ference is that Mn–N and Mn–O distances are somewhat longer because of Mn's larger radius.

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Supplementary Material Available: Tables of all bond distances and angles, anisotropic thermal parameters, hydrogen coordinates, and structure factors for **1**–**3** and chart of the disordered THF's in **2** (70 pages). Ordering information is given on any current masthead page.

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Syntheses and Acid Aquation Reactions of Pentakis(methylamine)cobalt(III) Complexes of the Neutral Ligands Urea, Dimethyl Sulfoxide, Dimethylformamide, Trimethyl Phosphate, and Acetonitrile

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Syntheses of $[Co(NH_2CH_3)_5L]^{3+}$ cations (L = urea, dimethyl sulfoxide, dimethylformamide, trimethyl phosphate, and acetonitrile) based on the $[Co(NH_2CH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ precursor are facile and high-yielding. Acid aquation reactions of these cations occur with rate constants at least 70-fold faster than those reported for the pentaammine analogues at 25 °C, this general rate enhancement being apparently steric in origin. While activation enthalpies for the pentakis(methylamine) and pentaammine complexes are similar, both activation entropies and activation volumes are more positive, yet not particularly sensitive to the size of the neutral leaving group. A dissociative I_d type mechanism operates. The more positive $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values for $Co(NH_2CH_3)_5L^{3+}$ compared with $Co(NH_3)_5L^{3+}$ imply a diminished role for an incoming water molecule in the dissociated transition state, which accords with the steric crowding known in pentakis(methylamine) complexes. These results parallel earlier observations of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ variation in the chloro analogues, although overall electrostrictive effects present with the charged leaving group are markedly diminished in this case where neutral leaving groups are employed.

Introduction

In recent attempts to gain a more intimate understanding of each of the apparently disparate mechanisms for spontaneous aquation reactions of cobalt(III) and chromium(III) amine complexes, we have been investigating various simple pentaamine systems.[3-5] Two systematic approaches have been adopted: first, study of complexes with neutral leaving groups;[3,4] second, study of the effect of varying the amine non leaving groups.[5] Both temperature and pressure dependence of aquation reactions have been probed to obtain a more extensive data base for analysis.

Where charged leaving groups are involved, solvent electrostriction changes in forming the transition state contribute significantly to both activation entropy ($\Delta S^{\ddagger}$) and activation volume ($\Delta V^{\ddagger}$).[6,7] When neutral leaving groups are employed, changes in electrostriction in the activation process are minimized;[3,8] $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ then define much more closely the intrinsic volume and entropy changes in attaining the transition state, and this is the basis for our first approach. The effect of the cation size and related steric effects had not been probed systematically until recently, when the system $M(NH_2R)_5Cl^{2+}$ (M = Co, Cr; R = H, CH_3) was studied.[5] The $M(NH_2R)_5Y^{n+}$ system is the current focus for our second approach, since it represents the simplest example of increased cation size with constant charge and leaving group, and since only unidentate ligands are involved, motions and rearrangements of chelate rings are not operating. In this work, we pursue these approaches in tandem, with a study of the $Co(NH_2CH_3)_5L^{3+}$ (L = unidentate neutral ligand) system and comparison with $Co(NH_3)_5L^{3+}$ analogues.

Aquation reactions of cobalt(III) and chromium(III) halo amines have been extensively studied in recent decades, leading to evidence of mechanistic disparity.[9-11] Reactions of cobalt(III) are generally accepted to be dominated by bond-breaking (dissociative) processes, while those of chromium(III) are apparently bond-making (associative) in character. This difference was defined in comparative studies of pentaammine and pentakis(methylamine) complexes since an increase in the rate of aquation in $Co(NH_2CH_3)_5X^{2+}$ compared with $Co(NH_3)_5X^{2+}$ ($X = Cl^-$, $CF_3SO_3^-$) is consistent with steric relief in a dissociated activated state, whereas the chromium(III) system exhibits retardation, appropriate for steric congestion of an associated transition state.[12,13] While a recent study has implied a significant change in the importance of bond-making and bond-breaking processes from the pentaammine- to the pentakis(methylamine)chlorochromium(III) complexes,[5] this did not lead to an assertion of mechanistic uniformity for cobalt(III) and chromium(III) overall; rather, the observation was based on a bond-making mechanism operating in the sterically uncrowded $Cr(NH_3)_5Cl^{2+}$. Yet it is with neutral leaving groups that mechanistic differentiation is most obvious. Solvent exchange on $Co(NH_3)_5(OH_2)^{3+}$ exhibits $\Delta V^{\ddagger} = +1.2$ cm^3 mol^{-1},[14] while on $Cr(NH_3)_5(OH_2)^{3+}$, $\Delta V^{\ddagger} = -5.8$ cm^3 mol^{-1},[15] for example. Dissociative interchange (I_d) and associative interchange (I_a) mechanisms operate respectively. Study of a range of $Cr(NH_3)_5L^{3+}$ complexes to complement the available data for $Co(NH_3)_5L^{3+}$ is under way[4] and will allow extension of this at present strictly limited comparison with neutral leaving groups.

