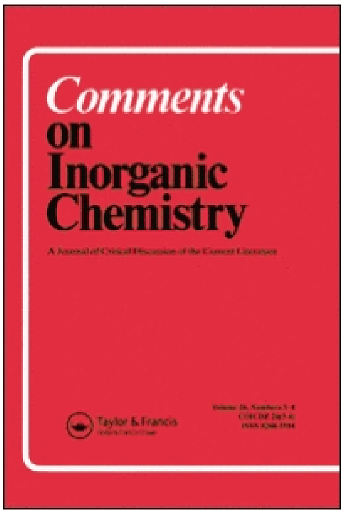

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New Insights into the Mechanisms of Spontaneous and Base-Catalysed Substitution Reactions of the Inert Metal Amine Complexes

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New Insights into the Mechanisms of Spontaneous and Base-Catalysed Substitution Reactions of the Inert Metal Amine Complexes

For Co(III) amine complexes, there is a large body of evidence that points to spontaneous substitution reactions occurring via interchange mechanisms in which bond breaking substantially precedes bond making in the transition state. The mechanisms of substitution of the Rh(III), Ir(III), Ru(III), Os(III) and Cr(III) analogues depend very much on a number of factors, such as the nature of the leaving group and steric factors, as well as the electronic configuration of the metal ion. On the balance of evidence, substitution reactions of the d^3 and d^5 complexes can proceed via interchange mechanisms in which either bond breaking precedes bond making or *vice versa*. For the spontaneous substitution reactions of $[M(NH_3)_5Cl]^{2+}$ complexes, the very large ionic solvation terms of the $[M(NH_3)_5]^{3+}$ and Cl^- components with respect to $[M(NH_3)_5Cl]^{2+}$ strongly favor a transition state in which there is substantial charge separation, i.e., dissociative interchange mechanisms are energetically more accessible than associative interchange mechanisms. New crystallographic evidence indicates strongly that the different kinetic behavior observed for Co(III), Rh(III) and Cr(III) on the addition of steric bulk into $[M(NH_2R)_5Cl]^{2+}$ complexes is not due to previously argued changes in mechanism with the nature of the metal ion. Rather, the kinetic differences reflect differences in the influence of π-bonding on the ground state and all of these complexes are believed to undergo substitution reactions via mechanisms in which bond breaking substantially precedes bond making. By contrast, the mechanisms of aquation reactions of the hexaammine complexes depend mainly on the electronic configuration and size of the central metal ion, since solvation terms in the transition state are similar to those in the ground state for either a dissociative or associative interchange mechanism. For these complexes, the preferred mechanism for substitution is an associative interchange for $[M(NH_3)_6]^{3+}$, M = Cr, Ru and Os, and a dissociative interchange mechanism for M = Co. All of the mechanisms of base-catalysed aquations of metal amine complexes appear to involve five-coordinate intermediates in a dissociative conjugate-base mechanism (D_{cb} or S_N1_{cb}), independent of the metal ion or the leaving group. However, the geometries of

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these intermediates vary with both the nature of the metal ion and the ancillary ligands. This variation can be explained by competing steric (molecular mechanics calculations) and ligand field contributions that favor different intermediates. In the case of the more sterically hindered ground states (e.g., $[Co(NH_3)_5X]^{n+}$ and $[Co(NH_2R)_5X]^{n+}$), the steric effects predominate and relatively long-lived trigonal bipyramidal intermediates are formed. In the case of the pentaammine complexes, the intermediate feels the influence of the leaving group in competition for different nucleophiles, and such a mechanism has been classified as a $(D_I)_{cb}$ mechanism. By contrast a true D_{cb} mechanism appears to occur for the $[Co(NH_2R)X]^{n+}$ complexes, where the observed competition ratios appear to be independent of the leaving group. In the less sterically hindered systems and/or systems with larger ligand field effects (e.g., the pentaammine complexes of M(III) complexes other than Co), the ligand field effects are dominant and the intermediates are much shorter-lived and are believed to be square pyramidal. These mechanisms appear to fall into the $(D_I)_{cb}$ region of the mechanistic continuum. Differences in the degree of base catalysis with the metal ions, leaving groups and ancillary ligands are rationalized by considering the combined effects of the rate of proton exchange, π bonding of the leaving group, and steric interactions.

Key Words: *mechanisms, spontaneous substitution, base-catalysed substitution, amine complexes*

INTRODUCTION

It has long been recognized that the mechanisms of spontaneous and base-catalysed substitution reactions of cobalt amine complexes are dissociative interchange (I_d) and dissociative or dissociative interchange conjugate-base (D_{cb} or S_N1_{cb}) mechanisms,[1–7] respectively. However, much more controversy has existed with respect to the substitution reactions (both spontaneous and base-catalysed) of the other metal ions, and in particular, Cr(III). Previous rationalizations of the mechanisms have concentrated on steric and electronic arguments, and often the ground states and solvent contributions have been incompletely assessed or ignored.

In this article, it will be shown that it is important to characterize the ground states in order to understand whether the differences in kinetic behavior are due to ground state effects (under a common mechanism), transition state effects (which imply mechanistic differences) or a combination of both. In addition, it will be shown that a neglect of the combined importance of M-L π-bonding (involving the leaving group) and of solvation has often led to incorrect conclusions of the mechanisms based on kinetic data alone.

A further difficulty has arisen due to the different working definitions of the symbols used to designate interchange mechanisms (I_a and I_d). The working definition that was originally adopted by Langford and Gray[1] is that, for an I_a mechanism, there is synchronous bond making with the incoming group and bond breaking with the leaving group giving rise to a transient intermediate of increased coordination number which is shorter lived than the timescale of solvent reorganization. Conversely, for an I_d mechanism, the leaving group is lost from the first coordination sphere to form an intermediate of reduced coordination number prior to the formation of a bond with the incoming nucleophile. Again this intermediate has a shorter lifetime than that required for solvent reorganization and, therefore, the intermediates in both the I_a and I_d mechanisms are so short-lived that they are effectively transition states. In theory, the definitions of Langford and Gray make the separation of mechanisms easy in terms of the sensitivity of the reactions to the nature of the incoming nucleophile. However, this rationale for assigning a mechanism cannot be applied to solvent self-exchange reactions in which the entering group and the leaving group are the same, by definition. A different definition of I_a and I_d was suggested by Merbach[2] in order to overcome these difficulties. In Merbach's nomenclature, an interchange mechanism that involves more bond breaking than bond making in the transition state is defined as an I_d mechanism and has a positive volume of activation, whereas a mechanism that involves more bond making than breaking in the transition state is defined as an I_a mechanism, and has a negative volume of activation. This different nomenclature that has arisen (for very good reasons) has led to further misunderstandings and conflict in the literature where different researchers have used different working definitions to describe the mechanisms of the same reactions. An excellent account of these problems and alternative nomenclature can be found in the 1983 review by Swaddle.[3]

THE MECHANISMS OF SOLVENT EXCHANGE REACTIONS OF HEXASOLVENT TRANSITION METAL COMPLEXES

Most spontaneous substitution reactions of octahedral complexes occur via a mechanism in which there is no discrete intermediate that is longer-lived than the time required for solvent reorganization, i.e., they are interchange mechanisms. Throughout this paper the terminology of Merbach will be used to describe interchange mechanisms. Figure 1[2] illustrates the different types of mechanisms that are possible for a spontaneous substitution reaction. Between the discrete boundaries which are formed by an associative mechanism (A) or a dissociative mechanism (D) lies a continuum of interchange mechanisms. These mechanisms will be further classified as associative interchange (I_a) in which bond making precedes bond breaking, interchange (I) in which there is an equal amount of bond making and breaking in the transition state and dissociative interchange (I_d) in which bond breaking precedes bond making.[2]

Two reviews by Merbach[2,7] have detailed the effects of electronic configuration on the mechanisms of solvent interchange reactions. Volumes of activation for such reactions have provided convincing evidence for the premise that the preferred mechanisms for substitution of isostructural complexes vary considerably as the metal ion is changed. These variations are in line with qualitative expectations of the effects of electronic configuration and size of the

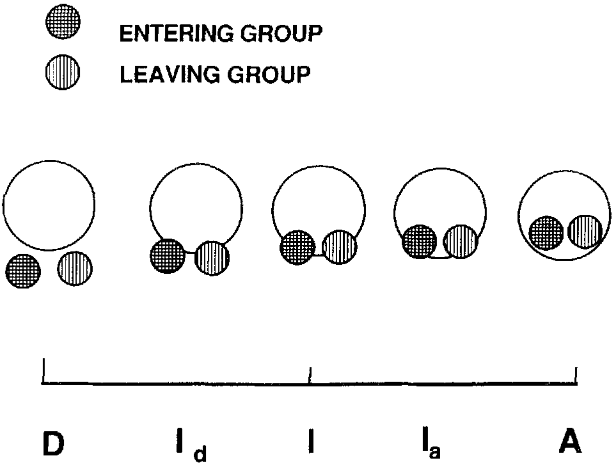


FIGURE 1 Classification of the mechanisms of spontaneous substitution reactions according to Merbach (Refs. 2 and 7).

metal ions on the relative stabilities of transition states of increased and decreased coordination numbers.[1-7] It appears that the energetically preferred mechanism can span almost the entire continuum that is represented in Fig. 1. The symmetric displacement of the leaving group and entering groups that are present in solvent exchange reactions is a necessary condition that arises from the concept of microscopic reversibility. For the more general situation where the entering group and leaving group are different, it is not a necessary condition that the strength of bonding of these two groups will be equal in the transition state. Indeed, in general the bonding is expected to be different and this is one of the difficulties in trying to classify a solvent exchange mechanism in the same mechanistic classification schemes that are appropriate to more general substitution reactions. Other problems are discussed in the review of Swaddle.[3]

While the mechanistic interpretations of the volume of activation data for solvent exchange reactions are fairly straightforward in aprotic solvents, the interpretations in protic solvents, such as water, are not as straightforward as is often espoused. Although the conclusions that have been drawn with regard to the degree of association/dissociation in the transition states of aqua exchange reactions are probably sound in a qualitative sense,[2,7] there are at least two terms that have been largely neglected in previous analyses of the significance of the values of $\Delta V^{\ddagger}$. The first term is that due to the changes in volume that arise from changes in hydrogen bonding of solvent molecules to the leaving and entering group in the transition state, as opposed to the ground state. $\Delta V^{\ddagger}$ for these solvent exchange reactions can, therefore, be divided into at least two terms as shown in Eq. (1):

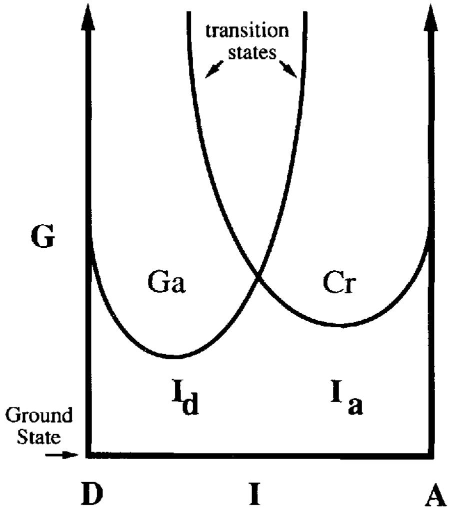
$$\Delta V^{\ddagger} = \Delta V^{\ddagger}_{\text{in}} + \Delta V^{\ddagger}_{\text{solv}} \tag{1}$$

where $\Delta V^{\ddagger}_{\text{in}}$ is the intrinsic or gas phase volume change for the solvent exchange reaction and $\Delta V^{\ddagger}_{\text{solv}}$ is the volume change due to changes in hydrogen bonding of the solvent to the entering and leaving groups in going from the ground state to the transition state. In the case of water, the latter term is expected to be significant. It arises because a lengthening of the metal-aqua bond results in a decrease in the hydrogen-bonding acidity of the aqua ligand. This, in turn, will result in the release of strongly hydrogen-bonded water molecules. This contribution will lead to a positive value of the $\Delta V^{\ddagger}_{\text{solv}}$ term. The converse is true for an associative interchange mechanism. Here, the partial binding of an incoming water molecule will increase its hydrogen-bonding acidity and result in a negative contribution to $\Delta V^{\ddagger}_{\text{solv}}$, which will more than counteract the positive hydrogen-bonding contribution due to a lengthening of the M–O bond of the leaving group. The likely net effect of the $\Delta V^{\ddagger}_{\text{solv}}$ term is to make values of $\Delta V^{\ddagger}$ more positive for a dissociative interchange mechanism and more negative for an associative interchange mechanism. That is, the differences in the values of $\Delta V^{\ddagger}$ are accentuated by the $\Delta V^{\ddagger}_{\text{solv}}$ term and may give a misleading indication as to the extent by which the mechanism changes with the metal ion. Although it is difficult to quantify the $\Delta V^{\ddagger}_{\text{solv}}$ term, a value of $\geq +3\ \text{cm}^3\ \text{mol}^{-1}$ may not be unreasonable on the basis of the contraction expected for a water molecule in the outer coordination sphere in the dissociative limit,[3] and will be negative for an associative mechanism. It is akin to (but of opposite sign to and smaller than) the electrostriction effects that are observed when there is a charged leaving group.[8,9]

The second term that is often neglected is that due to the contraction of the coordination sphere in a predominantly dissociative interchange mechanism and its expansion in a predominantly associative interchange mechanism.[3,10–12] This will tend to make the values of $\Delta V^{\ddagger}$ more negative for a dissociative mechanism and more positive for an associative mechanism than would otherwise be the case.[3,10–12] Therefore, such a contribution will tend to counteract the $\Delta V^{\ddagger}_{\text{solv}}$ term, with the net effect that the values of $\Delta V^{\ddagger}$ may fortuitously reflect the mechanism fairly well.

