyCH_2Cr(dienH)(H_2O)_3^{4+}$, 99708-70-0; 3-$HpyCH_2Cr(dap)_2(H_2O)^{3+}$, 99708-71-1; 3-picoline, 108-99-6; 1,2-dipyrid-3-ylethane, 4916-58-9.

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Hydrolysis of Coordinated Trifluoromethanesulfonate from Cobalt(III), Rhodium(III), Iridium(III), and Chromium(III) Pentaamines

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Base hydrolysis and aquation of $M(NH_3)_5(OSO_2CF_3)^{2+}$ (M = Co, Rh, Ir, Cr) and $M(NH_2CH_3)_5(OSO_2CF_3)^{2+}$ (M = Co, Rh, Cr) complexes at 25 °C and $I = 1.0$ M are reported. N-Methylation of the ammine ligand causes a marked enhancement of the rate of base hydrolysis reactions with k_{Me}/k_H of $>10^3$ (Co), 150 (Rh), and 800 (Cr). Only minor enhancements occur for aquation with Co and Rh, while there is a minor rate diminution with Cr. Positive activation entropies for base hydrolysis of $M(NH_3)_5(OSO_2CF_3)^{2+}$ (M = Co, Ir) and competition experiments with azide ion in basic solution as well as the absence of the competing ion in the rate law allow a dissociative conjugate-base mechanism for all complexes. The variation in rate enhancement from ammine to methylamine compounds and the competition studies in base with azide ion chiefly reflect differences in steric interactions due to differing metal–ligand bond lengths rather than any mechanistic diversity. Variations in competition behavior for rhodium(III), chromium(III), and cobalt(III) appear to reflect relative lifetimes of the intermediate of reduced coordination number. The variations in aquation are much smaller and do not allow any certainty in mechanistic assertions. Marked accelerations of rates for both acid and base hydrolyses (~10^3–10^6-fold) occur consistently for all trifluoromethanesulfonato complexes compared with those of halo analogues.

Introduction

Studies of hydrolysis reactions of amine complexes of inert d^3 (Cr^{III}) and d^6 (Co^{III}, Rh^{III}, Ir^{III}) ions have an extensive and venerable history, and this research has been widely reviewed.[3-6] Despite this activity, mechanistic aspects still need to be resolved. Overall, aquation reactions of the cobalt(III) complexes appear to be largely dissociative in nature; i.e., bond breaking substantially leads bond making. However, for chromium(III) complexes, more associative character appears to be evident.[7] The rate enhancement observed for cobalt(III) when the nonleaving groups are changed from pentaammine to pentakis(methylamine) with concomitant increase in steric strain contrasts with a rate reduction at chromium(III) in the same circumstances.[8,9] It can be argued that this is consistent with the assessment above. With rhodium(III), the effect is not so significant, and arguments[7] about the degree of associative character in that case are more tenuous. For base hydrolysis, a conjugate-base mechanism seems well-defined, although whether a limiting dissociative process (S_N1CB) obtains universally for these elements is more doubtful.[3,4]

Syntheses of labile trifluoromethanesulfonato ($-OSO_2CF_3$) complexes of inert d^3 and d^6 metal amines have been reported recently;[10-12] the Co(III) complexes aquate rapidly compared with their halo analogues and approach perchlorato complexes in lability.[13] In base, hydrolysis is even more rapid. Reactivity studies of the more kinetically inert metal ions such as Cr(III), Rh(III), and Ir(III) therefore become readily accessible if good leaving groups such as $CF_3SO_3^-$ are used. Here, we report the base

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Table I. Rate Constants for Aquation and Base Hydrolysis of $M(NH_2CH_3)_5(OSO_2CF_6)^{2+}$ Compounds at 25 °C, I = 1.0 M[a]

	k_{aq}, s^{-1}[b]			k_{OH}, $M^{-1}\ s^{-1}$		
M	R = H	R = CH_3	k_{Me}/k_H	R = H	R = CH_3	k_{Me}/k_H
Co	2.39 (5) × 10^{-2}[c]	≥1[e]	≥42	1.0 (1) × 10^4[d]	>10^7[e]	>10^3
Rh	1.91 (4) × 10^{-2}	3.47 (6) × 10^{-2}	1.8	46 (5)[f]	6.3 (3) × 10^3[f]	140
Ir	2.30 (3) × 10^{-4}[g]			1.36 (2) × 10^{-2}[d]		
Cr	1.09 (12) × 10^{-2}	6.43 (15) × 10^{-4}	0.06	2.5 (2)[d]	2.0 (1) × 10^3[d]	800

[a] Calculated from data deposited as supplementary material. [b] $[H^+]$ = 0.1 M. [c] In 0.1 M CF_3SO_3H (I = 0.1 M), $k = 2.70 \times 10^{-2}\ s^{-1}$. [d] In $NaClO_4$. [e] In NaCl. [f] In $NaOSO_2CF_3$. [g] In 0.1 M CF_3SO_3H (I = 0.1 M), $k = 2.61 \times 10^{-4}\ s^{-1}$.

hydrolysis and aquation of $M(NH_2R)_5(OSO_2CF_3)^{2+}$ complexes (M = Co, Rh, Ir, Cr; R = H, CH_3).

