Kinetics of the Formation, Reactivity and Crystal Structure of the Sulfite-bridged Cation Di-μ-hydroxo-μ-(sulfito-*O,O′*)-bis[(1,4,7-triazacyclononane)chromium(III)]†

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The kinetics of the formation of $[(tacn)Cr(\mu\text{-}OH)_2(\mu\text{-}OSO_2)Cr(tacn)]^{2+}$ (tacn = 1,4,7-triazacyclononane) from *trans*-$[(H_2O)(tacn)Cr(\mu\text{-}OH)_2Cr(tacn)(H_2O)]^{4+}$ in aqueous buffered sulfite solution have been studied spectrophotometrically. The formation takes place in two steps. The first step which is a rapid uptake of SO_2 was studied at 532 nm in the range $1.82 \leqslant pH \leqslant 5.93$, $0.03 \leqslant [S]_t \leqslant 0.05$ mol dm^{-3} ($[S]_t = [SO_2] + [HSO_3^-] + [SO_3^{2-}]$) and $19.9 \leqslant \theta \leqslant 29.9$ °C. The rate constant for SO_2 uptake at 25.2 °C was found to be 2.10 ± 0.09 dm^3 mol^{-1} s^{-1} with $\Delta H^\ddagger = 94 \pm 2$ kJ mol^{-1} and $\Delta S^\ddagger = 110 \pm 8$ J K^{-1} mol^{-1}. The second step in the formation is the pH-independent isomerization of the *trans*-aqua-sulfito species, to the *cis* analogue [$k_{iso} = (4.5 \pm 0.1) \times 10^{-3}$ s^{-1}, 25.2 °C]; followed by a fast unobserved ring-closure step. The sulfido-bridged product undergoes hydroxo bridge cleavage in acid solution ($0.030 \leqslant [H^+] \leqslant 1.0$ mol dm^{-3}) to form *cis*-$[(H_2O)(tacn)Cr(\mu\text{-}OH)(\mu\text{-}O_2SO)Cr(tacn)(H_2O)]^{3+}$ in which the sulfite bridge remains intact [$k = (6.1 \pm 0.1) \times 10^{-2}$ s^{-1}, 30.0 °C]. The crystal structure of $[(tacn)Cr(\mu\text{-}OH)_2(\mu\text{-}O_2SO)Cr(tacn)][ClO_4]_2\cdot 3H_2O$ shows that the sulfite moiety is bridging the two metal centres *via* two of its oxygen atoms with partial inversion of the sulfur.

The reactivity of mononuclear aquatransition-metal complex ions in aqueous sulfite solution has been well documented.[1-8] The kinetic data show that in each case the most significant initial step in the overall process is the rapid nucleophilic attack by ligand hydroxide on dissolved SO_2 to form an unstable O-bonded complex, a reaction that is readily reversible by immediate acidification. Subsequent reactions which include O- to S-bonded isomerization, internal redox or further sulfite addition depend on the pH, the N_4 or N_5 ligand grouping and the metal centre.

The reaction of hydroxo-bridged transition-metal complex ions in aqueous sulfite is not so well documented. The isolation of a sulfite-bridged cobalt(III) dimer has been reported.[9] This species was characterised using IR spectroscopy and was concluded to be doubly O-bonded. We recently reported[10] the formation and reactivity of the μ-hydroxo-μ-sulfito-bis[bis(1,2-diaminoethane)chromium(III)] cation. This species was also concluded to be doubly O-bonded based on comparison of IR data with those of the species of ref. 9. We now report the isolation of a very stable sulfito-bridged chromium(III) complex, elucidation of the mechanism of its formation, investigation of its reactivity in aqueous sulfite and in acidic solutions and the ultimate proof of the mode of co-ordination of the sulfite moiety in a crystal structure.

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 Co., MA), was used for all spectral investigations in solution. Solid $Na_2S_2O_5$ (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]

Crystallography.—*Crystal data.* $C_{12}H_{38}Cl_2Cr_2N_6O_{16}S$, $M = 729.4$, orthorhombic, space group *Pbnm*, $a = 9.009(3)$, $b = 14.461(4)$, $c = 22.032(6)$ Å, $U = 2870(1)$ Å^3, $Z = 4$ (the complex has crystallographic C_s symmetry), $D_c = 1.688$ g cm^{-3}, Cu-Kα radiation, $\bar{\lambda} = 1.541\ 78$ Å, μ(Cu-Kα) = 93.5 cm^{-1}, $F(000) = 1512$. Purple platy needles, crystal dimensions 0.10 × 0.13 × 0.30 mm.

Data collection and processing. Data were measured on a Nicolet R3m diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. 1988 Independent reflections were measured ($2\theta \leqslant 116°$) of which 1596 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors; a numerical absorption correction (face-indexed crystal) was applied; maximum and minimum transmission factors were 0.463 and 0.291 respectively.