It is difficult to judge which of the factors mentioned above will be the most important, but unless they cancel exactly, the degree of dissociation of the leaving group and/or association of the entering group in the transition state, from $\Delta V^{\ddagger}$ data alone, will tend to indicate greater or smaller mechanistic differences than actually occur in the protic solvents. However, it is clear from activation volume data that the mechanisms of solvent exchange in the Cr(III) and Ga(III) complexes, $[\text{M}(\text{OH}_2)_6]^{2+}$, which have similar sizes, are quite different. An energy diagram with a mechanistic coordinate is a useful way to represent both the continuum of interchange mechanisms and the position of the preferred mechanism on this continuum.[13] Figure 2 shows how this can be used to qualitatively illustrate the likely differences between Ga(III) and Cr(III) in the solvent exchange reaction of the $[M(OH_2)_6]^{3+}$ ions. The minimum energy transition states of these reactions fall in the I_a region of the mechanistic continuum for Cr(III) and in the I_d region of the mechanistic continuum for Ga(III).[2,3,7]

Since the strength of hydrogen bonding acidity increases with decreasing metal ligand bond length,[13–15] the $\Delta V^{\ddagger}_{solv}$ term will be more important for Co(III) in comparison to Cr(III), Ru(III), Rh(III) and Ir(III) if a similar mechanism is applicable to the series of aqua exchange reactions involving $[M(NH_3)_5(OH_2)]^{3+}$ ions[16–19] (i.e., there will be a more positive contribution to $\Delta V^{\ddagger}$ from the $\Delta V^{\ddagger}_{solv}$ term for Co(III) compared to the other ions). Therefore, some of the differences in $\Delta V^{\ddagger}$ observed for the $[M(NH_3)_5(OH_2)]^{3+}$ ions may be a result of changes in the $\Delta V^{\ddagger}_{solv}$



MECHANISTIC COORDINATE

FIGURE 2 Two-dimensional representation of the effects of the d electronic configuration and the M–O bond lengths on the mechanisms of substitution reactions of $[M(OH_2)_6]^{3+}$, M = Ga, and Cr.

term and the actual mechanisms of aqua exchange may be much closer than previously thought. In addition, the range in the values of $\Delta V^{\ddagger}$ for solvent exchange in the $[M(NH_3)_5(OH_2)]^{3+}$ ions is less than half that observed for the $[M(OH_2)_6]^{3+}$ ions (Table I) and the values for $[M(NH_3)_5(OH_2)]^{2+}$ lie in the middle of the range observed for $[M(OH_2)_6]^{3+}$. These results point to two important features of these mechanisms. Firstly, the mechanisms of aqua exchange of the $[M(NH_3)_5(OH_2)]^{2+}$ ions are near one another on the mechanistic continuum and, secondly, they lie towards the middle of this continuum. Similar conclusions have been made by Swaddle and Mak in their analysis of the correlation between the partial molar volumes of $[M(NH_3)_5(OH_2)]^{3+}$ ions and $\Delta V^{\ddagger}$ for aqua exchange.[10,16] While Swaddle[3,16] has alluded to the need to consider the whole assemblage, involving both the inner coordination sphere and the hydrogen-bonded water molecules, when interpreting the values of $\Delta V^{\ddagger}$ obtained from the aqua exchange reactions of the $[M(NH_3)_5(OH_2)]^{3+}$ complexes, the implicit problems

TABLE I

Crystallographic $M-OH_2$ bond lengths for $[M(OH_2)_6]^{3+}$ ions and $\Delta V^{\ddagger}$ values for the aqua exchange reactions of the $[M(NH_3)_5(OH_2)]^{3+}$ and $[M(OH_2)_6]^{3+}$ ions

Metal	$d(M-OH_2)$[a] Å	$\Delta V^{\ddagger}$ $(cm^3\ mol^{-1})$[b] $[M(OH_2)_6]^{3+}$	$\Delta V^{\ddagger}$ $(cm^3\ mol^{-1})$[b] $[M(NH_3)_5(OH_2)]^{3+}$
Co(III)	1.873(5)[c]		+1.2
Al(III)	1.877(3)[c]	+5.7	
Ga(III)	1.944(3)[c]	+5.0	
Cr(III)	1.959(3)[c]	−9.6	−5.8
V(III)	1.992(6)[c]	−8.9	
Fe(III)	1.995(4)[c]	−5.4	
Rh(III)	2.016(3)[d]	−4.2	−4.1
Ti(III)	2.028(5)[e]	−12.1	
Ru(III)	2.029(7)[c]	−8.3	−4.0
Ir(III)	2.041(3)[d]		−3.2

[a] All bond length data refers to the hexaaqua M(III) complex in $CsM(SO_4)_2.12H_2O$, except for Ru(III) which refers to $[Ru(OH_2)_6](C_7H_7SO_3)_3.3H_2O$.

[b] Ref. 7, except for the value for $[Ru(NH_3)_5(OH_2)]^{3+}$ which comes from Ref. 16 and $[Rh(OH_2)_6]^{3+}$ which comes from Ref. 23.

[c] Ref. 20.

[d] Ref. 21.

[e] Ref. 22.

mentioned here do not appear to have been addressed adequately previously.

From available crystallographic data on the $M-OH_2$ bond lengths,[20-22] it is apparent that there is a reasonable correlation between the value of $\Delta V^\ddagger$ for the aqua exchange reactions[2,7,16,23] and the M–O bond lengths (Table I). The data in Table I and Fig. 3 show, for both the $[M(OH_2)_6]^{3+}$ and $[M(NH_3)_5(OH_2)]^{3+}$ series, that such linear correlations, between the values of $d(M-OH_2)$ and $\Delta V^\ddagger$ exist for all of the complexes that have been studied, with the exception of Cr(III) (and Al(III) in the case of the $[M(OH_2)_6]^{3+}$ series). The importance of size in determining the mechanism has been argued previously,[2,7] but the graphs in Fig. 3 suggest that the electronic configuration may be less important in influencing the mechanisms of these substitution reactions than has been proposed in Merbach's reviews.[2,7] It is not clear why Cr(III) does not follow these trends in either series,[7] but the data indicate that the mechanism of aqua exchange in Cr(III) is more associative than would be expected on the basis of its size. This difference is not easily understood in terms of its electronic configuration, since the more electron deficient and much larger V(III) ion has a slightly less negative value of $\Delta V^\ddagger$. Merbach has also mentioned this potential anomaly.[7] Since specific ion-pairing may influence the values of $\Delta V^\ddagger$, it may be appropriate to repeat the experiments performed on the Cr(III) complexes, under identical conditions as those used for the labile complexes.

Apart from the consequences of hydrogen-bonding on the activation volumes, there will also be consequences for the position of the mechanisms of aqua exchange reactions on the mechanistic continuum. That is, the stretching of a $M-OH_2$ bond will weaken the strength of the hydrogen bonds to the solvent, which will cost energy. This will result in positive contributions to $\Delta G^\ddagger$ for dissociative interchange mechanisms, and the extent of destabilization of potential transition states will increase with the degree of stretching of the M–O bond. Conversely, this term will provide a negative contribution to $\Delta G^\ddagger$ for an associative interchange mechanism, with the hydrogen bonding contributions to the stabilization of the transition states becoming more important as the degree of association increases. This will tend to make the mechanisms of such reactions more associative than might be expected in the

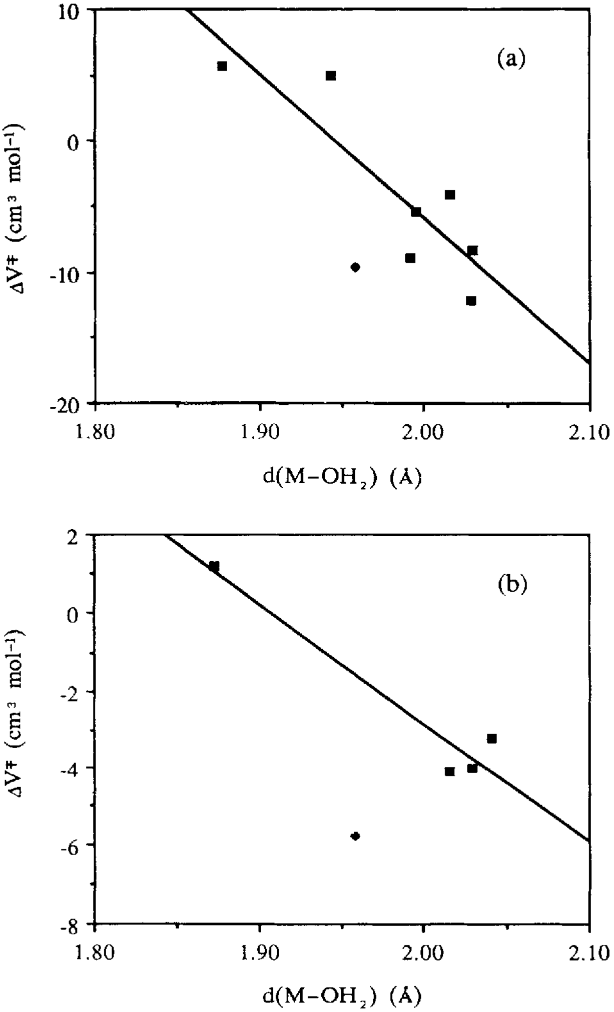


FIGURE 3 Plots of the values of d(M–OH_2) versus $\Delta V^{\ddagger}$ for aqua exchange in (a) $[M(OH_2)_6]^{3+}$ complexes and (b) $[M(NH_3)_5(OH_2)]^{3+}$ complexes. The diamond symbols represent the Cr(III) complexes.

absence of hydrogen bonding, which may explain the small positive value of $\Delta V^\ddagger$ observed in the aqua exchange reaction of $[Co(NH_3)_5(OH_2)]^{3+}$.

In summary, it is apparent that the changes in mechanisms of solvent exchange that are implicated by a simplistic analysis of $\Delta V^\ddagger$ data in protic solvents are probably reasonable in a general sense because of the cancellation of the terms that have been discussed in the previous paragraphs. Although mechanistic differences almost certainly exist, the activation volume data can only be taken as a semiquantitative guide and should not be taken as an absolute measure of the position along the mechanistic coordinate because of these complications. Possible difficulties in interpreting such data because of subtle solvent effects has also been alluded to in a recent review.[5] Secondly, it appears that the radii of the ions may have a more important influence on the value of $\Delta V^\ddagger$ than the d electronic configuration. The importance of the radii of the ions in determining the mechanism has been well illustrated by the work of Merbach on the trends in $\Delta V^\ddagger$ down a group.[2,7] In this author's opinion, the questions that need to be addressed by more detailed evaluations of the deductions made from the activation volume data are:

(i) What are the relative contributions of electronic configurations and size of the metal ions to the activation volume data and the mechanisms of solvent exchange reactions?
(ii) How important are the $\Delta V^\ddagger_{solv}$ contributions to the observed activation parameters for aqua exchange, and how do these impinge on the previous assignment of the extent of mechanistic differences?
(iii) Why does Cr(III) give anomalously large negative values of $\Delta V^\ddagger$ compared to other ions with similar sizes and/or similarly electron deficient metal centers? Is this a media effect?

It is clear that these are areas of research where more detailed investigations could be made.

The $\Delta V^\ddagger_{solv}$ complications that are mentioned above do not exist for solvent exchange reactions involving aprotic solvents. This is because the solvent (which is also the coordinated ligand) must be both a hydrogen-bonding acid and a hydrogen-bonding base in order to undergo the interaction that gives rise to the $\Delta V^{\ddagger}_{\text{solv}}$ term. Therefore, such terms are only expected to be significant in solvents such as water, alcohols, formamide, *N*-methylformamide, etc. For most other solvents, the main complication to the straightforward interpretation of the $\Delta V^{\ddagger}$ data will be the evaluation of the volume change due to the contraction of the radius of the coordination sphere in an I_d or D mechanism and its expansion in an I_a or A mechanism.[3,10-12]

AQUATION AND ANATION REACTIONS OF HEXAAMMINE COMPLEXES

Hexaammine complexes may be expected to be less susceptible to nucleophilic attack than hexaaqua complexes, for the following reasons. Firstly, the coordinated ammine ligands are weaker hydrogen-bonding acids than aqua ligands. This means that an incoming nucleophile will be less tightly bound to the outer sphere for hexaammine complexes compared to analogous hexaaqua complexes. Secondly, the M–OH$_2$ bonds are shorter in $[M(OH_2)_6]^{3+}$ (Table I[20-22]) than the M–NH$_3$ bonds in the corresponding $[M(NH_3)_6]^{3+}$ ions.[24-27] Therefore, the incoming nucleophile will be further away from the metal center in the ammine complex, thus being less able to form a partial bond in the transition state. Finally, the weaker hydrogen bonding of water molecules to coordinated NH$_3$, as opposed to coordinated OH$_2$, will minimize outer sphere effects that discriminate against an I_d mechanism (i.e., the contribution that results from the weakening of the ligand-solvent hydrogen bonds as the metal-ligand bond stretches will require less energy to be expended in stretching a M–NH$_3$ bond than a M–OH$_2$ bond). All of these effects will tend to make mechanisms of aquation of $[M(NH_3)_6]^{3+}$ ions more dissociative than those of $[M(OH_2)_6]^{3+}$ ions, whereas steric effects in the larger ammine complexes may tend to make their mechanisms more associative. The importance of the factors mentioned above appears clear when the mechanisms of substitution reactions of $[Cr^{III}(OH_2)_5X]^{x+}$ are compared with those of analogous $[Cr^{III}(NH_3)_5X]^{x+}$ complexes. There is a large amount of kinetic data that points to the substitution reactions of the former complexes being much more associative than their pentaammine analogues,[5] but as discussed in subsequent paragraphs, this analysis may be based on false assumptions and warrants further attention. It appears that the mechanisms of the aquation reactions of $[M(NH_3)_6]^{3+}$ ions are also influenced chiefly by the d-electronic configuration and size of the central ion, with those complexes having a partially empty non-bonding t_{2g} subset of d-orbitals and a larger size being more susceptible to nucleophilic attack. Thus, the d^3 complex, $[Cr(NH_3)_6]^{3+}$,[28] and the d^5 complex, $[Ru(NH_3)_6]^{3+}$,[29] almost certainly undergo spontaneous aquation reactions via an I_a (or A) mechanism, while the smaller $[Co(NH_3)_6]^{3+}$ complex, with a d^6 electronic configuration, undergoes aquation via an I_d mechanism.[3,30] Again, it is not clear whether the size of the ion or the electronic configuration is the more important factor and this is also an area where more detailed analysis may be appropriate.

