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Evidence for Bond Breaking Substantially Preceding Bond Making in the Mechanisms of Spontaneous Aquations of Penta-aminechloro-chromium(III), -cobalt(III), and -rhodium(III) Complexes: Crystal and Molecular Structure of Chloropentakis(methylamine)rhodium(III) Chloride

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The Rh–Cl bond is 0.017(2) Å shorter in the crystal structure of $[Rh(NH_2Me)_5Cl]Cl_2$ than in the structure of $[Rh(NH_3)_5Cl]Cl_2$; when combined with the corresponding differences of 0.003(3) Å for Co^{III} and 0.028(2) Å for Cr^{III}, this explains the trends in the substitution kinetics of these complexes, without a need to invoke changes in mechanisms.

When the rates of the spontaneous aquations of $[M(NH_2Me)_5Cl]^{2+}$ and $[M(NH_3)_5Cl]^{2+}$ are compared, the ratio of the rate constants for chloride substitution [*i.e.* $k(NH_2Me):k(NH_3)$] are 22, 0.5, and 0.030, respectively for Co, Rh, and Cr at 25 °C. This has been one of the keystones in assigning mechanistic differences between the substitution reactions of Co^{III}, Rh^{III}, and Cr^{III}.[1—4] It has been argued that the rate constant should increase on adding steric bulk to the amine ligands for a mechanism in which bond breaking substantially precedes bond making. The rationale for this is that steric strain is relieved in an activated state of lower co-ordination number relative to the ground state.[1,3] Thus, the observed ratio of rate constants for Co^{III} has been used to support such a mechanism. By contrast, the decrease in the rate constant observed for $[Cr(NH_2Me)_5Cl]^{2+}$ as compared to that observed for $[Cr(NH_3)_5Cl]^{2+}$ has been interpreted as providing strong evidence for a mechanism in which bond making precedes bond breaking.[1,2] The rhodium(III) complexes have intermediate behaviour and, accordingly, it has been claimed that the mechanism is intermediate between those in operation for Co^{III} and Cr^{III}.[4] In arriving at these conclusions, it was reasonably assumed that because the structures of $[Co(NH_3)_5Cl]Cl_2$[5] and $[Co(NH_2Me)_5Cl](NO_3)_2$[6] exhibited Co–Cl bond lengths that were the same, within experimental error, that the same would apply for the structures of the Cr^{III} and Rh^{III} analogues.[1] The corollary was that any differences in the series for the ratios of rate constants and activation parameters would reflect mechanistic (activated states) rather than ground state differences. However, the recently determined structure of $[Cr(NH_3)_5Cl]Cl_2$[7] provided strong evidence that the assumptions on which the above conclusions were made are spurious.[8,9] Thus, it was found that the Cr–Cl bond in $[Cr(NH_3)_5Cl]Cl_2$[7] is 0.028 Å longer than that in $[Cr(NH_2Me)_5Cl]Cl_2$.[8] This led to the conclusion that the observed differences in the ratios of $k(NH_2Me):k(NH_3)$ were due to ground state properties rather than due to differences in the activated states.[8,9] If this conclusion were also valid for the Rh analogues, then the Rh–Cl bond length in $[Rh(NH_2Me)_5Cl]Cl_2$ would be expected to be shorter than that of 2.356(1) Å in $[Rh(NH_3)_5Cl]Cl_2$.[10] In addition, the difference should be less than the difference in the bond lengths observed in the chromium analogues, in order to accommodate the ratios of $k(NH_2Me):k(NH_3)$. For these reasons, we undertook a precise *X*-ray crystal structure analysis of $[Rh(NH_2Me)_5Cl]Cl_2$.

$[Rh(NH_2Me)_5Cl]Cl_2$ was prepared in 80% yield from $RhCl_3{\cdot}3H_2O$[11] using a method similar to that published for the synthesis of $[Rh(NH_3)_5Cl]Cl_2$.[12] Suitable crystals were grown by slowly cooling a hot aqueous 0.001 M-HCl solution of the complex. The structure is isomorphous with the chromium analogue[6] and an ORTEP view of $[Rh(NH_2Me)_5Cl]^{2+}$ is given in Figure 1.† All hydrogen atoms were located and refined. The Rh–Cl bond length of 2.339(1) Å is 0.017(2) Å shorter than the Rh–Cl bond in $[Rh(NH_3)_5Cl]Cl_2$.[10] This is what was predicted from the ratios of $k(NH_2Me):k(NH_3)$ in the series Co^{III}, Rh^{III}, and Cr^{III}, on the basis of a common mechanism applying in which bond breaking substantially precedes bond making. As was observed in the other complexes containing the methylamine ligands,[6] the steric strain in $[Rh(NH_2Me)_5Cl]^{2+}$ is relieved by a lengthening of the average Rh–N bond by 0.03 Å as compared to that observed in $[Rh(NH_3)_5Cl]^{2+}$.[10]