Experimental Section

Syntheses. The preparations of the triflato complexes from chloro precursors using anhydrous trifluoromethanesulfonic acid have been described previously. The complexes $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (M = Co, Rh, Ir, Cr) and $[M(NH_2CH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (M = Co, Rh, Cr) were isolated as air-stable, but moisture-sensitive, analytically pure compounds.[10-11]

Kinetics. Reactions were monitored at fixed wavelengths with a Hewlett-Packard 8540A spectrophotometer and 89100A Thermoelectric temperature controller or with a Varian 635 spectrophotometer with thermostated cell holder. Solutions were 1.0 M in $NaClO_4$, $NaSO_3CF_3$, or NaCl. Buffer (HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid), TRIS (tris(hydroxymethyl)aminomethane), $BuNH_2$ (1-aminobutane), NaOAc (sodium acetate) with acid), NaOH, or acid was employed to control pH, which was measured with a Radiometer pH meter, Model 26, and a Radiometer standard combination electrode. Reactions were initiated by injection of the preequilibrated solvent onto the solid complex retained on a frit; then the mixture was injected directly into a spectrophotometer cell by using a mixing syringe previously described.[14] The reaction was monitored within seconds of mixing without any significant temperature change detected by an in situ thermocouple. Reactions in basic solution were monitored at 280 or 365 nm (Co), 280 nm (Rh), 235 nm (Ir), and 240 nm (Cr); in acid, wavelengths employed were 270 or 365 nm (Co), 345 nm (Rh), 290 nm (Ir), and 530 nm (Cr). Reactions were usually followed to completion, except where slow subsequent decomposition processes interfered with the determination. Rate constants were determined by standard nonlinear least-squares analysis, and quoted values are the average of at least three independent measurements, although up to eight determinations of any one reaction rate were made. $[OH^-]$ was determined from the measured pH and the appropriate values of K_w. In 1.0 M NaCl the value of pK_w has been assessed as 13.73 (25 °C).[15] Values of 13.77 and 13.80 (25 °C) have been reported for 1.0 M $NaClO_4$,[16] and we have used the former value. No data appear to exist yet for NaO_3SCF_3 solutions; however, we have assumed the same values as for the equivalent concentration of $NaClO_4$. Reactions in base were extremely rapid, and absorbance changes for the Rh complexes were not substantial. A slow decomposition occurred with the Cr complexes in base subsequent to trifluoromethanesulfonate hydrolysis, complicating the rate determinations for these compounds. Activation parameters were determined in base for Co and Ir complexes only.

Reactions in acid were simple water substitution processes. That the base hydrolysis reactions observed were due exclusively to $CF_3SO_3^-$ loss was monitored for each complex by chromatography and spectroscopy. Reactions in base were quenched with CF_3SO_3H after 5 half-lives, and the diluted solutions were absorbed on Dowex 50W-X2 (H^+ form) or SP Sephadex C-25 (Na^+ form) resin. Subsequent elution indicated only one species present within the limits of detection (≥97%), and the electronic spectrum of the eluate was fully consistent with that of authentic aquapentaammine complex in each case.

The rate of proton exchange in $Ir(NH_3)_5OSO_2CF_3^{2+}$ was determined by ammine deuteration employing a JEOL JNM-FX200 NMR spectrometer to monitor the ^1H signals. A TRIS buffer (pD 8.2) in mixed D_2O/Me_2SO (1:1) solvent, which separated the ammine signals from that of HOD, was employed (20 °C). Variations in the peak area with time from consecutive scans allowed a rate constant to be determined.

Competition Experiments. $[M(NH_2R)_5(OSO_2CF_3)](CF_3SO_3)_2$ (~0.5 g, accurately weighed) was dissolved directly into a solution of aqueous NaOH (0.1 M) that was 1.0 M in sodium azide, at 25 °C. After 5 half-lives of reaction, the hydrolysis was quenched by addition of an equal volume of 0.1 M triflic acid solution, and the solution was diluted 10-fold with iced water. The solution was absorbed on a column of Dowex 50W-X2 (H^+ form) resin and washed with a small amount of cold water. The azidopentaamine complex was eluted with 1 M $NaClO_4$; then the aquapentaamine was removed with 3 M acid. Elution was performed in the dark to limit any photochemical reactions of the azido complexes. For the rhodium complexes, elution was monitored spectrophotometrically with a flow-through cell. The eluates were diluted to known volumes, and the concentrations were determined by spectrophotometry and/or by atomic absorption techniques. Reactions were performed at least in duplicate, and mostly in triplicate.