The mechanisms of the anation reactions of the hexaammine complexes differ from the aquation reactions. In the case of chloride substitution into the coordination sphere of $[Ru(NH_3)_6]^{3+}$, the mechanism involves two steps. The slow, rate-determining step is the aquation of $[Ru(NH_3)_6]^{3+}$, which is followed by anation of $[Ru(NH_3)_5(OH_2)]^{3+}$ by chloride ions. This has been demonstrated by the observation that the rate constant of anation of $[Ru(NH_3)_6]^{3+}$ by chloride in aqueous HCl is independent of the concentration of Cl^-,[31] and is similar to the rate constant of aquation of $[Ru(NH_3)_6]^{3+}$ in aqueous CF_3SO_3H.[29] Moreover, the rate constant for loss of NH_3 is reduced by many orders of magnitude when the reaction is performed in neat CF_3SO_3H.[29] These results indicate that the first step in the anation mechanism is an associative or associative interchange mechanism for the formation of the aqua complex.[29] Similar two-step mechanisms are likely for the anation of other hexaammine complexes, except when the entering group is a stronger nucleophile than the solvent. The mechanisms of anation reactions are discussed in the following section.

MECHANISMS OF THE SPONTANEOUS AQUATIONS OF PENTAAMINECHLOROMETAL(III) COMPLEXES AND ANATION REACTIONS OF PENTAAMINEAQUAMETAL(III) COMPLEXES

While the evidence for a change in mechanism with the electronic configuration, and particularly the size of the metal ion, is fairly strong in the cases of aqua substitution into $[M(OH_2)_6]^{3+}$ and $[M(NH_3)_6]^{3+}$, it is not necessary to assume that the same mechanism will apply to all reactions of a particular metal ion. It has long been recognized that S_N substitution reactions about carbon can change from an S_N2 to an S_N1 mechanism depending on a number of factors. Similar situations are likely to apply in substitution reactions at most reaction centers.

In particular, it is often stated that all or most Cr(III) complexes undergo substitution reactions via I_a mechanisms.[5] From recent chemical information,[13,15,32–34] it is likely that the majority of aquation reactions of M(III) complexes with charged leaving groups occur via mechanisms that fall into the I_d region of the mechanistic continuum (using the nomenclature of Merbach). It is also probable that for many substitution reactions, the nature of the leaving group and solvation effects have larger influences on the mechanisms of these reactions than do the electronic configurations and sizes of the metal ion. To illustrate this point, an analysis of the kinetic evidence that is available for the aquations of the $[M(NH_2R)_5Cl]^{2+}$ ions will be discussed in detail, although similar arguments are applicable to reactions involving a charged leaving group other than Cl^-.

The π bonding of the leaving group to the metal ion appears to be an important factor in tuning the lowest energy pathway for substitution reactions.[13,32–34] It has also been used to rationalize the kinetic differences between Cr(III), Co(III) and Rh(III) for the aquation reactions of $[M(NH_2R)_5Cl]^{2+}$ on addition of steric bulk.[13,32–34] Table II contains a summary of M–Cl bond lengths in $[M(NH_2R)_5Cl]Cl_2$ complexes[14,33–38] and the rate constants of their spontaneous aquation reactions.[39–53] The remarkable feature about the structural data is that in all cases that have been examined, with the exception of Co(III), the value of the M–Cl bond length decreases with increasing steric bulk in going from the ammine to methylamine complexes. This gives a ground state rationalization for the differences in the ratios of the rate constants for aquation of the ammine and methylamine complexes, $k(NH_3):k(NH_2CH_3)$. The retardation of the rate of aquation of the Cr(III) complexes on the addition of steric bulk in comparison to the acceleration in the case of Co(III) is not due to a change in mechanism, as often argued. Rather it reflects the

TABLE II

Crystallographic M–Cl bond lengths for $[M(NH_2R)_5Cl]^{2+}$ ions in $[M(NH_2R)_5Cl]Cl_2$ and values of the rate constants at 25°C for the spontaneous aquation reactions of the $[M(NH_2R)_5Cl]^{2+}$ ions

Metal Ion	NH_3		NH_2CH_3		$NH_2CH_2CH_3$	
	M–Cl[a]	10^6k[b]	M–Cl	10^6k[b]	M–Cl	10^6k[b]
Cr	2.327(1)	8.70[f] 7.3[g]	2.299(1)[m]	0.261[f]	2.290(1)[p]	0.512[f] 0.42[g]
Ru	2.346(1) 2.343(1)[c]	0.93[h]				
Os	2.369(2)	~0.01[i]				
Co	2.286(2)[d]	1.72[j]	2.283(1)[n]	39.6[j](34.0[q])		165[q]
Rh	2.356(1)[e]	0.038[k]	2.339(1)[o]	0.022[k]	2.343(1)[p]	0.075[r]
Ir	2.371(2)	0.0011[l]	2.361(2)[p]			

[a] Å, Ref. 14, unless otherwise stated.

[b] s^{-1}, 25°C.

[c] For $[Ru(NH_3)_5Cl]Cl_{1.5}(BF_4)_{0.5}$, Ref. 35.

[d] Ref. 36.

[e] Ref. 37.

[f] Ref. 39.

[g] Calculated from the temperature dependence of the rate constants, Ref. 45.

[h] Ref. 39, calculated from the temperature dependence of the rate constant.

[i] Ref. 41.

[j] Ref. 46.

[k] Calculated from the temperature dependence of the rate constants, Ref. 43.

[l] Ref. 44.

[m] Ref. 38.

[n] $[Co(NH_2CH_3)_5Cl](NO_3)_2$, Ref. 38.

[o] Ref. 33.

[p] Ref. 34.

[q] Ref. 49.

[r] Ref. 50, calculated from extrapolation of the temperature dependence of the reaction $[Rh(EtNH_2)_5Cl]^{2+} + Br^- \rightarrow [Rh(EtNH_2)_5Br]^{2+} + Cl^-$, which has the aquation of the chloro complex as the rate determining step.

shortening of the Cr–Cl bond length in $[Cr(NH_2CH_3)_5Cl]^{2+}$ in comparison to that in $[Cr(NH_3)_5Cl]^{2+}$, which will act to slow the rate of substitution under the ambit of a common I_d mechanism.[32] Since the $k(NH_3)$:$k(NH_2CH_3)$ ratio for the analogous Rh ions is intermediate between those of the Cr(III) and Co(III) ions, it was argued[32] that a similar, but less pronounced, shortening of the Rh–Cl bond in $[Rh(NH_2CH_3)_5Cl]^{2+}$, as compared to $[Rh(NH_3)_5Cl]^{2+}$, would be found if the mechanism was also I_d in this case. Indeed, the predictions made on the basis of the kinetic data were shown to be correct when the crystal structure of $[Rh(NH_2CH_3)_5Cl]Cl_2$ was determined.[33]

The differences in M–Cl bond lengths in going from methylamine to ethylamine complexes[34] are small for both Cr(III) and Rh(III), which is also consistent with the small changes in the rate constants of aquation. Thus, all of the structural data are now consistent with a similar I_d mechanism applying for the aquation reactions of all of the $[M(NH_2R)_5Cl]^{2+}$ ions, where M = Co(III), Cr(III) and Rh(III).

The shortening of the M–Cl bond on the addition of steric bulk is surprising, since it might be expected that the opposite would occur. However, these results can be rationalized readily by consideration of M–Cl π-bonding effects. It has been shown from studies of the X-ray crystal structures of the isomorphous series of complexes, $[M(NH_3)_5Cl]Cl_2$, M = Cr, Ru, Os, Co, Rh, Ir, that M–Cl π bonding is more important for the d^3 and d^5 electronic configurations in comparison to the d^6 electronic configuration.[14] This is in line with chemical expectations as to where such bonding would be more prominent. It is apparent that, on the addition of steric bulk, the non-bonding interactions between the methylamine ligands tend to stretch the M–N bond lengths and, in the case of Cr, the weakening of these bonds is compensated by a strengthening of the M–Cl π bond. There is a further significant shortening of this bond in going from the methylamine to the ethylamine complex, but the difference is smaller. This arises because there are smaller changes in the degree of steric interactions in going from the methylamine to the ethylamine complex, in comparison to the differences between the ammine and methylamine complexes.[34] In the case of Rh(III), the same effects are observed, but they are less pronounced because π bonding is less pronounced in the M–Cl bond.[14] For Co, M–Cl π bonding is at a minimum in the isomorphous series[14] and, therefore, there is little difference between the Co–Cl bond lengths. The Ir–Cl bond lengths also decrease with the addition of steric bulk,[34] but not to the degree that might be expected from the trends in π bonding.[14] There are two possible reasons for this. Firstly, the Ir–Cl bond lengths have been determined less precisely than the other members of the series,[14,34] therefore the magnitude of the difference between the two bond lengths is known with less certainty. Secondly, there is a tendency for M–Cl π bonding to be similar for second- and third-row transition elements, because the second row elements have better energy overlap between the empty d-orbitals of the metal and the filled p-orbitals of the ligand, whereas the spacial overlap of the metal and ligand orbitals is better for ions of the third transition row of elements.[14,54] The balance between these two factors is also expected to be influenced by the auxiliary ligands since they will affect the ligand field, and hence the absolute energies of the d orbitals.

There are also effects of π bonding on the stabilities of potential transition states for these substitution reactions. In the cases of the Cr(III), Ru(III) and Os(III) complexes, the quite strong M–Cl π bonding means that the orbitals that were available for the formation of a bond with an incoming nucleophile in the hexaammine complexes are now already involved in π bonding in the $[M(NH_3)_5Cl]^{2+}$ ions. Since these substitution reactions are steroretentive,[55] the formation of a seven coordinate transition state has to proceed by the formation of a bond between the incoming nucleophile and the d-orbitals that are already used in the formation of the M–Cl π bond. Such a bond formation will be destabilized with respect to analogous substitution reactions in the hexaammine complexes. This means that arguments which justify an I_a mechanism on the basis of electronic configuration may not be valid when the leaving group is involved in substantial π bonding with the metal ion.[14] The other factors that influence the stabilities of the transition states are the steric requirements of the M–Cl multiple bond. These requirements are such that the average N–M–Cl bond angles are increased beyond 90° for Cr(III), Ru(III) and Os(III), while they are less than 90° for Co(III), Rh(III) and Ir(III) in the isomorphous pentaammine series.[14] Thus, in terms of the steric hinderance involved in forming seven-coordinate transition states, the greater steric requirements of the M–Cl multiple bond more than negate the increases in M–N bond lengths in the Cr(III), Ru(III) and Os(III) complexes. Since π bonding for Co(III) is much less significant, there will be little effect on the mechanism for Co(III). In general, the effect of π bonding for $[M^{III}(NH_3)_5X]^{n+}$ as compared to $[M(NH_3)_6]^{3+}$ is to move the mechanism towards an I_d mechanism on the mechanistic coordinate, as the strength of M–X π bonding increases. This effect will also increase as you go down the Co group, but the effect will not be as large as that expected for the d^3 and d^5 electronic configurations.[13,32,33] This analysis has been criticised[5] because of the effects of crystal packing forces and the precision by which the M–Cl bond lengths are determined in the X-ray analysis. However, we do not believe that such criticisms are valid. Firstly, we have been careful to compare structures that are isomorphous where changes in the packing forces will be minimized. Secondly, all of the structures that we have used in our analyses have been determined precisely. Finally, the Ru–Cl bond length in another precisely determined crystal structure ($[Ru(NH_3)_5Cl](BF_4)_{0.5}Cl_{1.5}$) is the same within experimental error as that in $[Ru(NH_3)_5Cl]Cl_2$, despite the quite different packing forces.[35]

