ABSTRACT

Reactivity of Dinuclear Hydroxo-bridged Complexes of Chromium(III) in Aqueous Sulfite

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The kinetics of the reaction of a series of di-hydroxo bridged dinuclear chromium(III) amine complexes in aqueous sulfite solution have been studied. The synthesis of a series of novel dinuclear chromium(III) complexes containing sulfite as a bridging bidentate ligand has also been achieved. The sulfite complexes were characterized by means of infra-red spectroscopy and the coordination of the sulfite bridge confirmed by X-ray diffraction on the complex di-μ-hydroxo-μ-sulfito-bis[1,4,7-triazacyclonane]chromium(III)]-dithionatetrahydrate. These sulfito complexes were isolated as intermediates or final product from the reactions of the hydroxo bridged complexes in aqueous sulfite solution.

Studies on the formation of μ-hydroxo-μ-sulfito-bis[bis(1,2-diaminoethane)chromium(III)], [(en)$_2$Cr(μ-OH)(μ-SO$_3$)Cr(en)$_2$]$^{3+}$; di-μ-hydroxo-μ-
sulfitobis[1,4,7-triazacyclononanechromium(III)], 
[[tacn]Cr(μ-OH)_2(SO_3)Cr(tacn)]^{2+}; μ-hydroxo-μ-sulfito-
bis[1,4,7,10-tetraazacyclododecanedecanechromium(III)], 
[[cyclen]Cr(μ-OH)(μ-SO_3)Cr(cyclen)]^{3+} and μ-hydroxo-μ-
sulfitobis[N,N-bis(2-aminoethyl)-1,2-diaminoethane-
chronium(III)], [[tren]Cr(μ-OH)(μ-SO_3)Cr(tren)]^{3+} by 
spectrophotometric methods over the range 2.0 ≤ pH ≤ 
5.5 have revealed that these reactions involve a rapid 
addition of a terminal aqua or hydroxo ligand from the 
ring opened mono-ol species, on sulfur dioxide or 
bisulfite ion, from the (en) and (tren) systems and the 
diol species from the (tacn) system, to form an 
oxygen-bonded sulfito species which undergoes a slower 
ring closure reaction to form a sulfite bridge complex.

Both the (en)-dil (k = 8.7 (± 0.1) x 10^7 dm^3 
mol^{-1} s^{-1}, 25 °C, ΔH^f = 6.5 (± 0.9) kJ mol^{-1}, ΔS^f = 
-71 (± 2) J mol^{-1} K^{-1}) and the (tacn)-dil (k = 2.10 (± 
0.08) dm^3 mol^{-1} s^{-1}, 25.2 °C, ΔH^f = 94 (± 8) kJ mol^{-1}, 
ΔS^f = 110 (± 8) J mol^{-1} K^{-1}) systems undergo sulfur 
dioxide uptake while in the (tren)-dil (k = 240 (± 1) 
dm^3 mol^{-1} s^{-1}, 25.0 °C) system bisulfite ion is the 
reactive species, all these being on the stopped-flow 
time scale. The reaction of the (cyclen)-dil (k = 
1.20 (± 0.02) x 10^{-2} dm^3 mol^{-1} s^{-1}, 24.6 °C, ΔH^f = 43 
(± 2) kJ mol^{-1}, ΔS^f = -138 (± 6) J mol^{-1} K^{-1}) is slow 
and it is thought that the ring opening of the bridge
is being observed.

The sulfite bridge is found to be labile under acid hydrolysis of \([\text{en}]_2\text{Cr}(\mu-\text{OH})(\mu-\text{SO}_3)\text{Cr}(\text{en})_3]^{3+}\), \((k = 7.8 (\pm 0.1) \times 10^{-5} \text{ s}^{-1}, 25.0 \degree\text{C})\) but very inert for the \(((\text{tacn})\text{Cr}(\mu-\text{OH})_2(\mu-\text{SO}_3)\text{Cr(\text{tacn})}]^{2+}\) species \((k = 6.1 (\pm 0.1) \times 10^{-2} \text{ s}^{-1}, 30.0 \degree\text{C})\) and the formation of a cis-\([(\text{H}_2\text{O})(\text{tacn})\text{Cr}(\mu-\text{OH})(\mu-\text{SO}_3)\text{Cr(\text{tacn})}(\text{OH}_2)]^{3+}\) species is proposed. The rate of hydrolysis was found to be independent and dependent for the former and the latter respectively over the range \(0.01 \leq [\text{H}^+] \leq 1.0 \text{ mol dm}^{-3}\).

The sulfite species \([(\text{en})_2\text{Cr}(\mu-\text{OH})(\mu-\text{SO}_3)\text{Cr(\text{en})}_2]^{3+}\) undergoes additional sulfite uptake \((k = 3.01 \times 10^{-4} \text{ s}^{-1}, 25.0 \degree\text{C}, \Delta H^\neq = 91 (\pm 8) \text{ kJ mol}^{-1}, \Delta S^\neq = -8.7 (\pm 29.6) \text{ J mol}^{-1} \text{ K}^{-1})\) to form a possible disulfite product a reaction independent of sulfite concentration but dependent on \([\text{H}^+]\).

No general mechanism was formulated for this series of complexes since their reactivity was found to vary greatly with the nature of the amine ligand.

The novel di-hydroxo bridged complex cation, \(((\text{tren})\text{Cr}(\mu-\text{OH})_2\text{Cr(\text{tren})}]^{4+}\) has also been synthesized and characterized by microanalysis and comparison with other known diols.