Kinetics and Mechanism of the Formation and Reactivity of μ-Hydroxo-μ-Sulfito-bis[bis(1,2-diaminoethane)chromium(III)]

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The kinetics of formation of $[(en)_2Cr(\mu\text{-}OH)(\mu\text{-}SO_3)Cr(en)_2]^{3+}$ cation from $[(en)_2Cr(\mu\text{-}OH)_2Cr(en)_2]^{4+}$ (en = 1,2-diaminoethane) in aqueous buffered sulfite solution has been studied spectrophotometrically. This formation consisted of two steps; first a rapid uptake of SO_2 by the ring-cleaved mono-μ-hydroxo species $[(OH)(en)_2Cr(\mu\text{-}OH)Cr(en)_2(OH)]^{3+}$ to form a terminal O-bonded sulfito intermediate. This reaction was studied at 600 nm in the ranges $3.78 \leqslant pH \leqslant 5.47$, $20 \leqslant \theta \leqslant 30$ °C and $0.03 \leqslant [S]_T \leqslant 0.05$ mol dm^{-3} ($[S]_T = [SO_2] + [HSO_3^-] + [SO_3^{2-}]$). The rate constant for uptake of SO_2 at 25 °C was found to be $(8.7 \pm 0.1) \times 10^7$ dm^3 mol^{-1} s^{-1} with $\Delta H^\ddagger = 6.5 \pm 0.9$ kJ mol^{-1} and $\Delta S^\ddagger = -71 \pm 2$ J K^{-1} mol^{-1}. The second step in which the sulfito intermediate undergoes a ring closure to form the $(\mu\text{-}OH)(\mu\text{-}SO_3)$ complex with the elimination of H_2O (or OH^-) was studied in the ranges $2.46 \leqslant pH \leqslant 4.46$, $19.9 \leqslant \theta \leqslant 29.9$ °C and $0.03 \leqslant [S]_T \leqslant 0.05$ mol dm^{-3}, and the rate constant for this process, k_3, was found to be 0.68 s^{-1} at 25.2 °C with $\Delta H^\ddagger = 28 \pm 1$ kJ mol^{-1} and $\Delta S^\ddagger = -155 \pm 3$ J K^{-1} mol^{-1}. The rate constant for ring closure with the loss of OH^- was found to be 0.15 s^{-1} at 25.2 °C with $\Delta H^\ddagger = 66 \pm 7$ kJ mol^{-1} and $\Delta S^\ddagger = -40 \pm 24$ J K^{-1} mol^{-1}. The $(\mu\text{-}OH)(\mu\text{-}SO_3)$ complex decomposes in acid to give free sulfite with a rate constant of $(7.8 \pm 0.1) \times 10^{-5}$ s^{-1} at 25 °C which is independent of $[H^+]$ over the range 0.01–1.0 mol dm^{-3} $HClO_4$. It undergoes additional sulfite uptake ($k = 3.01 \times 10^{-4}$ s^{-1}, 25 °C, $\Delta H^\ddagger = 91 \pm 8$ kJ mol^{-1}, $\Delta S^\ddagger = -8.7 \pm 29.6$ J K^{-1} mol^{-1}) to form a possible disulfito product. The reaction was found to be independent of $[S]_T$ but dependent on $[H^+]$ over the ranges $2.11 \leqslant pH \leqslant 7.28$, $0.03 \leqslant [S]_T \leqslant 0.05$ mol dm^{-3} and $20 \leqslant \theta \leqslant 30$ °C.

During recent years a number of systems have been studied which involve mononuclear aquatransition-metal complex ions in aqueous sulfite solution. These include reactions of the aquapentaammine complexes of cobalt(III),[1] chromium(III),[2] rhodium(III)[2] and platinum(IV),[3] *cis*- and *trans*-$[Co(en)_2(OH_2)_2]^{3+}$ (en = 1,2-diaminoethane),[4,5] *cis*-$[Co(tren)(OH_2)_2]^{3+}$ [tren = 1,2-bis(2-aminoethylaminoethane],[6] $[Co(tetren)(OH_2)]^{3+}$ (tetren = tetraethylenepentamine)[7] and the hexaaquachromium(III) cation.[8] The kinetic data show that in each instance the most significant first step in the overall process is rapid nucleophilic attack by ligand hydroxide on dissolved SO_2 to form an unstable O-bonded sulfito complex, a reaction that is readily reversible by immediate acidification. Metal-to-metal oxygen bonding is not involved in this reversible process, as confirmed by NMR measurements.[9] Reactions subsequent to the formation of the O-bonded intermediate include O- to S-bonded isomerization, internal redox, sulfite-ion addition, or a combination of these processes depending on the pH, the nature of the N_4 or N_5 ligand group and the metal centre.

