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Effect of Amine Substituents and Neutral Leaving Groups on the Activation Volume for Aquation of Octahedral Pentaamine Complexes of Cr^{III} and Rh^{III}

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The activation volumes were obtained for the aquation reactions of $[M(RNH_2)_5L]^{3+}$ (M = Cr, R = Me, L = Me_2SO, $HCONMe_2$ or $MeCONMe_2$; M = Rh, R = H or Me, L = Me_2SO or $HCONMe_2$); they are in accord with the existence of a dissociative shift in the substitution mechanism, not only with the size of the substituent R, but also with the size of the leaving ligands L.

Differences in the mechanistic behaviour of substitution reactions of pentaam(m)inemetal(III) complexes of cobalt, chromium and rhodium have attracted the attention of many groups in the past.[1] More recently the debate has been reopened,[2] and the measurement $\Delta V^{\ddagger}$ for the water exchange and spontaneous aquation reactions of $[M(MeNH_2)_5-(H_2^{17}O)]^{3+}$ and $[M(NH_3)_5L]^{3+}$ respectively (L = neutral ligands; M = Co^{III}, Cr^{III} or Rh$^{III\,3,4}$ has confirmed that a mechanistic differentiation does exist for the pentaam(m)ine complexes of these metal ions. We have now determined $\Delta V^{\ddagger}$ for the spontaneous aquation of $[M(RNH_2)_5L]^{3+}$ (M = Cr, R = Me, L = Me_2SO, $MeCONMe_2$ or $HCONMe_2$; M = Rh, R = H or Me, L = Me_2SO or $HCONMe_2$).

The compounds $[M(RNH_2)_5L][O_3SCF_3]_3$ were obtained by solvolysis of the corresponding triflato complexes, $[M(O_3SCF_3)(RNH_2)_5][O_3SCF_3]_2$, in the desired solvent.[5,6] Their elemental analyses, IR and UV/VIS spectra were consistent with the formulation given.* Dissolution of the complexes in 0.1 mol dm^{-3} HClO$_4$ produces quantitatively the corresponding aqua species. Table 1 collects the relevant kinetic and activation parameters for all the reactions studied. From these data it is clear that there are differences between the systems of Co^{III} and those of Cr^{III} and Rh^{III}.

For all the reactions indicated electrostriction factors have been minimized, consequently the values obtained should be indicative of the intrinsic mechanism. In this respect the values obtained for $\Delta V^{\ddagger}$ are especially valuable. While for M = Co^{III} the only effect observed is a positive shift of the activation volume on increasing the size of the amine substituent, for M = Cr^{III} and Rh^{III} important differences are also observed on changing the leaving ligand L.

For the accepted dissociatively activated interchange taking place in the cobalt(III) systems, probably the greater the steric constraint in the metal complex the more dissociative is the transition state and the more positive the activation volume. Changes in the leaving ligand do not seem to produce further modifications; probably the groups studied have similar binding energies to the cobalt(III) centre (as shown by the $\Delta H^{\ddagger}$ values) and the increases in volume on going to the transition state are also equivalent. On the other hand, for the analogous complexes of Cr^{III} and Rh^{III} the value of $\Delta V^{\ddagger}$ is affected in the same way by the size of the inert pentaamine skeleton, but a significant decrease in the span of the values of the activation volumes for the same series of reaction is observed. It is, in particular, very difficult to reconcile these facts with the associativeness of the mechanism found for the water-exchange reaction of the $[Cr(MeNH_2)_5(H_2O)]^{3+}$ complex.[3] The magnitude of the activation volume for the water-exchange reaction of $[M(MeNH_2)_5(H_2O)]^{3+}$ indicates an increase in dissociative character, when compared with $[M(NH_3)_5(H_2O)]^{3+}$ (M = Cr^{III} or Rh^{III}) (Table 1), and it is possible that a further increase in the strain of the molecule, caused by the size of the leaving ligand, could produce even a further shift to the dissociative part of the mechanistic continuum. Although such a positive $\Delta V^{\ddagger}$ shift is not apparent for the $[Cr(NH_3)_5L]^{3+}$ aquation, where all the values are clearly negative, for the more dissociatively activated aquation processes of $[Rh(NH_3)_5L]^{3+}$ and $[Cr(MeNH_2)_5L]^{3+}$ the bulkier leaving ligands have less negative activation volumes. For the even more dissociatively activated aquation reactions of $[Rh(MeNH_2)_5L]^{3+}$ all the activation volumes are positive, indicating a move towards a central mechanistic position (I mechanism).

