The Observation of an Intermediate in the Reaction Between Tetrachlorogold(III) and Thiocyanate Ions

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Summary In aqueous solution at 25 °C the substitution of one chloride ion in tetrachlorogold(III) by thiocyanate involves a readily detectable intermediate of 1 $AuCl_4^-$: 1 SCN^- stoicheiometry.

IT is widely assumed that substitution in square-planar complexes proceeds *via* a 5-co-ordinate intermediate.[1,2] In spite of the many kinetic studies of square-planar substitution direct evidence for such an intermediate has apparently been obtained with only one system.[1,2] This system[3] involved a somewhat elaborate rhodium complex and it has been suggested[1] that conditions favourable for the detection of such intermediates are, in general, rarely met. Certainly no 5-co-ordinate intermediate has yet been detected for gold(III) complexes. We report now the detection of an intermediate in the reaction between tetrachlorogold(III) and thiocyanate ions in aqueous solution at 25 °C.

In an aqueous solution of tetrachlorogold(III) ions (10^{-4} M) containing added chloride ions (0·10 M) hydrolysis is repressed and the gold species are virtually entirely[4] $AuCl_4^-$ ($\epsilon_{310} = 4200$). Addition of a 10—1000 fold excess of thiocyanate ions leads initially to a substantial, rapid increase in absorbance in the 310 nm region, followed by a somewhat slower fall in absorbance at these wavelengths. The thiocyanate ion does not itself absorb significantly at 310 nm. The evident reactions are most conveniently followed using stopped-flow spectrophotometry and we have shown that the system is properly represented by equation (1).

$$\begin{tikzcd} \mathrm{AuCl_4^-} + \mathrm{SCN^-} \arrow[r, shift left, "k_2"] & (\mathrm{C}) \arrow[l, shift left, "k_{-1}"] \arrow[r] & {[\mathrm{AuCl_3SCN}]^- + \mathrm{Cl^-}} \arrow[d, "\text{fast}"', "\text{excess SCN}^-"] \\ & & \mathrm{Au(SCN)_4^-} + 3\mathrm{Cl^-} \end{tikzcd} \qquad (1)$$

Significant concentrations of a 1:1 complex (C) are formed and with a 10 or more fold excess of thiocyanate present (C) is formed under approximately pre-equilibrium conditions. The two phases of the reaction, the formation of (C) and its conversion into products, can be studied reasonably independently. The equilibrium constant $K = k_1/k_{-1}$ is *ca.* 350 l mol^{-1} and (C) has ϵ_{310} *ca.* 7700. The observed rate constant for loss of (C) to product is $k_2^{\mathrm{obs}} = k_2K[\mathrm{SCN}]^-/(1 + K[\mathrm{SCN}^-])$ and at thiocyanate concentrations at which effectively all the tetrachlorogold(III) ions are converted into (C), k_2^{obs} reaches its constant, maximum value, k_2. For an ionic strength ($NaClO_4$) = 0·2 M we find $k_1 = 3{\cdot}33 \times 10^3$ l mol^{-1} s^{-1}, $k_{-1} = 9{\cdot}50$ s^{-1} and $k_2 = 10{\cdot}4$ s^{-1}. Further details, including the effects of added chloride ions on the reaction, will be given in our full report of this work. The simplest interpretation of our results is that (C) is the 5-co-ordinate intermediate usually assumed in theoretical discussions of square-planar substitution.

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