A Common Dissociative Interchange (I_d) Mechanism for the Aquations of Penta-aminechloro-cobalt(III) and -chromium(III) Complexes

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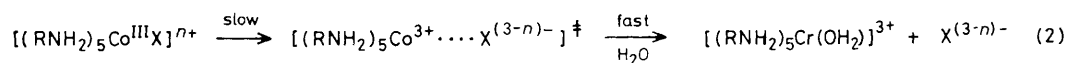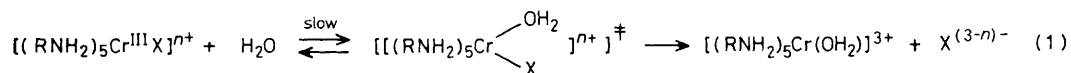
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The rate of aquation of $[Cr(NH_2Me)_5Cl]^{2+}$ is slower than that of $[Cr(NH_3)_5Cl]^{2+}$ because of a shorter Cr–Cl bond in the ground state of $[Cr(NH_2Me)_5Cl]^{2+}$, which is consistent with an I_d mechanism.

The currently accepted mechanism of the spontaneous substitution reactions of chromium(III)–amine complexes is an associative interchange mechanism (I_a, reaction 1). By contrast, that operating for the cobalt(III)–amine complexes is believed to be a dissociative interchange mechanism (I_d, reaction 2).[1] However, recent results on the aquation reactions of $[M(NH_2R)_5(OSO_2CF_3)]^{2+}$ have indicated that bond

breaking substantially precedes bond making in the substitution reactions of both Co^{III} and Cr^{III} (*i.e.* an I_d mechanism is operative for the substitution reactions of both metal ions).[2] In this communication, the assumptions behind another of the 'definitive' experiments by which a mechanistic difference between Co^{III} and Cr^{III} has been assigned, are refuted.

It has been argued often that one of the most compelling

$$[(RNH_2)_5Cr^{III}X]^{n+} + H_2O \;\underset{}{\overset{slow}{\rightleftharpoons}}\; [[(RNH_2)_5Cr{\overset{OH_2}{\underset{X}{\big<}}}]^{n+}]^{\ddagger} \longrightarrow [(RNH_2)_5Cr(OH_2)]^{3+} + X^{(3-n)-} \quad (1)$$

$$[(RNH_2)_5Co^{III}X]^{n+} \;\overset{slow}{\longrightarrow}\; [(RNH_2)_5Co^{3+}\cdots X^{(3-n)-}]^{\ddagger} \;\underset{H_2O}{\overset{fast}{\longrightarrow}}\; [(RNH_2)_5Cr(OH_2)]^{3+} + X^{(3-n)-} \quad (2)$$

pieces of evidence supporting an I_a mechanism for the substitution reactions of Cr^{III} complexes is that the rate of aquation of $[M(NH_2R)_5Cl]^{2+}$ is retarded in going from R = H to a more bulky alkyl group.[1,3] This is especially the case since the rate is accelerated by the introduction of steric bulk in the Co^{III} analogues[2,4] (where there is little dispute that an I_d mechanism is operative). Thus, the rate constant of aquation at 25 °C is 33 times smaller for $[Cr(NH_2Me)_5Cl]^{2+}$ than it is for $[Cr(NH_3)_5Cl]^{2+}$, but is 22 times larger for $[Co(NH_2Me)_5Cl]^{2+}$ than it is for $[Co(NH_3)_5Cl]^{2+}$. It has been assumed previously that these kinetic differences reflected differences in the activated states of the two metal ions during their substitution reactions. However, recent crystallographic evidence[5] indicates that these kinetic differences are due mainly to differences in the ground states, as discussed below.

This new evidence comes from the somewhat surprising result that the Cr–Cl bond observed in the structure of $[Cr(NH_3)_5Cl]Cl_2$[5] [2.327(1) Å] is significantly longer than that observed in the structure of the more sterically hindered $[Cr(NH_2Me)_5Cl]Cl_2$ [2.299(1) Å].[6] This result was totally unexpected because the Co–Cl bond lengths in $[Co(NH_2-Me)_5Cl](NO_3)_2$ [2.283(1) Å][6] and $[Co(NH_3)_5Cl]Cl_2$ [2.286(2) Å][7] are the same, within experimental error. In fact, the Cr–Cl bond length in the methylamine complex is much closer to a Co–Cl bond length than to the Cr–Cl bond length observed in the ammine complex. Therefore, the retardation of the rate of aquation of $[Cr(NH_2Me)_5Cl]^{2+}$ as compared to $[Cr(NH_3)_5Cl]^{2+}$ is explained readily within the framework of an I_d mechanism, since more energy is required to stretch the Cr–Cl bond in $[Cr(NH_2Me)_5Cl]^{2+}$ to a certain point near the dissociative limit than for the same bond in $[Cr(NH_3)_5Cl]^{2+}$. Consistent with this notion is that the enthalpy of activation for the aquation reaction of the methylamine complex is 17 kJ mol^{-1} greater than for the corresponding ammine complex.[3,8] This is to be contrasted with a difference of only 2 kJ mol^{-1} for the cobalt analogues,[3] where the bond lengths are virtually the same. Further, the differences in the entropies of activation for the methylamine and ammine complexes are about the same ($\sim$30 J K^{-1} mol^{-1}) for both metal ions, which militates against a change in mechanism. The acceleratory effect observed in the Co^{III} complexes on the introduction of steric bulk is due to an entropy effect (probably solvational in origin[8]). This same acceleratory effect exists for the Cr^{III} analogues, but is more than counterbalanced by the increase in the enthalpy term for the $[Cr(NH_2Me)_5Cl]^{2+}$ complex, which is due to the shortening of the Cr–Cl bond with respect to that observed in $[Cr(NH_3)_5Cl]^{2+}$. These results are entirely consistent with a common I_d mechanism and dispel the arguments which attribute the rate constant differences as being due to mechanistic changes.

