ABSTRACT

Mechanisms of Formation and Hydrolysis of Some Chromato Complexes of Chromium(III) Ions in Aqueous Solution

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The synthesis of a novel chromium(III) amine complex containing chromate as a bidentate ligand has been achieved, and the complex characterised by uv/visible and infrared spectroscopy.

This complex and the previously synthesised chromatopentaamminechromium(III) contain two chromium centres in different oxidation states which are separated by an oxo bridge i.e. Cr^{III}-O-Cr^{VI}. The reactivity of these complexes will be determined by the lability of the Cr^{III}-O and the Cr^{VI}-O bonds. Therefore, investigations on the mechanism of the formation and acid hydrolysis of these complexes were carried out and the results are presented in this thesis.

Studies on the formation of the chromato-pentaamminechromium(III), $[Cr(NH_3)_5CrO_4]^+$ and the chromato (rac-5,5,7,12,12,14 - hexamethyl - 1,4,8,11 - tetraazacyclotetradecane) chromium(III),

$[Cr(tetb)CrO_4]^+$ by spectrophotometric methods over the range of $3.5 \leq pH \leq 5.5$ and $0.40 \leq pH \leq 2.0$ respectively have revealed that these reactions involve a rapid addition of the aqua or hydroxo or diaqua amine chromium(III) to the Cr(VI) to form a monodentate complex. The reaction between aquapentaammine chromium(III) and chromate was complicated by catalysis by the buffers used. An attempt was made to identify a buffer system which would not catalyse the reaction but this was unsuccessful. In the case of the tetb complex, the mechanism involved the addition of the diaqua(tetb)chromium(III) ion to H_2CrO_4 (k_1 = 317 (± 11) mol^{-1} dm^3 s^{-1}, 24.7 ^oC, $\Delta H^{\#}$ = 60.0 (± 1) kJ mol^{-1}, $\Delta S^{\#}$ = 4.3 (± 3.9) J mol^{-1} K^{-1}) and to $HCrO_4^-$ (k_3 = 47.6 (± 1.8) mol^{-1} dm^3 s^{-1}, 24.7 ^oC, $\Delta H^{\#}$ = 53.2 (± 2.1) kJ mol^{-1}, $\Delta S^{\#}$ = 4.3 (± 3.9) J mol^{-1} K^{-1}) to form a monodentate chromato complex which undergoes a very rapid ring closure reaction to form the chelated chromato complex as the final product.

Acid hydrolysis of $[Cr(NH_3)_5CrO_4]^+$ was studied over the range $0.01 \leq [H^+] \leq 0.5$ mol dm^{-3}. It was observed that the reaction was rapid, indicating that the mechanism involves Cr^{VI}-O bond cleavage. The mechanism proposed for this reaction involves protonation of the chromato complex to form $Cr(NH_3)_5HCrO_4^+$ which decomposes to form $Cr(NH_3)_5OH_2^{3+}$ and

$HCrO_4^-$ (k_1 = 9.16 (± 0.13) s^{-1}, 25.3 ^oC, $\Delta H^{\#}$ = 50.5 (± 0.2) kJ mol^{-1}, $\Delta S^{\#}$ = -57 (± 10) J mol^{-1} K^{-1} and K_1 = (9.8 ± 1.0) x 10^{-2} mol dm^{-3}).

The $Cr(tetb)CrO_4^+$ ion is robust in acidic medium and does not hydrolyse even at pH = -1. Base hydrolysis occurs at very slow rates and is complete after about four days.

These results are compared with the reactions between cobalt(III) amine aqua complexes and chromate and the hydrolysis of the chromato complexes formed.