While the effects of π bonding offer a partial explanation as to why the mechanisms of spontaneous aquations of the $[M(NH_2R)_5Cl]^{2+}$ ions are expected to be similar, irrespective of the nature of M or R (i.e., they will tend to be dissociative interchange), there is a more compelling reason to expect a similar mechanism. This reason lies in the contribution of solvation effects to the preferred mechanistic pathway. In a limiting dissociative mechanism, the free energy of solvation of the pentacoordinate intermediate, $[M(NH_3)_5]^{3+}$, is estimated to be ~100 kJ mol^{-1}, while that of the ground state, $[M(NH_3)_5Cl]^{2+}$, is estimated to be ~60 kJ mol^{-1}.[15] Given that the value of $\Delta G^{\circ}_{\mathrm{solv}}$ for $Cl^-(aq)$ is approximately -300 kJ mol^{-1}, then $\Delta G^{\ddagger}_{\mathrm{solv}}$ for such a reaction is of the order of -350 kJ mol^{-1}. Even though it is known that a *D* mechanism does not apply to these reactions, it is clear that there is a very large discrimination for a more dissociative mechanism in these systems and this is a very strong driving force for an I_d mechanism. For either mechanism, the ground states of the reactants and products are both lowered in energy with respect to the gas phase by solvation, but the discrimination between the mechanisms is due to the effect of solvation on the energy of the transition state. This is illustrated in Fig. 4. Thus, from purely electronic and size considerations, an I_a mechanism is favored for the substitution reactions of the Cr(III) and Ru(III) complexes. However, when the effects of π bonding are considered together with the very large solvation energy terms, the activation barriers for I_d mechanisms are expected to be smaller than those for I_a mech-

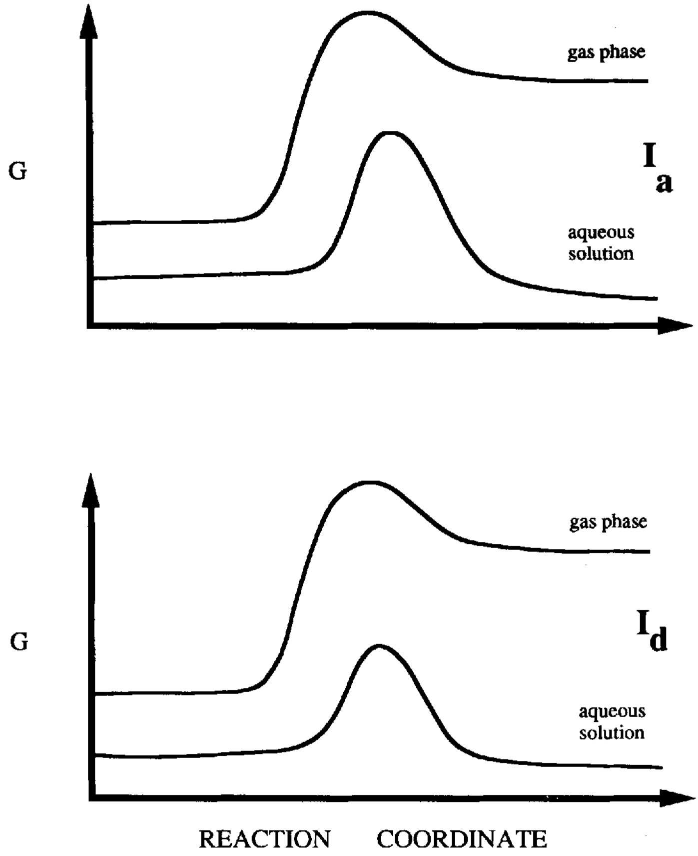


FIGURE 4 Reaction profiles for I_a and I_d mechanisms for the aquation of $[M(NH_3)_5Cl]^{2+}$ in the gas phase and in solution.

anisms.[13] This indeed appears to be the case for Cr(III). Conversely, activation volume data for the spontaneous aquation of $[Ru(NH_3)_5Cl]^{2+}$ was interpreted in terms of an A mechanism.[51] However, a pressure-dependent change in the mechanism, as shown in Scheme 1, is more consistent with the data.[56] At ambient pressures, the predominant pathway is believed to be I_d (i.e., that pathway represented by the rate constant k_2). At higher pressures, the position of the preequilibrium is moved towards the formation of more of the seven-coordinate intermediate to a sufficient extent

$$[Ru(NH_3)_5Cl]^{2+} + H_2O \xrightleftharpoons{K_1} [Ru(NH_3)_5(OH_2)Cl]^{2+}$$

$$[Ru(NH_3)_5Cl]^{2+} + H_2O \xrightleftharpoons[k_{-2}]{k_2} \{[Ru(NH_3)_5(OH_2)]^{3+}.Cl^-\}$$

$$[Ru(NH_3)_5(OH_2)Cl]^{2+} \xrightleftharpoons[k_{-3}]{k_3} \{[Ru(NH_3)_5(OH_2)]^{3+}.Cl^-\}$$

$$\{[Ru(NH_3)_5(OH_2)]^{3+}.Cl^-\} \xrightleftharpoons{K_4\text{, fast}} [Ru(NH_3)_5(OH_2)]^{3+} + Cl^-$$

SCHEME 1

to make the *A* mechanism the predominant reaction pathway. This highlights a potential problem in using activation volume data for interpreting the mechanism at ambient pressure, where there is a possibility of a pressure-dependent pre-equilibrium. A similar associative preequilibrium has been postulated to explain the decomposition of $[Ru(bpy)_3]^{3+}$,[57] but such a preequilibrium is expected to lie very much to the left in both instances, at ambient pressures.

The arguments about the effects of solvation on the mechanism of substitution do not apply for most neutral leaving groups, since solvation energy contributions to the mechanisms are small.[13,15,32] In pentaamine complexes with neutral leaving groups, there are distinct mechanistic differences between Co(III) and Cr(III),[58-61] which is to be expected on the basis of the differences in size and in d electronic configurations of the complexes.

Table II shows that there are still many gaps in our knowledge of the ground state structures and kinetics of substitution of the $[M(NH_2R)_5Cl]^{2+}$ ions. Most notable amongst these absences is the lack of any structural or kinetic data on the pentakis(alkylamine)chlororuthenium(III) and -osmium(III) complexes. While the ruthenium complexes have been reported to be prepared in solution,[62] they have not been fully characterized and no kinetic data has been reported for their substitution reactions. The kinetic studies on the Ru(III) and Os(III) complexes are expected to be difficult for a number of reasons, including the difficult synthetic procedures and the tendency for alkylamine complexes of Ru(III) and Os(III) to undergo oxidative dehydrogenation reactions of the ligands.[62,63] However, if the analyses of π bonding and solvation effects that have been given in the previous paragraphs are correct, then definite predictions as to what might be expected for the values of the missing data in Table II can be made. These are:

(i) The values of the M–Cl bond lengths in the $[M(NH_2R)_5Cl]^{2+}$ complexes (M = Ru, Os) are expected to decrease with respect to those observed in the analogous $[M(NH_3)_5Cl]^{2+}$ complexes, and this decrease should be comparable or slightly larger than that observed for the Cr analogues.

(ii) Small, but significant, decreases in the M–Cl bond lengths are expected in the $[M(NH_2CH_2CH_3)_5Cl]^{2+}$ ions (M = Ru, Os) in comparison to their $[M(NH_2CH_3)_5Cl]^{2+}$ analogues.

(iii) The values of the rate constants of aquation of the $[M(NH_2R)_5Cl]^{2+}$ (M = Ru, Os) ions are expected to be approximately two orders of magnitude smaller than in analogous $[M(NH_3)_5Cl]^{2+}$ ions, with only small differences in substitution rate constants between analogous methylamine and ethylamine complexes.

(iv) The values of the M–Cl bond lengths in $[M(NH_2CH_2CH_3)_5Cl]^{2+}$ (M = Co, Ir) are expected to be similar to those that are observed in the $[M(NH_2CH_3)_5Cl]^{2+}$ analogues.

(v) The values of the rate constants of spontaneous aquation of the $[Ir(NH_2R)_5Cl]^{2+}$ ions are expected to be similar to that observed for the $[Ir(NH_3)_5Cl]^{2+}$ ion.

Experiments are currently underway to fill in the gaps in the experimental data and test these predictions.

Table III contains a compilation of the available activation parameters for the spontaneous aquation reactions of the $[M(NH_2R)_5Cl]^{2+}$ ions.[39–53] These activation parameters support the arguments presented in the previous paragraphs that the mechanisms of spontaneous substitution reactions are very similar for Co(III) and Cr(III).[32] In terms of a common dissociative interchange mechanism, the reason for the decrease in the value of the rate constant for aquation of $[Cr(NH_2CH_3)_5Cl]^{2+}$ as compared to $[Cr(NH_3)_5Cl]^{2+}$ lies in the larger value of $\Delta H^{\ddagger}$ for the former complex. This is consistent with the greater energy that is required to stretch the Cr–Cl bond for the methylamine complex, as op-

TABLE III

Activation parameters for the spontaneous aquations of $[M(NH_2R)_5Cl]^{2+}$

Complex	$\Delta H^\ddagger$ kJ mol^{-1}	$\Delta S^\ddagger$ J K^{-1} mol^{-1}	$\Delta G^{\ddagger a}$ kJ mol^{-1}	$\Delta V^\ddagger$ cm^3 mol^{-1}
$[Co(NH_3)_5Cl]^{2+}$	93(1)[b]	−44(3)[b]	106(1)	−10.6(0.4)[j]
$[Co(NH_2Me)_5Cl]^{2+}$	95(1.5)[c]	−10(4)[c]	98(1.5)	−2.3(0.4)[c]
$[Co(NH_2Et)_5Cl]^{2+}$	89[d]	−9[d]	92	
$[Rh(NH_3)_5Cl]^{2+}$	101.5(1.2)[e]	−45.6(3.4)[e]	115(1)	−14.5(4.6)[k]
$[Rh(NH_2Me)_5Cl]^{2+}$	102(1)[e]	−50.2(2.3)[e]	117(1)	
$[Rh(NH_2Et)_5Cl]^{2+}$	101(3)[f]	−46(8)[f]	115(3)	
$[Ir(NH_3)_5Cl]^{2+}$	94[g]	−102[g]	124	
$[Cr(NH_3)_5Cl]^{2+}$	93(0.5)[h]	−29(1.5)[h]	102(0.5)	−10.8(0.3)[l]
$[Cr(NH_2Me)_5Cl]^{2+}$	110(0.5)[h]	−2(1.5)[h]	111(0.5)	+0.5(0.6)[c]
$[Cr(NH_2Et)_5Cl]^{2+}$	110(0.5)[h]	3(1.5)[h]	109(0.5)	
$[Ru(NH_3)_5Cl]^{2+}$	91.5[i]	−54[i]	109	−30.2[m]

[a] 25°C, calculated from the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ data.

[b] Ref. 47.

[c] Ref. 46.

[d] Ref. 49.

[e] Ref. 43.

[f] Ref. 50, the activation parameters are for the reaction, $[Rh(EtNH_2)_5Cl]^{2+} + Br^- \rightarrow [Rh(EtNH_2)_5Br]^{2+} + Cl^-$, which has the aquation of the chloro complex as the rate determining step.

[g] Ref. 44.

[h] Ref. 39.

[i] Refs. 16, 40.

[j] Ref. 8.

[k] Ref. 53.

[l] Ref. 48.

[m] Ref. 51.

posed to the ammine complex, in a dissociative interchange mechanism.[32] In the case of the Co(III) complexes, the Co–Cl bond lengths are the same within experimental errors and this is mirrored in the values of $\Delta H^\ddagger$. The similarities in the activation enthalpies of $[M(NH_3)_5Cl]^{2+}$, M = Co, Cr, are also consistent with a common mechanism, as are the activation entropy data. The more negative values of $\Delta S^\ddagger$ observed for the Co(III) complexes compared to their Cr(III) analogues are to be expected for a similar dissociative interchange mechanism. The Cr(III) complexes have larger radii than their Co(III) analogues, which will have the effect of increasing both the Born (dielectric continuum) and hydrogen bonding contributions of solvation of the Co(III) ions with respect to their

Cr(III) counterparts.[14,32,39,43,64,65] Thus the contribution to $\Delta S^{\ddagger}$ from electrostriction will be greater during the charge separation in the smaller ions and hence the values are more negative for the Co(III) ions in comparison to their Cr(III) counterparts.[32]

The less negative values of $\Delta S^{\ddagger}$ for $[Co(NH_2CH_3)_5Cl]^{2+}$ as compared to $[Co(NH_3)_5Cl]^{2+}$ appear to be the reason for the larger rate constant of aquation of the former complex. This probably arises because of the larger size and greater steric hindrance in the methylamine complex, which will decrease the contributions of solvation (Born and hydrogen bonding contributions) to the mechanism (i.e., electrostriction is less important because both the ground and transition states are less strongly solvated than in the pentaammine analogues).[39,43] The differences in $\Delta S^{\ddagger}$ values between the methylamine and ammine complexes are the same, within experimental error, for both Co(III) and Cr(III), which again points to the operation of a common mechanism.

