of the orderly electron-transfer properties, the conclusion can be drawn that intrinsic properties of the complexes, such as the pK_a of the amine protons or the formal potential, are much more sensitive to changes in the ligand, leading to differences in reactivity of several orders of magnitude. In this respect, the comparison between the closely related Ru(sar)$^{3+/2+}$ and Ru(tacn)$_2$$^{3+/2+}$ couples provides an excellent example.[46] Work on these questions is continuing.[48]

Acknowledgment. The authors are grateful to the Microanalytical Service Unit of ANU for analyses and to R. Wijeksera for a sample of the ligand tacn·3HCl.

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Contribution from the Chemistry Department,
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Kinetics of the Base Hydrolysis of Chloro(diamine)(triamine)chromium(III) Complexes: Evidence for the SN$_1$CB Mechanism in Chromium(III) Polyamine Complexes

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Spectrophotometrically determined kinetic parameters for the rate of base hydrolysis (μ = 0.1 M, NaCl) of *sfac*-CrCl(AA)(dien)$^{2+}$ [AA = en (I), tn (II)], *ufac*-CrCl(NMetn)(dien)$^{2+}$ (III), *mer*-CrCl(AA)(dpt)$^{2+}$ [AA = en (IV), pn (V), tn (VI), Me$_2$tn (VII)], *mer*-CrCl(tn)(2,3-tri)$^{2+}$ (VIII), *sfac*-CrCl(dien)(DMSO)$_2$$^{2+}$ (IX), and *cis*-CrCl(AA)$_2$(DMSO)$^{2+}$ [AA = en (X), tn (XI)] are (in order I–XI) as follows: $10^2k_{OH}(298.2)$ (M^{-1} s^{-1}) = 1.56, 1.85, 22.1, 10.5, 9.64, 60.6, 58.6, 73.5, 2.06, 0.500, 7.53; E_a (kJ mol^{-1}) = 104, 108, 109, 95.5, 98.1, 108, 84.7, 110, 102, 125, 105; $\Delta S_{298}^{\ddagger}$ (J K^{-1} mol^{-1}) = 61, 75, 101, 48, 56, 105, 26, 113, 58, 121, 84. Titrimetrically determined kinetic parameters for the rate of loss of chloride in acid (0.1 M HClO$_4$) for IX–XI are as follows: $10^6k_H(298.2)$ (s^{-1}) = 110, 24.4, 5.50; E_a (kJ mol^{-1}) = 68.0, 82.6, 96.2; $\Delta S_{298}^{\ddagger}$ (J K^{-1} mol^{-1}) = −100, −64, −31. Similar data for the rate of Hg^{2+}-assisted chloride release (μ = 1.0 M, HClO$_4$, determined spectrophotometrically): $10^3k_{Hg}(298.2)$ (M^{-1} s^{-1}) = 428, 43.0, 43.5; E_a (kJ mol^{-1}) = 74.4, 67.3, 73.3; $\Delta S_{298}^{\ddagger}$ (J K^{-1} mol^{-1}) = −7, −53, −33. Several of these complexes contain a meridional or "flat" *sec*-NH proton, but this gives only a small (<50 times) base hydrolysis rate increase with respect to related Cr(III) systems where this feature is absent. The observation that there is an inverse relationship between k_{OH} and k_H (aquation rate constant) is used to propose that a dissociative conjugate base mechanism is applicable to Cr(III) complexes of this type.

Introduction

Base hydrolysis (or base-catalyzed solvolysis[1,2]) of octahedral Co(III) polyamine complexes is a well-studied reaction, and considerable evidence for the conventionally accepted SN$_1$CB mechanism[1,2] has been accumulated.

A fairly general observation is that the presence of a meridional or "flat" *sec*-NH proton, cis to the leaving group, leads to high sensitivity toward base hydrolysis in Co(III) complexes.[2,3]

In a consideration of base hydrolysis studies of complexes with other inert transition-metal centers, the SN$_1$CB mechanism is generally assumed, although by no means as well established as for Co(III).[2] For Cr(III), in particular, the lower reactivity requires either less acidic NH protons or a less reactive conjugate base.[4,5]

In a recent review of base hydrolysis,[2] the significance of investigating the "flat *sec*-NH proton effect" for Cr(III) is commented on, as "the results should provide guidance about the importance of any trigonal-bipyramid intermediates."

We are now in a position to discuss these effects as we have recently synthesized[6] a series of *mer*-CrCl(AA)(3,3-tri)$^{2+}$ complexes[7] (AA = diamine) that incorporate this structural feature, and we report the results for their base hydrolysis kinetics, as well as base hydrolysis data for several other CrCl(L$_5$)$^{2+}$ complexes (Figure 1).

