

# Kinetics and Mechanism of Reaction of *Trans*-(diaqua)(*N,N'*-Ethylene-bis-Salicylideneimine) Chromium(III) with Sulfur(IV): The Labilizing Effect of Coordinated Sulfite

ANADI C. DASH, ACHYUTA N. ACHARYA, PRAKASH MOHANTY, ARABINDA DAS

Department of Chemistry, Utkal University, Bhubaneswar 751 004, India

Received 17 April 1997; accepted 22 September 1997

**ABSTRACT:** The reaction of  $\text{trans-[Cr(Salen)(OH}_2)_2]^+$  with aqueous sulfite yields  $\text{trans-[Cr(Salen)(OH}_2)(\text{OSO}_2\text{-O)]}^-$  (O-bonded isomer). The rate and activation parameter data for the formation of the sulfite complex are consistent with a mechanism involving rate-limiting addition of  $\text{SO}_2$  to the  $\text{Cr}^{\text{III}}\text{-OH}$  bond. The complex ions,  $\text{trans-[(OH}_2)\text{Cr(Salen)(OSO}_2\text{-O)]}^-$ , and  $\text{trans-[(OH)Cr(Salen)(OSO}_2\text{-O)]}^{2-}$ , undergo reversible anation by  $\text{NCS}^-$ ,  $\text{N}_3^-$ , imidazole, and pyridine resulting in the formation of  $\text{trans-[XCr(Salen)(OSO}_2\text{-O)]}^{(n+1)-}$  ( $n = 1$  for  $\text{X} = \text{N}_3^-$ ,  $\text{NCS}^-$ , and  $0$  for  $\text{X} = \text{imidazole}$  and  $\text{pyridine}$ ) predominantly via dissociative interchange mechanism. The labilizing action of the coordinated sulfite on the  $\text{trans-Cr}^{\text{III}}\text{-X}$  bond in  $\text{trans-[XCr(Salen)(OSO}_2)]^{(n+1)-}$  follows the sequence:  $\text{NCS}^- < \text{pyridine ca. N}_3^- \text{ ca. imidazole}$ . Data analysis indicated that the coordinated sulfite has little *trans* activating influence. © 1998 John Wiley & Sons, Inc. Int J Chem Kinet 30: 373–384, 1998

## INTRODUCTION

Substitution reactions of oxoanions ( $\text{XO}_n^{m-}$ ) have attracted increasing attention in the recent years [1]. Studies of the reactions of aquacobalt(III) and aqua-

chromium(III) cations with oxoanions have demonstrated the possibilities of proton ambiguities in several cases where establishment /or cleavage of  $\text{O-X}$  bond in  $\text{M}^{\text{III}}\text{O-XO}_{n-1}$  (rather than the  $\text{M}^{\text{III}}\text{-O}$  bond breaking or formation) is involved in the rate limiting step. Among the oxoanions,  $\text{SO}_3^{2-}$  is one which is believed to substitute at the cobalt(III) [2–7], rhodium(III) [8], chromium(III) [8,9], and platinum(IV) [10] centers by addition of  $\text{SO}_2$  to the  $\text{M}^{\text{III}}\text{-OH}$  bond. However, the rapid formation of  $\text{Cr(OH}_2)_5(\text{OSO}_2)^+$  has been interpreted equally well by Harris et al. [9]