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The effect of the non leaving groups on particularly the experimental activation volume has led to some controversy in the literature,[16-19] and recent studies show that there is obviously a significant effect when a charged leaving group is involved. With neutral leaving groups this effect is probably less significant,[20] but has not been systematically studied. As part of our continuing study in this area, we report the syntheses and acid aquation kinetics for the complexes $Co(NH_2CH_3)_5L^{3+}$ (L = urea, dimethyl sulfoxide, dimethylformamide, trimethyl phosphate and acetonitrile). While several of the products are readily hydrolyzed and not accessible by most routes, facile and high-yielding syntheses have been developed based on the (trifluoromethanesulfonato)pentakis(methylamine)cobalt(III) precursor.[21]

Experimental Section

Synthesis. The precursor complex $[Co(NH_2CH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ was prepared as previously described.[21] All solvents employed were dried and distilled AR grade; where a solvent molecule was introduced into the coordination sphere, reactions were performed with a crystal of 4-toluenesulfonic acid added to preclude any presumably rapid base-catalyzed solvolysis. Complexes were characterized by microanalysis, proton magnetic resonance spectroscopy, electronic spectroscopy, and infrared spectroscopy.

$[Co(NH_2CH_3)_5OC(NH_2)_2](S_2O_6)_{3/2}\cdot 1^1/_2H_2O$. (Trifluoromethanesulfonato)pentakis(methylamine)cobalt(III) trifluoromethanesulfonate (1.0 g) was dissolved in dry sulfolane (10 mL). Urea (1.0 g) was dissolved in with stirring, and then the stoppered flask of the solution was allowed to stand overnight. The reaction mixture was added slowly to ethanol (10 mL) at −20 °C, and then diethyl ether (250 mL) was slowly added to produce a purple-red oil. The mixture was stored at ~−20 °C for 2 h, the supernatant was decanted, and the oil was treated with ethanol (10 mL) at −20 °C and then with diethyl ether (250 mL). This process was repeated, then the oily precipitate was dissolved in methanol (50 mL) at −20 °C, and a solution of $Li_2S_2O_6$ (0.5 g) in methanol (25 mL) was added slowly to precipitate a purple solid. This was collected, suspended, and stirred in methanol (100 mL) at room temperature for 1 h and then collected, washed with ethanol (2 × 50 mL) and ether (2 × 10 mL), and dried (yield 0.53 g, 70%). Anal. Calcd for $C_6H_{32}N_7O_{11.5}S_3Co$: C, 13.31; H, 5.96; N, 18.11; S, 17.76. Found: C, 13.4; H, 5.7; N, 17.7; S, 18.0. Electronic spectrum (water, ~10 °C): 530 nm (ϵ ~70 M^{-1} cm^{-1}), 364 (ϵ ~80).

$[Co(NH_2CH_3)_5OP(OCH_3)_3](CF_3SO_3)_3$. (Trifluoromethanesulfonato)pentakis(methylamine)cobalt(III) trifluoromethanesulfonate (1.0 g) in dry trimethyl phosphate (5 mL) was allowed to stand at room temperature for 30 min. The purple solution was then added, over 5 min, to ethanol (10 mL) maintained at between −20 and −30 °C. Diethyl ether (200 mL) was added slowly to the rapidly stirring solution to produce an oil, which was separated and redissolved in ethanol (10 mL) at −20 °C. Slow addition of diethyl ether (50 mL) gave the product as a purple solid, which was collected, washed with diethyl ether (2 × 10 mL), and dried in vacuo. (yield 0.80 g, 65%). Anal. Calcd for $C_{11}H_{34}F_9N_5O_{13}PS_3Co$: C, 16.48; H, 4.28; N, 8.74; P, 3.86. Found: C, 16.0; H, 4.5; N, 8.7; P, 4.1. Electronic spectrum (trimethyl phosphate): 540 nm (ϵ 58 M^{-1} cm^{-1}), 362 (ϵ 56).

$[Co(NH_2CH_3)_5NCCH_3](CF_3SO_3)_3$. (Trifluoromethanesulfonato)pentakis(methylamine)cobalt(III) trifluoromethanesulfonate (2.0 g) was dissolved in dry acetonitrile (20 mL) with stirring at room temperature. After 30 min, diethyl ether (100 mL) was added slowly to precipitate orange needles, which were collected, washed with diethyl ether (2 × 10 mL), and dried in vacuo (yield 1.93 g, 90%). Anal. Calcd for $C_{10}H_{28}F_9N_6O_9S_3Co$: C, 17.10; H, 4.02; N, 11.96; S, 13.69. Found: C, 17.2; H, 3.9; N, 12.0; S, 13.55. Electronic spectrum (water): 486 nm (ϵ 81 M^{-1} cm^{-1}), 348 (ϵ 76.5). ^1H NMR spectrum (0.1 M $DClO_4$): δ 1.87 (t, J = 6 Hz, trans $\mathrm{C}\mathit{H}_3\mathrm{NH}_2$), 2.27 (t, J = 6 Hz, cis $\mathrm{C}\mathit{H}_3\mathrm{NH}_2$), 2.73 (s, CH_3CN), 4.37 (s, br, trans $\mathrm{N}\mathit{H}_2\mathrm{CH}_3$), 4.61 (s, br, cis $\mathrm{N}\mathit{H}_2\mathrm{CH}_3$).