The reactivity of the terminal aqua (or hydroxo) ligand towards free sulfite is fairly well documented by the above mentioned work. So far, there has been only one documented report[10] involving the reaction of a hydroxo-bridged complex in aqueous sulfite solution. The work included the isolation of a sulfito-bridged cobalt(III) dimer and characterization of this complex by infrared spectroscopy. The sulfite moiety was concluded to form a doubly O-bonded bridge. We now report the isolation of a stable sulfito-bridged chromium(III) complex, elucidation of the mechanism of its formation and investigation of its reactivity in aqueous sulfite and in acidic solutions.

Experimental

Materials.—All chemicals used were of reagent grade. Distilled water made from a stainless-steel distillation unit was used without further purification for all syntheses. Deionized water, made by passing distilled water through a Milli-Q ion-exchange purification unit (Millipore, Milford MA), was used for all spectral investigations in solution. Solid sodium metabisulfite $Na_2S_2O_5$ (BDH) was the source of sulfite; this salt is very stable in the solid form but hydrolyses rapidly and completely when dissolved in water to yield sulfite.[1] Sulfur dioxide gas was obtained from BDH (Poole).

Preparation and Characterization of Complexes.—cis-*Dichlorobis*(1,2-*diaminoethane*)*chromium*(III) *chloride.* This complex was prepared from $[Cr(en)_3]Cl_3$ by a literature[11] procedure, which was modified to obtain a purer product. The complex $[Cr(en)_3]Cl_3$ (20.3 g, 0.06 mol; recrystallized from 2% NH_4Cl in aqueous ethanol to give very fine crystals which decompose much faster than larger crystals obtained from recrystallization from water) was spread in a thin layer on a watch-glass and heated at 190 °C for 20 min to give a lumpy red-violet product. These lumps were crushed and the product heated for 20 min. At this stage a 30% loss in weight (corresponding to *ca.* 99% decomposition) was observed, yielding 14.2 g of product. This represents a vast improvement on the previous procedure.[11] The visible spectrum compared well with that reported earlier.[†,13]

Di-μ-hydroxo-bis[*bis*(1,2-*diaminoethane*)*chromium*(III)] *perchlorate.* This complex was prepared from the above *cis*-dichloro compound as described by Springborg and Schäffer.[11] The UV/VIS spectral parameters were in good agreement with those in the literature: λ 528 (ε 176) and 384 (115); lit.,[11] 528 (178) and 384 nm (115 dm^3 mol^{-1} cm^{-1}).

[†] The absorption coefficients are 68 and 66 dm^3 mol^{-1} cm^{-1} at 530 and 402 nm respectively (lit.,[12] 71 and 68 dm^3 mol^{-1} cm^{-1}).

μ-Hydroxo-μ-sulfito-bis[bis(1,2-diaminoethane)chromium(III)] perchlorate. Sulfur dioxide was bubbled slowly into water (3 cm^3, 0 °C) for 10 min. To this was added [(en)$_2$Cr(μ-OH)$_2$Cr(en)$_3$][ClO$_4$]$_4$ (0.5 g, 0.64 mmol) with stirring until dissolution was complete. To the red-pink solution a saturated solution (4 cm^3, room temperature) of NaClO$_4$ was added slowly with stirring in an ice-bath and cooling continued for 1 h. The red-pink crystals were filtered off, washed with two portions (1 cm^3) of 50% v/v ethanol–water, two portions (2 cm^3) of 95% ethanol, diethyl ether and dried in air. Yield: 0.4 g (82%). An identical product was obtained by replacing SO$_2$ with 0.3 g of Na$_2$S$_2$O$_5$. The purity was checked by microanalysis (done by Dr. E. Pascher, Mikroanalytisches Labor Pascher, Remegan) (Found: C, 12.65; H, 4.60; Cl, 14.6; Cr, 12.7; N, 15.1; S, 4.15. Calc. for $C_8H_{33}Cl_3Cr_2N_8O_{16}S$: C, 12.70; H, 4.65; Cl, 14.0; Cr, 13.7; N, 14.8; S, 4.25%). Visible spectrum: λ 518 (ε 202) and 385 nm (135 dm^3 mol^{-1} cm^{-1}). The IR spectrum showed vibrational frequencies assigned[10] to the bridging sulfite: δ_{OSO} 640w, ν_{SO} 832m, 866m, 912ms, 940s and 974s cm^{-1}.

Spectra.—The visible spectra were recorded on either a Varian Cary 219 or a Hewlett-Packard 8452A diode-array spectrophotometer, and the infrared spectra with either a Perkin Elmer 735B or a Philips Analytical SP3-300 spectrometer employing the KBr disc technique.

