Deprotonated Ruthenium(III) Hexa-ammine and its Role in Aquation and Proton Exchange Reactions

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Summary The deprotonated ruthenium(III) hexa-ammine complex is characterized by its absorption spectrum; its formation equilibrium constant is reported and its role in aquation and proton transfer reactions is discussed.

DEPROTONATED species of hexa-ammine complexes of transition-metal ions have been discussed as possible intermediates in base-catalysed substitution reactions of the complexes.[1] Except for the quadrivalent platinum complex[2] their existence has not been demonstrated, probably because of their low formation constant. We report evidence for the existence of the deprotonated ruthenium(III) hexa-ammine in alkaline aqueous solutions, and its absorption spectrum and formation equilibrium constant.

A typical absorption spectrum of $Ru(NH_3)_6Cl_3$ solution which was made alkaline and that of an identical solution which was acidified back to pH 8 are shown in the Figure.

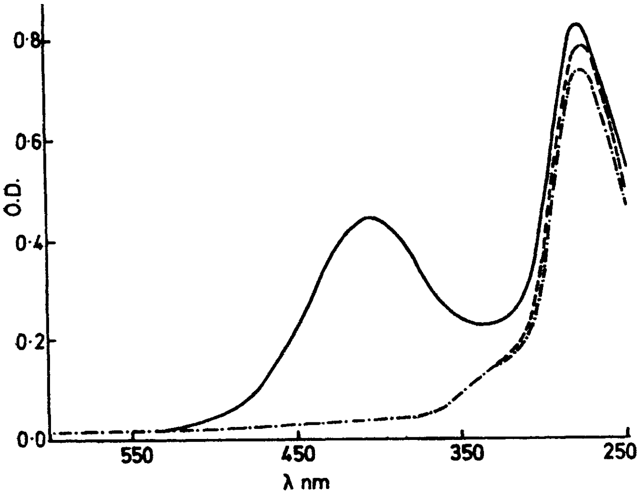

FIGURE. *Absorption spectra of* $Ru(NH_3)_6Cl_3$ *solution. Solid curve:* $Ru(NH_3)_6{}^{3+}$ *at* pH 12. – – – *absorption of alkaline solution acidified to pH* 8. -·-·- $Ru(NH_3)_6{}^{3+}$ *absorption in an acid solution* pH 4·5.

The absorption peak at 402 ± 2 nm that is observed for the alkaline solution and is absent from the spectrum of the acidified solution is undoubtedly responsible for the yellow colour of the alklaine solutions of $Ru(NH_3)_6^{3+}$ ion.[3] It can be assigned to the conjugate base which is formed according to equation (1):

$$Ru(NH_3)_6^{3+} + OH^- \underset{k_1}{\overset{k_1}{\rightleftharpoons}} Ru(NH_3)_5NH_2{}^{2+} + H_2O \qquad (1)$$

and not to $Ru(NH_3)_5OH^{2+}$ which has an absorption peak at 295 nm and the pK for its formation[4] is 4·2. Assignment of the new absorption peak at 402 nm to an ion pair of the complex and OH^- is unlikely. Preliminary experiments revealed that the absorption due to an ion pair of $Ru(NH_3)_6{}^3$ with chloride ions has a maximum below 300 nm,[5] well below the position of our observed absorption peak of 402nm, while ion pairs of hydroxide ions and transition-metal ions are expected to have charge-transfer absorption with an energy similar to those of chloride ions.[6]

The deprotonated ruthenium hexa-ammine complex is not stable and undergoes an aquation reaction:

$$Ru(NH_3)_5NH_2{}^{2+} + H_2O \rightarrow Ru(NH_3)_5OH^{2+} + NH_3 \qquad (2)$$

as is evident from the slow decrease of the 402 nm peak with a concomitant increased absorption at 295 nm. In slightly basic solutions the rate of the aquation of $Ru(NH_3)_6^{3+}$ is proportional to OH^- concentration. This proportionality levels off, however, at strongly basic solutions where appreciable fraction of the ruthenium hexa-ammine complex is deprotonated. We can conclude that the base-catalysed aquation reaction of $Ru(NH_3)_6^{3+}$ proceeds according to reactions 1 and 2, *i.e.*, it involves $Ru(NH_3)_5$-$NH_2{}^{2+}$ as an intermediate. We are currently investigating the kinetics of this reaction.

In order to determine the acid dissociation constant of the ruthenium hexa-ammine complex, the optical density at 420 nm was followed as a function of pH. The wavelength of 420 nm was chosen in order to minimize the interference from the absorption due to the hydroxopenta-ammine aquation product. Also, the absorbance for each solution was extrapolated to zero time in order to account for the partial decomposition during the experiment. The equilibrium constants of reaction (1) at various temperatures were calculated from the extrapolated absorbance values by a suitable linear plot of 1/[O.D.] against $1/[OH^-]$. The value obtained for the pK_a at 25° was 12·4 ± 0·5 and the enthalpy and entropy changes in reaction (1) were found to be $\Delta H^0 = 5{\cdot}1 \pm 0{\cdot}3$ kcal/mole and $\Delta S^0 = 32{\cdot}5 \pm 1{\cdot}0$ e.u.

The deprotonated species can play a role also in the base-catalysed proton exchange reaction between water and $Ru(NH_3)_6^{3+}$. The second-order rate constant for this reaction has a particularly high value of about 1×10^9 M^{-1} s^{-1} at room temperature.[7] Using n.m.r. we confirmed this value but also found a strong temperature dependence with an apparent activation energy of 20 ± 1 kcal/mole and an entropy of activation of 49 ± 3 e.u.[8] In addition to reaction (1) which gives rise to proton exchange between the complex and water, it is possible that the deprotonated species can exchange their protons with water fast enough to give an additional path for the exchange.

$$Ru(NH_3)_5NH_2{}^{2+} + \overset{*}{H}OH \xrightarrow{k_2} Ru(NH_3)_5NH\overset{*}{H}{}^{2+} + HOH \qquad (3)$$

Such a path would be dominant if k_2 exceeds k_{-1}. This may be the case here as the calculated $\Delta S^{\ddagger}_{-1}$ is 21 e.u. which is unusually positive for reactions involving separation of charges.[9]

Exchange reactions similar to reaction (3) were reported for the proton exchange between $Pt(NH_3)_5NH_2^{3+}$ and water[10] and also between $Cr(H_2O)_5OH^{2+}$ and water.[11]

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