Structure analysis and refinement. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. A ΔF map revealed the presence of one full-weight and four half-weight included water molecules, and of disorder in the perchlorate anions and the bridging sulfite group. Six different oxygen positions were identified within each perchlorate group and their site occupancies were refined. The disorder in the sulfite group involves an inversion of the sulfite centre, the position of the three oxygen atoms remaining fixed. The occupancies of the two sulfur positions were 0.9 and 0.1 respectively. Major-occupancy atoms were refined anisotropically and minor ones isotropically. The positions of the hydrogen atoms including those of the partial-weight water molecules were determined from a ΔF map. The positions of the CH and NH hydrogen atoms were idealised, they were assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C, N)$ and allowed

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

to ride on their parent C, N atoms. The OH hydrogens were refined isotropically [$U(\mathrm{H}) = 1.2U_{eq}(\mathrm{O})$] subject to an O–H distance constraint. Refinement was by full-matrix least squares (228 variable parameters) to give $R = 0.057$, $R' = 0.059$, [$w^{-1} = \sigma^2(F) + 0.001F^2$]. The maximum and minimum electron densities in the final ΔF map were 0.51 and -0.42 e Å^{-3}. Computations were carried out on a 486 PC using the SHELXTL program system (PC version 4.2).[11]

Preparation and Characterization of Complexes.—1,4,7-*Triazacyclononane trihydrochloride*. The hydrochloride of the macrocyclic ligand 1,4,7-triazacyclononane (tacn) was synthesized by the method of Richman and Atkins[12] in 73% yield. Proton NMR spectroscopy was used to confirm the structure; ^{1}H NMR (60 MHz, D_2O), δ (3.70, s, CH_2), m.p. 267–270 °C (lit.,[13] 260–270 °C).

Trichloro(1,4,7-*triazacyclononane*)*chromium*(III) [Cr(tacn)-Cl_3]. This complex was prepared from chromium(III) chloride hexahydrate and the above hydrochloride salt by the method of Weighardt *et al.*[14a] in 87% yield.

trans-*Diaqua-di-μ-hydroxo-bis*[(1,4,7-*triazacyclononane*)-*chromium*(III)] *tetraperchlorate* [(H_2O)(tacn)Cr(μ-OH)$_2$Cr-(tacn)(H_2O)][ClO_4]$_4$. This complex was prepared by the method of Weighardt *et al.*[14a] The UV/VIS spectral parameters were in good agreement with the literature.[14a]

Di-μ-*hydroxo*-μ-(*sulfito*-O,O′)-*bis*[(1,4,7-*triazacyclononane*)-*chromium*(III)]*diperchlorate trihydrate* [(tacn)Cr(μ-OH)$_2$(μ-O_2-SO)Cr(tacn)][ClO_4]$_2$·$3H_2O$. The *trans*-diaqua complex (1.0 g, 0.012 mol) was dissolved in water (20 cm^3) and $Na_2S_2O_5$ (1.2 g, 0.006 mol) was added with stirring until dissolution was complete. The solution was left in an air-conditioned room (20 °C) for 24 h to facilitate crystallization. The red-pink product was filtered off, washed with ice-cold ethanol–water (2 cm^3, 1 : 1 v/v), two portions (2 cm^3) of 95% ethanol, and dried in air. Yield 0.75 g (87%).

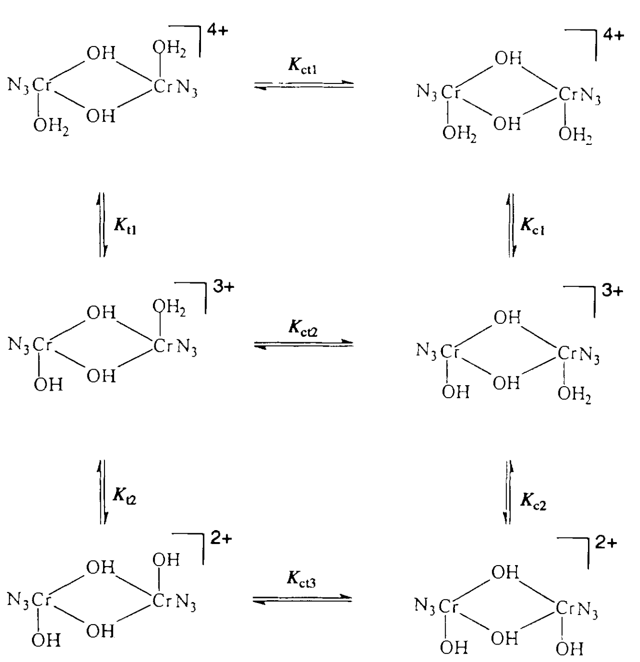
The visible spectrum of an aqueous solution of this complex showed absorption coefficients of 186 and 149 dm^3 mol^{-1} cm^{-1} at 532 and 406 nm respectively.

The purity was checked by microanalysis (by Dr. E. Pascher, Mikroanalytisches Labor Pascher, An der Pulvermuhle 3, D-5480 Remegan 8) (Found: C, 19.50; H, 5.15; N, 11.5; S, 4.45. $C_{12}H_{38}Cl_2Cr_2N_6O_{16}S$ requires C, 19.75; H, 5.25; N, 11.50; S, 4.40%).

The IR spectrum showed bands assignable[9] to the bridging sulfite, δ(OSO) 640w, ν(SO) 832m, 866m, 912ms, 940s and 974s cm^{-1}.

Spectral Measurements.—Visible spectra were recorded on either a Varian Cary 219 or a Hewlett-Packard 8452A diode array spectrophotometer, and IR spectra were measured with either a Perkin-Elmer 735B or a Pye-Unicam SP3–300 employing the KBr disc technique.

Kinetic Measurements.—The kinetic data for the fast reactions were obtained by following the absorbance change at 532 nm where there is an appreciable absorbance change between the reactant and the product (The absorption coefficients of the *trans*-diaqua cation and the sulfito complex are *ca.* 128 and 186 dm^3 mol^{-1} cm^{-1}, respectively). Analysis of the kinetic data at 406 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. The pH-jump technique was employed where sulfite and unbuffered 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.[14b]



Scheme 1 N_3 = 1,4,7-triazacyclononane

Table 1 Acid dissociation and equilibrium constants for *trans*-[$(H_2O)(N_3)Cr(\mu\text{-}OH)_2Cr(N_3)(H_2O)$]$^{4+}$ at 25 °C[16]

	N_3 = tacn	$(NH_3)_3$
pK_{t1}	5.08	6.15
pK_{t2}	7.25	7.48
pK_{c1}	2.82	4.19
pK_{c2}	8.80	9.05
pK_{ct1}	0.037	0.092
pK_{ct2}	6.85	82
pK_{ct3}	0.192	0.216

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[15] *viz.* 0.01 mol dm^{-3} $Na_2B_4O_7$·10 H_2O or 0.025 mol dm^{-3} KH_2PO_4–0.025 mol dm^{-3} Na_2HPO_4. For slow reactions the pH was measured both before and after the run. For fast reactions the pH was measured immediately after mixing.