Kinetic Measurements.—The kinetic data for the fast reactions were obtained at 600 nm where there is an appreciable absorbance change between the reactant and the product (the absorption coefficients of the di-μ-hydroxo cation and the sulfito complex are 62 and 34 dm^3 mol^{-1} cm^{-1}, respectively). Analysis of the data at other wavelengths (518 and 540 nm) gave comparable results. The ionic strength of the reaction mixtures was adjusted to 1 mol dm^{-3} with 4 mol dm^{-3} NaClO$_4$. Rate measurements for the uptake of SO$_2$ were made using the sulfite self-buffering technique[7] where calculated amounts of sodium hydroxide or perchloric acid are added to sulfite solutions to give the required pH. Sulfite and complex solutions were introduced separately into the reservoirs of a Hi-Tech Scientific stopped-flow SHU (SF-51) assembly connected to a Hi-Tech (SU-40) spectrophotometer unit interfaced to a 386-AT computer running the Hi-Tech analysis program RKDEM.

Rate measurements for the further addition of sulfite to, and acid hydrolysis of, the sulfito complex were made in a Cary-219 spectrophotometer equipped with a thermostatted cell compartment.

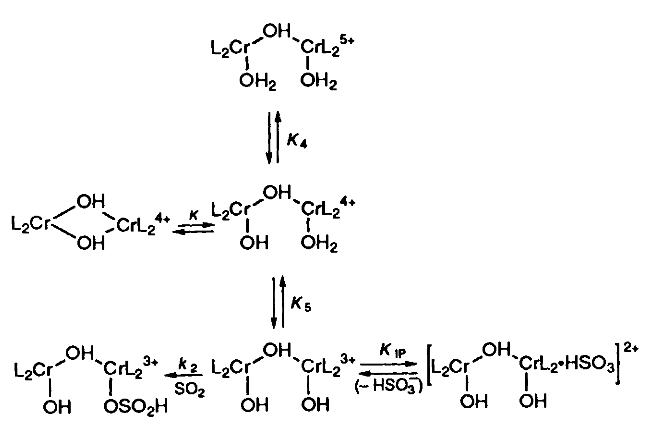
Reported k_{obs} values have a maximum error of ±5%, but most are within ±2% or less.

pH *Measurements.*—An Orion model 701, or a Beckmann model 1500, pH meter fitted with a combination glass electrode (Fisher, Markson or Corning) was used to measure pH. The meter was calibrated at the working temperature with standard buffer solutions,[14] *viz.* 0.01 mol dm^{-3} Na$_2$B$_4$O$_7$·10H$_2$O, 0.025 mol dm^{-3} KH$_2$PO$_4$ and 0.025 mol dm^{-3} Na$_2$HPO$_4$. For slow reactions the pH was measured before and after the run. For fast reactions the pH was measured immediately after mixing.

Results and Discussion

Acid Dissociation Constants.—The data were analysed on the basis of the values for the dissociation constants for the various equilibria present in aqueous sulfite as reported in the literature.[1] Values of pK_1 for sulfurous acid, 'H$_2$SO$_3$', have been reported as 1.85, 1.90 and 1.95 at 20, 25 and 30 °C respectively, while pK_2 is constant at 6.30 over the same range (I = 1.0 mol dm^{-3}). For the HSO$_3^-$/S$_2$O$_5^{2-}$ equilibrium, K_3 = 0.07 dm^3 mol^{-1} at 25 °C.

The complex salt [(en)$_2$Cr(μ-OH)$_2$Cr(en)$_2$][ClO$_4$]$_4$ is in rapid equilibrium[15] in aqueous solution as shown in Scheme 1. The value of K was reported[15] to be 0.76 at 25 °C and is independent of acid concentration. This means that the fraction of di-μ-hydroxo cation present in all kinetic solutions will be constant, irrespective of pH. The values of pK_4 and pK_5 were found to be 0.67 and 7.95 by spectrophotometric and conductometric methods respectively.[16] The large difference between these values is attributed[16] to extensive hydrogen bonding in the aquahydroxo mono-μ-hydroxo cation which gives it extra stability. Hence, this species will be the major form over the range pH 3.8–5.5 employed.



Scheme 1 L = en

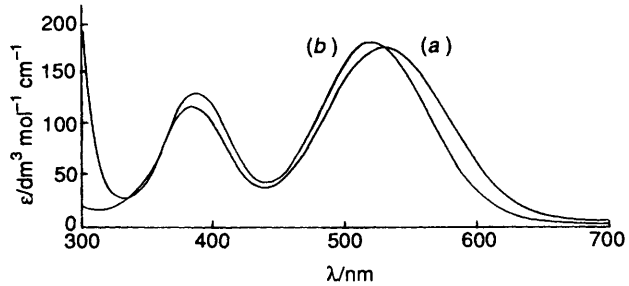


Fig. 1 Absorption spectra of (*a*) [(en)$_2$Cr(μ-OH)$_2$Cr(en)$_2$]$^{4+}$ and (*b*) [(en)$_2$Cr(μ-OH)(μ-SO$_3$)Cr(en)$_2$]$^{3+}$

Qualitative Observations.—Preliminary experiments in which Na$_2$S$_2$O$_5$ was added to solutions of the di-μ-hydroxo cation showed an instantaneous colour change from violet to red-pink corresponding to an increase, accompanied by blue shifts, in the two absorption maxima of the visible spectrum (see Fig. 1). No Cr→S charge-transfer bands were observed in the UV region of the spectrum. The final spectrum is identical to that in aqueous solution of the (μ-OH)(μ-SO$_3$) complex.