The stereoretentive nature of the substitution reactions of $[Co^{III}(NH_3)_5X]^{n+}$, and the similar activation enthalpies for $[Co(NH_2R)_5Cl]^{2+}$ ($R = H, CH_3$), appear to be consistent with a common I_d mechanism, with little relief of steric strain in the intermediate. If steric factors are most important in affecting the kinetics, then they would be expected to be most strongly reflected in the enthalpic rather than entropic contributions to the rate constant. However, the solvation contributions on the entropy of activation discussed in the previous paragraph will also result in large negative contributions to $\Delta H^{\ddagger}$, which will be greater for the smaller $[Co(NH_3)_5Cl]^{2+}$ ion, in comparison to the $[Co(NH_2CH_3)_5Cl]^{2+}$ ion. This will be compensated for by a more negative contribution to $\Delta H^{\ddagger}$ for relief of steric strain in $[Co(NH_2CH_3)_5Cl]^{2+}$ than $[Co(NH_3)_5Cl]^{2+}$. Therefore, the similarity in $\Delta H^{\ddagger}$ values for these two complexes may be fortuitous. The activation data for the Co(III) complexes also need to be reinvestigated in light of the studies on $[Co(NH_2R)_5Br]^{2+}$ ($R = H, CH_3, CH_2CH_3, CH_2CH_2CH_3, CH_2CH_2CH_2CH_3$), which show that $\Delta H^{\ddagger}$ is 10 kJ mol^{-1} less for the pentakis(alkylamine) complexes compared to $[Co(NH_3)_5Br]^{2+}$.[66] The latter result implies that the steric factors are significant. It remains to be seen whether the spontaneous substitution reactions of $[Co^{III}(NH_2R)_5X]^{n+}$, R = alkyl, are stereoretentive or indeed whether a short-lived intermediate occurs with reorganization in the transition state. If some rearrangement does occur, this may also contribute to the less negative values of $\Delta S^\ddagger$ that are observed for the $[M(NH_2CH_3)_5Cl]^{2+}$ complexes (M = Co, Cr).

The trends that are observed for the Co(III) and Cr(III) complexes are not as obvious in the Rh(III) analogues. However, the differences in $\Delta H^\ddagger$ that are expected on the basis of the differences in the Rh–Cl bond lengths in the ground state are within the experimental errors of the measurements. More surprising is the observation that the entropies of activation in the series $[M(NH_2R)_5Cl]^{2+}$ (R = H, Me, Et) are the same, within experimental error. Part of this, no doubt, lies in the weaker hydrogen bonding acidity of the coordinated amines of the Rh(III) complexes, which will reduce the solvent contributions to the entropy of activation, but this is not the entire answer. It appears that Rh(III) has a slightly different kinetic behaviour compared to Co(III) and Cr(III). Perhaps rearrangement occurs in the transition states (intermediates) for the $[M(NH_2CH_3)_5Cl]^{2+}$ complexes of Co(III) and Cr(III), but not Rh(III). However, the larger values of $\Delta H^\ddagger$ for Rh(III) complexes compared to their Co(III) analogues supports the previous assertions that an I_d mechanism operates for all three M(III) ions.[33]

The entropies of spontaneous aquation reactions of the pentaamminechloro complexes of the second-row transition metal ions, Ru(III) and Rh(III),[40,43] are the same, within experimental error, as that observed for the Co(III) analogue. This suggests that the substitution reactions of Rh(III) and Ru(III) are moved along the mechanistic continuum towards a more associative mechanism than that postulated for Co(III), since the electrostriction terms in the aquation of the larger Ru(III) and Rh(III) ions will be less important. On the basis of the size of the metal-ligand bond lengths,[14] the values of $\Delta S^\ddagger$ would follow the trend Co(III) < Rh(III) < Cr(III) < Ir(III) < Ru(III) < Os(III) for electrostriction about the $[M(NH_3)_5]^{3+}$ moiety, and Co(III) < Cr(III) < Ru(III) < Rh(III) < Os(III) ≈ Ir(III) for electrostriction about the Cl^- entity in partially separated transition states, where there is an equal amount of bond breaking for each complex. From these trends, it is expected that the value of $\Delta S^\ddagger$ for $[Ir(NH_3)_5Cl]^{2+}$ might be the least negative if a common mechanism was to apply, although the uncertainties in the values obtained for the Ir(III) complex may be large due to the experimental difficulties in obtaining the data at such high temperatures.[44] When the actual trends in $\Delta S^\ddagger$ are compared with those expected on the basis of electrostriction, for a common I_d mechanism, the experimental $\Delta S^\ddagger$ data suggest that the degree of dissociation in the transition state decreases in the order Co(III) $\geq$ Cr(III) $>$ Rh(III) $>$ Ru(III) $>$ Ir(III). This is not to say that the mechanism changes from an I_d to an I_a mechanism along this series, merely that the minimum energy transition state moves along the mechanistic coordinate. Indeed all of these mechanisms could be contained in a slice of the mechanistic continuum that lies in the I_d region. The enthalpy of activation data also indicates that the Ir(III) complex undergoes a less dissociative mechanism than the Co(III) and Rh(III) analogues, because if there is a similar degree of dissociation in the transition state, it would be expected that the values of $\Delta H^\ddagger$ would increase in the series Co(III) $<$ Rh(III) $<$ Ir(III) on the basis of ligand field effects.[67] However, it needs to be emphasized that the values of $\Delta H^\ddagger$, and particularly $\Delta S^\ddagger$, are the subject of a considerable degree of experimental uncertainty, often much larger than the quoted errors,[68] which makes activation volume data more reliable in interpreting mechanisms. Certainly for most other spontaneous aquation data involving charged leaving groups, the trend in $\Delta H^\ddagger$ (Co(III) $<$ Rh(III) $<$ Ir(III)) is consistent with an I_d mechanism.[68] Therefore, the published activation data for the aquation of $[\mathrm{Ir(NH_3)_5Cl}]^{2+}$ may well be in error and the kinetics of this reaction need to be reinvestigated. The data for $[\mathrm{Ru(NH_3)_5Cl}]^{2+}$ may also be complicated by a small contribution from the A pathway (Scheme 1), even at ambient pressures.[56]

The experimental difficulties quoted above have often been used to justify the use of $\Delta V^\ddagger$ data as better indicators of the mechanism. The activation volume data that is available (Table III) supports the assertions that have been made above. The fact that $\Delta V^\ddagger$ for the $[\mathrm{M(NH_3)_5Cl}]^{2+}$ ions, M = Co, Cr, are the same within experimental error supports a common mechanism.[32] It has been asserted that because of the effects of electrostriction it is not possible to use $\Delta V^\ddagger$ data to compare the mechanisms of Co(III) and Cr(III).[57] However, such arguments are flawed, since the values of $\Delta V^\ddagger$ are the sum of the intrinsic ($\Delta V^\ddagger_{\mathrm{int}}$) and electrostriction ($\Delta V^\ddagger_{\mathrm{el}}$) components, it follows that if the values of $\Delta V^\ddagger$ are similar for two complexes, then the most likely explanation is that the two components of $\Delta V^{\ddagger}$ are similar (i.e., a similar mechanism applies). There will be slightly different values of $\Delta V^{\ddagger}_{\text{int}}$ due to the different degrees of contraction of the $[M(NH_3)_5]^{3+}$ component of the transition state, but this effect will be small.[11,12] Again the values of $\Delta V^{\ddagger}$ for $[M(NH_2CH_3)_5Cl]^{2+}$ are similar for M = Co, Cr, but significantly more positive than those for the pentaammine analogues. The similarity in the values of $\Delta V^{\ddagger}$ for the Co(III) and Cr(III) complexes is again consistent with a similar mechanism operating. The more positive values of $\Delta V^{\ddagger}$ obtained for the pentakis(methylamine) complexes, compared to the pentaammine analogues, probably arise from the smaller electrostriction effects present in the dissociation of the ligand from larger pentakis(methylamine) complexes. Such an explanation is consistent with the entropy results.

Given the relatively small differences in the $\Delta V^{\ddagger}$ data for aqua exchange in $[M(NH_3)_5(OH_2)]^{3+}$ for Cr(III) and Ru(III), the large negative value (-30 cm^3 mol^{-1}) observed in the spontaneous aquation of $[Ru(NH_3)_5Cl]^{2+}$ is very surprising.[16,51] This value was initially taken to indicate that the mechanism for substitution in the Ru(III) complex was *A*,[51] but such data is inconsistent with the similarity in the values of $\Delta S^{\ddagger}$ between Co(III) and Ru(III), which would suggest that the two mechanisms are similar. It is also inconsistent with a number of other experimental details,[16,52] and the qualitative arguments that have been presented as to why, in general, such mechanisms should be dissociative interchange. These results are, however, consistent with the pressure-dependent change in mechanism (Scheme 1).[56]

Although the reactions of the pentaaminechlorocobalt(III) complexes are stereoretentive, many spontaneous aquation reactions of Co(III) amine complexes are not. The degree of stereoretention in these reactions has been discussed in detail.[4,55,69–71] Despite this, there is still debate whether such reactions occur via a single transition state or intermediate, or two competing intermediates or transition states, one being square pyramidal and the other being trigonal bipyramidal.[55,69–71] It has been claimed that the temperature dependence of the stereochemical change will resolve this issue,[55,68–70] but this is unlikely to be the case unless two distinct slopes are observed in the temperature dependence of the rate constant. This in turn will require the reaction to be monitored over a large temperature range in order to provide convincing evidence. A change in the degree of stereoretention with temperature cannot be taken as an indication of two separate intermediates, since if there is only one intermediate or transition state its preferred geometry is also likely to be temperature dependent (i.e., more rearrangement is expected as the temperature increases). In order to resolve this issue, quite extensive and careful experiments will need to be performed.

The degree of stereoretention in the spontaneous substitution reactions of $[Co^{III}(en)_2AX]^{n+}$ complexes has been rationalized, using ligand field theory, in terms of competing intermediates.[70,71] This is not compelling, however, since such a theory would also be consistent with a single intermediate that has a geometry that is between idealized square pyramidal and trigonal bipyramidal geometries. The geometry is simply more distorted towards a trigonal bipyramidal structure as the reaction becomes less stereoretentive. Any realistic calculation of the geometry of the intermediate must include ligand field contributions, steric contributions (molecular mechanics calculations) and the very large solvent contributions to the stabilization of the intermediates or transition states when there are charged leaving groups. To date, calculations have concentrated on only one of these contributions, i.e., ligand field[5,70,71] or steric contributions.[42,72] We are currently attempting to incorporate all three factors.

By invoking the concept of microscopic reversibility the anation reactions of the $[M(NH_2R)_5(OH_2)]^{3+}$ complexes with Cl^- (Table IV)[2-5,16,51,53,73-76] must also belong to the family of I_d mechanisms, at least for Cr(III), Co(III) and Rh(III). The reason for this process being near the dissociative limit also lies in the solvation energy terms. This arises because the formation of a seven-coordinate transition state will require a large amount of energy in terms of the energy required to partially desolvate $Cl^-(aq)$, which in turn will increase $\Delta G^\ddagger$. By contrast, an I_d mechanism near the dissociative limit will involve very little change in the solvation energy terms because the leaving group (OH_2) has no charge. This concept of microscopic reversibility is also illustrated in Fig. 4.

Therefore, the driving force for an I_d mechanism for both the spontaneous aquation reactions of $[M(NH_2R)_5Cl]^{2+}$ and the an-

TABLE IV

Rate constants at 25°C and activation volumes for the anation reactions of $[M(NH_3)_5(OH_2)]^{3+}$ with Cl^-[a]

Complex	$10^5k_{Cl^-}$[b] $M^{-1}\ s^{-1}$	$\Delta V^\ddagger$ $cm^3\ mol^{-1}$
$[Co(NH_3)_5(OH_2)]^{3+}$	0.28	+1.4(0.8)[c]
$[Rh(NH_3)_5(OH_2)]^{3+}$	0.68	+3.0(0.7)[c]
$[Ir(NH_3)_5(OH_2)]^{3+}$	230	
$[Cr(NH_3)_5(OH_2)]^{3+}$	0.35	
$[Ru(NH_3)_5(OH_2)]^{3+}$	12.0	−20(1.4)[d]

[a] Not corrected for ion-pair formation.

[b] 25°C, calculated from the published $\Delta H^\ddagger$ and $\Delta S^\ddagger$ data, where appropriate, Ref. 16.

[c] Ref. 53.

[d] Ref. 51.

ation reactions of $[M(NH_2R)_5(OH_2)]^{3+}$ is the solvation energies of the Cl^- ion and the 3+ ions. It follows that the mechanism of substitution of these complexes, and in particular the Cr(III) complexes, will become more associative in solvents that are less able to solvate Cl^-. However, such solvents will also favor the anation reaction, and Cl^- substitution will be difficult to measure because of both solubility problems and the fact that the equilibrium constant for the reaction shown below will lie very much to the left.

$$[M(NH_2R)_5Cl]^{2+}(solv) + solvent \rightleftarrows [M(NH_2R)_5(solvent)]^{3+}(solv) + Cl^-(solv)$$

There have been some studies of this type which are summarized in a recent review.[77] Where such studies have been performed with a charged leaving group, there is a strong correlation between the ability of the solvent to solvate the anionic leaving group (as measured by the solvent polarity and hydrogen bonding acidity) and the rate of reaction.[77,78] Such results point to the importance of solvent-assisted dissociative interchange mechanisms, but it is important to note that the position of the preferred mechanism on the mechanistic continuum of *I* mechanisms must change with the ability of the solvent to stabilize a more dissociated transition state. Indeed the mechanism for a given reaction may span almost the whole range of the continuum depending on the strength of solvation in the transition state. The importance of solvation of the transition state is also indicated by an analysis of the pressure dependence of $\Delta V^{\ddagger}$ in the aquation of $[M(NH_3)_5Cl]^{2+}$, M = Co, Cr.[8,48] This pressure dependence has been interpreted in terms of the 2–4 water molecules required during the activation process, i.e., the transition state is more strongly solvated than the ground state,[8,48] as a result of charge separation. The larger number of water molecules that are calculated to be involved in the case of Co(III) (i.e., 4) as compared to Cr(III) (i.e., 2) can be interpreted in at least two ways. Either the mechanism is less dissociative for Cr(III) as compared to Co(III),[8,48] or the smaller size of the Co(III) complex and the shorter Co–Cl bond length in comparison to that for Cr(III) will tend to increase the solvent electrostriction terms for Co(III) compared to Cr(III), in a similar mechanism. Hence, within the framework of a common mechanism, more solvent molecules will be involved in forming the transition state for the Co(III) complex. It is probable that the true answer lies somewhere between these two extremes in interpretation, i.e., the mechanisms for aquation of the Co(III) and Cr(III) complexes are similar, but the Cr(III) complex has a slightly less dissociated transition state.