Results and Discussion

Acid-dissociation and Equilibrium Constants.—The *trans*-diaquadi(μ-hydroxo)-bis[(1,4,7-triazacyclononane)chromium-(III)] cation was shown[16] to undergo a complex set of equilibria with its mono- and di-deprotonated forms and the corresponding *cis* isomers (Scheme 1). In this scheme the parameters K_t and K_c refer to the dissociation constants of the *trans* and *cis* isomers respectively and terms K_{ct} are the equilibrium constants for the *cis*/*trans* isomeric pairs; values of these parameters are given in Table 1. Inspection of these data reveals that the *trans*-diaqua and -dihydroxo species are dominant at low and high pH ranges respectively, whereas the *cis*-aquahydroxo form is dominant over a wide range of intermediate pH. This dominance of the *cis*-aquahydroxo form is attributed to hydrogen bonding between the *cis* aqua and hydroxo groups which gives it extra stability. This was also observed[17] for the *cis*-aquabis[bis(1,2-diaminoethane)-hydroxochromium(III)] cation.

Sulfur Dioxide Uptake.—When sulfite is added to an aqueous solution of the complex there is an immediate change in colour from violet to red-pink. This change corresponds to an increase in both absorption maxima as shown in Fig. 1, a reaction that is complete within 10 s.

The kinetics of the reaction were studied in the ranges, $1.82 \leqslant pH \leqslant 5.93$, $0.03 \leqslant [S]_t \leqslant 0.05$ mol dm^{-3} ($[S_T] = [SO_2] + [HSO_3^-] + [SO_3^{2-}]$), $19.9 \leqslant I \leqslant 31.0$ °C, with the complex concentration at 3.0×10^{-3} mol dm^{-3}, by the stopped-flow technique. The observed pseudo-first order rate constants are given in Tables 2 and 3.

A study of the aqueous chemistry[16] of the complex cation and sulfite reveals that there are nine possible reactive species (six from the complex and three from sulfite), which might have proved very difficult to analyse. However, based on the pK values of the complex cation and sulfuric(IV) acid, the pH range employed and the variation of k_{obs} with pH, the species of major significance are the *trans*-diaqua and -hydroxoaqua cations, SO_2 and HSO_3^-.

A stock solution of the complex has a pH of *ca.* 2.5 which means that virtually all (> 99%) the complex is in the diaqua form (*ca.* 96% *trans* and *ca.* 4% *cis*). At higher pH values the *trans*-hydroxoaqua cation would undergo reaction before it could isomerise to the *cis* form since uptake of sulfite is much faster than isomerization.

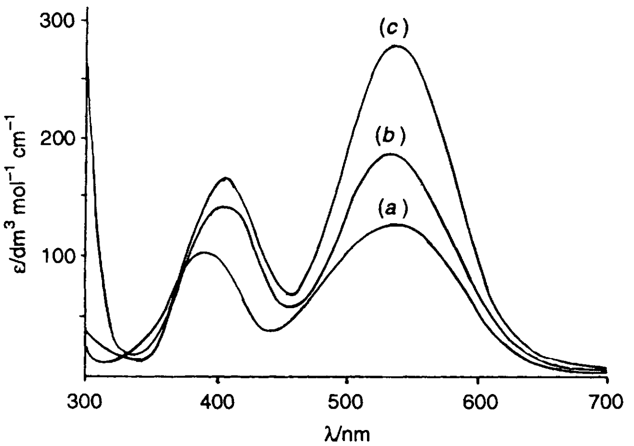


Fig. 1 Absorption spectra of (*a*) *trans*-$[(H_2O)(tacn)Cr(\mu\text{-}OH)_2Cr(tacn)(H_2O)]^{4+}$, (*b*) $[(tacn)Cr(\mu\text{-}OH)_2(\mu\text{-}O_2SO)Cr(tacn)]^{2+}$ and (*c*) *cis*-$[(H_2O)(tacn)Cr(\mu\text{-}OH)(\mu\text{-}O_2SO)Cr(tacn)(H_2O)]^{3+}$

Table 2 Pseudo-first order rate constants for the reaction of *trans*-$[(H_2O)(tacn)Cr(\mu\text{-}OH)_2Cr(tacn)(H_2O)]^{4+}$ in aqueous sulfite; $I = 1.0$ mol dm^{-3} ($NaClO_4$), [Complex] = 3×10^{-3} mol dm^{-3}. $[S]_t = 0.030$ mol dm^{-3}

T/°C 19.9		25.2		29.9	
pH	k_{obs}/s^{-1}	pH	k_{obs}/s^{-1}	pH	k_{obs}/s^{-1}
1.82	0.908	2.43	1.73	1.82	3.53
2.07	0.875	2.68	1.62	2.16	3.50
2.45	0.744	2.84	1.43	2.49	3.29
2.73	0.678	2.93	1.35	2.79	2.88
3.10	0.542	3.30	0.98	3.11	2.14
3.46	0.346	3.48	0.77	3.44	1.44
3.72	0.231	3.66	0.56	3.72	0.957
4.14	0.150	3.85	0.41	4.00	0.562
4.58	0.102	3.99	0.30	4.30	0.348
5.00	0.069	4.13	0.23	4.73	0.206
5.46	0.036	4.34	0.14	5.17	0.095
5.93	0.021	4.47	0.095	5.47	0.056
		4.64	0.062		