When the uptake of SO$_2$ was monitored on the stopped-flow spectrophotometer the rapid colour change corresponded to two fast reactions, the rates of which were studied separately using different time-scales. These fast reactions are followed by a much slower one, and will be discussed later. Identical spectra for the sulfito product were obtained for equimolar solutions of the di-μ-hydroxo cation and sulfite, with sulfite in excess, and for solutions of the isolated product. This supports a stoichiometric ratio of 1 : 1, and that the sulfito product is formed quantitatively from the di-μ-hydroxo species.

Sulfur Dioxide Uptake.—The kinetics of this reaction was studied in the ranges $3.78 \leqslant \text{pH} \leqslant 5.47$, $20.0 \leqslant \theta \leqslant 30.0$ °C, and $0.03 \leqslant [S]_T \leqslant 0.05$ mol dm^{-3} under pseudo-first-order conditions with 3.0×10^{-3} mol dm^{-3} complex using the stopped-flow technique, and observed rate constants are listed in Tables 1 and 2.

The aqueous chemistry summarized in Scheme 1 shows that there are four complex species in solution, the ring-closed di-μ-hydroxo and the three mono-μ-hydroxo cations. Since K (the equilibrium constant between the di-μ-hydroxo and mono-μ-hydroxo species) is independent[16] of pH it would be difficult to

Table 1 Pseudo-first-order rate constants for uptake of SO_2 by $[(en)_2Cr(\mu\text{-}OH)_2Cr(en)_2]^{4+}$; I = 1.0 mol dm^{-3} ($NaClO_4$), $[S]_T$ = 0.050 mol dm^{-3}, [Complex] = 0.005 mol dm^{-3} (pH variation)

20.0 °C		25.0 °C		30.0 °C	
pH	k_{obs}/s^{-1}	pH	k_{obs}/s^{-1}	pH	k_{obs}/s^{-1}
3.81	21.2	4.20	28.4	3.78	36.5
4.33	20.5	4.43	27.2	4.35	35.2
4.72	19.6	4.62	26.6	4.63	34.5
4.81	19.2	4.85	25.4	4.83	33.1
5.01	18.2	5.14	23.0	4.96	32.8
5.15	17.9	5.27	21.7	5.12	29.5
5.26	17.0	5.39	20.9	5.26	29.0
5.33	16.2	5.47	20.3	5.33	27.1
5.46	14.3			5.41	25.5

Table 2 Pseudo-first-order rate constants for uptake of SO_2 by $[(en)_2Cr(\mu\text{-}OH)_2Cr(en)_2]^{4+}$; $[S]_T$ variation, pH 4.45 ± 0.03, 25.0 °C

$10^2[S]_T$/mol dm^{-3}	k_{obs}/s^{-1}
3.0	15.9
3.5	19.2
4.0	21.0
4.5	24.1
5.0	27.1

determine the reactivity (if any) of the di-μ-hydroxo cation towards any of the three S^{IV}-containing species, so the analysis of the kinetic data is based entirely on the mono-μ-hydroxo species (the hydroxo-bridge has been shown[17] to be unreactive towards dissolved CO_2). The di-μ-hydroxo cation containing cyclen (= 1,4,7,10-tetraazacyclododecane) as ligand, which is believed[18] to contain only ring-closed species in solution, reacts very slowly[14] with sulfite. This would tend to suggest that the di-μ-hydroxo cation would contribute very little to the rate on the stopped-flow time-scale.

The total sulfite, $[S]_T$, variation data show that there is a direct dependence on $[S]_T$, which means that one (or more) of the sulfur(IV) species is involved in the reaction. The pH-variation data show that there is a possible dependence on $[SO_2]$ or $[HSO_3^-]$. The proposed mechanism is given in Scheme 1. The reactions of the aqua-hydroxo mono-μ-hydroxo cation with HSO_3^- and that of the dihydroxo mono-μ-hydroxo cation with SO_2 are kinetically indistinguishable and are related by the ratio of the acid dissociation constants [see equations (1) and (2)], where D^{4+} and D^{3+} are the aqua-hydroxo and dihydroxo forms of the mono-μ-hydroxo species, respectively.