$[Co(NH_2CH_3)_5OS(CH_3)_2]X_3$ (X = $CF_3SO_3^-$ or ClO_4^-). (Trifluoromethanesulfonato)pentakis(methylamine)cobalt(III) trifluoromethanesulfonate (1.0 g) was dissolved in dry dimethyl sulfoxide (5 mL) and left at room temperature for 30 min. The purple solution was then added, over 5 min. to ethanol (5 mL) at −20 °C, and then diethyl ether (500 mL) was added slowly to yield an oil. After the mixture was left standing at −18 °C overnight, the supernatant was decanted off and the oil was treated with ethanol (20 mL) at −20 °C. When the mixture was stirred, some precipitation occurred and this was completed by the slow addition of diethyl ether (200 mL). The product was collected, washed with diethyl ether, and dried in vacuo (yield 0.96 g, 85%). Anal. Calcd for $C_{10}H_{31}F_9N_5O_{10}S_4Co$: C, 16.24; H, 4.23; N, 9.47. Found: C, 16.3; H, 4.2; N, 9.5. This product was recrystallized by dissolution in methanol (25 mL) at 0 °C, since slow addition of a solution of $LiClO_4$ (2 g) in cold MeOH (5 mL) gave a purple precipitate. This was collected, washed with cold ethanol (2 × 10 mL) and diethyl ether (10 mL), and dried in vacuo (yield 0.62 g, 70%). Anal. Calcd for $C_7H_{31}Cl_3N_5O_{13}SCo$: C, 14.23; H, 5.29; N, 11.86; S, 5.43. Found: C, 14.4; H, 5.3; N, 11.8; S, 5.7. Electronic spectrum (water, ~10 °C): 540 nm (ϵ 75 M^{-1} cm^{-1}), 365 (ϵ 82). ^1H NMR spectrum (0.1 M $DClO_4$): δ 1.66 (t, J = 6 Hz, trans $\mathrm{C}\mathit{H}_3\mathrm{NH}_2$), 2.19 (t, J = 6 Hz, cis $\mathrm{C}\mathit{H}_3\mathrm{NH}_2$), 2.93 (s, CH_3S), 3.6 (s, br, trans $\mathrm{N}\mathit{H}_2\mathrm{CH}_3$), 4.7 (s, br, cis $\mathrm{N}\mathit{H}_2\mathrm{CH}_3$).

$[Co(NH_2CH_3)_5OCH\cdot N(CH_3)_2](CF_3SO_3)_3$. (Trifluoromethanesulfonato)pentakis(methylamine)cobalt(III) trifluoromethanesulfonate (1.0 g) was dissolved in dry dimethylformamide (5 mL) and left at room temperature for 30 min. The purple solution was added, over 5 min, to ethanol (5 mL) at −20 °C, followed by slow addition to diethyl ether (500 mL) to yield a purple oil. After the mixture was left standing at −18 °C overnight, the supernatant was decanted and the oil treated with ethanol (5 mL) at −20 °C. When the mixture was stirred, precipitation occurred, which was completed by the addition of diethyl ether (250 mL) (yield 1.0 g, 90%). Anal. Calcd for $C_{11}H_{32}F_9N_6O_{10}S_3Co$: C, 17.99; H, 4.39; N, 11.44; S, 13.10. Found: C, 17.9; H, 4.3; N, 11.3; S, 13.2. Electronic spectrum (water): 526 nm (ϵ 91 M^{-1} cm^{-1}), 363 (ϵ 77). ^1H NMR spectrum (0.1 M $DClO_4$): δ 1.74 (t, J = 6 Hz, trans $\mathrm{C}\mathit{H}_3\mathrm{NH}_2$), 2.14 (t, J = 6 Hz, cis $\mathrm{C}\mathit{H}_3\mathrm{NH}_2$), 3.02, 3.18 (s, $\mathrm{OCH\cdot N(C}\mathit{H}_3)_2$), 3.8 (s, br, trans $\mathrm{N}\mathit{H}_2\mathrm{CH}_3$), 4.7 (s, br, cis $\mathrm{N}\mathit{H}_2\mathrm{CH}_3$), 7.50 (s, $\mathrm{OC}\mathit{H}\mathrm{\cdot N(CH_3)_2}$).

Physical Methods. Electronic spectra were recorded on Hitachi 220A or Hewlett-Packard 8450A spectrophotometers. Infrared spectra were recorded with a Nicolet MX-1 FT-IR spectrometer, as KBr disks. Proton magnetic resonance spectra were recorded in 0.1 M $DClO_4$ on a JEOL FX200 spectrometer; shifts are with respect to sodium 3-(trimethylsilyl)propionate as internal reference, which occurs at −0.02 ppm vs. $SiMe_4$. Microanalyses were performed by the Australian National University Microanalytical Service.