Results

Hydrolyses of the trifluoromethanesulfonato pentaamine complexes in base were generally rapid, and all followed a simple rate law of the form

$$k_{obsd} = k_{aq} + k_{OH}[OH^-] \qquad (1)$$

at 25 °C and I = 1.0 M. For the relatively slow reaction of $Ir(NH_3)_5(OSO_2CF_3)^{2+}$, which can be followed directly in hydroxide ion solution, there is no departure from first-order behavior at least up to 0.7 M OH^-. The lability of the Co(III), Rh(III), and Cr(III) complexes required the use of buffer systems and limited pH ranges; however, good linear relationships of k_{obsd} with $[OH^-]$ were observed in all cases. Acid aquation rates were measured for each complex in 0.1 M H^+ (I = 1.0 M); in addition, intercepts from the application of eq 1 to data determined in basic solution were in agreement with these independent determinations, within experimental error. Detailed data for these hydrolyses have been deposited as supplementary material, while derived rate constants for acid aquation (k_{aq}) and base hydrolysis (k_{OH}) have been collected in Table I.

The temperature dependence of the hydrolysis of $Ir(NH_3)_5(OSO_2CF_3)^{2+}$ in acid yielded $\Delta H^\ddagger$ = 92 (±2) kJ mol^{-1} and $\Delta S^\ddagger$ = −6 (±6) J K^{-1} mol^{-1} and in base $\Delta H^\ddagger$ = 116 (±2) kJ mol^{-1} and $\Delta S^\ddagger$ = +107 (±6) J K^{-1} mol^{-1}. The rapid hydrolyses for other complexes in base severely restricted attempts to determine useful activation parameters. As a representative case, the activation parameters for $Co(NH_3)_5(OSO_2CF_3)^{2+}$ in base were determined as $\Delta H^\ddagger$ = 64 (±4) kJ mol^{-1} and $\Delta S^\ddagger$ = +48 (±12) J K^{-1} mol^{-1}. The large positive $\Delta S^\ddagger$ values for both the cobalt and the iridium complexes in base are typical of the behavior of d^6 metal amine complexes;[5] hence, there is no evidence for special behavior of trifluoromethanesulfonato complexes compared with other well studied leaving groups, nor is any special behavior expected.

The influence of ammine N-methylation on base hydrolysis is substantial (Table I), with rate increases greater than 10^3 observed. This consistent behavior for all the complexes is clearly different from the effect of N-methylation on aquation, where small rate increases for Co(III) and Rh(III) contrast with a rate decrease for Cr(III).[11] This acid and base behavior parallels results obtained with Cl^- as a leaving group.[7-9] It is notable that the rate enhancement Co > Cr ≈ Rh is related to the variation in average M–N bond lengths for these metal ions,[7,17,18] i.e. Co (1.99 Å) <

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Table II. Results of Competition Experiments on Pentaamine Complexes, Determined with 1 M NaN_3 in 0.1 M NaOH

$M(NH_2R)_5(OSO_2CF_3)^{2+}$		competition results[a]		
M	R	% azido (±0.4%)	% aquo (±0.4%)	$R = [CoN_3]/[CoOH][N_3^-]$
Co	H	9.7[b]	90.3[b]	0.11
Co	CH_3	36.0	64.0	0.56
Rh	H	2.0	98.0	0.02
Rh	CH_3	3.3	96.7	0.03
Cr	H	9.4	90.6	0.10
Cr	CH_3	12.0	88.0	0.14

[a] Average of duplicate or triplicate determinations $M(NH_2R)_5(OH_2)^{3+}$ and $M(NH_2R)_5(O_3)^{2+}$ products separated chromatographically; yields determined by electronic spectroscopy and/or atomic absorption spectroscopy. [b] Reference 14.

Cr (2.10 Å) ≈ Rh (~2.1 Å), implying that steric effects induced by the pentakis(methylamine) ligands influence the behavior significantly. The hydrolysis rates for the $Co(NH_2CH_3)_5(O_3SCF_3)^{2+}$ ion were rapid. Rate constants of $\geq 1\ s^{-1}$ in acid and $> 10^7\ M^{-1}\ s^{-1}$ in base at 25 °C were estimated.