Correspondence to: A. C. Dash

Contract grant Sponsor: Department of Science and Technology, New Delhi  
© 1998 John Wiley & Sons, Inc. CCC 0538-8066/98/050373-12

in terms of the reactions of both  $\text{HSO}_3^-$  and  $\text{SO}_2$  with  $\text{Cr}(\text{OH}_2)_5(\text{OH})^{2+}$ . Direct substitution of  $\text{SO}_3^{2-}$  at cobalt(III) [11,12], iron(III) [13,14], and palladium(II) [15] centers to yield S-bonded sulfito complexes have also been reported. This brings in mechanistic ambiguities in the formation/dissociation of the sulfito complexes. Further the chemistry of sulfur dioxide in relation to its environmental impacts has gained importance over the years. These considerations warrant further investigations of the kinetics and mechanism of reactions of  $\text{S}^{\text{IV}}$  with aqua metal ions. Our interest in the reactions of  $\text{SO}_2$  with aqua metal ions prompted us to investigate the sulfite substitution reaction using a labile (aqua)Cr(III) complex in order to explore the possibility if direct substitution of  $\text{SO}_3^{2-}/\text{HSO}_3^-$  at the Cr(III) center with Cr— $\text{OH}_2$  bond breaking is competitive with the  $\text{SO}_2$ ;  $\text{HSO}_3^-$ , or  $\text{SO}_3^{2-}$  addition to  $\text{Cr}^{\text{III}}\text{—OH}(\text{OH}_2)$  bond.

The *trans*-[Cr(Salen)(OH<sub>2</sub>)<sub>2</sub>]<sup>+</sup> (Salen = *N,N'*-ethylene-*bis*-salicylideneimine) is grossly distorted [16–18] along  $\text{OH}_2\text{—Cr}^{\text{III}}\text{—OH}_2$  axis. It is believed that distortion in the ground state of this complex imparts exceptional lability to substitution of the coordinated H<sub>2</sub>O by anionic and neutral ligands [19]. For this reason we have chosen this substrate to elucidate the mechanism of formation of its sulfito complex. Further the possibility of ligand isomerization ( $\text{Cr}^{\text{III}}\text{—OSO}_2 \rightarrow \text{Cr}^{\text{III}}\text{—SO}_3$ ) as reported by Harris et al. [8] in the  $\text{Cr}(\text{OH}_2)_6^{3+}/\text{S}^{\text{IV}}$  reaction, and the labilizing action of the coordinated sulfite in *trans*-[Cr(Salen)(OH<sub>2</sub>)(SO<sub>3</sub>)]<sup>−</sup> (either O— or S—bonded isomer) are also examined. The latter aspect was explored by studying the sulfite induced anation profile of the complex using  $\text{N}_3^-$ ,  $\text{NCS}^-$ , and imidazole (imH), py (pyridine) as entering ligands.

## EXPERIMENTAL

### Preparation of Complexes

*Trans*-[Cr(Salen)(OH<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub>, H<sub>2</sub>O: This complex was prepared by the published method [20] and purity checked by analysis of Cr (11.8%, calcd: 12.4%) {λ max, nm (ε, dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>): 275 (21700); 380 (4900); 465sh (145); 465 (165) [ref. 20]; ν (OH): 1630 cm<sup>−1</sup>, 1600 cm<sup>−1</sup> (for hydrate and coordinated water); and ν (C=N): 1550 cm<sup>−1</sup>}.

*Trans*-[Cr(Salen)(OH<sub>2</sub>)(OSO<sub>2</sub>—O)]Na: The *trans*-[Cr(Salen)(OH<sub>2</sub>)(OSO<sub>2</sub>—O)]Na was prepared as follows. An aqueous solution of *trans*-[Cr(Salen)(OH<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub>, H<sub>2</sub>O (1mmole) was treated with Na<sub>2</sub>SO<sub>3</sub> (2mmole) and pH adjusted to 6. The mixture was set aside at room temperature for a few hours. A yellowish brown solid formed which was isolated by filtration. It was washed successively with ethanol and diethyl ether and dried over silica gel in a desiccator. Anal: Cr, 11.7; C, 44.3; N, 6.8; H, 4.0; S, 7.2. Calcd. for [Cr(Salen)(OH<sub>2</sub>)(SO<sub>3</sub>)]Na: Cr, 12.0; C, 43.6; N, 6.4; H, 3.6; S, 7.3. λ max, nm (ε, dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>): 275 (20500), 380 (4600), 495 (103) (at pH = 6.2); ν (OH): 1640, 1600 cm<sup>−1</sup>; ν(C=N): 1540 cm<sup>−1</sup>; ν (SO), 970, 955, 1050, 1110 cm<sup>−1</sup>. The i. r. bands in the range 1110–955 cm<sup>−1</sup> are highly complex for both the diaqua and (aqua)(sulfito) complexes. However, the bands quoted for the (aqua)(sulfito) complex in this range (i.e., 1110–955 cm<sup>−1</sup>) were not observed for the diaqua complex thus indicating the presence of the coordinated sulfite. The 955 cm<sup>−1</sup> (weak) band for the sulfito complex may be indicative of O-bonded sulfite [21].