On the basis of microscopic reversibility, the anomalous volume of activation (Table IV) for the anation of $[Ru(NH_3)_5(OH_2)]^{3+}$ with Cl^- is to be expected given the large negative value for the aquation of $[Ru(NH_3)_5Cl]^{2+}$.[16,51] If our recent analysis of the aquation reaction is correct (Scheme 1), it follows that the predominant mechanism of the anation reaction is also I_d at ambient pressures.[56] The large negative value of $\Delta V^{\ddagger}$[51] is also explained by a pressure dependent change in the mechanism, whereby the A mechanism is favoured by high pressures.[56]

The interpretation of the activation parameters and rate data for these anation reactions is complicated by the formation of ion-pairs as a precursor to the anation event. Thus, there are contributions to $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ from the ion-pairing equilibria. Because of the difficulty in separating the contributions of such ion-pairing equilibria from the rate constant for substitution within the ion-pair, it is much more difficult to draw mechanistic conclusions from the kinetic data obtained from anation reactions as opposed to aquation reactions. This is complicated further by the range of ionic strengths and background electrolytes used in different studies reported in the literature. Therefore the use of the concept of microscopic reversibility and data from the aquation reactions is a more reasonable method for the assignment of anation mechanisms than trying to deconvolute the various contributions to the kinetics of anation reactions.

Apart from the effects of steric bulk on the kinetics of substitution, one of the cornerstones used for assigning different mechanisms is the use of relationships between the rate constants of aquations and the Gibbs free energies of the aquation/anation equilibria.[5,79–81] Such correlations have been quoted extensively as convincing evidence for mechanistic differences, especially by the proponents of the philosophy that the nature of the metal ion and ancillary ligands determine the mechanism (i.e., I_a for Cr(III) and I_d for Co(III).[5,79] An analysis of the slopes of these types of plots gives the following order in the degree of dissociation in the transition states for the aquation of $[M^{III}(NH_3)_5X]^{n+}$: Co(III) ≈ Ru(III) > Ir(III) > Rh(III) > Cr(III) > $[Cr(OH_2)_5X]^{n+}$ [5,79–81] However, as discussed in two recent reviews,[3,5] such relationships between the rate constants and the Gibbs free energies of the aquation/anation equilibria are open to both theoretical interpretation and experimental difficulties in determining the actual slope, especially with relative few data points. Moreover, in this author's opinion, the data actually validate the arguments that have been espoused in previous paragraphs that for charged leaving groups, such as Cl^-, all of the pentaamine complexes react via I_d mechanisms. Therefore, none of the data that has been used to assign significant mechanistic differences in these complexes stands up to close scrutiny.

The very fact that the relationship between $\Delta G^{\ddagger}$ and ΔG° for the aquation reactions of a range of pentaammine complexes has a slope of less than one points to the importance of the sensitivity of the mechanism to the nature of the leaving group. This is expected if the arguments with regard to solvation contributions to the mechanism are correct (i.e., the degree to which the mechanism changes with leaving group will be influenced by the degree to which solvation energies will favor a more dissociated transition state for Cr(III)). Plots of $\Delta V^{\ddagger}$ versus ΔV° tell a similar story, although they have been previously interpreted in terms of supporting mechanistic differences.[3,48] As we have argued earlier, the similar values of $\Delta V^{\ddagger}$ for the aquation reactions of $[M(NH_3)_5Cl]^{2+}$, M = Co, Cr, strongly suggest a similar degree of charge separation in the transition state for these two reactions. However, as you go down the leaving group series $Cl^- > Br^- > I^- > NCS^- >> OH_2$, the solvation contributions to stabilizing charge-separated transition states become less important and therefore the minimum energy pathway for the Cr(III) substitution reaction moves along the mechanistic continuum towards an I_a mechanism. Thus, it is expected that the mechanism for the aqua exchange reaction is in the I_a region of the mechanistic continuum. This is the likely reason for the lower slope that is observed for the Cr(III) series in comparison to the Co(III) series in plots of $\Delta V^{\ddagger}$ versus ΔV°, rather than a general change in mechanism between Co(III) and Cr(III). Moreover, since we have argued that the aqua exchange reaction of $[Cr(NH_3)_5(OH_2)]^{3+}$ has an I_a mechanism that lies towards the middle of the mechanistic continuum of I mechanisms, it follows that the substitution reactions of the Cr(III) complexes with charged leaving groups will generally occur via I_d mechanisms. The major differences in the mechanisms of spontaneous substitution reactions of $[Cr^{III}(NH_3)_5X]^{n+}$ complexes will be the degree of charge separation in the transition state as the leaving group is varied. This charge separation (i.e., position on the mechanistic continuum) will be much more sensitive to solvation effects on the leaving group than is the case for Co(III).

The greater sensitivity of the substitution kinetics of the pentaaquachromium(III) complexes, as opposed to their pentaammine analogues, may also be due to solvent effects. In terms of both their sizes and their hydrogen-bonding acidities, the $[M(OH_2)_5]^{3+}$ moiety, in a charge-separated transition state will be more strongly solvated than the $[M(NH_3)_5]^{3+}$ moiety. Therefore, the mechanisms of the former will be more susceptible to solvent effects, than those of the latter. Thus, the range of mechanisms of the pentaaqua complexes is expected to be larger than the pentaammine complexes, and hence the slope of the plots of $\Delta G^{\ddagger}$ versus ΔG° for the aquation reactions are expected to be less for the pentaaqua complexes than for the pentaammine complexes. This means that the aquation of $[Cr(OH_2)_5Cl]^{2+}$ is also expected to be an I_d mechanism, and in fact this reaction may proceed with a greater degree of charge separation in the transition state than the $[Cr(NH_3)_5Cl]^{2+}$ analogue.

It has also been concluded that the mechanisms of aquation of the $[M(NH_3)_5(OSO_2CF_3)]^{2+}$ (M = Co, Rh, Ir, Ru, Os and Cr) and $[M(NH_2CH_3)_5(OSO_2CF_3)]^{2+}$ (M = Cr, Co, Rh) complexes[54,82,83] proceed via a mechanism in which bond breaking substantially precedes bond making in the transition state.[83] This is particularly the case since there are close parallels in the ratios of the rate constants for aquation between the chloro complexes and the triflato complexes.[54,82,83] Therefore, it is likely that in general the preferred mechanisms for substitution in pentaammine and pentaaqua complexes containing a charged leaving group will reside in the I_d regime of the mechanistic continuum, i.e., the norm in such substitution reactions is that bond breaking substantially precedes bond making in the formation of the transition state.

There are three overriding points that emerge from the analyses that are presented in this section.

(i) If the mechanism is sensitive to the nature of the nucleophile, then it follows that there must be a range of different mechanisms over the range of entering/leaving groups.

(ii) The aquation reactions of pentaammine (and pentaaqua) complexes involving charged leaving groups generally appear to occur via mechanisms in which bond breaking substantially precede bond making. That is not to say that there is the same degree of bond breaking in the transition state for different metal ions with the same leaving group or for different leaving groups with the same metal ions, but just that the majority of these mechanisms lie within the I_d region of the mechanistic continuum.

(iii) Solvation effects are probably the overriding factor in determining the position of the mechanism of substitution on the mechanistic continuum for all of the M(III) complexes discussed here, except for Co(III).

MECHANISMS OF BASE HYDROLYSIS OF PENTAAMINEACIDOMETAL(III) AND RELATED COMPLEXES

It is generally accepted that the mechanism for base hydrolysis is an S_N1_{cb} mechanism (Scheme 2), at least for Co(III); however, there is still controversy as to the lifetime of this five-coordinate intermediate.[4,6,84,85] In the case of Co(III), there is debate as to whether the rate determining step of substitution in the conjugate base is an I_d or D mechanism (i.e., whether this intermediate has a lifetime that is longer than the time required for solvent reorganization.[4,6,86–90] An E_2 mechanism (i.e., a mechanism in which deprotonation and elimination of the leaving group to form a five-coordinate intermediate is concerted) has also been proposed in some cases where deprotonation is rate limiting,[91,92] but the need for such a mechanism has been subsequently challenged.[84]

There is an even greater degree of debate as to the mechanisms by which the other metal ions undergo base-catalysed hydrolyses,

$$[\mathrm{M^{III}(NH_2R)_5X}]^{n+} + \mathrm{OH^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{M(NH_2R)_4(NHR)X}]^{(n-1)+} + \mathrm{H_2O}$$

$$[\mathrm{M(NH_2R)_4(NHR)X}]^{(n-1)+} \xrightarrow{k_2} [\mathrm{M(NH_2R)_4(NHR)}]^{2+} + \mathrm{X}^{(3-n)-}$$

$$[\mathrm{M(NH_2R)_4(NHR)}]^{2+} + \mathrm{H_2O} \xrightarrow{\text{fast}} [\mathrm{M(NH_2R)_4(NHR)(OH_2)}]^{2+}$$

$$[\mathrm{M(NH_2R)_4(NHR)(OH_2)}]^{2+} \xrightarrow{\text{fast}} [\mathrm{M(NH_2R)_5(OH)}]^{2+}$$

$$[\mathrm{M(NH_2R)_4(NHR)}]^{2+} + \mathrm{Y^-} \xrightarrow{\text{fast}} [\mathrm{M(NH_2R)_4(NHR)Y}]^{+}$$

$$[\mathrm{M(NH_2R)_4(NHR)Y}]^{+} + \mathrm{H_2O} \xrightarrow{\text{fast}} [\mathrm{M(NH_2R)_5Y}]^{2+} + \mathrm{OH^-}$$

SCHEME 2

where different workers have argued that the rate determining step involving the conjugate base for Cr(III) and Rh(III) is a *D*, I_d or I_a mechanism.[4,6,93–95] For Ru(III), the story is even more complex, where it has been argued recently that the mechanism is not even an S_N1_{cb} mechanism, but is an *A* mechanism that involves nucleophilic attack of OH^- as the initial step.[96] In this author's opinion, all such mechanisms are S_N1_{cb} and fall within the *D*, or at least the I_d, classification near the dissociative limit, with the possible exception of Ru(III). As discussed in the following sections, the kinetic differences can be understood in terms of competing ligand field, π bonding and steric effects on the stabilization of different geometries of potential intermediates. The rate constant, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ data for base hydrolysis of the $[M(NH_2R)_5Cl]^{2+}$ complexes are compiled in Table V, and activation volume data are contained in Table VI.[39,43,85,93–104]

By far the most data on base-catalysed hydrolysis reactions have been obtained for Co(III). Apart from the debate about the possibility of an E_2 mechanism in some specialized cases,[84,91,92] the

TABLE V

Rate constants and activation parameters for the base hydrolyses of $[M(NH_2R)_5Cl]^{2+}$ ions.

Complex	k_{OH}[a] $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}	$\Delta G^{\ddagger a}$ kJ mol^{-1}	Ref.
$[Co(NH_3)_5Cl]^{2+}$	0.24	114	140	75	97[c]
$[Co(NH_2Me)_5Cl]^{2+}$	0.8×10^3	75	72	54	98[c]
$[Co(NH_2Et)_5Cl]^{2+}$	1.1×10^3	75	75	53	98[c]
$[Rh(NH_3)_5Cl]^{2+}$	1.8×10^{-4}	114.8(0.7)	66(2)	95(1)	43
$[Rh(NH_2Me)_5Cl]^{2+}$	1.59×10^{-3}	110(1)	71(6)	89(1)	99
		108.6(1.8)	74(6)	86.5(2)	43
$[Rh(NH_2Et)_5Cl]^{2+}$	3.53×10^{-3}	107(4)	66(12)	87(4)	99
$[Ir(NH_3)_5Cl]^{2+}$	4.8×10^{-8}	139(3)	79.5(9)	115(3)	100
$[Cr(NH_3)_5Cl]^{2+}$	1.92×10^{-3}	111.7(0.5)	77(1)	89(0.5)	39
	1.8×10^{-3}	110	54	94	101
$[Cr(NH_2Me)_5Cl]^{2+}$	0.432	106.3(0.5)	103(1)	75(0.5)	39
$[Cr(NH_2Et)_5Cl]^{2+}$	1.61	105.4(0.5)	114(1)	71.5(0.5)	39
$[Ru(NH_3)_5Cl]^{2+}$	5.2(4.9[b])	112	143	69	102
	2.15	73(3)	−36	84	96

[a] 25°C; calculated from the values of $\Delta H^{\dagger}$ and $\Delta S^{\dagger}$.

[b] Ref 40.

[c] Recalculated data are quoted, Ref. 85.

