ABSTRACT

SYNTHESES, CHARACTERISATION, AND REACTIVITY OF SOME COORDINATED OXO-MOLYBDENUM(VI) COMPLEXES IN AQUEOUS SOLUTION.

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The synthesis of some cobalt/chromium(III) ammine complexes, containing the molybdate(VI) oxoanion as a monodentate and bidentate ligand, has been achieved, and the complexes characterised by uv/visible spectroscopy, infrared spectroscopy, ^{95}Mo NMR spectroscopy, and X-Ray Powder Diffraction. These complexes are unsymmetrical binuclear compounds containing two different metal centres, cobalt and molybdenum or chromium and molybdenum, which bear different charges, and are separated by an oxo bridge, $Co^{III}—O—Mo^{VI}$ or $Cr^{III}—O—Mo^{VI}$. The reactivity of the complexes depends on the relative lability of the $Co^{III}—O$ or $Cr^{III}—O$ and $Mo^{VI}—O$ bonds. The reactivity of the complexes, namely, their formation and hydrolysis in acidic and basic media have been investigated thoroughly. The electron transfer reactions involving $[Co(NH_3)_5MoO_4]ClO_4$ and (1) aqueous sulfite solution, (2) $K_4Fe(CN)_6$, (3) L-ascorbic acid, and (4) L-cysteine, have also been investigated thoroughly. All of these results are reported in this thesis.

Studies on the formation of $Co(NH_3)_5MoO_4^+$, molybdatopenta-amminecobalt(III), $Cr(NH_3)_5MoO_4^+$, molybdatopentaamminechromium(III), and $Co(tren)MoO_4^-$, molybdato(2, 2', 2''-triaminotriethylamine)cobalt(III), by spectrophotometric methods over the range $7.13 \leq pH \leq 8.18$ have revealed that these reactions involve rapid nucleophilic addition of the aqua or hydroxo ammine cobalt/chromium(III) group to the Mo(VI) centre to produce a monodentate molybdato complex. With the 2,

2', 2''-triaminotriethylamine complex, the initially formed monodentate molybdato complex undergoes a very rapid ring closure reaction of the molybdate group to form a chelated molybdato complex as the final product. Similar rate and activation parameters are obtained for the formation reactions and the magnitudes of the rate constants suggest that cleavage of the Mo^{VI}—O bond occurs during formation.

The acid hydrolysis of the complexes in aqueous media has been investigated over the range $0.01 \leq [H^+] \leq 0.45$ mol dm^{-3}, and a general mechanism has been proposed to explain the reaction. The monodentate molybdato complexes, $Co(NH_3)_5MoO_4^+$ and $Cr(NH_3)_5MoO_4^+$, hydrolyse to the $Co(NH_3)_5H_2O^{3+}$ ion and $Cr(NH_3)_5H_2O^{3+}$ ion, respectively at stopped-flow rates, thus indicating that there is Mo^{VI}—O bond cleavage. Unlike other acid catalysed aquation, the rates of reactions were inversely dependent on $[H^+]$. There was an expansion of the coordination number of the Mo(VI) centre from four to six on protonation, along with resonance stabilisation of the six coordinate species. Both $Co(NH_3)_5HMoO_4^{2+}$ (or $Cr(NH_3)_5HMoO_4^{2+}$) and $Co(NH_3)_5OMoO(OH)_2(H_2O)_2^{3+}$ (or $Cr(NH_3)_5O$-$MoO(OH)_2(H_2O)_2^{3+}$) are formed, but only $Co(NH_3)_5HMoO_4^{2+}$ and $Cr(NH_3)_5HMoO_4^{2+}$ are the reactive species, which subsequently decompose to the $Co(NH_3)_5H_2O^{3+}$ ion and $Cr(NH_3)_5H_2O^{3+}$ ion, respectively, along with polymolybdates. The species with a four coordinate Mo(VI) centre undergoes molybdate elimination during acid hydrolysis as opposed to the species with a six coordinate Mo(VI) geometry (this is stabilised by resonance). In the case of the bidentate molybdato complexes, molybdato-bis(1, 2-diaminoethanecobalt(III), $Co(en)_2MoO_4^+$ and molybdato(2, 2', 2''-triamino-triethylamine)cobalt(III), $Co(tren)MoO_4^+$, only the elimination of molybdate was seen. The mechanism for this step is similar to that given for $Co(NH_3)_5MoO_4^+$ and $Cr(NH_3)_5MoO_4^+$, with the formation of the respective diaqua complexes and polymolybdates. The rates of hydrolysis are of the same magnitude as the monodentate complexes. Similar rate and activation parameters are obtained for the acid hydrolysis reactions and the magnitudes of the rate constants suggest that cleavage of the $Mo^{VI}—O$ bond occurs during hydrolysis.

The base hydrolysis of the complexes has been studied. The D_{CB} mechanism has been proposed for $Co(NH_3)_5MoO_4^+$ and $Cr(NH_3)_5MoO_4^+$, while a dual mechanism has been proposed for $Co(en)_2MoO_4^+$ and $Co(tren)MoO_4^+$; first there was the ring opening step which went via the ion-pair mechanism, and then there is the elimination of molybdate which goes via the D_{CB} mechanism.

The kinetics of the electron-transfer reactions between $Co(NH_3)_5MoO_4^+$ and (1) aqueous sulfite, (2) $K_4Fe(CN)_6$, (3) L-ascorbic acid, and (4) L-cysteine have been studied. With the first three reductants an outer-sphere electron-transfer process has been proposed, with the reduction of the Co(III) centre to $Co^{2+}{}_{(aq)}$. The Mo(VI) centre, however, remained unaffected. Similar activation parameters are obtained for these reactions. With L-cysteine there was a complex reaction, with the reduction of the Mo(VI) centre to Mo(V); the Co(III) centre, however, remained unaffected. The reaction was biphasic in nature, with the first stage consisting of a series of steps to give a binuclear diamagnetic Mo(V) species linked to Co(III) via an oxo bridge. The first stage was autocatalysed by an intermediate formed. The second stage was also complex, with cysteine catalysing structural rearrangement of the intermediate. Electron Spin Resonance (ESR) was used to detect the very reactive Mo(V) monomer formed in the first stage.

Electrochemical studies were performed on the complexes in the pH range $5.79 \leq pH \leq 8.01$.