*Trans*-[Cr(Salen)(X)(OSO<sub>2</sub>—O)]Na<sub>*n*</sub> {*n* = 2, X =

**Table I** Analytical and uv-Visible Spectral Data for *trans*-[Cr(Salen)(OSO<sub>2</sub>—O)(X)]Na<sub>*n*</sub>

Complex <sup>a</sup>	Cr	S	Na	λ <sub>max</sub> <sup>b</sup> /nm	ε <sub>max</sub> <sup>b</sup> /dm <sup>3</sup> mol <sup>−1</sup> cm <sup>−1</sup>
[Cr(Salen)(OSO <sub>2</sub> —O)(imH)]Na	11.0 (10.6)	7.0 (6.5)	3.9 (4.7)	400	4739
[Cr(Salen)(OSO <sub>2</sub> —O)(py)]Na	9.8 (10.4)	7.3 (6.4)	3.7 (4.6)	385	6207
[Cr(Salen)(OSO <sub>2</sub> —O)(N <sub>3</sub> )]Na <sub>2</sub>	11.2 (10.2)	5.6 (6.3)	8.8 (9.0)	385	8029
[Cr(Salen)(OSO <sub>2</sub> —O)(NCS)]Na <sub>2</sub>	11.0 (10.3)	— (9.1)	9.3	385	8015

<sup>a</sup> imH = imidazole, py = pyridine, and calculated values based on molecular formula are parenthesised.

<sup>b</sup> From the spectra of the in situ generated complexes: *trans*-[Cr(Salen)(OH<sub>2</sub>)<sub>2</sub>]<sup>+</sup> = 1.0 × 10<sup>−4</sup>; [S<sup>IV</sup>]<sub>T</sub> = 0.05; [X]<sub>T</sub> = 0.2 mol dm<sup>−3</sup> (X = imH, py, N<sub>3</sub><sup>−</sup>, and NCS<sup>−</sup>) at pH = 6.8; and ε = ΔA × (1 + K<sub>e</sub>C<sub>2</sub>)/(K<sub>e</sub>C<sub>1</sub>C<sub>2</sub>) + A<sub>0</sub>/C<sub>1</sub> where A and A<sub>0</sub> denote absorbances of the mixture and only the sulfito complex at λ max, ΔA = A − A<sub>0</sub>, and K<sub>e</sub> is the equilibrium constant for the formation of *trans*-[XCr(Salen)(OSO<sub>2</sub>—O)]<sup>(n+1)−</sup>, C<sub>1</sub> = [Cr(Salen)(OH<sub>2</sub>)<sub>2</sub>(OSO<sub>2</sub>—O)]<sup>−</sup> = [Cr<sup>III</sup>]<sub>T</sub>, and C<sub>2</sub> = [X<sup>n−</sup>]<sub>T</sub>/(1 + [H<sup>+</sup>]/K<sub>d</sub><sup>HX</sup>) and K<sub>d</sub><sup>HX</sup> is the acid dissociation constant of HX.