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† *Crystal data:* $C_5H_{25}Cl_3N_5Rh$, $[Rh(NH_2Me)_5Cl]Cl_2$, $M = 364.6$, monoclinic, space group $P2_1/c$, $a = 11.486(3)$, $b = 8.084(2)$, $c = 15.244(6)$ Å, $\beta = 93.11(2)°$, $D_x = 1.713$ g cm^{-3}, $U = 1413.4(7)$ Å^3, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 16.91$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å. Reflections were measured ($2° < 2\theta < 55°$) on an Enraf–Nonius CAD4-F four-circle diffractometer. The structure was solved by analogy with the isostructural chromium complex and refined by full-matrix least-squares methods to an R value of 0.026 on 2794 F [$I > 2.5\sigma(I)$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1

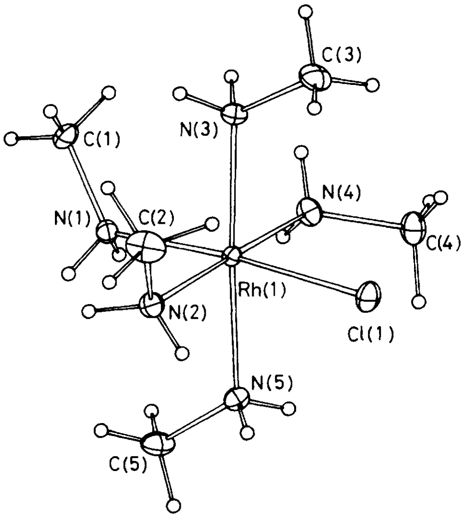

Figure 1. ORTEP drawing of the $[Rh(NH_2Me)_5Cl]^{2+}$ cation. Selected bond lengths: Rh–Cl 2.339(1), Rh–N(1) 2.091(2), Rh–N(2) 2.083(3), Rh–N(3) 2.091(2), Rh–N(4) 2.081(3), Rh–N(5) 2.089(3) Å.

The observation that $\Delta H^‡$ is equal within experimental error for $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_2Me)_5Cl]^{2+}$, but is significantly greater for $[Cr(NH_2Me)_5Cl]^{2+}$ than for $[Cr(NH_3)_5Cl]^{2+}$,[1—3] supports the inference that the kinetic differences between Co^{III} and Cr^{III} are dominated by ground state effects {*i.e.* the M–Cl bond in the ground state of $[M(NH_2Me)_5Cl]^{2+}$ strengthens relative to that of $[M(NH_3)_5Cl]^{2+}$ as one goes from Co^{III} to Cr^{III}}.[8,9] The case is not as clear cut for Rh^{III} as $\Delta H^‡$ is also equal for the two complexes.[4] However, solvent contributions to $\Delta H^‡$ are dependent on the nature of the amine ligand and on the radii of the complexes.[9] When the corrections for solvation are made,[9] the ratio, $\Delta H^‡$ (NH_3) : $\Delta H^‡$ (NH_2Me) is expected to increase in the order $Cr^{III} < Rh^{III} < Co^{III}$.

The shortening of the Cr–Cl bond in $[Cr(NH_2Me)_5Cl]^{2+}$ as compared with that in $[Cr(NH_3)_5Cl]^{2+}$ was rationalized in terms of an increase in π-bonding within the Cr–Cl bond.[8,9] This argument is consistent with the observation that the shortening for Rh^{III} is intermediate between that observed in the Co^{III} and Cr^{III} complexes, since the order of the strength of π-bonding is $Co^{III} < Rh^{III} < Cr^{III}$.[7] In addition, molecular mechanics calculations[13] do not predict the observed shortening of the M–Cl bonds in $[M(NH_2Me)_5Cl]^{2+}$, but these calculations do not allow for changes in π-bonding. Rather the molecular mechanics calculations predict a lengthening of the M–Cl bonds in all cases.

These results illustrate the problems of assigning reaction mechanisms on the basis of differences in rate constants when changes in the ground state properties of the reactants are not taken into consideration. It is clear from these, and other studies,[14] that the spontaneous substitution mechanisms of penta-amine complexes of Co^{III}, Rh^{III}, and Cr^{III} are more similar than is generally believed. On the balance of evidence the penta-amine complexes of all three metal ions undergo substitution reactions *via* mechanisms in which bond breaking substantially precedes bond making. We are currently attempting to semi-quantify the bond length changes observed in the ground state with the appropriate activation parameters on the basis of this common mechanism.

The above analysis applies only to leaving groups which have a substantial degree of π-bonding. It is likely that there are greater mechanistic differences in the substitution reactions of $[M(OH_2)_6]^{3+}$ and, in particular, $[M(NH_3)_6]^{3+}$, within this series of metal ions.[9]

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