TABLE VI

Activation volume parameters for the base catalysed hydrolyses of $[M(NH_2R)_5Cl]^{2+}$

Complex	$\Delta V^{\ddagger}$ cm^3 mol^{-1}	Ref.
$[Co(NH_3)_5Cl]^{2+}$	33	103,104
$[Co(NH_2Me)_5Cl]^{2+}$	32.8(1.7)	93
$[Co(NH_2Et)_5Cl]^{2+}$	31.1(0.5)	93
$[Rh(NH_3)_5Cl]^{2+}$	18.7(0.7)	95
$[Cr(NH_3)_5Cl]^{2+}$	17.0(0.9)	94
$[Cr(NH_2Me)_5Cl]^{2+}$	34.8(1.7)	94

only argument as to the mechanism is whether the five-coordinate intermediate is longer or shorter-lived than solvent reorganization (i.e., is the rate determining step a D or I_d mechanism). It is clear from studies of competition between different nucleophiles for the putative five-coordinate intermediate obtained from the base-hydrolysis of $[Co^{III}(NH_3)_5L]^{n+}$ that there is a small effect of the leaving group on the competition between water and other nucleophiles for this intermediate.[90] Therefore, most evidence now points to the formation of a five-coordinate intermediate that is sufficiently long-lived to show some discrimination for the entering nucleophile, but is sufficiently short-lived to be influenced by the nature of the leaving group. This leads to problems as to whether you apply the label D or I_d to the mechanism. Using the definition of Merbach, these results would place the mechanism within the D region of the mechanistic continuum, whereas the definitions used by other workers would place this in the I_d region of the mechanistic continuum. I believe that the latter definition is inappropriate, since as pointed out by Swaddle,[4] the process of complete ion-pair separation can be a million times slower than the process of bond breaking, i.e., the intermediate can be very long-lived compared to the process of bond breaking and solvent reorganization, but still be influenced by the nature of the leaving group. Thus, the mechanism can be a long way away from a concerted interchange mechanism that is defined as I_d in the Merbach nomenclature. Perhaps a more reasonable viewpoint would be to subdivide dissociatively activated mechanisms into three classes, with the caveat mentioned previously that it should always be recognized that there is a continuum of transition states and intermediates. In keeping with the nomenclature of Merbach, I_d would represent a dissociatively activated process in which bond breaking and bond making is concerted, i.e., there is no intermediate. A new symbol D_I could represent a mechanism in which bond breaking occurs to form an intermediate of lower coordination number, but this intermediate is short enough lived to feel the influence of the leaving group, and the D mechanism occurs when the intermediate is long enough lived so that it does not feel the influence of the leaving group (Fig. 5). It is easy to distinguish between a D and a D_I mechanism under this definition, since a true D mechanism will have competition ratios that are independent of the nature of the leaving group. Using this criterion, it is clear that the mechanisms of base hydrolysis of $[Co^{III}(NH_3)_5L]^{n+}$ complexes fall within the D_I definition. This is not to say that all mechanisms of base-catalysed substitution reactions of pentaamine

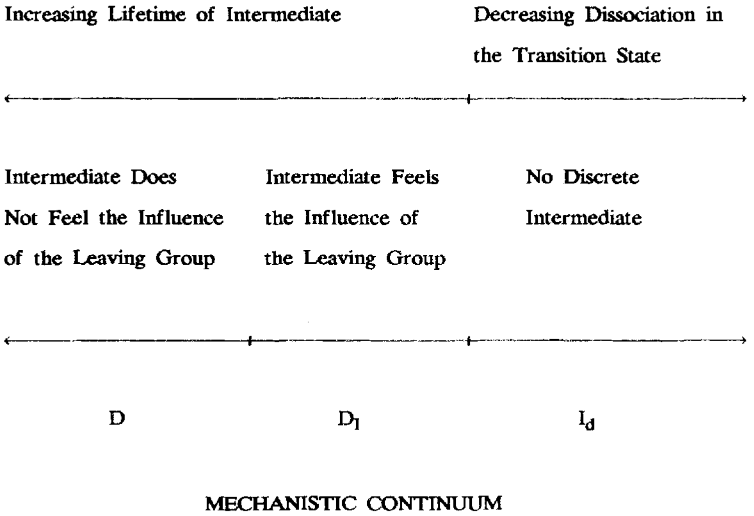


FIGURE 5 Mechanistic continuum for dissociatively activated processes. The continuum in the D and D_I regions corresponds to the lifetime of the intermediate (i.e., the depth of the potential well in which it is contained). The dividing line between the D_I and D mechanisms (i.e., the lifetime of the intermediates) will depend critically on a number of factors, including the charge of the leaving group, specific ion-pairing effects, etc.

complexes fall into this category. Indeed, longer-lived intermediates are expected where steric factors stabilize a five-coordinate intermediate, and a number of such cases are expected to fall within the true *D* definition of a mechanism. This is well illustrated by a comparison of azide competition for the five-coordinate intermediate generated from $[Co(NH_2R)_5X]^{2+}$ ($R = H, CH_3$; $X = Cl^-, CF_3SO_3^-$).[42,83,90] Azide competes for the five-coordinate intermediate generated from the methylamine complexes 5.5–6 times more effectively than for the intermediate generated from the ammine complexes. This indicates that the former is much longer-lived than the latter. This is confirmed by the competition ratios since there is a small but measurable difference of ~13% between the abilities of the five-coordinate intermediates that are generated from $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5(OSO_2CF_3)]^{2+}$ to compete for azide,[90] whereas the intermediates generated from the methylamine analogues have identical abilities to compete for azide.[42,83] The argument is even more compelling since the much larger competition ratios for the methylamine complexes enables small differences between them to be detected with much more precision. These results combined suggest that the mechanism for base-hydrolysis of the pentaammine complexes fall in the D_I region of the mechanistic continuum, whereas those for the pentakis(methylamine) complexes fall within the true *D* region of the mechanistic continuum. However, the latter needs to be treated with some caution until more extensive competition experiments have been performed. Clearly, competition experiments involving the pentakis(methylamine) complexes with the dimethyl sulfoxide and F^- or SO_4^{2-} leaving groups are desirable, since it is with these leaving groups that the greatest differences in competition ratios are observed in the case of the pentaammine complexes.[90]

In order to understand the changes in the rate constants of the base-catalysed hydrolysis reactions of the pentaamine complexes on the addition of steric bulk into the amine ligands (Table V), it is necessary to consider the effects on the rate constants of both the formation of the conjugate base and the formation of the five-coordinate intermediate from the conjugate base. While the rate constant of proton exchange in $[Co(NH_2CH_3)_5Cl]^{2+}$ increases only by a factor of 6 over the rate constant for $[Co(NH_3)_5Cl]^{2+}$, the rate constant for base hydrolysis increases by a factor of 13,000, which shows that the major contribution to the rate enhancement occurs in the dissociation of the leaving group from the conjugate base.[42] This large rate enhancement is reflected in a large decrease in $\Delta H^{\ddagger}$, which is consistent with the release of steric strain in the formation of a five-coordinate intermediate. We have tested whether such an argument is valid by the use of molecular mechanics calculations.[34] Indeed our preliminary calculations show that nearly all of the differences in $\Delta H^{\ddagger}$ that are observed in the series $[Co(NH_2R)_5Cl]^{2+}$ (M = H, CH_3, CH_2CH_3) can be explained by the release of steric strain (Table VII). These calculations are somewhat crude in the sense that they treat all of the ligands as amine ligands in the five-coordinate intermediate. While the deprotonated amine ligand would be expected to have a shorter Co–

TABLE VII

Molecular mechanics calculations of the release of steric strain in the formation of a five-coordinate intermediate in the base hydrolysis of $[M(NH_2R)_5Cl]^{2+}$ [34]

Complex	ΔU[a] kJ mol^{-1}	$\Delta(\Delta U)_{ma}$[b] kJ mol^{-1}	$\Delta(\Delta H^{\ddagger})_{ma}$[c]	$\Delta(\Delta U)_{ca}$[d] kJ mol^{-1}	$\Delta(\Delta H^{\ddagger})_{ca}$[e] kJ mol^{-1}
$[Co(NH_3)_5Cl]^{2+}$	−23.8	−32.3	−39	−29.5	−39
$[Co(NH_2Me)_5Cl]^{2+}$	−56.1				
$[Co(NH_2Et)_5Cl]^{2+}$	−53.3				
$[Rh(NH_3)_5Cl]^{2+}$	−11.4	−28.1	−5	−28.1	−6
$[Rh(NH_2Me)_5Cl]^{2+}$	−39.5				
$[Rh(NH_2Et)_5Cl]^{2+}$	−40.4				
$[Ir(NH_3)_5Cl]^{2+}$	−5.8				
$[Cr(NH_3)_5Cl]^{2+}$	−8.5	−24.6	−5(−22[f])	−25.4	−6(−23[f])
$[Cr(NH_2Me)_5Cl]^{2+}$	−33.1[g]				
$[Cr(NH_2Et)_5Cl]^{2+}$	33.9[g]				
$[Ru(NH_3)_5Cl]^{2+}$	−5.3				
$[Os(NH_3)_5Cl]^{2+}$	−3.9				

[a] Difference in strain energy for the minimized ground states and five-coordinate intermediates.

[b] Difference in ΔU for analogous ammine and methylamine complexes.

[c] Differences in activation enthalpies for ammine complexes and analogous methylamine complexes.

[d] Difference in ΔU for analogous ammine and ethylamine complexes.

[e] Differences in activation enthalpies for ammine complexes and analogous ethylamine complexes.

[f] Corrected for the extra energy required to break the shorter Cr–Cl bonds in the alkylamine complexes (see the text).

[g] Molecular mechanics calculations predict a small bond lengthening of the Cr–Cl bond on addition of steric bulk, instead of a significant bond shortening.

N bond length than the others, on the basis of the X-ray structure of the deprotonated hexaamine complex, $[Co((NO_2)_2\text{-sar-}H)]Cl_2.4H_2O$,[105] the calculations are in good semi-quantitative agreement with the observed differences. In all cases, the five-coordinate intermediate minimizes to a trigonal bipyramidal structure which is consistent with the stereochemical course of such reactions.[34]

It has been argued from the activation volume results that the similar values of $\Delta V^\ddagger$ observed for the base-catalysed aquations of $[Co(NH_2R)_5Cl]^{2+}$ (M = H, CH_3, CH_2CH_3; Table VI)[93] is also indicative of the formation of a five-coordinate intermediate, but the interpretation of such results has to be treated with caution. The electrostrictive solvation contributions during charge separation will be quite different for the ammine and alkylamine complexes as argued previously for the spontaneous substitution reactions. Moreover, there may be quite different intrinsic contributions to $\Delta V^\ddagger$ from the generation of the five-coordinate species from the conjugate base for the different ligands. Therefore, the similarity in the values of $\Delta V^\ddagger$ is likely to be fortuitous.

The generally slower rates of base-catalysed substitution of Cr(III) complexes compared to their Co(III) analogues has long been a source of controversy.[4,6] However, when the combined effects of π-bonding and of steric factors are considered, the reasons for these differences become obvious.[32,34] In the case of $[M(NH_3)_5Cl]^{2+}$, the chloro group undergoes significant π bonding with Cr(III), but the interaction is much smaller with Co(III).[14] The postulated reason for the large rate enhancement found for base-catalysed hydrolysis is activation of the M–Cl bond by forming a $M{=}NR_2$ π bond.[67] Such a mechanism is supported by the shortening of the $Co{=}NR_2$ bond and the lengthening of the trans $Co{-}NHR_2$ bond that has been found in the crystal structure of $[Co((NO_2)_2\text{-sar-}H)]Cl_2.4H_2O$.[105] A similar activation of the M–Cl bond could be expected in the conjugate base formed during the base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$. However, the extent of π bonding in the Cr–Cl bond is much larger than in the Co–Cl bond[14]; therefore this will destabilize the formation of a $Cr{=}NR_2$ bond in the conjugate base in comparison to Co(III). In other words, the activation of the M–Cl bond is expected to be less in the conjugate base of the Cr(III) complex in comparison to the Co(III) complex.

plexes by competition for π bonding between the Cr–Cl and Cr–NR_2 bonds is supported by the available data on the proton exchange kinetics of Co(III) and Cr(III) complexes. The rate constants for proton exchange in $[M(NH_3)_6]^{3+}$ and $[M(en)_3]^{3+}$ complexes, M = Co(III), Cr(III), differ by only a factor of less than two for analogous complexes,[106] but the rate constants of proton exchange of various tetraaminedichlorochromium(III) complexes are two or more orders of magnitude smaller than their Co(III) analogues.[6,107,108] Therefore, part of the lower extent of catalysis in Cr(III) complexes, compared to their Co(III) analogues, is due to the less favourable deprotonation step, since the conjugate base is destabilized with respect to the Co(III) analog, by the Cr–Cl π bonding. The reaction is further retarded by the weaker activating effect of the conjugate base on the Cr–Cl bond.

In comparing the reactivity patterns of analogous Co(III) and Cr(III) complexes towards base catalysis, it has been stated that "There has never been a satisfactory explanation of the leaving group effect which shows up well in the change in the k_{OH}^{Co}/k_{OH}^{Cr} ratio along the series for $[M(NH_3)_5X]^{2+}$, X = NO_3^- (500) > Cl (200) > Br^- (35) > I^- (1.6) and reaches a point where, in the iodo complexes, the reactivities of the two complexes are almost the same."[6] However, the arguments espoused in the previous paragraph offer a simple explanation of such reactivity trends. Since π bonding to the hard Cr(III) center is expected to decrease in the order $NO_3^- > Cl^- > Br^- > I^-$, both the conjugate base is expected to be stabilized down the series (more rapid proton exchange) and the labilizing effect of the Cr=NH_2 bond will increase in this order, and hence the rate of dissociation in the conjugate base. Therefore, these observations are entirely consistent with the π bonding arguments that are used throughout this review. They are also consistent with the greater degree of base catalysis (i.e., the ratio of the base-catalysed and spontaneous rate constants) in the same series,[6] which increases with the π bonding ability of the leaving group to Cr(III) (i.e., the ratios are 15, 196, 690 and 3700, for NO_3^-, Cl^-, Br^- and I^-, respectively).