When hydrolysis was carried out in aqueous base in the presence of azide ion, both hydroxo and azido pentaamine complexes were formed. Competition by azide ion or water for the coordination site vacated by the $CF_3SO_3^-$ leaving group, R = [azido]/[aquo][N_3^-], was determined by chromatographic separation and subsequent analysis of the products of the acid-quenched base hydrolysis reaction. Aquation and hydrolysis reactions of the azido complexes of Co(III), Cr(III), and Rh(III) and anation of the aqua complexes by azide were sufficiently slow[19-21] to permit separation and characterization without significant interference. The results of the competition experiments are collected in Table II. It is notable that competition increases in all cases from pentaammine to pentakis(methylamine). Further, while competition for pentaammine Co(III) and Cr(III) is essentially the same, there is a much greater competition for the pentakis(methylamine) Co(III) than for the Cr(III) analogue. However, competition for Rh(III) in the pentaammine case is only about one-fifth of that of the pentaammine Co(III), while the competition effect observed for the methylamine case is more comparable to that observed for Cr(III) than for Co(III). Although there is a greater R value for the more crowded methylamine complexes generally, it is apparent that the metal ion dominates the behavior.

The lability of trifluoromethanesulfonate in both acid and base for all metal ions is clear from a comparison with data for Cl^- and Br^- as leaving groups (Table III). Rate enhancements in the range 10^3–10^6 are observed, and in fact are larger for the second- and third-row ions Rh and Ir than for first-row Co and Cr. The ligands $CF_3SO_3^-$ and Cl^- are adjacent in the spectrochemical series, but the reactivity differences have been ascribed earlier[11] to a lower energy for the purely electrostatic component of bonding combined with a very low covalent contribution to bonding by $CF_3SO_3^-$, which allows it to be readily removed. In base, the rate enhancements for the $M(NH_2R)_5X^{2+}$ complexes are comparable to those in acid; i.e., the $k_{aq}(^-OSO_2CF_3)/k_{aq}(Cl^-)$ and $k_{OH}(^-OSO_2CF_3)/k_{OH}(Cl^-)$ ratios are 1.4×10^4 and 1.2×10^4 for Co(III), 5.0×10^5 and 4.2×10^5 for Rh(III), 2.1×10^5 and 2.8×10^5 for Ir, and 1.3×10^3 and 1.3×10^3 for Cr(III), respectively. Within the errors of the combined determinations, these ratios in acid and base are essentially constant for the same metal ions.

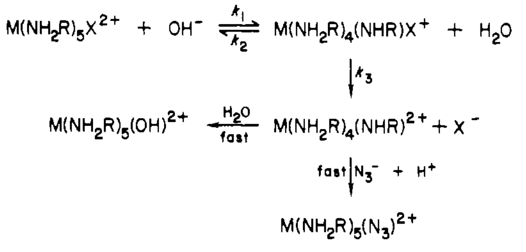
Some rate measurements were also carried out in the presence of various anions such as ClO_4^-, N_3^-, and acetate to evaluate their effects. For example, in 0.1 M TRIS buffers at pH 9.22 containing 1 M $NaClO_4$ and 1 M NaN_3, respectively, the rate constants for $Co(NH_2CH_3)_5Cl^{2+}$ were 5.1 (1) × $10^{-2}\ s^{-1}$ ($k_{OH} = 1800\ M^{-1}\ s^{-1}$) and 4.0 (1) × $10^{-2}\ s^{-1}$ ($k_{OH} = 1400\ M^{-1}\ s^{-1}$) at 25 °C. Similar measurements in 0.1 M TRIS buffers containing 1 M $NaClO_4$ and 1 M $NaOOCCH_3$ at pH 8.77 gave rate constants of $1.8 \times 10^{-2}\ s^{-1}$ ($k_{OH} = 1800\ M^{-1}\ s^{-1}$) and $1.6 \times 10^{-2}\ s^{-1}$ ($k_{OH} = 1600\ M^{-1}\ s^{-1}$). These variations are consistent with the change in activity coefficient of H^+ in the different media ($\gamma_{H^+} = 0.6288$ in 1 M $NaClO_4$ and $\gamma_{H^+} = 0.7594$ in 1 M $NaOOCCH_3$ at 25 °C),[22] and after correction is made for such variations the derived second rate constants are the same within the errors of the measurements.