A mechanism in which the diaqua cation and the hydroxoaqua cation are reacting with HSO_3^- and SO_2 respectively was considered (Scheme 2). The mechanism was considered plausible owing to the proven reactivity of terminal hydroxide with dissolved sulfur dioxide.[1–8,10]

In this scheme the pathways described by k_1 and k_2 are kinetically indistinguishable, and k_1 and k_2 are related by the ratio of the acid dissociation constants [equation (1)]. Separate

$$k_1 = k_2(K_{t1}/K_1) \qquad (1)$$

fits could be made for both the k_1 and k_2 steps but were linear for only a very small range of the data under highly acid conditions (pH < 2.5). The inclusion of an acid hydrolysis step into the mechanism did not improve the fit.

The inability of the above mechanism (which operates for mononuclear and previously reported dinuclear systems)[10] to account for the kinetic data led us to consider a different pathway, involving the formation of an adduct with sulfur dioxide (Scheme 3).

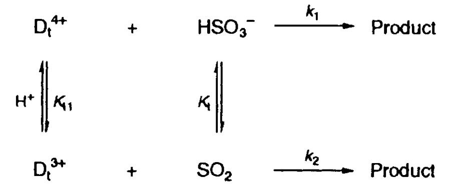
The expression for the observed rate constant based on the mechanism presented in Scheme 3 is given by equation (2).

$$k_{obs} = k_3K_{ad}[H^+][SO_2]/([H^+] + K_{t1} + K_{ad}[H^+][SO_2]) \qquad (2)$$

Equation (2) can be rearranged to give equation (3), the

$$1/k_{obs} = 1/k_3 + (1/k_3K_{ad})([H^+] + K_{t1})/([H^+][SO_2]) \qquad (3)$$

inverted linear form, where a plot of $1/k_{obs}$ *vs.* $([H^+] + K_{t1})/([H^+][SO_2])$ gave good straight lines for all three temperatures. The parameters k_3 and K_{ad} were derived from the intercept and slope respectively. The plots for all three



Scheme 2 D_t^{4+} and D_t^{3+} are the *trans*-diaqua and *cis*-hydroxoaqua species respectively

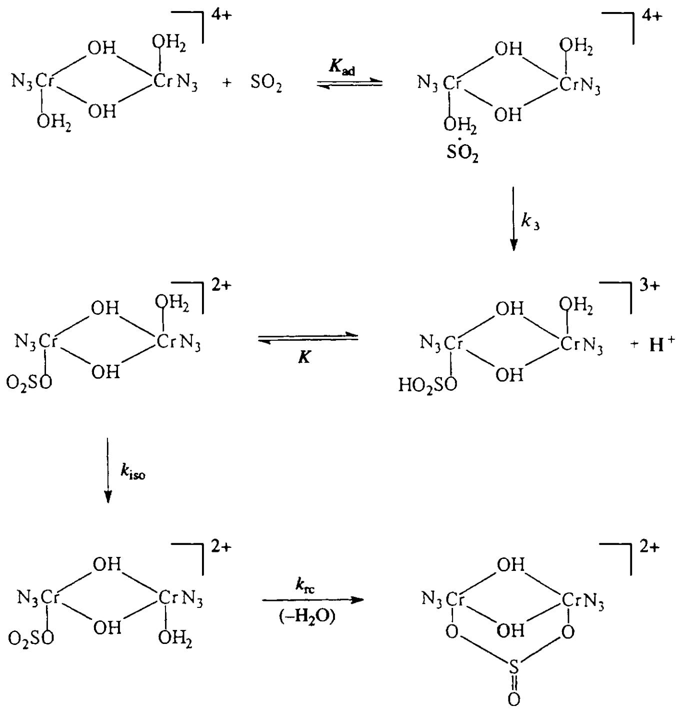
Table 4 Calculated rate and equilibrium constants for reaction of *trans*-$[(H_2O)(tacn)Cr(\mu\text{-}OH)_2Cr(tacn)(H_2O)]^{4+}$ with SO_2

T/°C	k_3/s^{-1}	K_{ad}/dm^3 mol^{-1}
19.9	0.94 ± 0.05	860
25.2	2.10 ± 0.09	755
29.9	3.97 ± 0.11	627

$\Delta H^\ddagger = 94 \pm 2$ kJ mol^{-1}
$\Delta S^\ddagger = 110 \pm 8$ J K^{-1} mol^{-1}
$\Delta H^\circ = 21.3 \pm 1.7$ kJ mol^{-1}
$\Delta S^\circ = 0.12 \pm 0.01$ J K^{-1} mol^{-1}

Table 3 Pseudo-first order rate constants for the reaction of *trans*-$[(H_2O)(tacn)Cr(\mu\text{-}OH)_2Cr(tacn)(H_2O)]^{4+}$ in aqueous sulfite; $I = 1.0$ mol dm^{-3} ($NaClO_4$), [Complex] = 3 mmol dm^{-3}, 25 °C, pH 3.03 (± 0.02)

$10^2[S]_t$/mol dm^{-3}	1.5	2.0	3.0	3.5	4.0	4.5	5.0
k_{obs}/s^{-1}	0.54	0.63	1.29	1.65	2.03	2.37	2.64