Experimental Section

Analytically pure[6,8–9b] tetrachlorozincate(II) salts of *sfac*-CrCl(en)(dien)$^{2+}$ (I),[8] *sfac*-CrCl(tn)(dien)$^{2+}$ (II),[8] *ufac*-CrCl(NMetn)(dien)$^{2+}$ (III),[9a] *mer*-CrCl(AA)(3,3-tri)$^{2+}$,[6] [AA = en (IV, pn (V), tn (VI), Me$_2$tn (VII)], *mer*-CrCl(en)(2,3-tri)$^{2+}$ (VIII),[6] *sfac*-CrCl(dien)(DMSO)$_2$$^{2+}$ (IX),[9b] and *cis*-CrCl(AA)$_2$(DMSO)$^{2+}$ [AA = en (X), tn (XI)][9b] were prepared according to the literature methods. These were converted to zinc(II)-free salts [either Cl$^-$·ClO$_4$$^-$ (I, II), NO$_3$$^-$·ClO$_4$$^-$ (VII, VIII, X, XI), (I$^-$)$_2$ (III), or (ClO$_4$$^-$)$_2$ (IX)] or else the directly prepared chloride salts[6] (IV–VI) were used without further purification. (*Caution*! ClO$_4$$^-$ salts are potentially explosive.)

Base hydrolysis kinetic data were obtained spectrophotometrically by using repeated continuous- (700–300 nm) or repeated fixed-wavelength scans (Table I) with a Varian DMS-100 recording spectrophotometer.

NaOH solutions (μ = 0.1 M, NaCl) were standardized by HCl titration and adjusted to the appropriate temperature. Small samples of the complex were added, and after dissolution (usually rapid), the solution was transferred by syringe into a temperature-controlled 5.00-cm cell (approximately 6-mL capacity). The complex:NaOH ratio was always less than 1:8, even at the most dilute NaOH concentration (0.01 M). Pseudo-first-order rate constants (k_{obsd}, s^{-1}) were calculated from the fixed-wavelength data over 3–4 half-lives by using 12–15 data points, and the average results are reported in Table I. These have been converted to k_{OH} (M^{-1} s^{-1}) (Table I) by using the expression $k_{obsd} = k_{OH}[OH^-]^{-1}$. Satisfactory linear Arrhenius plots of ln [k_{OH}] vs T^{-1} over a 10-fold [OH$^-$] range confirm the relationship between k_{obsd} and k_{OH}. Activation

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(7) Abbreviations used: en = NH$_2$(CH$_2$)$_2$NH$_2$, pn = *R,S*-NH$_2$CH(CH$_3$)CH$_2$NH$_2$, tn = NH$_2$(CH$_2$)$_3$NH$_2$, NMetn = CH$_3$NH(CH$_2$)$_3$NH$_2$, Me$_2$tn = NH$_2$CH$_2$C(CH$_3$)$_2$CH$_2$NH$_2$, dien = 2,2-tri = NH$_2$(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$, dpt = 3,3-tri = NH$_2$(CH$_2$)$_3$NH(CH$_2$)$_3$NH$_2$, 2,3-tri = NH$_2$(CH$_2$)$_2$NH(CH$_2$)$_3$NH$_2$.

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Table I. Rate Constants for the Base Hydrolysis of $CrCl(L_5)^{2+}$ Complexes at $\mu = 0.1$ M[a]