Kinetics. Acid aquation reactions at ambient pressure were followed by spectrophotometry in the thermostated (±0.1 °C) cell holders of spectrophotometers described above, in 0.1 M $HClO_4$. Samples of the complex were dissolved directly in preequilibrated solutions in the spectrophotometer cell, and reactions were monitored continuously to about 4 half-lives of reaction. First-order rate constants were determined by conventional computational methods, and least-squares fitting to a single exponential. The pressure dependence of the acid aquation for several complexes was determined in a thermostated high-pressure optical cell mounted in a Varian 635 spectrophotometer, at pressures up to 1700 bar. The activation volume ($\Delta V^{\ddagger}$) for each reaction was determined from plots of log k_p vs. pressure, as previously described.[22] The temperature dependence of each acid aquation reaction was determined over a temperature range of at least 25 °C, and activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) were obtained from plots of log k_T vs. $1/T$ in the usual manner.

Base hydrolysis of the $Co(NH_2CH_3)_5(NCCH_3)^{3+}$ ion was followed at 25 °C in (tris(hydroxymethyl)amino)methane–$HClO_4$ buffer (I_{buffer} = 0.1 M) or in dilute base. Reaction was initiated when complex and base solutions thermostated in a dual-compartment spectrophotometer cell were mixed. Chromatography of a selected solution in the cold on SP Sephadex C-25 resin, following adjustment of the pH to ~5 upon reaction completion, indicated that the reaction produced only one product, which was not the aquo complex and whose absorption spectrum in acid and base was consistent with an acetamido complex by comparison with the well-known pentaammine analogue.[23]

Results

Reaction of (trifluoromethanesulfonato)pentakis(methylamine)cobalt(III) trifluoromethanesulfonate directly with coordinating solvent or neutral ligand in the poorly coordinating solvent sulfolane proceeded smoothly to form the $Co(NH_2CH_3)_5L^{3+}$ complexes. These reactions parallel those reported previously for the $Co(NH_3)_5L^{3+}$ analogues,[3,21] but enhanced sensitivity of the pentakis(methylamine) complexes particularly to moisture required

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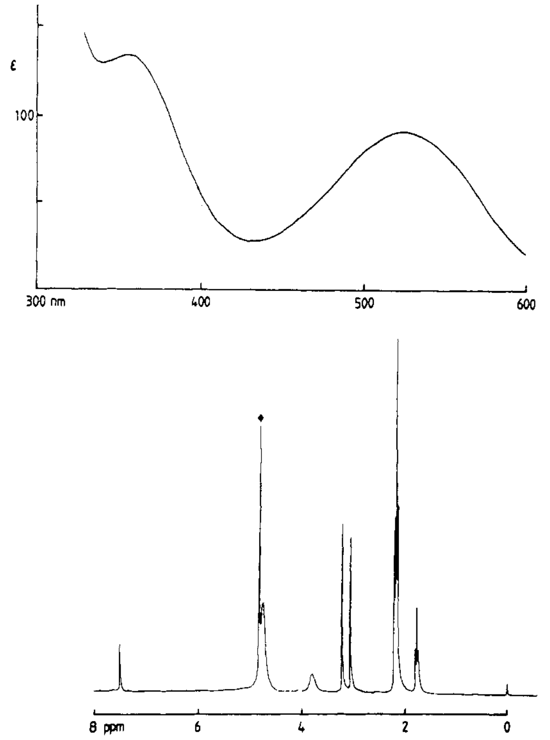

Figure 1. Visible absorption spectrum in water (top) and ^1H NMR spectrum in 0.1 M $DClO_4$ (bottom) of $[Co(NH_3)_5(OCH{\cdot}N(CH_3)_2)](CF_3SO_3)_3$ (♦ marks the HDO signal in the NMR spectrum).

much more rigorous control of reaction conditions. While complexes can be recrystallized if required from alcohol as perchlorate or mixed perchlorate–trifluoromethanesulfonate salts, as isolated they are microanalytically and spectroscopically pure. This is clear from the proton NMR spectrum of the $[Co(NH_2CH_3)_5(OCH{\cdot}N(CH_3)_2)](CF_3SO_3)_3$ complex shown in Figure 1. Expected signals for cis and trans methyl and amine protons of the methylamine ligands and for the coordinated solvent molecule are observed in $DClO_4$ in the appropriate ratios. Electronic spectra of the complexes exhibit the expected octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ envelope transitions in the visible region. The low-energy maximum for the urea (530 nm), trimethyl phosphate (540 nm), dimethyl sulfoxide (540 nm), and dimethylformamide (526 nm) complexes are at lower energy than for the aqua complex (510 nm), consistent with O-bonding, while the same maximum for N-bound acetonitrile is at higher energy (486 nm). With coordinated urea, where N-bonding is a prospect, further support for O-bonding comes from infrared spectroscopy, since no detectable IR band occurs here in the region 1720–1740 cm^{-1}, where a sharp and prominent band characteristic for N-bound urea occurs in $Rh(NH_3)_5(NH_2CONH_2)^{3+}$.[24] All complexes show an asymmetry in the low-energy absorption band in the electronic spectrum, consistent with the real C_{4v} symmetry in these ions; the spectrum is illustrated in Figure 1 for the dimethylformamide complex.

