Hydrolysis of *cis*-Dichlorobis(bipyridyl)-cobalt(III) and -chromium(III) Ions, and of Their Phenanthroline Analogues with and without a Catalyst

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Summary Hydrolysis of the dichlorobis(bipyridyl)-cobalt(III) and -chromium(III) ions and their phenanthroline analogues is slow without a catalyst, but is fast in the presence of the corresponding metal(II) complexes: for the metal(III) complexes the hydrolysis is also base-catalysed, even though a conjugate base mechanism is not possible.

IN the literature there is a lack of agreement with regard to the rate of hydrolysis of *cis*-$[Co(N{-}N)_2Cl_2]^+$ [(N–N) = 2,2′-bipyridyl(bipy) or 1,10-phenanthroline (phen)]. Some authors state that the hydrolysis is fast,[1–5] others claim it to be more or less slow.[6–9] We report among other qualitative kinetic phenomena, the catalytic influence of small amounts of cobalt(II) complexes with the (N–N) ligands, thereby clarifying the situation.

Solutions of $[Co(N{-}N)_2Cl_2]^+$ in 0·01 M-hydrochloric acid or water are much more stable toward hydrolysis than the corresponding ethylenediamine complex, as shown by their visible spectra remaining unchanged for several hours; further, neither silver(I) nitrate nor mercury(II) acetate are able to cause a fast hydrolysis, while reducing agents and bases are.

Cobalt(II) chloride, added to the stable solutions of the chlorides of $[Co(N{-}N)_2Cl_2]^+$ in water (0·1 g to 15 ml.), has, in a test tube experiment, no apparent effect upon the rate of hydrolysis. However, the addition of minute amounts of one of the somewhat inert[4] bivalent cobalt(II) salts $Co(N{-}N)_2Cl_2$ or $Co(N{-}N)_3Cl_2$, results in immediate hydrolysis of $[Co(N{-}N)_2Cl_2]^+$ to $[Co(N{-}N)_2Cl(H_2O)]^{2+}$, and on longer standing at least some equilibration with regard to the heterocyclic ligand, giving rise to the formation of some $Co(N{-}N)_3{}^{3+}$ complex, takes place. This ion can be formed quickly and quantitatively from $Co(N{-}N)_2Cl_2{}^+$ by adding an excess of (N–N) ligand plus a little cobalt(II) chloride which acts as a catalyst through its immediate formation of $Co(N{-}N)_2Cl_2$ or $Co(N{-}N)_3Cl_2$.

In Pfeiffer's synthesis[2] of *cis*-$[Co(phen)_2Cl_2]Cl$ by treating the tris-salt under reflux with chloroform, the same type of catalysis occurs. Thus, the reaction does not take place with cobalt(II)-free $[Co(phen)_3]Cl_3$.

Since a conjugate-base mechanism is out of the question for the hydrolysis of the first chloride of $Co(N{-}N)_2Cl_2{}^+$ it is particularly interesting that treatment with base makes this hydrolysis fast. With the weak base ammonia only the first chloride is hydrolysed, while hydroxide ions also cause the second chloride to be hydrolysed. This latter reaction is extremely slow without catalysis.

These catalytic phenomena for cobalt(III) (N–N) systems are also valid for the corresponding chromium(III) systems. Only the chromium(III) systems are much less oxidizing[4] and therefore much less likely to be contaminated with chromium(II) systems. With amalgamated zinc in hydrochloric acid, $Cr(N{-}N)_2Cl_2{}^+$ and $Co(N{-}N)_2Cl_2{}^+$ behave analogously apart from the fact that the thermodynamically less stable chromium-to-chloride bonds become hydrolysed further than in the cobalt case.

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