$$\begin{tikzcd}
D^{4+} \arrow[d, shift left, "K_5"] & + & HSO_3^- \arrow[r, "k_1"] \arrow[d, shift left, "K_1"] & \text{Product} \\
D^{3+} \arrow[u, shift left] & + & SO_2 \arrow[r, "k_2"] \arrow[u, shift left] & \text{Product}
\end{tikzcd} \qquad (1)$$

$$k_1 = k_2(K_5/K_1) \qquad (2)$$

Mechanisms in which each step was considered without the other were postulated and reasonably good fits were obtained (in the lower pH range), but it was observed that calculated k_{obs} values were higher than the experimentally obtained ones at the higher pH values and the deviation increased with increasing pH. This led us to propose a mechanism in which an unreactive HSO_3^- ion pair was formed, and this gave an excellent fit. The sulfite concentration $[SO_3^{2-}]$ is very small in the pH range investigated and was found to have very little influence on the mechanism. The occurrence of the unreactive HSO_3^- ion pair would therefore rule out the reaction of the aqua-hydroxo mono-μ-hydroxo cation with HSO_3^-, hence the mechanism in Scheme 1.

Table 3 Kinetic parameters for uptake of SO_2 by $[(en)_2Cr(\mu\text{-}OH)_2\text{-}Cr(en)_2]^{4+}$

T/°C	$10^{-7}k_2$/dm^3 mol^{-1} s^{-1}	K_{IP}/dm^3 mol^{-1}
20.0	8.1 ± 0.1	51 ± 15
25.0	8.7 ± 0.1	50 ± 10
30.0	9.2 ± 0.1	49 ± 15

$\Delta H^{\ddagger}$ = 6.5 ± 0.9 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −71 ± 2 J K^{-1} mol^{-1}.

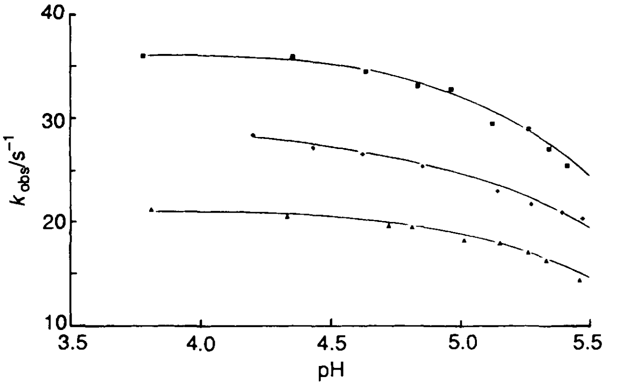


Fig. 2 Plots of k_{obs} *vs.* pH for uptake of SO_2 by $[(en)_2Cr(\mu\text{-}OH)_2\text{-}Cr(en)_2]^{4+}$. Solid lines are calculated from equation (3). Temperature: (▲) 20, (◆) 25 and (■) 30 °C

From the proposed mechanism the expression (3) can be derived. Values of k_2 and K_{IP} were calculated using the STATGRAPHICS computer program in the non-linear regression mode, and are given in Table 3. The calculated value for k_2 [(8.73 ± 0.05) × 10^7 dm^3 mol^{-1} s^{-1}, 25 °C] compares very well with reported[1–7] values for mononuclear hydroxoamine metal complexes reacting with SO_2 (*ca.* 10^8 dm^3 mol^{-1} s^{-1}).

$$k_{obs} = k_2\left(\frac{K}{1+K}\right) \left(\frac{K_4K_5[SO_2]}{[H^+]^2 + K_4[H^+] + K_4K_5 + K_4K_5K_{IP}[HSO_3^-]}\right) \qquad (3)$$

Plots of k_{obs} *vs.* pH for the reaction of the di-μ-hydroxo species with SO_2 are shown in Fig. 2 where the solid lines were calculated from equation (3).

Over the pH range investigated the aqua-hydroxo mono-μ-hydroxo cation is the major mono-μ-hydroxo species[16] in all kinetic solutions, and one would expect it to be reactive towards SO_2 since it has a terminal hydroxide ligand which is a potential reactive site. The strong hydrogen bonding between the *cis* aqua and hydroxo groups of this species, which makes it dominant over the range, could be the factor that makes the terminal hydroxide unreactive (or much less reactive) towards SO_2.

The activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were determined from the temperature-dependence data (Table 3) utilizing Eyring's equation[19] and least-squares analysis. The value of $\Delta H^{\ddagger}$ for the reaction was found to be 6.5 ± 0.9 kJ mol^{-1} which is not unusual for this type of reaction.[1–7] The value of $\Delta S^{\ddagger}$ was −71 ± 2 J K^{-1} mol^{-1} which is similar to the reported[7] value of −88 ± 15 J K^{-1} mol^{-1} for the $[Co(tetren)(OH)]^{2+}$ cation reacting with SO_2. In general, for uptake of SO_2 and CO_2, $\Delta S^{\ddagger}$ is either small or negative indicating a highly ordered transition state. This is quite possible in the dihydroxo mono-μ-hydroxo cation since it has two *cis* hydroxide groups which can form hydrogen bonds (and possibly S···O dipole–dipole interactions) as shown.