Acid aquation of each complexes proceeds to form only $Co(NH_2CH_3)_5(OH_2)^{3+}$, since the electronic spectra of the products are identical with the spectrum of an authentic sample (maxima at 510 (ϵ 61 M^{-1} cm^{-1}) and 360 nm (ϵ 62)). Further, chromatography of the products on SP-Sephadex C-25 resin or on Dowex 50W-X2 cation resin shows only one band within the accuracy of the method (≥97%). All complexes except the urea compound exhibit strictly first-order kinetics for a single reaction. In the case of urea, the kinetics followed in the ultraviolet region showed an interfering reaction in the initial stages, despite the favorable microanalysis and spectroscopic characterization. While this did not interfere with the determination of rate constants to any marked extent, its presence is notable since this is the only compound where isomers are possible and may indicate an O-bound $\rightleftharpoons$ N-bound equilibrium in addition to hydrolysis, although no trace of N-bound urea was detected in the solid state by IR. Alternatively, it could indicate the presence of a trace of $Co(NH_2CH_3)_5(OHC_2H_5)^{3+}$ formed during isolation, since we have been unable to isolate an analytically pure sample of this compound due to its extreme lability and sensitivity to moisture, and it is an obvious possible impurity. This interfering reaction is ~10-fold faster than the major reaction at 25 °C, so could be readily separated.

Table I. Temperature Dependence of the Rate Constants for Aquation of $Co(NH_2CH_3)_5L^{3+}$ Complexes in 0.1 M $HClO_4$

L	T, °C	10^3k_{obsd}, s^{-1}
dimethyl sulfoxide	20.0	1.36 ± 0.02
	25.1	2.80 ± 0.12
	32.3	8.19 ± 0.15
	39.8	21.0 ± 0.6
	45.0	41.5 ± 1.5
dimethylformamide	25.1	0.115 ± 0.003
	32.4	0.327 ± 0.008
	39.8	0.918 ± 0.018
	45.8	2.03 ± 0.02
	52.4	5.00 ± 0.10
trimethyl phosphate	20.0	14.8 ± 0.4
	25.0	27.8 ± 0.4
	30.0	51.3 ± 1.0
	35.0	94.9 ± 1.2
	40.0	170.0 ± 2.0
urea	15.0	1.68 ± 0.02
	25.0	7.28 ± 0.03
	30.0	14.2 ± 0.4
	35.0	26.9 ± 0.7
	40.0	47.3 ± 0.5
	45.0	78.3 ± 0.8
acetonitrile	25.4	0.0112 ± 0.0004
	32.7	0.0325 ± 0.0008
	39.9	0.104 ± 0.003
	45.6	0.310 ± 0.008
	52.4	0.663 ± 0.009

Table II. Pressure Dependence of the Rate Constants for Aquation of Several $Co(NH_2CH_3)_5L^{3+}$ Complexes in 0.1 M $HClO_4$

L	pressure, bar	10^3k_{obsd}, s^{-1}
dimethyl sulfoxide[a]	1	2.05 ± 0.04
	680	1.75 ± 0.05
	1360	1.48 ± 0.02
	1700	1.35 ± 0.05
dimethylformamide[b]	1	0.772 ± 0.008
	680	0.641 ± 0.013
	1360	0.555 ± 0.007
	1700	0.508 ± 0.009
acetonitrile[c]	1	0.291 ± 0.012
	680	0.257 ± 0.009
	1360	0.210 ± 0.005
	1700	0.199 ± 0.003

[a] T = 22.8 °C. [b] T = 38.5 °C. [c] T = 45.1 °C.

Rate constants for aquation of $Co(NH_2CH_3)_5L^{3+}$ complexes at ambient pressure and various temperatures are collected in Table I. The pressure dependence of aquation rate constants for the complexes with L = dimethyl sulfoxide, dimethylformamide, and acetonitrile are collected in Table II. Data were not collected on the urea and trimethyl phosphate complexes due both to the rapidity of these reactions and to complications in the former reaction discussed above, which introduced technical difficulties with available facilities. As it happens, from activation parameters collected in Table III, both the pentaammine and pentakis(methylamine) complexes show a good correlation between ΔS^{*} and ΔV^{*}, so ΔS^{*} data for the urea and trimethyl phosphate complexes suffice to support an obvious trend. This trend is simply that while ΔH^{*} values for $Co(NH_3)_5L^{3+}$ and $Co(NH_2CH_3)_5L^{3+}$ are very

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Table III. Activation Parameters for Aquation of $Co(NH_2CH_3)_5L^{3+}$ in 0.1 M $HClO_4$ and Comparative Aquation Rate Constants and Activation Parameters for $Co(NH_3)_5L^{3+}$

	$Co(NH_2CH_3)_5L^{3+\,a}$				$Co(NH_3)_5L^{3+\,a}$				
L^b	k_{obsd}(25 °C)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	k_{obsd}(25 °C)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	$k_{NH_2CH_3}/k_{NH_3}$
Me_2SO	2.8×10^{-3}	103.4 (±1.0)	+53 (±3)	+5.9 (±0.2)	1.8×10^{-5}	103	+10	+2.0	156
TMP	2.8×10^{-2}	90.8 (±0.5)	+30 (±2)		2.5×10^{-4}				112
DMF	1.15×10^{-4}	108.6 (±1.0)	+44 (±3)	+6.3 (±0.3)	1.6×10^{-6}	111	+16	+2.6	72
urea	7.3×10^{-3}	95.5 (±1.5)	+35 (±5)		5.5×10^{-5}	94	−10	+1.3	151
ACN	1.1×10^{-5}	118.4 (±3.0)	+57 (±9)	+6.0 (±0.5)	$\sim 2 \times 10^{-8}$				~500
Cl^-	4.0×10^{-5}	95	−10	−2.3	1.7×10^{-6}	93	−35	−9.9	23

[a] Units: k, s^{-1}; $\Delta H^\ddagger$, kJ mol^{-1}; $\Delta S^\ddagger$, J K^{-1} mol^{-1}; $\Delta V^\ddagger$, cm^3 mol^{-1}. [b] Me_2SO = dimethyl sulfoxide; TMP = trimethyl phosphate; DMF = dimethylformamide; ACN = acetonitrile.

