ABSTRACT

Studies on the Reactivity of the Chromate Ion Attached to Some Cobalt(III) Amine Complexes In Aqueous Solution

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The synthesis of some Cobalt(III) amine complexes containing chromate as a bidentate and monodentate ligand has been achieved, and the complexes characterised by uv/visible and infrared spectroscopy.

These complexes can be considered as unsymmetric binuclear compounds containing two different metal centres, Cobalt and Chromium, which bear different charges and are separated by a oxo bridge i.e. Co^{3+}-O-Cr^{6+}. The reactivity of these complexes will therefore depend on the relative lability of the Co^{3+}-O and Cr^{6+}-O bonds. Some aspects of the reactivity of these complexes namely their formation and hydrolysis in acidic and basic media have been thoroughly investigated, the results of which are reported in this thesis.

Studies on the formations of the Chromatopentaamminecobalt(III), $Co(NH_3)_5CrO_4^+$, Chromato(2,2',2''-triaminotriethylamine)cobalt(III), $Co(tren)CrO_4^+$, and Chromato(1,2-diaminoethane)cobalt(III) $Co(en)_2CrO_4^+$, by spectrophotometric methods over the range $6.0 \leq pH \leq 8.0$ have revealed that these reactions involve a relatively rapid nucleophilic addition of the aquo or hydroxo amine cobalt(III) group to the Cr(VI) centre to produce

a monodentate chromato complex. With the 1,2-diaminoethane and 2,2',2''-triaminotriethylamine complexes, the initially formed monodentate chromato complex undergoes a slower ring closure reaction of the chromate group to form a chelated chromato complex as the final product. Similar rate and activation parameters are obtained for these formation reactions and the magnitudes of the rate constants suggest that cleavage of the Cr-O bond occurs during formation.

The hydrolysis of these complexes in aqueous acidic media has also been investigated over the range $0.01 \leqq [H^+] \leqq 1.0$ mol dm^{-3}, and a general mechanism proposed to explain these reactions. With the monodentate chromato complex $Co(NH_3)_5CrO_4^+$, hydrolysis to the $Co(NH_3)_5OH_2^{3+}$ ion occurs at stopped flow rates, again indicating the Cr-O bond cleavage. The mechanism proposed for this reaction involves protonation of the chromato complex to both mono and diprotonated species $Co(NH_3)_5HCrO_4^{2+}$ and $Co(NH_3)_5H_2CrO_4^{3+}$, which subsequently decompose to the $Co(NH_3)_5OH_2^{3+}$ ion and the various protonated chromate ions. The diprotonated ion however hydrolyses at a much faster rate ($\sim 10^4$ times) than the monoprotonated resulting from the further weakening of the Cr-O bond by the additional proton.

Acid hydrolysis of the bidentate chromato complexes $Co(tren)CrO_4^+$, $Co(en)_2CrO_4^+$ and $Co(NH_3)_4CrO_4^+$ to the corresponding cis diaqua complexes occurs via two steps, the first being the acid catalysed ring opening of the complexes to the corresponding monodentate aquachromato complexes. This is followed by elimination of the chromato group from these monodentate complexes to give the diaqua complexes. Even though the mechanism for this second step is similar to that given for the $Co(NH_3)_5CrO_4^+$ complex, hydrolyses of the aquachromato complexes occur at much slower rates (~ 10^3 times) than the $Co(NH_3)_5CrO_4^+$.

The base hydrolysis of the $Co(tren)CrO_4^+$ ion has also been studied and this is believed to be occurring by a D_{CB} mechanism.