Scheme 3 N_3 = 1,4,7-triazacyclononane

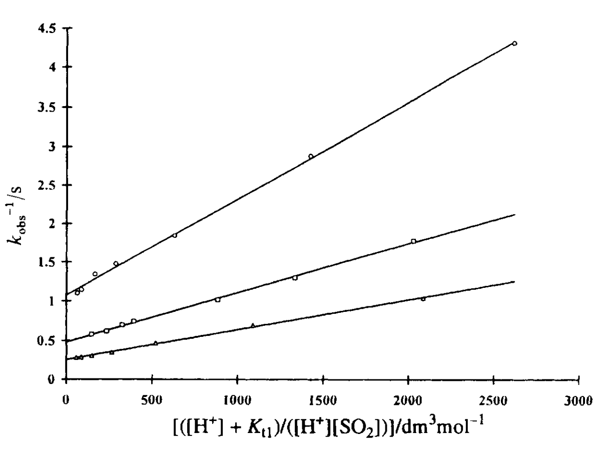


Fig. 2 Plot of $1/k_{obs}$ *vs.* $([H^+] + K_{t1})/([H^+][SO_2])$ for the reaction of *trans*-$[(H_2O)(tacn)Cr(\mu\text{-}OH)_2Cr(tacn)(H_2O)]^{4+}$ in aqueous sulfite. T = 19.9 (○), 25.2 (□) or 29.9 °C (△)

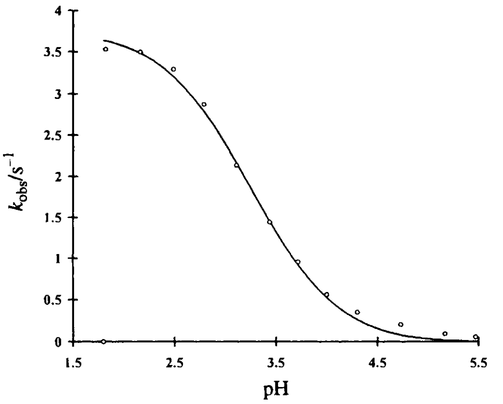


Fig. 3 Plot of k_{obs} *vs.* pH for SO_2 uptake by *trans*-$[(H_2O)(tacn)Cr(\mu\text{-}OH)_2Cr(tacn)(H_2O)]^{4+}$ at 29.9 °C. The solid line is calculated from equation (2)

temperatures are shown in Fig. 2 and the calculated values of k_3 and K_{ad} along with the corresponding activation parameters are given in Table 4.

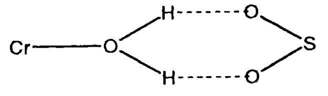
Fig. 3 shows a fit for the experimentally obtained values of k_{obs} (at 29.9 °C) *vs.* pH to that of a curve generated from the calculated rate and equilibrium constants from Table 4.

The value obtained for k, for the uptake of SO_2 is *ca.* eight orders of magnitude (10^8) less than that found for the corresponding process in reported aqua-mononuclear systems.[1-8] This large difference arises from the different reaction mechanism found in the present system as shown in Scheme 2.

Here uptake is not occurring *via* the rapid 'direct addition' mechanism in which there is no metal–oxygen bond breakage in the nucleophilic attack by terminal hydroxide ligand on sulfur dioxide. Rather, the rate-determining step, k_3, is the relatively slow rearrangement of a SO_2 adduct formed with the terminal aqua ligand of the complex. The activation energy for this step, $\Delta H^\ddagger = 94 \pm 2$ kJ mol^{-1}, is *ca.* three to four times greater than found for the corresponding SO_2 uptake for mononuclear hydroxoamine-metal complexes, demonstrating the increased difficulty of the reaction of the aqua ligand with SO_2. The increase in $\Delta H^\ddagger$ can be viewed as arising from an increased energy barrier in the concerted loss of two protons from the aqua ligand compared to the loss of only one proton in the case of the hydroxo ligand. The additional proton in the aqua ligand also makes it less nucleophilic towards SO_2 and contributes to the higher $\Delta H^\ddagger$ value. The $\Delta S^\ddagger$ value for most of the mononuclear systems and the recently reported[10] dinuclear system $[(en)_2Cr(\mu\text{-}OH)_2Cr(en)_2]^{4+}$ (en = 1,2-diaminoethane) for SO_2 uptake are either small or negative[1-8] which implies a highly ordered (or compact) transition state. The much higher value of $\Delta S^\ddagger$ for our system suggests that the solvation sphere of the transition state is loosened. If free-energy requirements are similar in all cases the increased value of $\Delta H^\ddagger$ can be seen as a compensation effect for the higher value of $\Delta S^\ddagger$.

The adduct formation constant, K_{ad}, decreases with an increase in temperature and reflects the exothermic nature of the adduct formation.

The fairly large value of K_{ad} (755 dm^3 mol^{-1}, 25.2 °C) is unusual since SO_2 is uncharged and therefore a much smaller association constant is expected. Comparatively large values were also found for SO_2 adduct formation constants for the dinuclear cobalt(III) cation, $[(en)_2Co(\mu\text{-}OH)_2Co(en)_2]^{4+}$ in our laboratory.[18] Ion-pair formation constants of 279, 125 and 27 dm^3 mol^{-1} for the respective ion pairs, $Cr(H_2O)_6^{3+} \cdots S_2O_5^{2-}$, $Co(tetren)(H_2O)^{3+} \cdots SO_3^{2-}$ and $Co(tetren)(H_2O)^{3+} \cdots SO_4^{2-}$ (tetren = tetraethylenepentamine) were reported.[7,8] The high association constant found here could be due to extensive hydrogen bonding between the two protons of the aqua ligand and the two oxygens of the bent sulfur dioxide molecule resulting in a six-membered ring transition state **I**. However, this reasoning is at variance with the fairly high value found for $\Delta S^\ddagger$. Instead, the high association constant could be a consequence of a strong attraction between the highly charged (4+) cation and the negatively charged oxygen atoms of the polar S–O bonds in the sulfur dioxide molecule.