Table IV. Rate Constants for Base Hydrolysis of $Co(NH_2CH_3)_5(NCCH_3)^{3+}$ at 25 °C and I = 1.0 M (ClO_4^-)

pH	OH^-	k_{obsd}, s^{-1}	k_{OH}, M^{-1} s^{-1}
8.99	1.565×10^{-5}	0.000 189 (±0.000 010)	12.0
9.35	3.585×10^{-5}	0.000 435 (±0.000 016)	12.1
9.90	1.272×10^{-4}	0.002 2 (±0.000 15)	11.4
	2.5×10^{-3}	0.029 8 (±0.0008)	11.9

similar, both $\Delta S^\ddagger$ and $\Delta V^\ddagger$ values are more positive for the pentakis(methylamine) complexes (Table III). In addition, at 25 °C, rate constants for the O-bound ligand hydrolyses are between 70- and 150-fold greater for $Co(NH_2CH_3)_5L^{3+}$ complexes compared with those for their pentaammine analogues. With N-bound acetonitrile, the enhancement is slightly greater, although the aquation rate constant for $Co(NH_3)_5(NCCH_3)^{3+}$ is not well-defined.[25]

Hydrolysis in basic solution of the $Co(NH_2CH_3)_5(NCCH_3)^{3+}$ complex occurs with attack at the nitrile to form the bound amide, analogous to the $Co(NH_3)_5(NCCH_3)^{3+}$ compound.[23] The second-order rate constant (Table IV) for this process is about 12 M^{-1} s^{-1}, which is actually slightly faster than the value of 3.1 M^{-1} s^{-1} reported for $Co(NH_3)_5(NCCH_3)^{3+}$ at 25 °C. While steric effects of the alkylamines may have been thought likely to inhibit the process, since OH^- digonal attack at the carbon should occur at about 60° from the Co–N side of the nitrile,[26] perhaps the nitrile carbon is sufficiently remote from the center to limit steric effects somewhat. Further, electronic effects in changing from ammine to methylamine ligands will differ. In addition, the Co–N(sp) bond of the nitrile should be shorter than the Co–N(sp^2) bond of the acetamide, so the reaction itself alleviates strain. This type of reaction is clearly outside the initial scope of this work, but it appears that some analysis of the effect of non leaving groups on bound nitrile hydrolysis may prove revealing and will be addressed separately.

Discussion

The effect of leaving group charge on activation volume and activation entropy is now well documented.[6,7,22] For simple complexes and leaving groups of similar molar volumes, the variation is best represented by parameters for aquation of $Co(NH_3)_5(SO_4)^+$ ($\Delta V^\ddagger$ −18.3 cm^3 mol^{-1}; $\Delta S^\ddagger$ −42 J K^{-1} mol^{-1}),[10,27] $Co(NH_3)_5Cl^{2+}$ ($\Delta V^\ddagger$ −10.6 cm^3 mol^{-1}; $\Delta S^\ddagger$ −35 J K^{-1} mol^{-1}),[10,28] and $Co(NH_3)_5(OH_2)^{3+}$ ($\Delta V^\ddagger$ +1.2 cm^3 mol^{-1}; $\Delta S^\ddagger$ +27 J K^{-1} mol^{-1}).[14] Since the leaving group charge varies from 2− to 1− to 0, the trend can be ascribed to variation in charge separation in forming the transition state and subsequent changes in solvent electrostriction. For activation volume, the experimental $\Delta V^\ddagger$ can be separated into two components: $\Delta V_{intr}^\ddagger$ represents the intrinsic contribution arising from nuclear displacement at the reaction center upon activation, while $\Delta V_{solv}^\ddagger$ results from the rearrangement of solvent molecules about the reacting species.[29] Where charges separate, the changes in electrostriction ($\Delta V_{el}^\ddagger$) dominate the latter term. A like conceptualization may be applied to the experimental $\Delta S^\ddagger$, but here the situation is complicated by, for example, rotational contributions, which do not of course appear in the volume model. For the pentaamine complexes discussed above, the increasingly negative $\Delta V^\ddagger$ values from OH_2 to Cl^- to SO_4^{2-} can be tied to an increase in the $\Delta V_{el}^\ddagger$ term. Notably, with anionic but mechanistically similar $Co(CN)_5X^{3-}$, aquation occurs with a large positive $\Delta V^\ddagger$, and a decrease in electrostriction in the dissociated transition state is anticipated in that case.[30]