Table III. Comparative Data for Aquation and Base Hydrolysis of the $M(NH_2R)_5X^{2+}$ Compounds at 25 °C

M	R	X	k_{aq}, s^{-1}	k_{OH}, $M^{-1}\ s^{-1}$	ref
Co	H	$CF_3SO_3^-$	2.39×10^{-2}[b]	1.0×10^4[c]	*a*
		Cl^-	1.7×10^{-6}[d]	0.24[c]	*m, n*
		Br^-	6.5×10^{-6}[d]	1.4[c]	*m, n*
Co	CH_3	$CF_3SO_3^-$	≥ 1[b]	$> 10^7$[e]	*a*
		Cl^-	3.7×10^{-5}[f]	1.8×10^3[e,b]	*o*, 9
Rh	H	$CF_3SO_3^-$	1.91×10^{-2}[b]	46[g]	*a*
		Cl^-	3.8×10^{-8}[h]	1.1×10^{-4}[i]	*q, r*, 7
		Br^-	3.4×10^{-8}[h]	9.6×10^{-5}[i]	*q, r*
Rh	CH_3	$CF_3SO_3^-$	3.47×10^{-2}[b]	6.3×10^3[e]	*a*
		Cl^-	2.6×10^{-8}[f]	4.4×10^{-3}[i]	7
Ir	H	$CF_3SO_3^-$	2.30×10^{-4}[b]	1.36×10^{-2}[c]	*a*
		Cl^-	1.1×10^{-9}[f]	4.8×10^{-8}[j]	*s, t*
		Br^-	1.1×10^{-9}[f]	2.2×10^{-8}[j]	*s, t*
Cr	H	$CF_3SO_3^-$	1.09×10^{-2}[b]	2.5[c]	*a*
		Cl^-	8.7×10^{-6}[k]	1.9×10^{-3}[l]	*u*, 8
		Br^-	6.8×10^{-5}[k]	7.2×10^{-2}[i]	*u, v*
Cr	CH_3	$CF_3SO_3^-$	6.43×10^{-4}	2.0×10^3[c]	*a*
		Cl^-	2.6×10^{-7}[l]	4.3×10^{-1}[l]	8

[a] This work. [b] I = 1.0 M (CF_3SO_3H). [c] I = 1.0 M ($NaClO_4$). [d] I = 0.1 M (HNO_3). [e] I = 1.0 M (NaCl). [f] I = 0.1 M ($HClO_4$). [g] I = 1.0 M ($NaOSO_2CF_3$). [h] I = 0.2 M (NH_4X, X = Cl^- or Br^-). [i] I = 0.1 M ($NaClO_4$). [j] $I \rightarrow 0$ (extrapolated). [k] I = 1.0 M ($HClO_4$). [l] I = 0.2 M (ClO_4^-). [m] Adamson, A. W.; Basolo, F. *Acta Chem. Scand.* **1955**, *9*, 1261. [n] Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *Inorg. Chem.* **1968**, *7*, 174. [o] Chan, S. C.; Hui, K. Y. *Aust. J. Chem.* **1967**, *20*, 2529. [p] Recalculated by using pK_w = 13.73.[15] [q] Poë, A. J.; Shaw, K.; Wendt, M. J. *Inorg. Chim. Acta* **1967**, *1*, 371. [r] Chan, S. C. *Aust. J. Chem.* **1967**, *20*, 61. [s] Schmidt, G. B. *Z. Phys. Chem. (Munich)* **1966**, *50*, 222. [t] Lalor, G. C.; Cavington, T. *J. Chem. Soc., Dalton Trans.* **1972**, 55. [u] Ogard, A. E.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 1084. [v] Levine, M. A.; Jones, T. P.; Harris, W. E.; Wallace, W. J. *J. Am. Chem. Soc.* **1961**, *83*, 2453.

Scheme I



The rate constant for proton exchange in the $Ir(NH_3)_5OSO_2CF_3^{2+}$ ion was found to be 0.0015 ± 0.002 s^{-1} at 20 °C and pD ~8.2. Assuming a second-order term in the rate law, we deduce a rate constant $k_{OH} \approx 900\ M^{-1}\ s^{-1}$, which approaches that measured by Palmer and Basolo (2000 $M^{-1}\ s^{-1}$) for the $(NH_3)_5IrCl^{2+}$ ion.[23] Unfortunately, the proton exchange for the triflato complex had to be followed in a D_2O/Me_2SO mixture in order to separate the ammine proton signal from that of HOD, but the agreement with the earlier study in water indicates the deduction has a coarse validity. Only one proton-exchange rate was observed for the triflato and chloro complexes, and it must be largely the cis-proton-exchange rate that was observed. The

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rate of exchange for the trans proton may be somewhat faster than that for the cis proton in keeping with the $(NH_3)_5CoCl^{2+}$ results,[24] but that was not discerned. The exchange rate is therefore at least 10^5-fold greater than the base hydrolysis rate.