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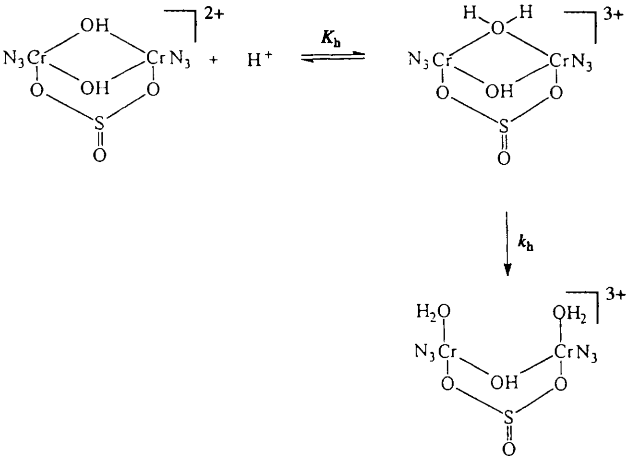
Reaction Subsequent to SO_2 *Uptake.*—After the sulfur dioxide uptake reaction a much slower process occurs which leads to the formation of a bridging sulfite species. This reaction

Table 5 Acid hydrolysis of $[(tacn)Cr(\mu-OH)_2(\mu-O_2SO)Cr(tacn)]^{2+}$; $I = 1.0$ mol dm^{-3} ($NaClO_4$), 30.0 °C

$[H^+]$/mol dm^{-3}	1.00	0.50	0.30	0.10	0.08	0.04	0.03
10^2k_{obs}/s^{-1}	5.60	5.66	5.51	4.46	3.90	3.32	2.60



Scheme 4 N_3 = 1,4,7-triazacyclononane

is represented by the two steps k_{iso} (isomerization) and k_{rc} (ring closure) in Scheme 3.

Investigation of this reaction revealed an observed first-order rate constant [$k_{obs} = (4.5 \pm 0.1) \times 10^{-3}$ s^{-1}, 25 °C) which was independent of both pH and $[S]_T$ in the ranges studied. This could imply that the rate-determining step here is totally internal and could be due to the isomerization (k_{iso}) of the *trans*-aquasulfito cation to the *cis*-aquasulfito cation. This isomerization step could then be followed by a much faster ring-closure (sulfite bridge formation) reaction, represented by k_{rc} in Scheme 3. A precedent for rapid ring closure of the *cis*-aquasulfito cation comes from a value of 0.68 s^{-1} (25 °C) found for a similar species[10] *cis*-$[(OSO_2)(en)_2Cr(\mu-OH)Cr(en)_2(H_2O)]^{3+}$.

This bridging sulfite species is fairly stable in water at room temperature and X-ray quality crystals were isolated as the perchlorate salt by slow evaporation. This is the most stable of our bridging sulfite complexes thus allowing the growth of good crystals which was virtually impossible for the bis[bis(1,2-diaminoethane)chromium(III)] system.[10]

Acid Hydrolysis of $[(tacn)Cr(\mu-OH)_2(\mu-O_2SO)Cr(tacn)]^{2+}$.—The acid catalysed hydrolysis of the above cation was studied in the range $0.030 \leqslant [H^+] \leqslant 1.0$ mol dm^{-3} at 30.0 °C. The data are given in Table 5 and the proposed mechanism is given in Scheme 4.

The hydrolysis product was analysed using cation-exchange and UV/VIS spectrophotometry. Upon formation of the bridging sulfito-cation, $[(tacn)Cr(\mu-OH)_2(\mu-O_2SO)Cr(tacn)]^{2+}$, from the *trans*-diaqua diol there is an increase in the absorbance in the visible spectrum. Acid hydrolysis of this sulfito-bridged cation is accompanied by a further increase in absorbance. This observation would suggest that the hydrolysis product is not the *trans*-diaqua diol and therefore the hydrolysis does not involve the removal of sulfite from the bridge. If the *cis*-diaqua diol was the hydrolysis product formed by the removal of sulfite from the bridge then it would isomerise to the more favourable *trans*-diaqua diol under acid conditions. This argument is strongly supported by the ion-exchange work in which no free sulfite was found in the hydrolysis mixture. It therefore seems that what is occurring is the cleavage of one of the hydroxo bridges to form a *cis*-diaqua-μ-hydroxo-μ-sulfito cation as shown in Scheme 4. This is very similar to the reported[19] hydrolysis of the carbonate-bridged cation, $[(tacn)Co(\mu-OH)_2(\mu-O_2CO)Co(tacn)]^{2+}$ in which one hydroxo bridge cleaves to form a *cis*-diaqua-μ-hydroxo-μ-carbonato cation. Attempts to isolate a solid product from the hydrolysis mixture were unsuccessful.

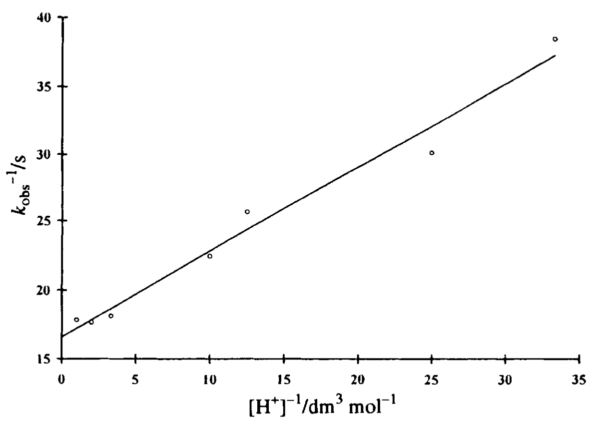


Fig. 4 Plot of $1/k_{obs}$ *vs.* $[H^+]^{-1}$ for the acid hydrolysis of $[(tacn)Cr(\mu-OH)_2(\mu-O_2SO)Cr(tacn)]^{2+}$ at 30 °C

The kinetic data in Table 5 show that at $[H^+] > 0.3$ mol dm^{-3} the value of k_{obs} is essentially constant and decreases at lower concentrations. This kind of behaviour is indicative of a mechanism involving proton pre-equilibration as outlined in Scheme 4.

