ABSTRACT

Dinuclear hydroxobridged complexes of cobalt (III) and rhodium (III) are prepared, the non-participating ligand in all cases being the tridentate macrocycle 1,4,7-triazacyclononane. Investigations of the behaviour in aqueous acid, in aqueous sulfite, in basic solutions and in carbonate media are reported and the results compared to show the effect of the macrocyclic ligand relative to simpler ligands and also to show the effect of the change in metal centre among analoguous complexes.

The tribridged complexes, tri-μ-hydroxobis [1,4,7-triazacyclononane) metal (III)] perchlorates, hereafter referred to as 'cobalt (III) triol' and 'rhodium (III) triol' for the metals cobalt and rhodium respectively, are found to undergo acid catalysed cleavage of one hydroxide bridge in dilute acid solutions to yield the trans-diaqua- complexes as product. The amount of trans-diaqua- product is pH dependent and equilibrium constants are reported; $K = 10 \pm 2\ M^{-1}$ ($\Delta H^{\circ} = -105.9 \pm 0.2$ kJ mol^{-1}, $\Delta S^{\circ} = -0.3 \pm 0.1$ J mol^{-1}K^{-1}) and $15 \pm 2\ M^{-1}$ ($\Delta H^{\circ} = -134.3 \pm 0.4$ kJ mol^{-1}, $\Delta S^{\circ} = 0.4 \pm 0.1$ J mol^{-1}K^{-1}) at 20°C for the cobalt (III) triol

and rhodium (III) triol complexes respectively. Acid dissociation constants for the trans-diaqua-products are also reported; pKa_1 for the cobalt (III) complex is 4.10±0.05, pKa_1 and pKa_2 for the rhodium (III) complex are 5.16±0.02 and 8.00±0.02 respectively at 22°C. Kinetic investigations of the above mentioned bridge cleavage process by stopped flow spectrophotometry show two equilibrium steps, a relatively fast proton assisted bridge cleavage and formation step K_1 followed by rate determining cis- trans isomerisation, K_2. For the rhodium (III) triol complex, k_2K_1=11.0±0.5 $M^{-1}s^{-1}$ and k_{-2} =(2.2±0.2) x $10^{-2}s^{-1}$ ($\Delta H_2^{\neq}$ = 57 ± 9 kJ mol^{-1}, $\Delta S_2^{\neq}$= -825± 1 J $mol^{-1}K^{-1}$) at 20°C.

The triol complexes are found to undergo rapid sulfite uptake reactions in aqueous sulfite media. Novel sulfito complexes as a result of these investigations, are reported. These are the di-μ-hydroxo-μ-sulfito bis[1,4,7-triazacyclononane) cobalt (III)] perchlorate salt and the aquabisulfito-μ-hydroxo-μ-sulfito bis[1,4,7-triazacyclononane metal (III)] perchlorate salts (metal = cobalt and rhodium). The kinetics of formation of these complexes are investigated and the proposed mechanisms involve the reaction of bridging hydroxide with HSO_3^- species, the k_1 path

and reaction of terminal hydroxide with SO_2 species, the k_2 path. For the cobalt (III) complex, k_1=15.0 ±0.2$M^{-1}s^{-1}$($\Delta H^{\ddagger}$ = 35±3 kJ mol^{-1}, $\Delta S^{\ddagger}$ = -103±1 J K^{-1} mol^{-1}) and $k_2K_1K_2$=75.6±0.4 $M^{-1}s^{-1}$ at 20°C for the uptake of the first sulfite species. In the case of the rhodium (III) complex, k_1=(7.2±0.2 $M^{-1}s^{-1}$ ($\Delta H^{\ddagger}$=1.5±0.5 kJ mol^{-1}, $\Delta S^{\ddagger}$ =284±4 J $K^{-1}mol^{-1}$) at 20°C. The uptake of the second sulfite follows a similar mechanism in some respects to the first uptake reaction, and k_1 for the rhodium complex is (3.2±0.5)x$10^2M^{-1}s^{-1}$($\Delta H^{\ddagger}$=37±2 kJ mol^{-1}, $\Delta S^{\ddagger}$=-71.8±0.2 J $K^{-1}mol^{-1}$); $k_2K_1K_2$=(6.06±0.41) x 10^4 $M^{-1}s^{-1}$. Uptake of the second sulfite species immediately prcedes an isomerisation reaction in which the initially formed O- bonded monodentate ligand isomerises to S- bonded. The rate constant for the rhodium (III) complex at 25°C is k_3=(9.3±0.4)x10^{-3} s^{-1} ($\Delta H^{\ddagger}$=32.5±0.1 kJ mol^{-1}, $\Delta S^{\ddagger}$=-174.7 ±0.1 J K^{-1} mol^{-1}). For the cobalt complex, k_3 = (3.1±0.1) x $10^{-5}s^{-1}$ at 25°C.

In aqueous carbonate media, CO_2 is taken up by the cobalt (III) triol complex in a slow reaction to form the di-μ-hydroxo-μ-carbonato bis [(1,4,7-triazacyclononane)cobalt (III)] complex. The mechanism involves reaction of the bridging hydroxide as well as terminal hydroxide ligands produced via base hydrolysis with CO_2. The obtained rate constants are respectively,