L_5	λ,[f] nm	T, °C [K]	$[OH^-]$, M	$10^3 k_{obsd}$, s^{-1}	$10^2 k_{OH}$,[b] $M^{-1}\ s^{-1}$	$10^5 k_{OH(calcd)}$,[c] $M^{-1}\ s^{-1}$
sfac-(en)(dien) (I)	505	19.1 [292.3]	0.1	0.672 (10)	0.672 (10)	0.669
		25.0 [298.2]	0.1	1.53 (4)	1.53 (4)	1.56
				1.58 (3)	1.58 (3)	
		31.0 [304.2]	0.05	1.79 (4)	3.58 (8)	3.57
sfac-(tn)(dien) (II)	505	19.1 [292.3]	0.1	0.774 (11)	0.774 (11)	0.770
		25.0 [298.2]	0.1	1.84 (2)	1.84 (4)	1.85
				1.84 (3)	1.84 (3)	
		30.6 [303.8]	0.05	2.07 (6)	4.14 (12)	4.12
ufac-(NMetn)(dien) (III)	375	11.8 [285]	0.1	2.87 (10)	2.87 (10)	2.86
		14.7 [287.9]	0.05	2.27 (3)	4.54 (6)	4.56
		25.0 [298.2]	0.01	2.21 (6)	22.1 (6)	22.1
mer[d]-(en)(dpt) (IV)	375	9.8 [283.0]	0.1	1.29 (7)	1.29 (7)	1.33
				1.25 (3)	1.25 (3)	
		14.7 [287.9]	0.1	2.54 (3)	2.54 (3)	2.65
				2.51 (3)	2.51 (3)	
		18.8 [292.0]	0.05	2.27 (2)	5.67 (4)	4.65
				2.29 (4)	5.72 (8)	
		25.0 [298.2]	0.01	1.02 (3)	10.2 (3)	10.5
				0.929 (39)	9.3 (4)	
				1.00 (5)	10.0 (5)	
mer[d,e]-(pn)(dpt) (V)	375	9.8 [283.0]	0.1	1.18 (2)	1.18 (2)	1.15
				1.11 (4)	1.11 (4)	
		14.7 [287.9]	0.1	2.37 (4)	2.37 (4)	2.34
		25.0 [2.98.2]	0.01	0.96 (2)	9.6 (2)	9.64
mer[d]-(tn)(dpt) (VI)	375	9.8 [283.0]	0.05	2.89 (7)	5.78 (14)	5.81
				2.89 (14)	5.78 (28)	
		14.7 [287.9]	0.01	1.26 (6)	12.6 (6)	12.7
				1.32 (4)	13.2 (4)	
		18.8 [292.0]	0.01	2.47 (8)	24.7 (8)	24.0
				2.57 (15)	25.7 (15)	
				2.23 (7)	22.3 (7)	
				2.31 (7)	23.1 (7)	
		25.0 [298.2]				60.6
mer[d]-(Me_2tn)(dpt) (VII)	375	9.8 [283.0]	0.05	4.79 (7)	9.58 (14)	9.34
		14.7 [287.9]	0.01	1.63 (11)	16.3 (11)	17.2
		18.8 [292.0]	0.01	2.91 (3)	29.1 (3)	28.3
				2.85 (6)	28.5 (6)	
		25.0 [298.2]				58.6
mer[d]-(en)(2,3-tri) (VIII)	375	9.8 [283.0]	0.05	3.38 (4)	6.76 (8)	6.77
				3.33 (10)	6.66 (20)	
		14.7 [287.9]	0.01	1.56 (4)	15.6 (4)	15.0
		18.0 [291.2]	0.01	2.52 (6)	25.2 (6)	25.3
		18.8 [292.0]	0.01	2.81 (4)	28.1 (4)	28.6
		25.0 [298.2]				73.5
sfac-(dien)$(DMSO)_2$ (IX)	550	15.2 [288.4]	0.1	0.502 (7)	0.502 (7)	0.505
		25.0 [298.2]	0.1	2.05 (7)	2.05 (7)	2.06
				2.12 (5)	2.12 (5)	
		30.0 [303.2]	0.1	4.06 (9)	4.06 (9)	4.08
			0.05	2.02 (2)	4.04 (4)	
cis-$(en)_2$(DMSO) (X)	505	25.0 [298.2]	0.1	0.496 (8)	0.496 (8)	0.500
				0.502 (11)	0.502 (11)	
		30.0 [303.2]	0.1	1.17 (2)	1.17 (2)	1.15
				1.14 (2)	1.14 (2)	
		34.8 [3.8.0]	0.1	2.47 (5)	2.47 (5)	2.48
cis-$(tn)_2$(DMSO) (XI)	440	10.9 [284.1]	0.1	0.887 (5)	0.887 (5)	0.883
		15.2 [288.4]	0.1	1.74 (7)	1.74 (7)	1.74
		25.0 [298.2]	0.01	7.46 (4)	7.46 (4)	7.53
			0.05	3.72 (3)	7.44 (6)	
		30.0 [203.2]	0.01	1.56 (3)	1.56 (3)	15.3

[a] Maintained by using 0.1 M NaCl. [b] $k_{OH} = k_{obsd}[OH^-]^{-1}$. [c] Calculated from the activation parameters cited in Table II. [d] In this configuration the *sec*-NH proton is remote from the coordinated chloro ligand.[6] Such a configuration has been described as (H↓)[6] or anti.[14] [e] Two isomers are possible due to end-for-end orientation of the unsymmetrical diamine ligand. The isomeric composition from this source is unknown. [f] Wavelength used to monitor the reaction.

parameters were computer-calculated from k_{OH} vs T data (Table II).

Acid hydrolysis rate data (0.1 M $HClO_4$) for the three complexes containing DMSO (IX–XI) were determined by chloride ion release titration.[6] Separation of the colored cations by filtration of a suitable aliquot through a short column of Dowex cation-exchange resin (Na^+ form) was required, prior to each titration. Pseudo-first-order rate constants (k_H, s^{-1}) (Table III) were calculated from the volume vs time data, and activation parameters (Table IV) were obtained from the variation of k_H with T.

Mercury(II)-assisted chloride release rate data for IX–XI ($\mu = 1.0$ M, $HClO_4$) were obtained spectrophotometrically by using methods previously described[4] (Tables V and VI).

