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cis-Activation by the Nitrato-ligand in Amminechromium(III) Ions

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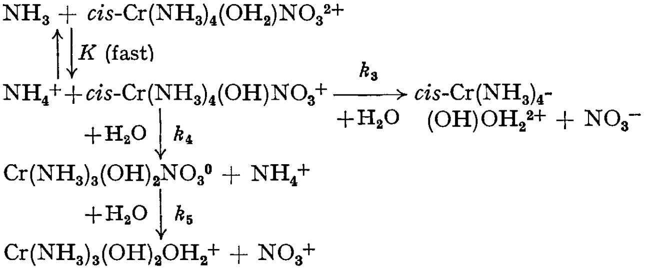
Summary Nitrato-ligands in Cr^{III} ammines strongly accelerate the aquation of NH_3 ligands in the *cis*-positions.

WE have found, by use of cation-exchange chromatography and specific NH_4^+ and NO_3^- ion electrodes, that the spontaneous thermal aquation of $Cr(NH_3)_5NO_3^{2+}$ ion in 0·1M-NH_4ClO_4 (pH 6) at 25° yields 100 ± 5% of NO_3^- as expected, but only 34% of $Cr(NH_3)_5OH^{2+}$; the other products are NH_4^+ (100 ± 10%), *cis*-$Cr(NH_3)_4(OH)OH_2^{2+}$ (35%) (but none of the *trans*-isomer), and a mixture of *fac*- and *mer*-$Cr(NH_3)_3(OH)_2OH_2^+$.

The spectrum (260—700 nm) of the $Cr(NH_3)_5NO_3^{2+}$ solution changed during aquation in accordance with the formation of these products; isosbestic points were precisely maintained, and the rate of change of optical absorbance at 275, 400, and 560 nm showed that the rate of disappearance of $Cr(NH_3)_5NO_3^{2+}$ was accurately first-order in $[Cr(NH_3)_5NO_3^{2+}]$, with rate coefficient $k(NO_3) = (2·4 \pm 0·1) \times 10^{-3}$ s^{-1}. The rates of formation of free NO_3^- and NH_4^+ ions yielded this same rate coefficient, within the experimental uncertainty. The pH remained constant at *ca.* 6 because acidic aquo-ligands were being introduced concomitantly with NH_3 release.

The complexes $Cr(NH_3)_5OH_2^{2+}$ and *cis*-$Cr(NH_3)_4(OH)OH_2^{2+}$ were found not to aquate significantly in 0·1M-perchlorate media (pH 6) at 25° over a period greater than 10 half-lives of the $Cr(NH_3)_5NO_3^{2+}$ aquation (and were not significantly affected by our ion-exchange procedure), while the aquations of $Cr(NH_3)_5Br^{2+}$ and $Cr(NH_3)_5I^{2+}$ yield *exclusively* $Cr(NH_3)_5OH^{2+}$ and halide ion under comparable conditions over even longer periods.[1,2] Thus, the observed characteristics of the aquation of $Cr(NH_3)_5NO_3^{2+}$ constitute clear evidence for a strong activation of ligands *cis* to a nitrato-ligand in Cr^{III} complexes. The aquations of $Cr(NH_3)_5F^{2+}$ and $Cr(NH_3)_5Cl^{2+}$ do involve some ammonia release,[3] but this is because the rates of replacement of F and Cl by H_2O are comparable with the rate of ammonia aquation of, *e.g.*, $Cr(NH_3)_6^{3+}$ to $Cr(NH_3)_5OH_2^{3+}$ ($k = 8 \times 10^{-5}$ s^{-1} at 75° in 0·5 M-$HClO_4$ for all six ammine ligands)[4] and not because of activation by F or Cl.

These observations are consistent with the following Scheme, in which $k_1 = 0·8 \times 10^{-3}$ s^{-1}, $k_2 = 1·6 \times 10^{-3}$ s^{-1}, and k_3, k_4, and k_5 are assumed to be high (with k_3/k_4 *ca.* 1·1); this assumption is consistent with the observation[5] that a pathway with inverse $[H^+]$ dependence is detectable in the aquation of $Cr(H_2O)_5NO_3^{2+}$ even in the pH range 0—1.



SCHEME

At pH 6, the equilibrium K will lie almost entirely toward the presumably labile ion *cis*-$Cr(NH_3)_4(OH)NO_3^+$ (pK_a estimated to be *ca.* 5—6), and the rate of aquation of $Cr(NH_3)_5NO_3^{2+}$ will be controlled by k_1 and k_2 alone and is therefore cleanly first-order. However, in 0·1M-$HClO_4$, *cis*-$Cr(NH_3)_4(OH)NO_3^+$ formation will be greatly suppressed, and the slow step k_2 should be followed by the further *slow* aquation of *cis*-$Cr(NH_3)_4(OH_2)NO_3^{2+}$ to *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$ and $Cr(NH_3)_3(NO_3)(OH_2)_2^{2+}$, if *cis*-activation by the nitrato-ligand is again operative; the last-named species should in turn slowly yield $Cr(NH_3)_3(OH_2)_3^{3+}$ isomers. Indeed, we observed that the products of the aquation at pH 1 were essentially the same as at pH 6, but isosbestic points were *not* maintained, and the spectrophotometric reaction rate was slower overall and *not* first-order, being instead indicative of a series of at least two consecutive slow reactions operating concurrently with the process k_1, exactly as the above Scheme requires. Our results confirm and explain Monacelli's observations[6] that the spectrophotometric rate of disappearance of $Cr(NH_3)_5NO_3^{2+}$ is depressed by increasing $[H^+]$ and deviates considerably from first-order in $[Cr(NH_3)_5NO_3^{2+}]$ at high acidities.

We believe that simple substitutions at Cr^{III} centres occur by associative (I_a or S_N2) mechanisms,[1] and therefore suggest that the stereospecific expulsion of *cis*-ligands by the nitrato-group in Cr^{III} complexes may occur *via* an associative ring-closure process leading to a transiently bidentate nitrato-complex. This could operate equally well with other potentially bidentate ligands such as sulphate, sulphite, carbonate, nitrite, or carboxylate. Thus, we have an explanation for numerous apparent anomalies in Cr^{III} co-ordination chemistry, such as labilization by the nitrito-ligand[7] and by carboxylate.[8] Similarly, the marked acceleration of the rate of decomposition of Cr^{III} ammines in aqueous nitrate,[9,10] sulphate[9] and sulphite[4] media *vis-à-vis* perchlorate or halide solutions[4,9] can be understood in terms of the formation of small amounts of the oxyaniono-complexes (perchlorate excepted, being a poor complexing agent); significantly, attempts to isolate salts of $Cr(NH_3)_5SO_4^+$ have so far failed.[4]

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