Dissociation of a neutral ligand from a cationic complex is, in the absence of significant variation in specific nonelectrostatic solute–solvent interactions, relatively free of changes in solvational contributions to activation parameters $\Delta V^\ddagger$ and $\Delta S^\ddagger$. At least for the experimental $\Delta V^\ddagger$, the dominant component will be the $\Delta V_{intr}^\ddagger$ term. For a series of $Co(NH_3)_5L^{3+}$ complexes, the observation of similar $\Delta V^\ddagger$ values (~+2 cm^3 mol^{-1}) for a range of neutral leaving groups of different molar volumes is consistent with this proposition.[3] Perhaps the covalent radius of the bonded atom alone is important in defining the volume change, since the more remote components of the ligand may be innocent in a mechanistic sense, retaining largely their environmental integrity. With $Co(NH_3)_5(OCH{\cdot}N(CH_3)_2)^{3+}$, activation volumes for both solvent exchange ($\Delta V^\ddagger$ +3.2 cm^3 mol^{-1})[31] and aquation ($\Delta V^\ddagger$ +2.6 cm^3 mol^{-1})[3] are very similar despite the variation in solvent, thus further supporting a minor role for solvent terms. From these studies with neutral leaving groups, unidentate ligand dissociation from an amminecobalt(III) complex was asserted to be characterized by a small, positive $\Delta V_{intr}^\ddagger$ term.[3] Variations with charged leaving groups from this basis are substantial and reflect significant changes in $\Delta V_{el}^\ddagger$, so that effects in the second and later coordination spheres dominate in those cases, masking mechanistically significant terms.

Even when displacement of a neutral leaving group is involved, there is variation in the $\Delta V^\ddagger$ and $\Delta S^\ddagger$ terms with non leaving groups. For example, solvent exchange of $Co(NH_3)_5(OH_2)^{3+}$ ($\Delta V^\ddagger$ +1.2 cm^3 mol^{-1})[14] and *trans*-$Co(en)_2(OH_2)_2^{3+}$ (+5.9 cm^3 mol^{-1})[32] illustrates the effect. With charged leaving groups the effect is much more marked; the chloro analogues of the above complexes exhibit $\Delta V^\ddagger$ values of −9.9[28] and +11 cm^3 mol^{-1},[33] respectively. The opportunity to make these type of comparisons has been until recently essentially fortuitous, since they were unplanned. In the above complexes, variations in the cation size, number of different types of donor atoms, and introduction of chelate rings in one example complicate any interpretation of the role of the non leaving groups. The system $M(NH_2R)_5Y^{n+}$ (R = H, CH_3) represents the simplest example of increased cation size with constant charge and leaving group, unfettered by motions and rearrangements of chelate rings. The Y = Cl^- system has recently been studied,[5] with both $\Delta S^\ddagger$ and $\Delta V^\ddagger$ becoming more positive

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from R = H to R = CH_3 (Table III); here, with various neutral Y, the same trend is observed.

The crystal structure of $Co(NH_2CH_3)_5Cl^{2+}$ has been reported,[34] and substantial steric crowding is observed. However, there is no obvious bond lengthening in the M–Cl bond in $Co(NH_2CH_3)_5Cl^{2+}$ (2.283 Å)[34] compared with that in $Co(NH_3)_5Cl^{2+}$ (2.286 Å).[35] Although no data is available, we presume a like situation applies with the neutral ligand complexes, although Cl^- has a larger covalent radius than O or N donors, and some structural study with a neutral donor would be interesting. With the charged leaving group, the trend in $\Delta V^\ddagger$ and $\Delta S^\ddagger$ was ascribed to an appreciable decrease in electrostricted solvent reorganization in the larger ions associated with a less organized solvent sheath for the pentakis(methylamine) complex.[5] A constancy for $\Delta H^\ddagger$ did not favor variation in the M–Cl separation in the activation state with non leaving group, and a similar constancy is observed here with the neutral leaving groups. Notably, $\Delta(\Delta V^\ddagger)$ and $\Delta(\Delta S^\ddagger)$ from $Co(NH_3)_5Cl^{2+}$ to $Co(NH_2CH_3)_5Cl^{2+}$ of +7.6 $cm^3\ mol^{-1}$ and +34 $J\ K^{-1}\ mol^{-1}$ are somewhat different than average $\Delta(\Delta V^\ddagger)$ and $\Delta(\Delta S^\ddagger)$ values for $Co(NH_2R)_5L^{3+}$ analogues of +4 $cm^3\ mol^{-1}$ and +40 $J\ K^{-1}\ mol^{-1}$ but lie in the same direction. If we accept that $\Delta V_{el}^\ddagger$ terms with neutral ligands are minimal, the above data for $Co(NH_2R)_5L^{3+}$ complexes suggests a more dissociated activated state (more positive $\Delta V_{intr}^\ddagger$) for the R = CH_3 complex. This could simply mean less participation of incoming water in the transition state in that complex, which would be quite consistant with the known steric crowding. The similar trend for the chloro complexes, where $\Delta V_{el}^\ddagger$ changes might have been expected to be more substantial, suggests that the variation may arise from a more positive $\Delta V_{intr}^\ddagger$ term when R = CH_3 in that case also, although the similarity may be fortuitous.