Results

The rates of base hydrolysis (Table I) for a series of $CrCl(L_5)^{2+}$ complexes of known stereochemistry have been measured spectrophotometrically. No marked visible color change occurs during the reaction, but for the mer complexes, the absorbance at the 380-nm maxima decreases, while that at the 520-nm maxima increases with an isosbestic point at about 395 nm. Occasionally, base hydrolysis reactions in Cr(III) systems are accompanied by

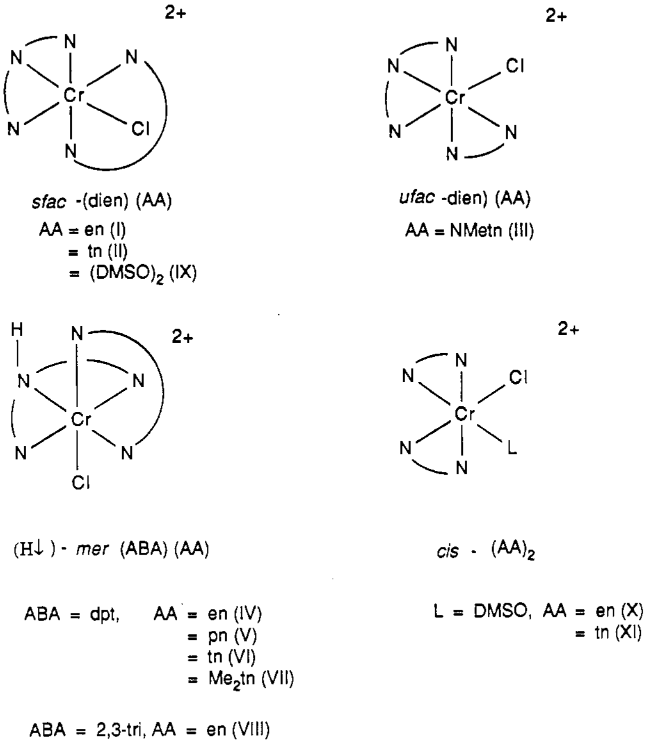

Figure 1. Schematic representations of the geometric isomers of $CrCl(N_5)^{2+}$.

Table II. Kinetic Parameters for the Base Hydrolysis of $MCl(L_5)^{2+}$ Complexes at 298 K and $\mu = 0.1$ M

M = Cr

L_5	k_{OH}, $M^{-1}\,s^{-1}$	E_a, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	ref
$(NH_3)_5$	1.8×10^{-3}	109	+99	*a*
sfac-(en)(dien)	1.56×10^{-2}	104 ± 2	+61 ± 4	*b, c*
ufac-(NMetn)(dien)	2.21×10^{-1}	109 ± 1	+101 ± 2	*b*
$(NH_2Me)_5$	$>4.3 \times 10^{-1}$	109	+104	*a, d*
mer-(en)(dpt)	1.05×10^{-1}	99.5 ± 5	+48 ± 10	*b*
mer-(pn)(dpt)	9.64×10^{-2}	98.1 ± 2	+56 ± 4	*b*
mer-(tn)(dpt)	6.06×10^{-1}	108 ± 3	+105 ± 6	*b*
mer-(Me_2tn)(dpt)	5.86×10^{-1}	84.7 ± 4	+26 ± 8	*b*
mer-(en)(2,3-tri)	7.35×10^{-1}	110 ± 2	+113 ± 4	*b*
sfac-(dien)$(DMSO)_2$	2.06×10^{-2}	102 ± 1	+58 ± 2	*b*
cis-$(en)_2$(DMSO)	5.00×10^{-3}	125 ± 2	+121 ± 4	*b*
cis-$(tn)_2$(DMSO)	7.53×10^{-2}	105 ± 1	+84 ± 2	*b*

M = Co

L_5	k_{OH}, $M^{-1}\,s^{-1}$	E_a, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	R^e	ref
$(NH_3)_5$	8.6×10^{-1}	116	+140	478	*f*
sfac-(en)(dien)	4.71	87	+72	3078	*g*
sfac-(tn)(dien)	1.06×10^{1}	123	+179	5380	*h*
mer-(en)(dpt)	2.2×10^{3}			20952	*f*
ufac-(NMetn)-(dien)	7.57	83	+82	35	*h*
$(NH_2Me)_5$	8×10^{2}	77.7	+72	1860	*f*
mer-(tn)(dpt)	2.8×10^{3}	102	+175	4620	*h*
mer-(en)(2,3-tri)	1.24×10^{3}	92.4	+116	1687	*i*

[a] Data from ref 12. [b] This research. [c] See ref 4 for data at $\mu = 1.0$ M. [d] $\mu = 0.2$ M, with the reaction characterized by a negative salt effect. [e] Ratio of $k_{OH}[Co(III)]/k_{OH}'[Cr(III)]$. [f] Reference 3. [g] Foo Chuk Ha; House, D. A. *Inorg. Chim. Acta* **1980**, *38*, 167. [h] Lim Say Dong; House, D. A. *Inorg. Chim. Acta* **1976**, *19*, 23. [i] House, D. A.; Gainsford, A. R.; Blunt, J. W. *Inorg. Chim. Acta* **1982**, *58*, 141.