$N_3^-$ ;  $NCS^-$   $n = 1$ ,  $X = imH$  (imidazole),  $py$  (pyridine)}: An aqueous solution of *trans*-[Cr(Salen)(OH<sub>2</sub>)(OSO<sub>2</sub>)]-Na (1mmole) was mixed with NaN<sub>3</sub>/NaNCS/pyridine/imidazole in 1:2 mole proportion and pH of the solution was adjusted to 6. The mixture was set aside for a few hours at room temperature in a closed glass vessel after which the desired complex precipitated out. It was collected by filtration, washed with ethanol and diethyl ether and dried over silica gel in a desiccator. The purities of samples were checked by analysis of Cr, S, and Na. The analytical and spectral data of the complexes are collected in Table I.

### Solutions and Reagents

Analar grade reagents were used in kinetics experiments. Solutions were prepared in doubly distilled water, the second distillation being made from alkaline KMnO<sub>4</sub> in an all glass distillation apparatus. Sodium metabisulfite, Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, was the source of S<sup>IV</sup>. This salt is very stable in solid state but hydrolyses rapidly to equilibrium mixture of SO<sub>3</sub><sup>2-</sup>/HSO<sub>3</sub><sup>-</sup>/SO<sub>2</sub> when dissolved in water. Fresh solutions of sulfite was prepared just before commencing the kinetic experiments. Stock solution of NaClO<sub>4</sub>, used to adjust ionic strength, was estimated by a combined ion-exchange alkalimetric procedure. Dowex 50W-X8 resin in H<sup>+</sup> form was used for ion-exchange experiments. NaNCS and pyridine were estimated by Volhard's method [22] and pH titration, respectively. NaN<sub>3</sub> and imidazole were used as received.

### Physical Measurements

The pH measurements were made with an Elico LI120 digital pH meter using a glass-Ag/AgCl, Cl<sup>-</sup> (2 mol dm<sup>-3</sup> NaCl) combination electrode CL 51. Standard buffers of pH 4.01, 6.86 and 9.2 were used to calibrate the pH meter. Uv-visible spectra were recorded on a JASCO 7800 spectrophotometer using 10 mm matched quartz cells. The i.r. spectra were recorded on a JASCO FT i. r. spectrophotometer model 5300. The C, H, N, analysis was done at Central Drug Research Laboratory, Lucknow, India; Cr and Na were estimated by atomic absorption spectrometry on a Perkin Elmer atomic absorption spectrometer model 3100. Sulfur was estimated as BaSO<sub>4</sub> after oxidizing the sulfito complex with ammoniacal hydrogen peroxide.

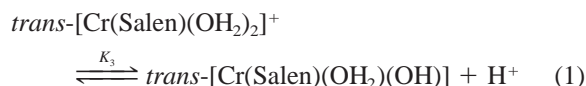
### Kinetic Measurements

The kinetics of formation of the sulfito complex was investigated under pseudo-first-order conditions in self-

buffered sulfite with [Cr(Salen)(OH<sub>2</sub>)<sub>2</sub>]<sup>+</sup>]<sub>T</sub> = 5.0 × 10<sup>-5</sup>, 0.03 ≤ [S<sup>IV</sup>]<sub>T</sub>/mol dm<sup>-3</sup> ≤ 0.11, 6.50 ≤ pH ≤ 7.2, 15.0 ≤ *t*/°C ≤ 30.0, and I = 0.3 mol dm<sup>-3</sup>. The reaction was monitored on a HITECH (U. K.) SF51 stopped flow spectrophotometer interfaced with an APPLE II GS P.C. The flow module and the solutions in drive syringes were thermostatted to the desired temperature by circulating water from a C85-D thermostat through a cooler FC 200 (U.K.). The complex solution and the sulfite buffer both adjusted to the same ionic strength were loaded separately in two syringes and were thermally equilibrated. These were rapidly mixed and the decrease of absorbance with time were monitored at 285 nm. The absorbance-time curves were single exponentials characteristic of the first-order kinetics. At least five replicate measurements were made for each run to calculate the mean value of *k*<sub>obs</sub> and its standard deviation σ(*k*<sub>obs</sub>). The rate constants are collected in Table II.