From the proposed mechanism in Scheme 4 the derived rate law is given by equation (4), which can be rearranged to give the inverted form [equation (5)].

$$k_{obs} = k_hK_h[H^+]/(1 + K_h[H^+]) \qquad (4)$$

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

A plot of $1/k_{obs}$ *vs.* $1/[H^+]$ gave a straight line (see Fig. 4) from which k_h [$(6.1 \pm 0.1) \times 10^{-2}$ s^{-1}] and K_h (26 ± 3 dm^3 mol^{-1}) were derived from the intercept and slope respectively.

Crystal Structure of $[\{Cr(tacn)(OH)\}_2(\mu-SO_3)][ClO_4]_2\cdot3H_2O$.—Purple platy needles of the complex were prepared by slow evaporation of an aqueous solution of the *trans*-diaqua complex and $Na_2S_2O_5$; recrystallization was not necessary. The structure of the cation with atom labelling is shown in Fig. 5. Atomic coordinates are listed in Table 6 and selected bond lengths and angles in Table 7.

The crystal structure shows the chromium atom to be six-co-ordinate, being bonded to three tacn nitrogen atoms, two bridging hydroxy atoms and an oxygen atom of a bridging sulfite group. The co-ordination geometries are distorted octahedral with angles at Cr in the ranges 79.7(2)–99.2(2) and 169.5(2)–176.7(2)°. The complex has crystallographic C_s symmetry about a plane perpendicular to the Cr $\cdots$ Cr axis and passing through the bridging hydroxy oxygens and the sulfur and one of the oxygen atoms of the bridging sulfite. There is partial inversion (*ca.* 10%) of the sulfite atom as illustrated in Fig. 5.

The Cr–N distances are in the range 2.061(5)–2.073(5) Å and do not differ significantly from those reported for related Cr(tacn) and Cr(tmtacn) complexes (tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane).[14a,20–25] The bridging Cr–OH dis-

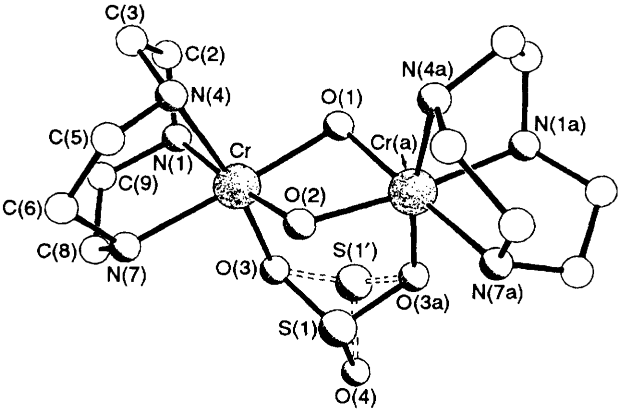


Fig. 5 The crystal structure of the cation [(tacn)Cr(μ-OH)$_2$(μ-O$_2$SO)Cr(tacn)]$^{2+}$

Table 6 Atomic coordinates (× 10^4, × 10^5 for Cr) for [(tacn)Cr(μ-OH)$_2$(μ-O$_2$SO)Cr(tacn)][ClO$_4$]$_2$·3H$_2$O

Atom	*x*	*y*	*z*
Cr	123 422(10)	−28 232(6)	68 318(4)
N(1)	13 810(5)	−3 090(3)	6 129(2)
C(2)	14 813(8)	−2 260(5)	6 107(3)
C(3)	13 921(8)	−1 405(5)	6 116(3)
N(4)	12 701(5)	−1 481(3)	6 551(2)
C(5)	11 255(8)	−1 136(5)	6 328(3)
C(6)	10 549(8)	−1 825(5)	5 905(3)
N(7)	10 808(5)	−2 777(3)	6 132(2)
C(8)	11 411(8)	−3 430(5)	5 655(3)
C(9)	13 019(8)	−3 265(6)	5 549(3)
O(1)	13 803(6)	−2 787(4)	7 500
O(2)	11 072(6)	−2 412(4)	7 500
S(1)[a]	10 921(3)	−4 426(2)	7 500
S(1′)[b]	12 173(27)	−4 612(16)	7 500
O(3)	11 895(4)	−4 149(3)	6 944(2)
O(4)	10 928(7)	−5 456(4)	7 500
Cl	7 599(2)	527(1)	5 768(1)
O(5)	7 317(9)	1 415(7)	5 532(4)
O(6)	8 868(10)	447(6)	6 120(7)
O(7)	6 611(13)	668(9)	6 284(4)
O(8)	6 814(19)	−22(15)	5 384(9)
O(9)	7 083(31)	−361(19)	5 775(13)
O(10)	8 844(20)	388(11)	5 333(10)
O(11)	8 718(12)	953(9)	7 500
O(12)	6 790(11)	2 493(9)	7 231(6)
O(13)	7 080(12)	−892(10)	7 749(6)

[a] Occupancy 90%. [b] Occupancy 10%.

