ABSTRACT

Cobalt (III) complexes of the type $[Co(dmg)_2X_2]^-$ ($X = Cl^-, Br^-, I^-, N_3^-$) react in aqueous sulfite solution to produce trans-$[Co(dmg)_2(SO_3)_2]^{3-}$. Of the various sulfur-containing species present in solution only the sulfite ion reacts with the cobalt(III) complexes according to the expression

$$\text{rate} = k[SO_3^{2-}][\text{complex}]$$

At 30 °C the rate constants are 6.8, 3.3 and 0.5 $M^{-1}s^{-1}$ for the dichloro-, dibromo- and diiodo- complexes respectively. For the diazido complex the rate constant is 1.6 $M^{-1}s^{-1}$ at 32.0 °C. The dipyridine complex, trans-$[Co(dmg)_2py_2]^+$ reacts extremely slowly with sulfite ion to form the trans-disulfito species.

The kinetics are consistent with a mechanism involving direct replacement of the X^- species by the sulfite ion in a slow step followed by a rapid reaction. This rapid reaction involves the replacement of the other X^- species by another sulphite ion because of the large trans-effect of the coordinated sulfite.

The equilibrium constants for the formation of the disulfito complex are of the order of magnitude 10^{13}. At 25.5 °C they are 2.78×10^{13}, 1.03×10^{13} and $3.54 \times 10^{13} M^{-2}$ for the dichloro-, dibromo- and diiodo- complexes respectively. These large equilibrium constants suggest that the

equilibrium lies towards the formation of the disulfito complex.

The aquation of dichloro-, dibromo- and diiodobis-(dimethylglyoxime)cobalt (III) ions to their corresponding aqua-halogeno-complexes gave first-order rate constants of 2.5, 1.7 and 0.35 s^{-1} respectively at 25 ^{o}C. The order of reactivity observed for the aquation being $Cl^{-} > Br^{-} > I^{-}$ which is consistent with the order of reactivity observed for the formation of the bis(dimethylglyoxime) disulfito cobalt (III) complex. The order of reactivity for the replacement of the first halide by water in dihalogenobis-(dimethylglyoxime)cobalt (III) ions reported by Ablov was the inverse of what we observed.

Attempts to prepare cis-bis(dimethylglyoxime) cobalt (III) complexes by methods reported by Ablov et al were all futile. However,syntheses of dinuclear complexes with dmg incorporated as terminal ligands were successful. The dinuclear complexes prepared were $[NH_3(dmg)_2Co{-}O_2{-}Co(dmg)_2NH_3]$ and $[(NH_3)_2(dmg)Co(\mu\text{-}OH)(\mu NH_2)Co(dmg)_2]NO_3$