Discussion

There is substantial evidence for a conjugate-base mechanism for hydrolysis of d^3 and d^6 pentaamine metal ion complexes in basic solution.[6,25] Frequently, the reactions involve a preequilibrium of the type shown in Scheme I, followed by rate-determining loss of X from the conjugate base. Rate-determining proton abstraction (k_1) is possible,[6] but we have established that it does not apply for this study. It follows that dissociation of the leaving group is rate-determining. This part of the process leads to competitive capture of the nucleophiles in solution, in this instance N_3^- and H_2O. A contentious issue still is whether they capture a five-coordinate intermediate or are intimately involved in the activated complex for loss of the leaving group.

The $Co(NH_2CH_3)_5X^{2+}$ complexes offer an especially good test of the latter prospect since in the presence of 1 M N_3^- the ratio of hydroxo to azido product approaches unity and the appearance of a competing ion in the activated complex would be evident in the rate law. However, the rate in the presence of 1 M N_3^- was not much different from that in 1 M ClO_4^- under analogous conditions and clearly there is not a first-order term in the rate law involving the N_3^- ion. In fact, the rate is slightly less in the presence of 1 M N_3^- than in the presence of 1 M ClO_4^-. It could be argued that N_3^- is merely substituting for ClO_4^- in the activated complex and that both ions yield, accidentally, the same rate of extrusion of X^-. Perchlorate ion entry would not be observed because of very fast base hydrolysis of the resulting $Co(NH_2CH_3)_5OClO_3^{2+}$ ion. Analogous experiments with 1 M acetate ion were therefore carried out, and the rate constant in this medium (1600 ± 200 M^{-1} s^{-1}) is not appreciably different from that in 1 M ClO_4^- (1800 ± 200 M^{-1} s^{-1}) at 25 °C when allowance is made for the activity coefficients of H^+ in the media. Also, acetate ion is a poor competitor for the intermediate of reduced coordination number in this instance.[9] We can be confident therefore that the anion is at most a spectator of the activated complex and is not intimately involved in extruding the leaving group. Capture of the intermediate of reduced coordination number may be the result of the proximity of anion and five-coordinate intermediate, but clearly the pentakis(methylamine) species is showing much more discrimination than the pentaammine derivative in this respect.

The other complexes are subject to the same test, but they are not so discriminating because the amount of azido competition product is much less and consequently the rate change that could be expected in the presence of the competitor anion is also relatively small (≤10%). However, in these instances also no evidence for the presence of the anion in the rate-determining step has been found.

The current competition ratios also imply a common intermediate arising from the different leaving groups for each set of the $(NH_3)_5CoX^{2+}$ and $(CH_3NH_2)_5CoX^{2+}$ (X = Cl, CF_3SO_3) ions and an increased lifetime for $(CH_3NH_2)_4(CH_3NH)Co^{2+}$ relative to $(NH_3)_4(NH_2)Co^{2+}$. The latter observation is consistent with an earlier study on the pentakis(methylamine)cobalt(III) complex.[9] There it was argued that the large rate increase (~10^4) for release of Cl^- from $(CH_3NH)Co(NH_2CH_3)_4Cl^+$ relative to the same process for $(NH_2)Co(NH_3)_4Cl^+$ was due to relief of steric strain in the methylamine complexes as the Co–Cl bond was stretched in the transition state. A consequence of this argument is that entry of a nucleophile into the crowded five-coordinate intermediate is not as facile as into $(NH_2)Co(NH_3)_4^{2+}$ and the intermediate becomes more selective toward the type of nucleophile. It also militates against entry of the competitor while the leaving group is still present. Such an expanded activated complex would be even more strained than the ground-state complex and would result in a rate decrease relative to the case of the pentaammine complexes.

These results, in general, are consistent with the bulk of the evidence, which points to a genuine five-coordinate intermediate arising from base hydrolysis of the Co(III) amine complexes provided the leaving group is reasonable,[26] i.e. $k_{OH} \geq 10^{-2}$ M^{-1} s^{-1}. Even so, the intermediates are clearly short-lived and do not survive much beyond the relaxation of their solvation sphere at least for the $Co(NH_2)(NH_3)_4^{2+}$ ion. In this instance, the competition ratios appear to be somewhat dependent on the charge of the leaving group but relatively constant for each charge type.[27] These results are interpreted to mean that the intermediate captures the solution atmosphere of its precursor. Further evidence for the discreteness of the intermediate has arisen from competition studies[25] in the presence of anions that form measurable ion pairs such as CO_3^{2-}, PO_4^{3-}, and SO_4^{2-}. In such instances, little or no competition was observed nor did these ions seriously impede the capture of good competitors such as N_3^-. Moreover, competition between two anions such as N_3^- and $S_2O_3^{2-}$, for the intermediate, occurs in such a manner that one competitor does not influence the other.[25,28] Both sets of experiments attest the presence of a discrete five-coordinate intermediate even if its lifetime is short and barely survives the collapse of the precursor's solvation atmosphere.