Table III. Titrimetrically Determined Pseudo-First-Order Rate Constants for the Thermally Activated Loss of Chloride Ion from Monochlorochromium(III) Complexes Containing DMSO[a]

T, °C	K	10^5k_H, s^{-1}	10^5k_{calcd},[b] s^{-1}
	$CrCl(tn)_2(DMSO)^{2+}$ (XI)		
25.0	298.2		0.550
28.7 (3)[c]	301.9	0.911 ± 0.05	0.888
34.3 (6)	307.5	1.77 ± 0.04	1.78
42.1 (4)	297.3	4.26 ± 0.05	4.51
47.0 (4)	320.2	8.29 ± 0.07	7.91
	$CrCl(en)_2(DMSO)^{2+}$ (X)		
17.2 (5)	290.4	1.00 ± 0.10	0.998
25.0	298.2		2.44
28.7 (5)	301.9	3.63 ± 0.14	3.67
34.3 (6)	307.5	6.73 ± 0.08	6.69
	$CrCl(dien)(DMSO)_2{}^{2+}$ (IX)		
17.2 (5)	290.4	5.24 ± 0.20	5.24
25.0	298.2		11.0
28.7 (4)	301.9	15.3 ± 0.73	15.3
34.3 (10)	307.5	25.1 ± 0.86	25.1

[a] In 0.1 M $HClO_4$. [b] Calculated by using the activation parameters cited in Table IV. [c] Number of data points used to obtain mean k_{obsd} values. Individual, rather than mean, k_{obsd} data were used in the calculation of activation parameters.

Table IV. Kinetic Parameters for the Rate of Chloride Release from $CrCl(L_5)^{2+}$ Complexes at 25 °C

L_5	10^7k_H, s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\ddagger}{}_{298}$, J K^{-1} mol^{-1}	ref
sfac-(dien)$(DMSO)_2$	1100	68.0 ± 0.9	−100 ± 2	*a*
cis-$(en)_2$(DMSO)	244	82.6 ± 1.5	−64 ± 3	*a*
sfac-(en)(dien)	224	89.2	−43	*b*
sfac-(tn)(dien)	218	91.0	−37	*b*
$(NH_3)_5$	95	89.3	−50	*c*
cis-$(tn)_2$(DMSO)	55.0	96.2 ± 1.5	−31 ± 3	*a*
ufac-(NMetn)(dien)	37.0	93.0	−45	*d*
mer-(en)(dpt)	5.34	99.2	−40	*e*
mer-(tn)(dpt)	5.04	82.8	−96	*e*
mer-(en)(2,3-tri)	2.87	90.9	−73	*e*
$(MeNH_2)_5$	2.48	113	−2	*c*

[a] This research (0.1 M $HClO_4$). [b] Reference 4. [c] Data from ref 3. [d] Reference 9. [e] Reference 6.

Cr–N bond rupture, but this was not the case in the present series. Indeed, the reaction sequence $CrCl(N_5)^{2+} + OH^- \rightarrow Cr(OH)(N_5)^{2+} \rightarrow Cr(N_5)(OH_2)^{3+} \rightarrow CrCl(N_5)^{2+}$ can be achieved without appreciable loss and with complete stereochemical retention (by IR spectroscopy of starting material and product).

The situation is not quite the same for the three complexes containing DMSO (IX–XI), as precipitation [$Cr(OH)_3$?] is evident at long reaction times at high [OH^-]. Nevertheless, we believe the measured spectrophotometric change represents the conventional base-catalyzed chloride release reaction, as the observed rate constants fit the pattern established for the $CrCl(N_5)^{2+}$ systems. We cannot, however, eliminate the alternative path via DMSO release viz.

$$CrCl(N_4)(DMSO)^{2+} + OH^- \xrightarrow{\text{rate determining}} CrCl(OH)(N_4)^+ + DMSO$$

$$CrCl(OH)(N_4)^+ + OH^- \xrightarrow{\text{rapid}} Cr(OH)_2(N_4)^+ + Cl^-$$

Indeed, $CrCl(dien)(DMSO)_2{}^{2+}$ (which reacts more rapidly than expected) may well have a contribution via this alternative route.