In reality, of course, the "separation" of $\Delta V^\ddagger$ (experimental) into two components[29] is too simplistic. However, it is attractive to assign one solvent molecule from the second coordination sphere as "special", since its fate is to coordinate to the metal ion; then the $\Delta V_{intr}^\ddagger$ term may be reduced to a localized variation in the spatial arrangement of that water molecule and the leaving group in a "sea" of electrostricted solvent relative to the metal ion. The $\Delta V_{solv}^\ddagger$ term then encompasses all other motions in the outer sphere about the complex ion. A more positive $\Delta V_{intr}^\ddagger$ term is then associated with both entering and leaving group being further from the metal ion in the activated state. Their actual location will of course impinge on the reorganization of the solvent layers in general. The intermediate of reduced coordination number (in terms of a "bond-breaking" mechanism) can be created on the subpicosecond time scale in a vibration-like action.[36] Its lifetime will be exceptionally short. Even the "long-lived" conjugate base intermediates such as $Co(NH_3)_4(NH_2)^{2+}$ have lifetimes of probably <10 ps and do not survive long enough to equilibrate completely with their surroundings.[37,38] So the environment of the activated dissociated complex is partly inhereted. With $Co(NH_3)_5X^{2+}$ ions, it has been suggested that the activated complex may approach but does not achieve the solvation sheath of a true 3+ ion.[3] With a neutral leaving group, charge from precursor to activated complex is preserved, limiting $\Delta V_{solv}^\ddagger$ and $\Delta S_{solv}^\ddagger$ terms. For a charged leaving group, the $\Delta V_{solv}^\ddagger$ and $\Delta S_{solv}^\ddagger$ terms will be affected by cation size and lifetime of the transition state. Larger cations will have, on a spherical model, a lower surface charge density and a less tightly bound and ordered solvation sheath. Lifetime of any intermediate may be affected by its size and the type of donor atoms and therefore will be related to the type of non leaving groups. Both cation size and non leaving groups will affect the extent and significance of solvent reorganization when a charged group is displaced.

The significance of intermediate lifetime and configuration on activation parameters can be seen from comparison of data for water exchange of *trans*-$Co(en)_2(OH_2)_2^{3+}$ ($\Delta V^\ddagger$ +5.9 $cm^3\ mol^{-1}$)[32] and the slower isomerization ($\Delta V^\ddagger$ +14 $cm^3\ mol^{-1}$).[39] Clearly, these reactions do not involve the same transition state. A relatively short-lived tetragonal-pyramidal intermediate would suffice for water exchange, but such a species must convert or relax to a trigonal-bipyramidal species necessarily for isomerization, with greater disruption of the solvent environment.[36] Steric congestion in *trans*-$Co(en)_2(OH_2)_2^{3+}$ should be markedly less than in $Co(NH_2CH_3)_5L^{3+}$, yet $\Delta V^\ddagger$ in the former is of a size similar to the latter and may reflect a role for the chelate rings "sweeping" solvent molecules in forming the transition state. Solvent molecules transferred from the electrostricted second coordination sphere to outer less ordered spheres will each experience an increase in molar volume of several $cm^3\ mol^{-1}$,[22] so apparently minor effects can contribute markedly to an experimental activation volume at least.

The rate enhancements observed for $Co(NH_2CH_3)_5L^{3+}$ are substantial and parallel similar enhancements observed with anionic leaving groups (Table III). The more rapid rate constants in the sterically crowded ions are fully consistent with a dominantly bond-breaking dissociative mechanism, which has been assumed in the above discussion, in concert with the generally held view of substitution in cobalt(III) amines. The operation of a limiting dissociative (D) mechanism is unlikely in view of our conceptualization of intermediate lifetimes and the view that the intermediate has a "memory" of the departing group and of the precursor environment. More positive $\Delta V^\ddagger$ and $\Delta S^\ddagger$ values from $Co(NH_3)_5L^{3+}$ to $Co(NH_2CH_3)_5L^{3+}$ indicate no mechanistic disparity, but merely a trend towards less participation of the incoming water molecule and perhaps a longer lived intermediate with increasing size and steric crowding of the complex. Variation of the non leaving groups, at least about cobalt(III), do not appear to require any gross change in aquation mechanism; rather, they mediate the various extents of bond-breaking and bond-making in an essentially dissociative interchange mechanism.

Registry No. $[Co(NH_2CH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 90065-88-6; $[Co(NH_2CH_3)_5OC(NH_2)_2](S_2O_6)_{3/2}$, 100681-43-4; $[Co(NH_2CH_3)_5OP(OCH_3)_3](CF_3SO_3)_3$, 100681-45-6; $[Co(NH_2CH_3)_5NCCH_3](CF_3SO_3)_3$, 100681-47-8; $[Co(NH_2CH_3)_5OS(CH_3)_2](CF_3SO_3)_3$, 100681-49-0; $[Co(NH_2CH_3)_5OS(CH_3)_2](ClO_4)_3$, 100681-50-3; $[Co(NH_2CH_3)_5OCHN(CH_3)_2](CF_3SO_3)_3$, 100681-52-5; $[Co(NH_2CH_3)_5(OH_2)]^{3+}$, 32424-84-3.

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