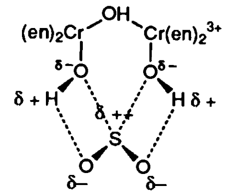
Table 4 Observed rate constants for ring closure of $[(en)_2Cr(\mu\text{-}OH)_2(en)_2]^{4+}$. [Complex] = 0.003 mol dm^{-3}, $[S]_T$ = 0.030 mol dm^{-3}, I = 1.0 mol dm^{-3} ($NaClO_4$)

19.9 °C		25.2 °C		29.9 °C	
pH	k_{obs}/s^{-1}	pH	k_{obs}/s^{-1}	pH	k_{obs}/s^{-1}
2.46	0.420	2.46	0.536	2.43	0.681
2.52	0.410	2.61	0.512	2.61	0.673
2.62	0.365	2.77	0.434	2.76	0.613
2.82	0.334	2.87	0.407	2.88	0.582
2.90	0.311	3.05	0.366	3.01	0.516
3.10	0.280	3.25	0.342	3.19	0.481
3.19	0.244	3.43	0.304	3.36	0.455
3.48	0.214	3.63	0.274	3.52	0.414
3.66	0.195	3.96	0.201	3.72	0.400
3.96	0.148	4.46	0.137	4.04	0.276
4.36	0.087			4.42	0.260

Table 5 Rate constants, dissociation constants and activation parameters for the formation of the sulfite bridge (ring closure)

T/°C	k_3/s^{-1}	k_4/s^{-1}	pK_6	pK_7
19.9	0.55	0.099	1.54	2.94
25.2	0.68	0.15	1.49	2.98
29.9	0.83	0.25	1.39	3.08

$\Delta H_3^‡ = 28 \pm 1$, $\Delta H_4^‡ = 66 \pm 7$, $\Delta H_6^{-} = 23 \pm 4$ and $\Delta H_7^{\ominus} = -22 \pm 5$ kJ mol^{-1}; $\Delta S_3^‡ = -155 \pm 3$, $\Delta S_4 = -40 \pm 24$, $\Delta S_6^{\ominus} = 0.37 \pm 0.08$ and $\Delta S_7^{\ominus} = -0.97 \pm 0.09$ J K^{-1} mol^{-1}.

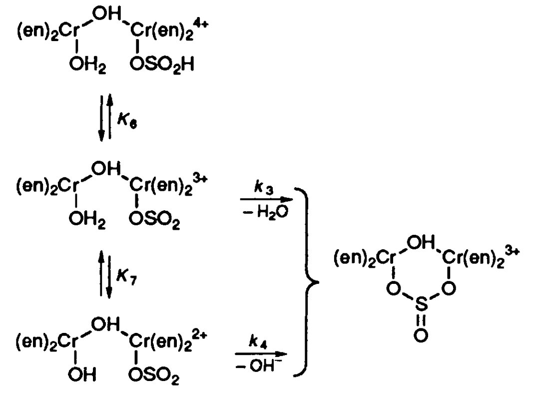


Formation Of Bridging Sulfite (*Ring Closure*).—This reaction was studied in the ranges $2.43 \leqslant pH \leqslant 4.46$, $20.0 \leqslant \theta \leqslant 29.9$ °C and $0.03 \leqslant [S]_T \leqslant 0.05$ mol dm^{-3}. It was found to be independent of $[S]_T$. The primary kinetic data in Table 4 show a decrease in k_{obs} with increasing pH, which could suggest that the protonated form of some species formed from the sulfur dioxide uptake reaction is the more (or most) reactive in this step. The proposed mechanism is shown in Scheme 2 where the assumption is made that the aqua(hydrogensulfito) mono-μ-hydroxo cation would not undergo ring closure but eliminate sulfur dioxide due to the activation of the proton (as reported[1-7] for mononuclear cases).

From the proposed mechanism the expression for k_{obs} would take the form (4). The values of k_3, k_4, K_6 and K_7 were

$$k_{obs} = (k_3K_6[H^+] + k_4K_6K_7)/([H^+]^2 + K_6[H^+] + K_6K_7) \quad (4)$$

calculated by a non-linear regression method using the STATGRAPHICS computer program, and are given in Table 5 along with their activation parameters. A fit of the experimental data by the curve generated from the values given in Table 5 is shown in Fig. 3.