For anation of *trans*-[Cr(Salen)(OH<sub>2</sub>)(OSO<sub>2</sub>)]<sup>-</sup> by NCS<sup>-</sup>, N<sub>3</sub><sup>+</sup>, pyridine(py), and imidazole (imH), the preformed sulfito complex ([S<sup>IV</sup>]<sub>T</sub>]/[Cr(Salen)(OH<sub>2</sub>)<sub>2</sub>]<sup>+</sup>]<sub>T</sub> = 200–700, pH = 6, and I = 0.5 mol dm<sup>-3</sup>) was loaded in one syringe and the other syringe was loaded with the anating agent at the same ionic strength. The two solutions were rapidly mixed and the formation of the product was monitored at 400 nm. In every case the increase of absorbance with time fitted excellently to the first order kinetic expression:  $A_{\infty} - A_t = (A_{\infty} - A_0)\exp(-k_{obs}t)$ . The rate constants (average of at least five replicate measurements) are collected in Table III. All other calculations were made on a IBM compatible 486 P. C.

*pK* of *trans*-[Cr(Salen)(OH<sub>2</sub>)<sub>2</sub>]<sup>+</sup>: The *pK* of the diaqua complex was determined by potentiometric titration. A solution (100 cm<sup>3</sup>) of the complex (1.0 × 10<sup>-3</sup>, I = 0.3 mol dm<sup>-3</sup>) was titrated potentiometrically against 0.049 mol dm<sup>-3</sup> NaOH. We obtained *pK*<sub>3</sub> = 7.35 ± 0.05 (see eq. (1)) for the diaqua complex at 25°C in excellent agreement with the reported value (7.54) [20].



The second step acid dissociation of the diaqua complex was not observed below pH 9. Loret et al [20] reported a value of 10.47 for the *pK* of *trans*-[Cr(Salen)(OH<sub>2</sub>)(OH)]. As against this we calculated a value 10.5 ± 0.1 for the same from the pH titration data in the range 9 ≤ pH ≤ 11.

*pK* of *trans*-[Cr(Salen)(OH<sub>2</sub>)(OSO<sub>2</sub>H)]: 90.0 cm<sup>3</sup> of 0.003 mol dm<sup>-3</sup> sulfito complex, {*trans*-[Cr(Salen)

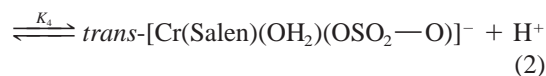
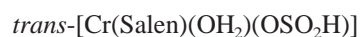
**Table II** Rate Constants for the Formation of  $[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2\text{—O})]^+$ <sup>a</sup>