In base, enhanced hydrolysis rates of metal ion amine complexes are observed at least for Co(III), Cr(III), Rh(III), Ir(III), and Ru(III).[6] In some instances, competition by anions for the supposed intermediate has been observed. For example, both Cr(III) and Rh(III) show the competition effect;[28,29] in the other instances it has not been sought to our knowledge. On the whole, the S_N1CB mechanism appears appropriate in all these instances except that the data to support the mechanism are not as voluminous as for Co(III) chemistry. Consistent patterns emerge.

In basic solution, all the pentaammine complexes show a rate increase upon N-methylation when either Cl^- or $CF_3SO_3^-$ is the leaving group. This common increase does imply a significant component in bond breaking arising from the increase in strain in the ground state that is relieved in the transition state. The large and positive $\Delta S^{\ddagger}$ values observed for the $M(NH_3)_5OSO_2CF_3^{2+}$ (M = Co, Ir) hydrolyses are consistent with those observed for other anionic leaving groups.[5] They are also consistent with the S_N1CB mechanism and inconsistent with an associative process.[5] In this respect it is now known[30] that analogous amine deprotonations in at least two instances have entropy changes close to zero so that the bulk of the positive entropy of activation for the overall hydrolysis is likely to arise from the dissociation of the leaving group, contrary to a previous analysis.[5] Even so, the conclusion concerning mechanism remains the same, i.e. a dissociative process overall. Azide competition in base shows an increased competition ratio for $M(NH_2R)_5O_3SCF_3^{2+}$ ions from R = H to R = CH_3, consistent with arguments for a dissociative activation step and an enhanced stability of the deprotonated pentakis(methylamine) intermediate. Further, competition ratios for $Co(NH_3)_5O_3SCF_3^{2+}$ and $Cr(NH_3)_5O_3SCF_3^{2+}$ with the N_3^- ion in base are much the same, consistent with a common mechanism.

The effect of the deprotonated amine on the leaving group lability is also reflected in the base-catalyzed path for isomerization of $(NH_3)_5MONO^{2+}$ ions (M = Co, Rh, Ir) to their respective $(NH_3)_5MNO_2^{2+}$ counterparts.[31] Here, the rate ratios of spon-

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[24] Bramley, R.; Creaser, I. I.; Mackey, D. J.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 244–248.

[25] Jackson, W. G.; Hookey, C. N.; Randall, M. L.; Comba, P.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2473–2482.

[26] There is evidence for anomalous behavior for hydrolysis of fluoro complexes. For example, see: Green, M.; Taube, H. *Inorg. Chem.* **1963**, *2*, 948–950. Jackson, W. G.; Begbie, C. M. *Inorg. Chem.* **1981**, *20*, 1654–1659.

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[30] Comba, P.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1985**, 51–52.

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taneous to the base-catalyzed isomerization are directly proportional to the rates of proton exchange in the relevant $M(NH_3)_6^{3+}$ ions. Presumably, the same bond-labilizing effect operates for these rearrangements as for the loss of a ligand in the instances where the leaving group is better. Evidence for a substantial bond lengthening trans to a deprotonated amine site has also been seen recently in an X-ray crystallographic study on a cobalt(III) amine complex.[32] Such a bond extension can be equated to increased labilization of the attached group.

There are some apparent anomalies in the behavior of the cations however. The rate increase in base upon N-methylation is not uniform, varying from >2000 for Co to 800 for Cr to 150 for Rh. Azide competition for the Rh complexes is no more than one-fifth that of the Co analogues. Azide competition during $Co(NH_2CH_3)_5O_3SCF_3^{2+}$ base hydrolysis is substantially higher than for the Cr(III) analogue despite the similar behavior in the pentaammines. Possible reasons for these variations need some discussion.

The rate enhancement trend from ammonia to methylamine with metal ion, Co > Cr > Rh, bears some relationship to metal–ligand bond length variations. For the d^6 second-row Rh(III) ion and the d^3 first-row Cr(III) ion, the relatively longer M–N bonds would create less steric compression in the ground state compared to that of the Co(III) complex. Other factors that could impinge on this argument are a variation in the pK_a ratio for the amine complexes and the solvation of the ions in each instance. It is doubtful, however, if these latter effects could accommodate the rate differences observed. Variations between the NH_3 and CH_3NH_2 complexes might be significant, but the relative variation from one metal ion to another would not be expected to alter in degree with such saturated ligands. The bulk of the change is therefore most likely to come from the variation in steric compression in the pentakis(methylamine) complexes as the M–N bond lengths change.

