# Abnormal Behaviour in the Acid Hydrolysis of an Octahedral Cobalt (III)-Amine Complex Cation in Aqueous Solution

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*Summary* Acid hydrolysis of *trans*-chloroammino-(1,4,8,11-tetra-azacyclotetradecane)cobalt(III) cation in aqueous solution leads abnormally to the release of the co-ordinated ammonia whereas the $Hg^{2+}$ ion-catalysed hydrolysis and the base hydrolysis of the same complex cation are normal with the release of the co-ordinated chloride.

IT is well known that co-ordinated ammonia in octahedral cobalt(III)-amine complexes is very stable with respect to substitution by other ligands in solutions. Thus, all the well studied substitution reactions of complexes of the type $[Co(NH_3)_5X]^{n+}$, (X = F, Cl, Br, I, AcO, $N_3$, NCS, $NO_2$, $H_2PO_4$, and $HC_2O_4$), and of the type *cis*- and *trans*-$[Co(en)_2NH_3X]^{2+}$ (en = ethylenediamine; X = Cl or Br) in aqueous solution only involve the release of the group X.[1] Release of $NH_3$ has not been observed under normal conditions; $[Co(NH_3)_5Cl]Cl_2$[2] and $[Co(en)_2NH_3Cl]Cl_2$[3] remain intact even in boiling hydrochloric acid solution for hours.

We noticed, however, that co-ordinated $NH_3$ is relatively unstable in cobalt(III) complexes containing various macrocyclic quadridentate secondary amines. When *trans*-

$[Co(cyclam)NH_3Cl]Cl_2$ was dissolved in 0·01M-$HClO_4$ (or $HNO_3$), (cyclam = 1,4,8,11-tetra-azacyclotetradecane), the visible absorption spectrum slowly changed, with isosbestic points at 467 and 590 nm. The final solution was green and its spectrum was consistent with the presence of a mixture of *trans*-$[Co(cyclam)Cl_2]^+$ and *trans*-$[Co(cyclam)ClOH_2]^{2+}$. A green precipitate of *trans*-$[Co(cyclam)Cl_2]ClO_4$ was isolated from the cooled final solution. The same final green solution was obtained in the reaction with the nitrate salt. We infer, therefore, that $NH_3$ is released according to reactions (1) and (2). The first-order rate constant was

$$trans\text{-}[Co(cyclam)NH_3Cl]^{2+} + H_2O \xrightarrow{slow} trans\text{-}[Co(cyclam)OH_2Cl]^{2+} + NH_3 \quad (1)$$

$$trans\text{-}[Co(cyclam)OH_2Cl]^{2+} + Cl^- \overset{fast}{\rightleftharpoons} trans\text{-}[Co(cyclam)Cl_2]^+ + H_2O \quad (2)$$

estimated to be $2 \times 10^{-5}\,s^{-1}$ at 74 °C. This aquation is *ca.* 20 times slower than that of *trans*-$[Co(cyclam)Cl_2]^+$ at the same temperature.[4]

This seemingly abnormal behaviour of *trans*-$[Co(cyclam)NH_3Cl]^{2+}$ in aqueous solution can be explained in terms of the influence of nephelauxetic effects of various amine ligands on the thermodynamic and kinetic stability of octahedral cobalt(III)–amine complexes. It has been pointed out that the central $Co^{III}$ ion in cyclam complexes would very much prefer negatively charged ligands, such as $Cl^-$ and $OH^-$, to neutral molecules, such as $NH_3$ and $OH_2$, than the corresponding bisethylenediamine and ammine complexes.[5] The relative stability of *trans*-$[Co(L)ClOH_2]^{2+}$ with respect to *trans*-$[Co(L)NH_3OH_2]^{3+}$ would, therefore, be expected to increase with L as follows: $(NH_3)_4 < (en)_2 <$ cyclam. Kinetically, the relative weakening of the Co–$NH_3$ bond with respect to the Co–Cl bond would also increase similarly with change of L.

In basic medium, however, $NH_3$ is not released and the system undergoes a normal base hydrolysis. This seems to indicate that the weaker Co–$NH_3$ bond in the ground state is replaced by the much stronger Co–$NH_2$ bond with the subsequent release of the chloride ligand in the transition state.

*trans*-$[Co(cyclam)NH_3Cl]^{2+}$, also behaves normally in acid medium when sufficient $Hg^{2+}$ has been added to the solution. Here the chloride ligand is converted into the much more labile leaving group, $-(ClHg)^+$.

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