$[\text{S}^{\text{IV}}]_{\text{T}}/$ mol dm <sup>-3</sup>	pH	$k_{\text{obs}}/\text{s}^{-1}$	$[\text{S}^{\text{IV}}]_{\text{T}}/$ mol dm <sup>-3</sup>	pH	$k_{\text{obs}}/\text{s}^{-1}$
15.0 ± 0.1°C					
0.030	6.62	7.3 ± 0.8	0.080	6.58	43 ± 2
0.040	6.75	8.9 ± 0.7	0.080	6.66	28 ± 2
0.050	6.74	10.0 ± 0.5	0.080	6.72	22 ± 1
0.060	6.77	16 ± 2	0.080	6.83	19 ± 1
0.070	6.76	18 ± 1	0.080	6.97	12 ± 1
0.080	6.78	19 ± 1	0.080	7.03	7.2 ± 0.5
0.090	6.73	20 ± 1	0.100	6.72	23 ± 2
20.0 ± 0.1°C					
0.030	6.65	10.1 ± 0.3	0.080	6.59	50 ± 2
0.040	6.67	14 ± 1	0.080	6.66	37 ± 1
0.050	6.70	18 ± 1	0.080	6.72	29 ± 2
0.060	6.81	20 ± 1	0.080	6.81	28 ± 1
0.070	6.76	24 ± 1	0.080	6.98	13 ± 1
0.080	6.74	28 ± 2	0.080	7.03	9.0 ± 0.1
0.090	6.73	30 ± 1	0.100	6.78	32 ± 1
25.0 ± 0.1°C					
0.030	6.71	12 ± 1	0.080	6.60	55 ± 5
0.040	6.69	17 ± 1	0.080	6.62	48 ± 5
0.050	6.74	26 ± 1	0.080	6.70	39 ± 2
0.060	6.71	28 ± 2	0.080	6.66	43 ± 3
0.070	6.63	34 ± 2	0.070	6.91	13 ± 2
0.080	6.73	30 ± 2	0.080	6.90	21 ± 3
0.090	6.60	43 ± 5	0.090	6.98	24 ± 2
0.080	6.98	15 ± 1	0.080	7.13	9.4 ± 1.1
0.090	6.55	50 ± 2	0.050	6.81	21 ± 2
0.10	6.80	34 ± 2	0.070	6.57	37 ± 3
0.11	6.84	34 ± 3	0.070	6.63	34 ± 7
30.0 ± 0.1°C					
0.030	6.76	17 ± 1	0.080	6.52	71 ± 4
0.040	6.72	20 ± 1	0.080	6.71	43 ± 1
0.050	6.71	31 ± 1	0.080	6.81	36 ± 1
0.060	6.71	36 ± 2	0.080	6.81	36 ± 1
0.070	6.73	39 ± 1	0.080	6.90	24 ± 1
0.080	6.69	44 ± 2	0.080	6.98	19 ± 1
0.090	6.73	48 ± 3	0.080	7.14	12 ± 1
0.100	6.74	51 ± 2			

<sup>a</sup> I = 0.3 mol dm<sup>-3</sup>, λ = 285 nm; HSO<sub>3</sub><sup>-</sup>/SO<sub>3</sub><sup>2-</sup> buffer.

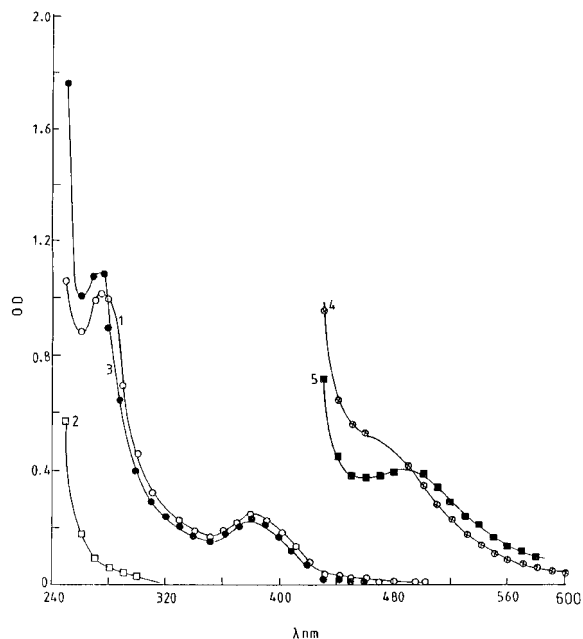
(OH<sub>2</sub>)(OSO<sub>2</sub>—O)]<sup>-</sup> (I = 0.5 mol dm<sup>-3</sup>, 25°C)) was pH titrated with 0.1009 mol dm<sup>-3</sup> HClO<sub>4</sub>. The pH titration data indicated protonation of the sulfite complex (see eq. (2)). The pH data in the range 7.1–5.9 were used to calculate pK of the protonated sulfite complex { $K_4 = [\text{H}^+](1 - n_{\text{H}})/n_{\text{H}}$ ,  $n_{\text{H}}$  = average number of H<sup>+</sup> bound per complex ion). We obtained  $K_4 = (1.4 \pm 0.5) \times 10^{-6}$  mol dm<sup>-3</sup>. At pH values

lower than 5.9 the calculated values of  $K_4$  increased rapidly presumably due to the acid catalyzed decomposition of the protonated complex and loss of SO<sub>2</sub>.

