

## 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 dihydroxo 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- $\mu$ -hydroxo- $\mu$ -sulfitobis[1,4,7-triazacyclononanechromium(III)]-dithionatetrihydrate. These sulfite 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  $\mu$ -hydroxo- $\mu$ -sulfitobis[bis(1,2-diaminoethane)chromium(III)],  
 $[(en)_2Cr(\mu-OH)(\mu-SO_3)Cr(en)_2]^{3+}$ ; di- $\mu$ -hydroxo- $\mu$ -

sulfitobis[1,4,7-triazacyclononanechromium(III)],  
 $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\text{SO}_3)\text{Cr}(\text{tacn})]^{2+}$ ;  $\mu$ -hydroxo- $\mu$ -sulfito-  
bis[1,4,7,10-tetraazacyclododecanechromium(III)],  
 $[(\text{cyclen})\text{Cr}(\mu\text{-OH})(\mu\text{-SO}_3)\text{Cr}(\text{cyclen})]^{3+}$  and  $\mu$ -hydroxo- $\mu$ -  
sulfitobis[N,N-bis(2-aminoethyl)-1,2-diaminoethane-  
chromium(III)],  $[(\text{tren})\text{Cr}(\mu\text{-OH})(\mu\text{-SO}_3)\text{Cr}(\text{tren})]^{3+}$  by  
spectrophotometric methods over the range  $2.0 \leq \text{pH} \leq$   
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)-diol ( $k = 8.7 (\pm 0.1) \times 10^7 \text{ dm}^3$   
 $\text{mol}^{-1} \text{ s}^{-1}$ ,  $25 \text{ }^\circ\text{C}$ ,  $\Delta H^\ddagger = 6.5 (\pm 0.9) \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger =$   
 $-71 (\pm 2) \text{ J mol}^{-1} \text{ K}^{-1}$ ) and the (tacn)-diol ( $k = 2.10 (\pm$   
 $0.08) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $25.2 \text{ }^\circ\text{C}$ ,  $\Delta H^\ddagger = 94 (\pm 8) \text{ kJ mol}^{-1}$ ,  
 $\Delta S^\ddagger = 110 (\pm 8) \text{ J mol}^{-1} \text{ K}^{-1}$ ) systems undergo sulfur  
dioxide uptake while in the (tren)-diol ( $k = 240 (\pm 1)$   
 $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $25.0 \text{ }^\circ\text{C}$ ) system bisulfite ion is the  
reactive species, all these being on the stopped-flow  
time scale. The reaction of the (cyclen)-diol ( $k =$   
 $1.20 (\pm 0.02) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $24.6 \text{ }^\circ\text{C}$ ,  $\Delta H^\ddagger = 43$   
 $(\pm 2) \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -138 (\pm 6) \text{ J mol}^{-1} \text{ K}^{-1}$ ) 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  $[(en)_2Cr(\mu-OH)(\mu-SO_3)Cr(en)_3]^{3+}$ , ( $k = 7.8 (\pm 0.1) \times 10^{-5} \text{ s}^{-1}$ ,  $25.0 \text{ }^\circ\text{C}$ ) but very inert for the  $[(tacn)Cr(\mu-OH)_2(\mu-SO_3)Cr(tacn)]^{2+}$  species ( $k = 6.1 (\pm 0.1) \times 10^{-2} \text{ s}^{-1}$ ,  $30.0 \text{ }^\circ\text{C}$ ) and the formation of a *cis*- $[(H_2O)(tacn)Cr(\mu-OH)(\mu-SO_3)Cr(tacn)(OH_2)]^{3+}$  species is proposed. The rate of hydrolysis was found to be independent and dependent for the former and the latter respectively over the range  $0.01 \leq [H^+] \leq 1.0 \text{ mol dm}^{-3}$ .

The sulfite species  $[(en)_2Cr(\mu-OH)(\mu-SO_3)Cr(en)_2]^{3+}$  undergoes additional sulfite uptake ( $k = 3.01 \times 10^{-4} \text{ s}^{-1}$ ,  $25.0 \text{ }^\circ\text{C}$ ,  $\Delta H^\ddagger = 91 (\pm 8) \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -8.7 (\pm 29.6) \text{ J mol}^{-1} \text{ K}^{-1}$ ) to form a possible disulfite product a reaction independent of sulfite concentration but dependent on  $[H^+]$ .

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,  $[(tren)Cr(\mu-OH)_2Cr(tren)]^{4+}$  has also been synthesized and characterized by microanalysis and comparison with other known diols.