Base hydrolysis rates for *sfac*-$CrCl(AA)(dien)^{2+}$ (AA = en, tn) have been measured previously at $\mu = 1.0$ M.[4] The present values (at $\mu = 0.1$ M) are about 2 times greater, supporting the observation that base hydrolysis kinetics of this type are subject to a negative salt effect.[3]

Discussion

The S_N1CB mechanism for the base hydrolysis (base-catalyzed substitution) of Co(III) polyamine complexes is now well established. While a few subtle points, such as the site of deprotonation and the possibility of internal proton interchange,[9c] remain to be clarified, the overall dissociative nature of the reaction involving a trigonal-bipyramidal intermediate is generally accepted.[2]

Table V. Observed and Calculated Rate Constants for the Hg^{2+}-Assisted Chloride Release from $CrClL_5^{2+}$ Complexes ($\mu = 1.0$ M)[a]

T, °C	K	$[Hg^{2+}]_i$, mM	10^3k_{obsd}, s^{-1}	10^3k_{Hg},[b] M^{-1} s^{-1}	$10^3k_{Hg(calcd)}$,[c] M^{-1} s^{-1}
L_5 = (dien)(DMSO)$_2$[d]					
9.4	282.6	20.4	2.52 (3)	124 (2)	125
			2.59 (5)	127 (3)	
14.2	287.4	20.4	4.41 (9)	216 (4)	213
			4.29 (3)	210 (2)	
25.0	298.2				658
L_5 = (en)$_2$(DMSO)[e]					
14.2	287.4	93.4	1.45 (4)	15.5 (4)	15.5
			1.46 (5)	15.6 (5)	
25.0	298.2				43.0
25.2	298.4	44.7	1.82 (3)	40.7 (7)	43.7
			2.00 (7)	44.7 (2)	
			2.00 (6)	44.7 (1)	
30.0	303.2	20.9	1.37 (5)	65.5 (2)	67.2
			1.38 (2)	66.0 (1)	
			1.50 (5)[f]	71.7 (2)	
L_5 = (tn)$_2$(DMSO)[e]					
14.2	287.4	93.4	1.34 (7)	14.3 (7)	14.3
			1.91 (9)[f]	20.4 (9)	20.3
20.4	293.6	93.4	3.34 (7)[f]	35.8 (7)	35.9
22.4	295.6	93.4	3.99 (7)[f]	42.7 (7)	43.0
25.0	298.2				43.5
					54.0[f]
30.0	303.2	44.7	3.04 (11)	68.0 (3)	70.8
			3.01 (6)	67.3 (1)	
			3.73 (13)[f]	83.4 (3)	83.0
		20.9	1.53 (6)	73.2 (3)	
			1.57 (7)	75.1 (3)	

[a] Determined spectrophotometrically by using fixed-wavelength scans (400 nm) with time. [b] $k_{Hg} = k_{obsd}[Hg^{2+}]_i^{-1}$. [c] Calculated from the activation parameters cited in Table VI. [d] In HNO_3. [e] In $HClO_4$. [f] Using the $ZnCl_4^{2-}$ salt.

Table VI. Kinetic Parameters for the Rate of Mercury(II)-Assisted Chloride Release from $CrCl(L_5)^{2+}$ Complexes at 25 °C ($\mu = 1.0$ M)

L_5	10^4k_{Hg}, M^{-1} s^{-1}	E_a, kJ mol^{-1}	ΔS^{*}_{298}, J K^{-1} mol^{-1}	ref
sfac-(dien)(DMSO)$_2$	4280[f,g]	74.4 ± 3[g]	−7 ± 6[g]	*a*
(NH$_3$)$_5$	480	62	−56	*b*
cis-(tn)$_2$(DMSO)	540[h]	64.5 ± 1	−70 ± 2	*a*
	435[g]	73.3 ± 3[g]	−33 ± 6[g]	*a*
cis-(en)$_2$(DMSO)	430	67.3 ± 2	−53 ± 4	*a*
sfac-(en)(dien)	236			*c*
sfac-(tn)(dien)	216			*c*
mer-(tn)(dpt)	26.7	85.7	−15	*d*
mer-(Me$_2$tn)(dpt)	21.8	78.6	−41	*d*
ufac-(NMetn)(dien)	20.1	64.2	−90	*e*
mer-(en)(dpt)	5.95	78.1	−53	*d*
mer-(en)(2,3-tri)	1.79	80.1	−56	*d*

[a] This research, with chloride-free anions in $HClO_4$ media. [b] Data from ref 3. [c] Reference 4. [d] Reference 6. [e] Reference 9. [f] Adjusted to $\mu = 1.0$ M $HClO_4$ from the $\mu = 1.0$ M HNO_3 data (Table V) by using the relationship $k_{Hg}(HClO_4) = 0.65k_{Hg}(HNO_3)$: House, D. A. *Inorg. Chim. Acta* **1981**, *51*, 273. [g] Data from two temperatures only. [h] Using the $ZnCl_4^{2-}$ salt.