Scheme 2

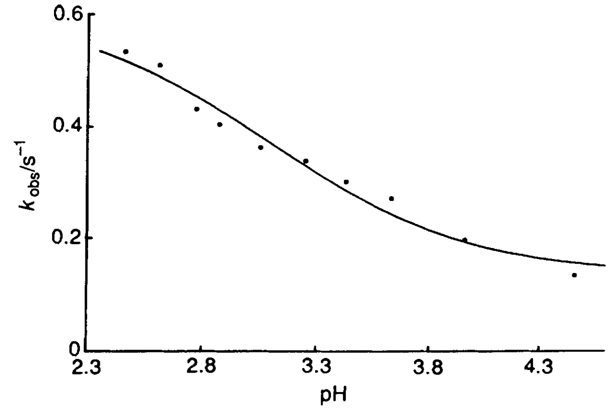
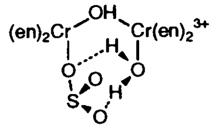
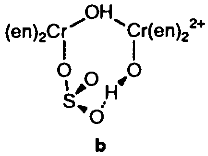


Fig. 3 Plot of k_{obs} *vs.* pH for the formation (ring closure) of the sulfito-bridged species $[(en)_2Cr(\mu\text{-}OH)(\mu\text{-}SO_3)Cr(en)_2]^{3+}$. Solid line calculated from equation (4)

At a first glance at this mechanism the k_4 step is expected to be very much slower than k_3, since a hydroxide is being lost in the former and an aqua ligand in the latter. In general, hydroxide is a poor leaving group. The data show that k_4 is indeed less but only by a factor of about four on average. This could be due to the formation of a transition state which allows the hydroxide to leave without much difficulty. The more negative value of $\Delta S^‡$ for the k_3 step could be indicative of a more ordered transition state as depicted. Since there is more hydrogen bonding involved in the transition state **a**, its Cr–OH_2 bond should be somewhat weaker than the Cr–OH bond of **b**. The 'free' oxygen in **b** can assist in cleavage of the Cr–OH bond. This is therefore an associative interchange (I_a) type mechanism which exhibits the anchimeric effect.[15]



a



b

Acid Hydrolysis of $[(en)_2Cr(\mu\text{-}OH)(\mu\text{-}SO_3)Cr(en)_2]^{3+}$.—Kinetic runs in $HClO_4$ solution show that the rate constant, (7.8 ± 0.1) × 10^{-5} s^{-1} at 25 °C, for the decomposition of the (μ-OH)(μ-SO_3) species is independent of $[H^+]$ over the range 0.01–1.0 mol dm^{-3}. Attempted characterization of the hydrolysis product *via* ion-exchange chromatography and UV/VIS spectrophotometry was unsuccessful. Free sulfite was detected but the di-μ-hydroxo cation was not. The possible hydrolysis product, *cis*-$[Cr(en)_2(OH_2)_2]^{3+}$ was not detected; therefore, the mixture probably contains cations with partially or fully hydrolysed 1,2-diaminoethane ligand. This is possible since the Cr–N bond is very susceptible to hydrolysis.[20]

Reactivity of $[(en)_2Cr(\mu\text{-}OH)(\mu\text{-}SO_3)Cr(en)_2]^{3+}$ *in Aqueous Sulfite*.—A product isolated from this reaction could have one of two formulae, $[Cr_2(en)_2(OH)_2(SO_3)_2]\cdot H_2O$ or $[Cr(en)(OH)(SO_3)(OH_2)]$ according to the elemental microanalysis results. We were not able to determine the formula weight

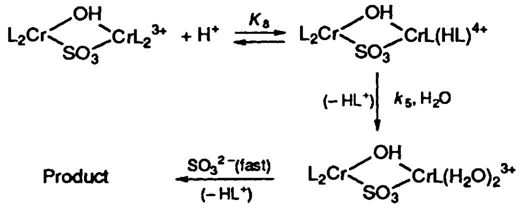
Table 6 Kinetic data for the further addition of sulfite to $[(en)_2Cr(\mu\text{-}OH)(\mu\text{-}SO_3)Cr(en)_2]^{3+}$; varying pH, [Complex] = 0.003 mol dm^{-3}, I = 1.0 mol dm ^{3} ($NaClO_4$), $[S]_T$ = 0.030 mol dm^{-3}

20.0 °C		25.0 °C		30.0 °C	
pH	$10^4k_{obs}/s^{-1}$	pH	$10^4k_{obs}/s^{-1}$	pH	$10^4k_{obs}/s^{-1}$
2.22	1.40	2.11	2.90	2.15	4.97
2.76	1.43	2.46	2.96	2.74	4.90
3.28	1.49	2.82	2.85	3.30	4.98
3.85	1.48	3.15	3.07	3.84	4.78
4.38	1.39	3.49	3.11	4.35	4.21
4.78	1.34	3.75	3.01	4.81	3.61
5.16	1.15	4.11	3.11	5.19	2.40
5.79	0.67	4.46	2.86	5.76	1.09
6.48	0.35	4.82	2.55	6.51	0.219
7.26	0.17	5.15	2.22	7.28	0.040
		5.74	1.21		
		6.08	0.91		
		6.46	0.48		
		6.88	0.23		