Summarizing, a fine balance seems to exist regarding the mechanism of the aquation reactions of $[M(RNH_2)_5L]^{3+}$ (M = Cr or Rh; R = H or Me; L = $H_2^{17}O$, Me_2SO, $HCONMe_2$ or $MeCONMe_2$). While an increase in the size of the R substituents produces a definite shift to a dissociative activation mechanism, smaller changes associated with changes in the size of the L ligands seem to produce a further, although not so important, displacement. All in all, the classical view of the inert skeleton of the $[M(amine)_5L]^{3+}$ complexes being uniquely responsible for the intimate mechanism of their substitution reactions only seems to hold for systems well away from the intermediate I mechanistic position.

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* A typical preparation consists in the dissolution of the triflato complex (0.5 g) in ligand L (5 cm^3) at room temperature for 3 d (M = Cr), or at 60–70 °C for 4–5 h (M = Rh). UV/VIS spectroscopic data in 0.1 mol dm^{-3} HClO$_4$ [λ/nm (ε/mol dm^{-3} cm^{-1})] for $[M(RNH_2)_5L]$-$[O_3SCF_3]_3$: M = Cr, R = Me, L = Me_2SO, 516 (57), 378 (51); M = Cr, R = Me, L = $HCONMe_2$, 502 (69), 372 (48); M = Cr, R = Me, L = $MeCONMe_2$, 516 (97), 378 (84); M = Rh, R = H, L = Me_2SO, 324 (139); M = Rh, R = H, L = $HCONMe_2$, 324 (263); M = Rh, R = Me, L = Me_2SO, 340 (215); M = Rh, R = Me, L = $HCONMe_2$, 332 (311).

Table 1 Kinetic and activation parameters for a series of spontaneous aquation reactions of neutral ligands in $[M(RNH_2)_5L]^{3+}$ complexes

M	R	L	$k^{298}_{extrapolated}/s^{-1}$	$\Delta H^{\ddagger}/$ kJ mol^{-1}	$\Delta S^{\ddagger}/$ J K^{-1} mol^{-1}	$\Delta V^{\ddagger}/$ cm^3 mol^{-1}	Ref.
Co	H	H_2O	6×10^{-6}	111 ± 1	$+28 \pm 4$	$+1.2 \pm 0.2$	7
		Me_2SO	2×10^{-5}	103 ± 3	$+10 \pm 7$	$+2.0 \pm 0.4$	8
		$HCONMe_2$	2×10^{-6}	111 ± 4	$+16 \pm 8$	$+2.6 \pm 0.4$	8
	Me	H_2O	7×10^{-4}	99 ± 6	$+27 \pm 22$	$+5.7 \pm 0.2$	3
		Me_2SO	3×10^{-3}	103 ± 1	$+53 \pm 3$	$+5.9 \pm 0.2$	6
		$HCONMe_2$	1×10^{-4}	109 ± 1	$+44 \pm 3$	$+6.3 \pm 0.3$	6
Cr	H	H_2O	5×10^{-5}	97 ± 2	0 ± 7	-5.8 ± 0.2	9
		Me_2SO	2×10^{-5}	95 ± 1	-15 ± 3	-3.2 ± 0.1	4
		$HCONMe_2$	1×10^{-5}	93 ± 2	-25 ± 5	-7.4 ± 0.1	4
		$MeCONMe_2$	2×10^{-5}	92 ± 2	-30 ± 6	-6.2 ± 0.4	4
	Me	H_2O	4×10^{-6}	99 ± 3	-18 ± 10	-3.8 ± 0.3	3
		Me_2SO	8×10^{-7}	110 ± 2	$+8 \pm 1$	-0.8 ± 1.1	This work
		$HCONMe_2$	6×10^{-7}	94 ± 3	-48 ± 3	-0.5 ± 0.3	This work
		$MeCONMe_2$	5×10^{-6}	89 ± 5	-49 ± 5	-0.1 ± 1.2	This work
Rh	H	H_2O	8×10^{-6}	103 ± 1	$+3 \pm 5$	-4.1 ± 0.4	9
		Me_2SO	2×10^{-6}	91 ± 3	-33 ± 2	$+1.5 \pm 1.2$	This work
		$HCONMe_2$	1×10^{-6}	105 ± 6	-5 ± 1	-2.9 ± 0.3	This work
	Me	H_2O	1×10^{-5}	113 ± 2	$+38 \pm 6$	$+1.2 \pm 1.1$	3
		Me_2SO	3×10^{-5}	98 ± 2	-2 ± 1	$+1.5 \pm 0.6$	This work
		$HCONMe_2$	1×10^{-5}	100 ± 9	$+13 \pm 2$	$+1.7 \pm 0.4$	This work

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