The reasons for the different Cr–Cl bond lengths probably arise from the effects of π-bonding and the differing ionic radii of Co^{III} and Cr^{III}. Single crystal X-ray studies on the isomorphous series $[M(NH_3)_5Cl]Cl_2$ have provided evidence for a much greater degree of π-bonding in the M–Cl bond within the Cr^{III} complex than that within the Co^{III} complex[5] (which is to be expected on the grounds of their electronic configurations). The effect of the bulky methylamine ligands is to lengthen the M–N bonds as compared to those in the ammine complexes, in order to relieve steric clashes between neighbouring ligands.[5—7] This enables the the Cr–Cl bond to shorten and, thus, increase both its σ- and π-bonding. Consistent with an increase in π-bonding is that the average Cl–Cr–N(cis) bond angle increases slightly (0.4°) in going from the ammine to the methylamine complex. By contrast, the same angle in the cobalt analogues closes (1°) in order to relieve steric interactions between the methylamine ligands,

thus adding strain on the Co–Cl bond. This effect appears to counterbalance the expected shortening of the Co–Cl bonds due to lengthening of the Co–N bonds, in the methylamine complex. Thus, the differences between the structures of the complexes for the two metal ions is probably a function of the greater importance of π-bonding for the Cr^{III} complexes and the smaller ionic radius of Co^{III} as compared to Cr^{III}. Although the bond length evidence relates to the solid state, it is likely that these differences will carry over into solution, because the arguments for the differences are the same no matter whether the compound is in the solid state, or in solution.

A further point to note is that the π-bonding in the Cr–Cl bonds will inhibit an I_a mechanism, because any incoming nucleophile would have to interact with d-orbitals already involved in π-bonding (in order to attack in a position cis to the leaving group). Such a cis-attack to form the seven-coordinate intermediate would be required in order to explain the stereoretentive nature of Cr^{III} aquation reactions.[9] Thus, an associative interchange mechanism is retarded as much in the d^3 Cr^{III} complexes as in the d^6 Co^{III} complexes, in terms of the availability of empty d-orbitals which can participate in bond making. Further, the steric requirements of the Cr–Cl multiple bonds[5] would tend to negate the arguments that the larger Cr^{III} ion is more able to undergo aquations via an I_a mechanism than are the Co^{III} analogues.

Finally, the activation volume, $\Delta V^{\ddagger}$, increases by 7.6 cm^3 mol^{-1} in going from $[Co(NH_3)_5Cl]^{2+}$ to $[Co(NH_2-Me)_5Cl]^{2+}$, while the corresponding increase in the Cr^{III} complexes is 11.1 cm^3 mol^{-1}.[3] It is reasonable to assume that the 7.6 cm^3 mol^{-1} difference in the cobalt complexes corresponds to the same factors that give rise to the increase in the entropy.[10] If a common I_d mechanism were to apply, the additional 3.5 cm^3 mol^{-1} observed for the chromium complexes is consistent with the shorter Cr–Cl bond length in $[Cr(NH_2Me)_5Cl]^{2+}$ as opposed to $[Cr(NH_3)_5Cl]^{2+}$ {$i.e.$ the Cr–Cl bond in $[Cr(NH_2Me)_5Cl]^{2+}$ has to stretch more than that in $[Cr(NH_3)_5Cl]^{2+}$, hence, the more positive value of $\Delta V^{\ddagger}$}. Further, the similarity in the value of the compressibility coefficients of activation[3] ($\beta^{\ddagger}$ $\sim$0 cm^3 kbar^{-1} mol^{-1}), militates against a change in mechanism for the pentakis-(methylamine) complexes. Therefore, all the activation parameter data point to a common I_d mechanism in the aquations of the $[M(NH_2R)_5Cl]^{2+}$ ions, M = Co, Cr.

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