Table 7 Rate and equilibrium constants and activation parameters for further sulfite addition

T/°C	$10^4k_5/s^{-1}$	$10^{-5}K_8/dm^3\ mol^{-1}$
20.0	1.43	8.0
25.0	3.01	3.8
30.0	5.04	1.5

$\Delta H^\ddagger = 91 \pm 8$ kJ mol^{-1}, $\Delta S^\ddagger = -8.7 \pm 29.6$ J K^{-1} mol^{-1}, $\Delta H^\ominus = 124 \pm 9$ kJ mol^{-1}, $\Delta S^\ominus = -4.5 \pm 0.4$ J K^{-1} mol^{-1}.



Scheme 3 L = en

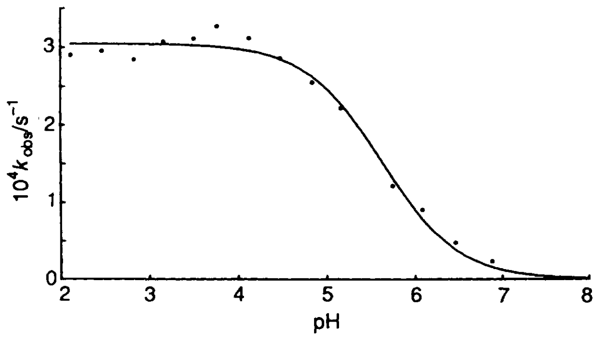


Fig. 4 Plot of k_{obs} *vs.* pH for further addition of sulfite to $[(en)_2Cr(\mu\text{-}OH)(\mu\text{-}SO_3)Cr(en)_2]^{3+}$. Solid line calculated from equation (5)

because of its insolubility (probably due to its neutrality) and so the product is somewhat uncertain. This product could also be polymeric, which is not unusual for Cr^{III},[21] and this could account for its insolubility.

An inspection of the primary kinetic data, given in Table 6, shows that proton pre-equilibration is important in the rate-determining step. Although this reaction requires the presence of sulfite to proceed, it was independent of $[S]_T$ over the range 0.03–0.05 mol dm^{-3} (k_{obs} = 2.92 ± 0.02 s^{-1}, pH = 4.12, θ = 25 °C). In some experiments in which the reaction mixture was not buffered it proceeded with an increase in pH. This could be due to loss of the 1,2-diaminoethane ligand. It is therefore proposed that the rate-determining step involves the acid-catalysed loss of 1,2-diaminoethane ligand followed by rapid addition of sulfite as shown in Scheme 3.

From the mechanism proposed expression (5) can be derived

$$k_{obs} = (k_5K_8[H^+])/(1 + K_8[H^+]) \qquad (5)$$

which can be rearranged to form (6). A plot of $1/k_{obs}$ *vs.* $1/[H^+]$

$$1/k_{obs} = (1/k_5K_8)/[H^+]^{-1} + (1/k_5) \qquad (6)$$

gave a good straight line, where k_5 and K_8 can be derived from the intercept and slope, respectively. The calculated values along with activation parameters are given in Table 7. At 25 °C pK_8' (where $K_8' = 1/K_8$) was calculated to be 5.6 which would suggest that at low pH (< 4) basically all the complex is in the protonated form which would give a more or less constant value of k_{obs}, as was the case.

A plot of k_{obs} *vs.* pH for the experimentally obtained values and the calculated line generated from the values in Table 7 is shown in Fig. 4.

Conclusion

The reactivity of the μ-hydroxo-μ-sulfito dinuclear complex is very similar to that of mononuclear complexes previously investigated, in that the terminal hydroxide was found to react with dissolved SO_2 at a rate comparable to those of the mononuclear hydroxo complexes.

A startling feature of this work is the unreactivity of the *cis*-aquahydroxo complex towards dissolved SO_2. This unreactivity (or very low reactivity) is attributed to the extensive hydrogen bonding in this species which literally ties up the terminal hydroxide.

The possible formation of a disulfito product is also very interesting, but this needs further characterization.

One of the main aims of this project has not been realized, and that is the reactivity of the hydroxide bridge. Further work is being done in this area.

Acknowledgements

This work was supported by grants provided by the Research and Publications Fund Committee and by the Board of Postgraduate Studies, University of the West Indies. P. T. M. thanks the Alumina Company of Canada (Jamaica) Ltd. for providing a postgraduate research fellowship which helped to finance the study.

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Received 8*th January* 1993; *Paper* 3/00138E