Azide competitions during the base hydrolyses of $M(NH_3)_5O_3SCF_3^{2+}$ (M = Co, Cr) were much the same and equal to the competition ratios for a range of $Co(NH_3)_5X^{2+}$ ions in base.[27] Comparative data for Cr(III) ammines, in general, are not available due to competing ammonia loss, which complicates the process.[33] This complication, however, was not evident with the labile $CF_3SO_3^-$ ligand. It is significant that the enhanced N_3^- competition in the change from $Co(NH_3)_5O_3SCF_3^{2+}$ ($R = 0.11$) to $Co(NH_2CH_3)_5O_3SCF_3^{2+}$ ($R = 0.56$) parallels closely the data for Cl^- as the leaving group ($R = 0.10$ and 0.56, respectively).[9] This correlation also supports the assignment of a limiting dissociative mechanism. Competition for the intermediate derived from $Cr(NH_2CH_3)_5O_3SCF_3^{2+}$ is higher than for that derived from $Cr(NH_3)_5O_3SCF_3^{2+}$ but not markedly so (Table II), and it is much less than for the Co(III) analogue. The same argument that accounts for the reduced rate of hydrolysis of $Cr(NH_2CH_3)_5O_3SCF_3^{2+}$ relative to the Co(III) analogue also accounts for the reduction in the competition ratio. The reduced strain in the ground state is reflected in a shorter lifetime for the intermediate and thus a reduction in the selectivity for the incoming nucleophile. Clearly, N_3^- (1 M) is preferred over the more abundant H_2O (55 M) as a competitor, and this selectivity is greatest for the longest lived intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ and reduced for those intermediates of shorter life.

An associative path for N_3^- entry is clearly not favored with the bulky alkylamine complexes despite the reduction in steric compression for the ions with the larger M–N bond lengths.

The competition observed in the hydrolysis of $Rh(NH_3)_5O_3SCF_3^{2+}$ and $Rh(NH_2CH_3)_5O_3SCF_3^{2+}$ is much lower than that observed for the Co(III) and Cr(III) analogues ($\sim ^1/_5$). This behavior parallels that seen previously for Rh(III) complexes.[29] It probably reflects the higher ligand field strength of Rh(III) complexes and the demand they have therefore for six-coordination. Such an effect would tend to limit the lifetimes of the five-coordinate intermediates, their selectivity for the nucleophile in solution, and the rearrangement of the remaining ligands.

Overall, aquation reactions of cobalt(III) amine complexes appear to be largely dissociative; i.e., bond breaking substantially leads bond making. For chromium(III) the same general pattern is evident; i.e., the rates show a substantial dependence on the charge of the complex and little dependence on the entering group. Even so, the associative aspect appears to be enhanced relative to the analogous Co(III) complexes.[7] For $Co(NH_3)_5Cl^{2+}$ and $Co(NH_2CH_3)_5Cl^{2+}$, the rate enhancement observed as the ion becomes more compressed is consistent with the primarily dissociative character of the process. In contrast, however, the Cr(III) ions display a rate reduction under the same circumstances. Although the effect is not large, it can be argued that an increase in bond making by water relative to the Co(III) ions would accommodate the change in pattern.[9] The Rh(III) complexes, however, show very little difference in rate.

Although the rates of aquation are generally faster for the triflato complexes, the relative rates for the pentaammines and pentakis(methylamine) complexes remain in the same order and the same arguments about mechanistic balance apply. Generally, for the aquation and anation paths however, the rate differences are smaller than those observed in the base hydrolysis reactions. Also, to date, there is no sign of a strong dependence of the rate of substitution on the entering group even when a good nucleophile such as RS^- is used. It must be concluded therefore that bond breaking leads bond making by a substantial margin in the chemistry cited in this paper.

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Registry No. $Co(NH_3)_5(OSO_2CF_3)^{2+}$, 75522-49-5; $Rh(NH_3)_5(OSO_2CF_3)^{2+}$, 84254-56-8; $Ir(NH_3)_5(OSO_2CF_3)^{2+}$, 84254-58-0; $Cr(NH_3)_5(OSO_2CF_3)^{2+}$, 84254-60-4; $Co(NH_2CH_3)_5(OSO_2CF_3)^{2+}$, 84254-64-8; $Rh(NH_2CH_3)_5(OSO_2CF_3)^{2+}$, 84254-65-9; $Cr(NH_2CH_3)_5(OSO_2CF_3)^{2+}$, 84254-66-0.

Supplementary Material Available: Tables showing the observed rate constants for the base hydrolysis and aquation of the complexes and the temperature dependence of the rate constants (4 pages). Ordering information is given on any current masthead page.

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