

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

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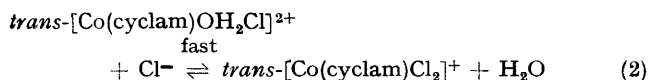
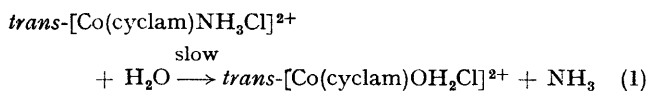
**Summary** Acid hydrolysis of *trans*-chloroammino-(1,4,8,11-tetra-azacyclotetradecane)cobalt(III) cation in aqueous solution leads abnormally to the release of the co-ordinated ammonia whereas the  $\text{Hg}^{2+}$  ion-catalysed hydrolysis and the base hydrolysis of the same complex cation are normal 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  $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ , ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{AcO}, \text{N}_3, \text{NCS}, \text{NO}_2, \text{H}_2\text{PO}_4$ , and  $\text{HC}_2\text{O}_4$ ), and of the type *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{NH}_3\text{X}]^{2+}$  ( $\text{en} = \text{ethylenediamine}; \text{X} = \text{Cl}$  or  $\text{Br}$ ) in aqueous solution only involve the release of the group X.<sup>1</sup> Release of  $\text{NH}_3$  has not been observed under normal conditions;  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ <sup>2</sup> and  $[\text{Co}(\text{en})_2\text{NH}_3\text{Cl}]\text{Cl}_2$ <sup>3</sup> remain intact even in boiling hydrochloric acid solution for hours.

We noticed, however, that co-ordinated  $\text{NH}_3$  is relatively unstable in cobalt(III) complexes containing various macrocyclic quadridentate secondary amines. When *trans*-

[Co(cyclam)NH<sub>3</sub>Cl]Cl<sub>2</sub> was dissolved in 0.01M-HClO<sub>4</sub> (or HNO<sub>3</sub>), (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<sub>2</sub>]<sup>+</sup> and *trans*-[Co(cyclam)-ClOH<sub>2</sub>]<sup>2+</sup>. A green precipitate of *trans*-[Co(cyclam)Cl<sub>2</sub>]ClO<sub>4</sub> 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<sub>3</sub> is released according to reactions (1) and (2). The first-order rate constant was



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

This seemingly abnormal behaviour of *trans*-[Co(cyclam)-NH<sub>3</sub>Cl]<sup>2+</sup> 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<sup>III</sup> ion in cyclam complexes would very much prefer negatively charged ligands, such as Cl<sup>-</sup> and OH<sup>-</sup>, to neutral molecules, such as NH<sub>3</sub> and OH<sub>2</sub>, than the corresponding bisethylenediamine and ammine complexes.<sup>5</sup> The relative stability of *trans*-[Co(L)ClOH<sub>2</sub>]<sup>2+</sup> with respect to *trans*-[Co(L)NH<sub>3</sub>OH<sub>2</sub>]<sup>3+</sup> would, therefore, be expected to increase with L as follows: (NH<sub>3</sub>)<sub>4</sub> < (en)<sub>2</sub> < cyclam. Kinetically, the relative weakening of the Co-NH<sub>3</sub> bond with respect to the Co-Cl bond would also increase similarly with change of L.

In basic medium, however, NH<sub>3</sub> is not released and the system undergoes a normal base hydrolysis. This seems to indicate that the weaker Co-NH<sub>3</sub> bond in the ground state is replaced by the much stronger Co-NH<sub>2</sub> bond with the subsequent release of the chloride ligand in the transition state.

*trans*-[Co(cyclam)NH<sub>3</sub>Cl]<sup>2+</sup>, also behaves normally in acid medium when sufficient Hg<sup>2+</sup> has been added to the solution. Here the chloride ligand is converted into the much more labile leaving group, -(ClHg)<sup>+</sup>.

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