Another important factor in differentiating the base catalysis behaviour of Co(III) and Cr(III) is the effect of steric bulk. Tobe has alluded to the smaller steric factors for Cr(III) being a reason for the observed differences,[6] but these have not been quantified until recently.[34] Our molecular mechanics calculations support this notion (Table VII), where the difference in the release of strain energy is larger for Co(III) in comparison to Cr(III).[34] When this difference is combined with the extra energy required to stretch the shorter Cr–Cl bond in the $[Cr(NH_2R)_5Cl)Cl_2$ complexes (R = CH_3, CH_2CH_3)[34,38] of 17 kJ mol^{-1},[32] the difference in the ratios of $k_{OH}(H):k_{OH}(CH_3):k_{OH}(CH_2CH_3)$ for Co(III) and Cr(III) is in good quantitative agreement with the molecular mechanics calculations (Table VII) in terms of a common mechanism. This is strong support for a common D_I mechanism for the base-catalyzed substitution rates of the Co(III) and Cr(III) complexes.

The notion of a common mechanism for the base-hydrolysis of $[M^{III}(NH_3)_5L]^{n+}$ (M = Co, Cr) is also supported by competition experiments with azide in the base hydrolysis of $[M(NH_3)_5(OSO_2CF_3)]^{2+}$, where the competition ratios for the capture of azide are identical within experimental error for the Co(III) and Cr(III) complexes.[83] It is difficult to reconcile this result if the mechanisms are not the same and the lifetimes of the intermediates are not similar. When competition studies were performed with the more sterically hindered system, i.e., $[Cr(NH_2CH_3)_5(OSO_2CF_3)]^{2+}$, the competition ratio for azide increased by a factor of 1.4 over that observed for $[Cr(NH_3)_5(OSO_2CF_3)]^{2+}$, consistent with an increase in the lifetime of the five-coordinate intermediate.[83] The fact that this increase is not as large as that observed for the Co(III) analogues is probably a reflection of the smaller steric stabilization of the five-coordinate intermediate for the Cr(III) complexes. Unfortunately, there have been few reliable studies on the competition ratios for the intermediates produced in the base-catalyzed hydrolysis reactions of Cr(III), chiefly because of the interferences due to side-reactions during the course of such reactions,[55] but this is an area that needs to be pursued. In addition, it would be very interesting to be able to follow the steric course of the reactions for the base-catalyzed reactions of $[Cr^{III}(NH_2R)_5L]^{n+}$. Again complications brought about by loss of amine ligands and other side reactions can be negated if labile leaving groups such as $CF_3SO_3^-$ or weakly bound solvent ligands are used in such studies.

On the basis of much smaller volumes of activation for base-catalyzed substitution reactions of pentaamminechromium(III) catalyzed substitution reactions of pentaamminechromium(III) complexes, as compared to their Co(III) analogues, it has been proposed that an associative interchange conjugate base mechanism occurs for Cr(III).[94] By contrast, the volume of activation of $[Cr(NH_2CH_3)_5Cl]^{2+}$ is the same within experimental error as that observed for $[Co(NH_2CH_3)_5Cl]^{2+}$,[93,94] which is taken as evidence for the normal S_N1_{cb} mechanism operating in the more sterically hindered system.[94] While the latter conclusion appears to be reasonable, the conclusion that the reaction of the conjugate base in the mechanism for base-catalyzed hydrolysis of $[Cr(NH_3)_5Cl]^{2+}$ occurs via an I_d mechanism[94] is not compelling, for the reasons that have been outlined above. The differences in the observed volume changes for the Co(III) and Cr(III) pentaammine complexes may well have something to do with the geometry of the five-coordinate intermediate and the different solvent packing around different intermediates. What stereochemical evidence that is available suggests that the intermediate in the case of Cr(III) is square pyramidal, whereas those for Co(III) are trigonal bipyramidal.[55] A square pyramidal geometry is likely to have the leaving group and or solvent weakly associated in the sixth site and, therefore, the volume of activation would be expected to be smaller. By contrast the more sterically hindered tetrakis(methylamine)-(methylaminato(1-))chromium(III) intermediate is more likely to adopt a trigonal bipyramidal geometry.

There has been less work done on the base hydrolysis of the Rh(III) and Ir(III) analogues. The results that have been obtained show clearly that the extent of base-catalysis is much less than for their Co(III) analogues. There appear to be at least four reasons for this observation:

(i) The deprotonation preequilibrium becomes less favourable down the series, which results in a smaller degree of acceleration at a given pH.[6]
(ii) These ions are significantly larger[14] and therefore the relief of steric strain that is brought about by the formation of a five-coordinate intermediate is less.[34]
(iii) Since the ligand field strength increases down the group, the energy required to form a five-coordinate intermediate will increase down the group.[70,71]

(iv) The metal ions become softer down the group; therefore, the extent of π-bonding of the leaving group increases down the d^6 triad. This in turn will decrease the activating effect of the π bonding NR_2^- group on the M–X bond in the conjugate base.

The low level of azide competition for the putative five-coordinate intermediates generated from the base-hydrolysis of $[Rh(NH_2R)_5(OSO_2CF_3)]^{2+}$ (M = H, CH_3) shows that if true intermediates are formed, their lifetimes are very short-lived. This is supported by the molecular mechanics calculations, which show that the observed differences in activation energy between the amine and methylamine or ethylamine complexes are much smaller than those calculated.[34] Thus, either a five-coordinate intermediate is not formed, or it is too short-lived to undergo significant rearrangement before it captures an incoming nucleophile. It is likely that similar situations apply for the Ir(III) complexes. This would mean that the elementary step within the S_N1_{cb} mechanism that involves the conversion of the conjugate base to a five-coordinate intermediate or transition state is on the borderline of the I_d and D_I mechanisms.

In summary, all of the kinetic data indicate that a similar mechanism applies in the base-hydrolysis of the pentaamine complexes of Cr(III), Co(III), Rh(III) and Ir(III). The only likely differences are the lifetimes of the intermediates and their geometries, which can be semi-quantitatively rationalized in terms of steric effects and ligand field contributions.

In the spontaneous aquations of pentaammineruthenium(III) complexes, we have postulated that there is a preequilibrium between water and the complex which enables the reactions to occur via parallel I_d and A mechanisms (Scheme 1). Although it appears that the I_d mechanism predominates at room pressure, it is expected that competing mechanisms would also apply in the case of base catalysis. In this instance, there would be competition between the A mechanism, in which OH^- acts as a nucleophile, and the S_N1_{cb} mechanism (Scheme 3). In light of the known disproportionation chemistry of Ru(III),[109,110] a third mechanistic pathway which involves such a reaction to generate catalytic amounts of a Ru(IV) complex, as a first step, could contribute to the ob-

$$[\mathrm{Ru(NH_3)_5Cl}]^{2+} + \mathrm{OH} \underset{}{\overset{K_1}{\rightleftharpoons}} [\mathrm{Ru(NH_3)_5(OH)Cl}]^{+}$$

$$[\mathrm{Ru(NH_3)_5(OH)Cl}]^{+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Ru(NH_3)_5(OH)}]^{2+} + \mathrm{Cl}^{-}$$

$$[\mathrm{Ru(NH_3)_5X}]^{n+} + \mathrm{OH}^{-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{Ru(NH_3)_4(NH_2)X}]^{(n-1)+} + \mathrm{H_2O}$$

$$[\mathrm{Ru(NH_3)_4(NH_2)X}]^{(n-1)+} \xrightarrow{k_4} [\mathrm{Ru(NH_3)_4(NH_2)}]^{2+} + \mathrm{X}^{(3-n)-}$$

$$[\mathrm{Ru(NH_3)_4(NH_2)}]^{2+} + \mathrm{H_2O} \xrightarrow{\text{fast}} [\mathrm{Ru(NH_3)_4(NH_2)(OH_2)}]^{2+}$$

$$[\mathrm{Ru(NH_3)_4(NH_2)(OH_2)}]^{2+} \xrightarrow{\text{fast}} [\mathrm{Ru(NH_3)_5(OH)}]^{2+}$$

SCHEME 3

served base-catalysis. Since both the Ru(IV) and Ru(II) oxidation states are more labile than Ru(III), this could lead to the observed base-catalysis. This proposition has been tested by the addition of oxidant to the solution during the kinetic procedure.[40] Ce(IV) and O_2 have no effect on the rate constant, but aging of the solutions for several hours or the addition of $[\mathrm{Ru^{IV}Cl_5OH}]^{2-}$ or ruthenium red gave increased hydrolysis rates when added at concentrations of 10^{-5} and 10^{-4} M, respectively.[40] The latter experiments suggest a possible role for disproportionation in catalyzing such reactions; however, in the absence of such additional catalysis, the activation parameters for the base-catalysed aquation of $[\mathrm{Ru(NH_3)_5Cl}]^{2+}$ (large value of $\Delta H^{\ddagger}$ and large positive value of $\Delta S^{\ddagger}$)[40] are consistent with those observed for other S_N1_{cb} mechanisms. The relatively low enthalpy of activation and the moderately negative entropy of activation found in subsequent studies are more consistent with the *A* mechanism, despite the fact that a similar value was obtained for the second order rate constant at 25°C.[96] It seems difficult to reconcile these two contradictory sets of values, but the answer may lie in a competing second order reaction which interferes with the base-catalyzed hydrolysis reaction.[6,111] It is possible that one set of data was obtained for the true base-catalyzed hydrolysis and the other inadvertantly for side reactions. One way to distinguish between the three possible mechanisms is to perform experiments in the presence of other good nucleophiles and to do the isotopically labelled experiments that will enable water and OH^- to be distinguished as an entering group. In the competition experiments, the rate constant of a reaction, as well as the competition ratio, will be affected when the concentration or nature of the nucleophile is altered if an *A* mechanism predominates. By contrast, the rate constant will be independent of the concentration and nature of the nucleophile if the S_N1_{cb} mechanism predominates. This is an area which needs to be investigated further.

It would also be of interest to study the rates and mechanisms of the base-hydrolysis reactions of the complexes, $[Ru^{III}(NH_2R)_5X]^{n+}$. Such reactions will be complicated by the base-catalysed disproportionation of the Ru(III) complexes, with subsequent oxidative dehydrogenation of the ligands.[62,63] However, the base-catalysed substitution reaction is likely to be faster than the disproportionation reaction, since studies with oxidizable amine ligands have been reported.[6,95] Studies on Ru(III) complexes with good leaving groups, such as triflate, should enable reliable data to be obtained which is free from such complications. If the *A* mechanism operates, then such a substitution reaction will be inhibited by the bulky ligand, but acceleration will be expected in the S_N1_{cb} mechanism. This is another area that we hope to pursue in the near future.

CONCLUSIONS

We have outlined, in qualitative and semi-quantitative arguments, how changes in solvation, leaving group, electronic factors, steric factors and π bonding can influence the minimum energy transition state in an aquation reaction and the lifetime of intermediates in the base-catalysed reactions. In summary, there are several points that are general to the analysis of the mechanisms of substitution reactions:

(i) The electronic structures and the sizes of the central metal ions are not as important in determining the mechanism of spontaneous substitution reactions as previously thought, but are only two of several important factors.

(ii) Solvation effects are likely to be the overriding factor in controlling the mechanism of spontaneous substitution reactions with charged leaving groups.

(iii) The mechanisms of spontaneous substitution reactions involving neutral leaving groups will be much more sensitive to factors such as electronic configuration and size of the ion. The mechanisms of such substitution reactions can vary widely over the mechanistic coordinate for related complexes with different metal ions.

(iv) The mechanisms of spontaneous substitution reactions of metal ions such as Cr(III) may vary over most of the mechanistic coordinate, depending on a number of factors. In the case of aquations of Cr(III) complexes with charged leaving groups, such as Cl^-, the mechanisms almost certainly lie in the I_d region of the mechanistic continuum, and near the dissociative limit. However, other mechanisms can lie in the I_a region of the mechanistic continuum depending on a number of factors including the leaving group, solvent, steric interactions, etc.

(v) The base-catalysed substitution reactions of the pentaammine complexes of Cr(III), Co(III), Rh(III) and Ir(III) all appear to occur via similar mechanisms of substitution (S_N1_{cb}), but they differ in both the lifetimes and the geometries of the intermediates. These differences can occur between analogous complexes with different metal ions and between different complexes of the same metal ion. For analogous complexes, the lifetimes of the intermediates decrease in the order Co(III) > Cr(III) > Rh(III) > Ir(III). The quite different degrees of base-catalysis in analogous complexes of different metal ions are readily explained when the factors of Bronsted acidity of the amine ligands, π-bonding of the leaving group, steric interactions and ligand field interactions are considered.

(vi) In the case of the base-catalysed hydrolysis of Ru(III) and Os(III) complexes, a great deal more work needs to be completed. From the limited data that is available, the kinetic results could be interpreted in terms of either an A, an S_N1_{cb}, or a disproportionation-catalysed mechanism.

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