tances, 1.957(4) and 1.975(4) Å, differ significantly but are still within the range observed in other related complexes.[14a,20–25] The Cr–OH–Cr angles [96.4(2) and 97.5(2)°] are also normal. The Cr–O(sulfito) distances of 1.975(4) Å are the same as the Cr–OH bond lengths and similar to those reported for Cr–O(sulfate)–Cr complexes.[26,27] There are, we believe, no other reported examples of crystallographic studies on Cr–OSO$_2$–Cr or indeed any Cr–OSO$_2$ complexes. The only example of a sulfite-bridged dinuclear first-row transition metal complex is a μ-oxo-di-μ-sulfito iron(III) tmtacn complex.[28] In this iron(III) complex the Fe–O(sulfito) distances of 1.984 Å again do not differ significantly from those we have observed here. The internuclear non-bonded Cr • • • Cr distance of 2.944 Å is appreciably longer than that observed in [(tmtacn)Cr^{III}(μ-OH)$_3$Cr^{III}(tmtacn)]$^{3+}$[20] but very similar to that (2.898 Å) in [(tacn)Cr^{III}(μ-OH)$_2$(μ-CO$_2$)Cr^{III}(tacn)]I$_2$·H$_2$O.[21] It is interesting that this latter complex crystallises in the same space group (*Pbnm*) and has very similar unit-cell dimensions to the present complex.

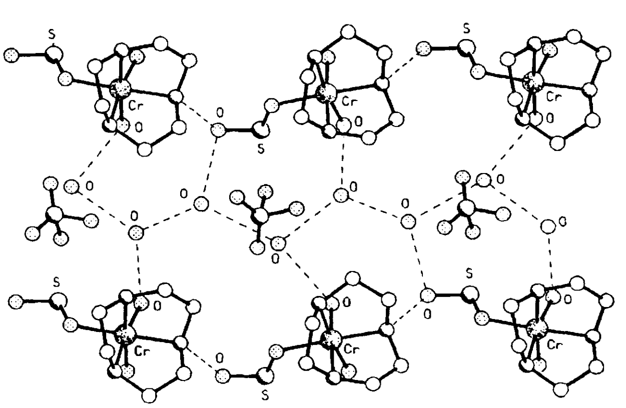


Fig. 6 Part of the network of hydrogen bonds linking the cations and water molecules in the structure of [(tacn)Cr(μ-OH)$_2$(μ-O$_2$SO)-Cr(tacn)][ClO$_4$]$_2$·3H$_2$O

Table 7 Selected bond lengths (Å) and angles (°) for [(tacn)Cr(μ-OH)$_2$(μ-O$_2$SO)Cr(tacn)][ClO$_4$]$_2$·3H$_2$O with estimated standard deviations (e.s.d.s) in parentheses

Cr–N(1)	2.073(5)	Cr–N(4)	2.061(5)
Cr–N(7)	2.072(5)	Cr–O(1)	1.975(4)
Cr–O(2)	1.957(4)	Cr–O(3)	1.975(4)
Cr • • • Cr(a)	2.944(2)	N(1)–C(2)	1.503(9)
N(1)–C(9)	1.485(8)	C(2)–C(3)	1.474(10)
C(3)–N(4)	1.464(9)	N(4)–C(5)	1.479(9)
C(5)–C(6)	1.506(10)	C(6)–N(7)	1.483(9)
N(7)–C(8)	1.514(8)	C(8)–C(9)	1.487(10)
O(1)–Cr(a)	1.975(4)	O(2)–Cr(a)	1.957(4)
S(1)–O(3)	1.558(4)	S(1)–O(4)	1.489(6)
S(1)–O(3a)	1.558(4)	S(1′)–O(3)	1.418(13)
S(1′)–O(4)	1.658(25)	S(1′)–O(3a)	1.418(13)

N(1)–Cr–N(4)	81.5(2)	N(1)–Cr–N(7)	82.8(2)
N(4)–Cr–N(7)	81.5(2)	N(1)–Cr–O(1)	97.9(2)
N(4)–Cr–O(1)	95.4(2)	N(7)–Cr–O(1)	176.7(2)
N(1)–Cr–O(2)	172.6(2)	N(4)–Cr–O(2)	91.8(2)
N(7)–Cr–O(2)	99.2(2)	O(1)–Cr–O(2)	79.7(2)
N(1)–Cr–O(3)	92.5(2)	N(4)–Cr–O(3)	169.5(2)
N(7)–Cr–O(3)	89.3(2)	O(1)–Cr–O(3)	93.9(2)
O(2)–Cr–O(3)	94.7(2)	Cr–O(1)–Cr(a)	96.4(2)
Cr–O(2)–Cr(a)	97.5(2)	O(3)–S(1)–O(4)	104.8(2)
O(3)–S(1)–O(3a)	103.5(2)	O(4)–S(1)–O(3a)	104.8(2)
O(3)–S(1′)–O(4)	103.2(11)	O(3)–S(1′)–O(3a)	119.4(17)
O(4)–S(1′)–O(3a)	103.2(11)	Cr–O(3)–S(1)	117.6(2)
Cr–O(3)–S(1′)	122.1(9)		

Inspection of the packing of the molecules reveals extensive intermolecular hydrogen bonding (Fig. 6). All six amino NH groups are involved in N–H • • • O hydrogen bonds; four with perchlorate oxygen atoms (2.98–3.15 Å) and two with the sulfito oxygen atom O(4) (2.85 Å). Both bridging hydroxo groups are involved in O–H • • • O hydrogen bonds with water molecules of crystallization at distances of 2.65 and 2.88 Å.

Conclusion

The unusual preference for reaction of SO$_2$ with the terminal aqua over the bridging hydroxo group has been observed accompanied by much slower rate constants and higher enthalpy of activation than seen in previously studied systems. The product contains an extremely stable sulfito bridge as established by crystallographic studies.

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