Table VII. Comparison of Aquation and Base Hydrolysis Rate Constants for $CrCl(L_5)^{2+}$ Complexes

L_5	10^2k_{OH},[a] M^{-1} s^{-1}	10^7k_H, s^{-1}	ref[b]
(NH$_2$Me)$_5$	>43[c]	2.5	*d, d*
mer-(en)(2,3-tri)	73.5	2.9	*e, f*
mer-(tn)(dpt)	60.6	5.0	*e, f*
mer-(Me$_2$tn)(dpt)	58.6		*e*
mer-(en)(dpt)	10.5	5.3	*e, f*
mer-(pn)(dpt)	9.64		*e*
ufac-(NMetn)(dien)	22.1	37	*e, g*
cis-(tn)$_2$(DMSO)	7.46	55	*e, e*
(NH$_3$)$_5$	0.18	95	*d, d*
sfac-(tn)(dien)	1.85	218	*e, d*
sfac-(en)(dien)	1.56	224	*e, d*
cis-(en)$_2$(DMSO)	0.50	244	*e, e*
sfac-(dien)(DMSO)$_2$	2.06	1100	*e, e*

[a] $\mu = 0.1$ M (NaCl)[e] unless otherwise stated. [b] First reference to k_{OH}; second reference to k_H. [c] $\mu = 0.2$ M, and the reaction is characterized by a negative salt effect. [d] Data from ref 3. [e] This research. [f] Reference 6. [g] Reference 9.

For acid hydrolysis of similar types of Co(III) complexes a dissociative process is also postulated.[1] Here, the lifetime and geometry of the intermediate are subject to rather more uncertainty, but there is accumulating evidence to support movement toward a trigonal bipyramid,[10] even though steric change is not always observed.

The parallel between acid and base hydrolyses has been commented on earlier,[3] and there is an approximate linear relationship, $\log k_{OH} = (1.29 \pm 0.22) \log k_H + (7.35 \pm 1.86)$, supporting the general dissociative nature in the rate-determining step, for both processes.

The situation for Cr(III) complexes is much less certain. Aquation processes are believed to be more associative (I_a), and there is no direct correlation between k_H[Cr(III)] and k_H[Co(III)].[6] Indeed, the observation that $CoCl(NH_2Me)_5^{3+}$ aquates 19 times faster than $CoCl(NH_3)_5^{2+}$, whereas $CrCl(NH_2Me)_5^{2+}$ aquates 38 times more slowly than $CrCl(NH_3)_5^{2+}$, is compelling evidence for a mechanistic change. The limited data available for interpretation[6] would reinforce the suspicion that systems which aquate rapidly for Co(III) are slow for Cr(III), and vice versa, i.e., an inverse relationship.

The acid hydrolysis rate data reported here (Tables III and IV) for the three Cr(III) complexes containing DMSO do not provide any additional information on this point, as the corresponding data for Co(III) are not all available.[10b]

We do, however, provide more data for a comparison of the Hg^{2+}-assisted aquation rates (Tables V and VI) with the thermal aquation rates. These support our previous arguments[6] that there is a direct relationship between these parameters. The entry of data in Tables IV and VI is in order of fastest to slowest for both k_H and k_{Hg}, and there is a reasonable 1:1 correspondence between the listed complexes. Thus, we believe the mechanism of Hg^{2+}-assisted halide release for Cr(III) complexes to be much more associative than previously proposed.[12b]

Base hydrolysis rates for Cr(III) systems are characterized by reactivities of some orders of magnitude less than those for analogous Co(III) systems.[2,12a] Consequently, if the conjugate base mechanism is operative, either the NH protons are less acidic or the conjugate base is less reactive or both.[4,5] We now argue that the conjugate base mechanism is operating for Cr(III) systems and that the lower reactivity can be accounted for with this mechanism. The extended range of base hydrolysis data presented here shows that there is a direct correlation between k_{OH}[Cr(III)] and k_{OH}[Co(III)] (Table II) with an average (excluding extremes) k_{OH}[Co(III)]/k_{OH}[Cr(III)] ratio of 3300. This is in keeping with the idea that similar mechanisms will show direct correlation. Logical extension of this argument would predict that k_{OH}[Cr(III)] and k_H[Cr(III)] should show an inverse correlation due to the mechanistic change for k_H[Cr(III)]. Inspection of the data in Table VII shows that this is indeed the case with large k_{OH} corresponding to small k_H.

The only other series of Cr(III) complexes with constant leaving group where k_{OH}:k_H data are available for comparison is the $CrCl(NH_2R)_5^{2+}$ (R = H, Me, Et, *n*-Pr, *n*-Bu) system.[13] The inverse relation holds for R = H vs R = Me (Table II), but from then on there is a monotonic increase in both k_H and k_{OH}. We would attribute this to entropy effects dominating any inverse

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k_H:k_{OH} trends, as the size of the ion is increasing with increasing alkyl chain length.[13]

The present series of Cr(III) complexes (IV–VIII) also contains for the first time systems with meridional or "flat" *sec*-NH protons.[6] In Co(III) chemistry, the introduction of such a structural feature cis to the leaving group results in a 200–1000 times increase in base hydrolysis rate relative to that for isomers with "bent" *sec*-NH proton systems,[14] and this information can be used in structural assignments. Isomeric comparisons in the Cr(III) series cannot be made, but we do have both facial (I–III) and meridional triamine systems. The best acceleratory factor of 48[k_{OH}(VIII)/k_{OH}(I)] is nowhere nearly as dramatic as in the Co(III) case where k_{OH}(VIII)/k_{OH}(I) is 263.

Mechanistically, the "flat *sec*-NH proton effect" in Co(III) polyamines is attributed to both an increase in –NH acidity and to an increase in the lability of the resultant conjugate base.[2] Any process that will facilitate the formation of a five-coordinate amido intermediate in the dissociatively activated process will facilitate base hydrolysis. Thus, for a MX(diamine)(triamine)$^{2+}$ system, in the mer configuration the flat deprotonated *sec*-NH nitrogen will allow good p_π–d_π overlap in the formation of a five-coordinate intermediate, with the triamine in the trigonal plane, and only minor bond movement of the diamine is required. Bent triamines require considerably more bond distortion to achieve the same geometry.[15]

Co(III) complexes are well-known for their ability to undergo stereochemical change during base hydrolysis.[16] Obviously, bond movements and trigonal-bipyramidal intermediates are easily achieved in such systems. On the other hand Cr(III) complexes are very much less stereomobile,[12a] although the steric course of base hydrolysis has yet to be investigated in depth.

The fact that the "flat *sec*-NH nitrogen effect" is very much weaker in Cr(III), and that base hydrolysis rates are much slower, is fully consistent with the above generalizations that bond movement in Cr(III) complexes is considerably more difficult than in related Co(III) systems.

We thus attribute the general lack of sensitivity of Cr(III) systems to base hydrolysis to the difficulty in generating suitable trigonal-bipyramidal intermediates.

In three cases we have pairs of Cr(III) complexes where only the ring size is changed, viz. *cis*-CrCl(AA)$_2$(DMSO)$^{2+}$, *mer*-CrCl(AA)(dpt)$^{2+}$, and *sfac*-CrC(AA)(dien)$^{2+}$ (AA = en, tn). A change from five- to six-membered rings in Co(III) systems induces a marked increase in aquation lability.[3] This is attributed to the more flexible six-membered ring allowing a more facile generation of the dissociatively activated trigonal-bipyramidal intermediate.[10a,17] What effect this change would have on an associative mechanism is difficult to predict, but the data presented here, and for other Cr(III) systems (e.g. *trans*-CrCl$_2$(N$_4$)$^+$),[18] show that there is, in fact, a suspicion of an inhibitory effect. Indeed, this could be expected if the larger six-membered rings are assumed to restrict the approach of the water molecule relative to the five-membered-ring analogues.

In base hydrolysis of Co(III) complexes, the six-membered-ring effect is less marked with a rate increase of about 12 times that for the *trans*-CoCl$_2$(AA)$_2^+$ (AA = en, tn) systems.[17] Similar k_{OH} rate increase factors of 2–100 have been found for isomers of CoCl(AA)(dien)$^{2+}$ (AA = en, tn).[3] Subtle differences in the nature of the base-catalyzed amido type trigonal bipyramid relative to that of the uncatalyzed direct dissociative trigonal bipyramid may need to be considered before the lower sensitivity of base hydrolysis to the six-membered-ring effect can be accounted for. However, this may not be necessary if the factor of ca. 1500 for k_H between the *trans*-CoCl$_2$(AA)$_2^+$ complexes (AA = en, tn) is the extreme. Nevertheless, if base hydrolysis of chloro(amine)chromium(III) systems proceeds via the S$_N$1CB mechanism and trigonal-bipyramidal intermediates, then on the basis of the above arguments, an accelatory six-membered-ring effect should be observed. This is indeed the situation for the presently studied series of complexes (Table II) with tn:en k_{OH} rate ratios of 15, 5.8, and 1.2 for the three pairs, in the above order. It should be noted that the largest acceleratory effect is observed in the system with two six-membered rings.

Finally, the activation parameters presented in Table II are normal for this type of reaction, which is characterized by a large positive entropy of activation. This trend has been used to support the assignment of the S$_N$1CB mechanism for Co(III) complexes[19] but would scarcely be convincing if taken in isolation.

Conclusion

The measurement of rates of base hydrolysis for a series of 11 CrClL$_5^{2+}$ complexes has allowed a sequence of reactivity patterns to emerge. These are interpreted in terms of the dissociative S$_N$1CB mechanism, first, on the basis of an inverse correlation between k_{OH} and the more associatively activated acid hydrolysis rate data. Second, there is a distinct six-membered-ring acceleratory effect in base hydrolysis that favors trigonal-bipyramid formation, whereas the opposite is observed for aquation. Finally, although the S$_N$1CB mechanism is postulated, there is rather more difficulty in generating a trigonal-bipyramidal intermediate for Cr(III) than for Co(III), as the *sec*-NH proton acceleratory effect for base hydrolysis is not large and the general sensitivity to base hydrolysis is small.

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(14) Reference 2, Table 6.
(15) See Figure 8 of ref 2.
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