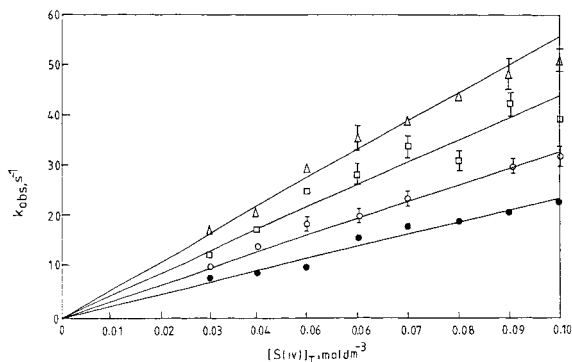


## RESULTS AND DISCUSSION

**Formation of  $trans-[Cr(Salen)(OH_2)(OSO_2-O)]^-$ :** Addition of  $trans-[Cr(Salen)(OH_2)_2]^+$  to sulfite buffer (pH = 6.0) results in a rapid spectral change in the range 200–400 nm. The spectra of the diaqua and the aqua sulfite complexes are presented in Figure 1. The formation of sulfite  $Cr^{III}$  species of  $Cr(OH_2)_6^{3+}$  and  $Cr(NH_3)_5(OH_2)^{3+}$  [8] have been reported earlier and such reactions have been shown to be fast (ms time scale) unlike other ligand substitution reactions of aqua  $Cr^{III}$  cations. The uv-visible spectra of the reaction mixtures containing  $S^{IV}$  and  $trans-[Cr(Salen)(OH_2)_2]^+$  ( $[S^{IV}]_T$  in excess, pH 6) did not reveal any further change over extended time period. Hence, the initially formed sulfite  $Cr^{III}$  species was stable to any further change. This discounts the possibilities of ligand isomerization ( $Cr^{III}-OSO_2 \rightarrow Cr^{III}-SO_3$ ) in the present system unlike the same observed by Harris et al.[9] in the  $Cr(OH_2)_6^{3+}/S^{IV}$  reaction as also any reaction between  $S^{IV}$  and coordinated Salen. The absorbances (240–400 nm) of the reaction mixtures at equilibrium with  $[Cr^{III}]_T = 0.5 \times 10^{-4}$  and  $[S^{IV}]_T = 0.03-0.11 \text{ mol dm}^{-3}$  (pH = 6.55–7.20, I =  $0.3 \text{ mol dm}^{-3}$ ), after correcting for the absorbances of



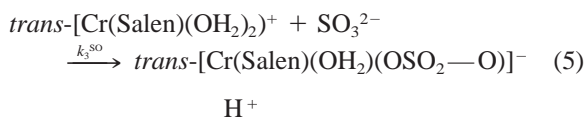
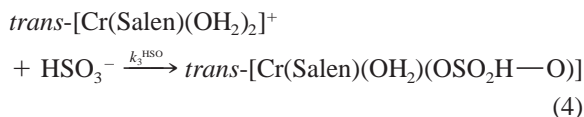
**Figure 1** Uv-visible spectra of  $trans-[Cr(Salen)(OH_2)_2]^+$  and  $trans-[Cr(Salen)(OH_2)(OSO_2-O)]^-$  at pH = 6.6. (1)  $trans-[Cr(Salen)_2(OH_2)_2]^+$  ( $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ); (2)  $S^{IV}$  ( $0.04 \text{ mol dm}^{-3}$ ); (3)  $trans-[Cr(Salen)(OH_2)(OSO_2-O)]^-$  ( $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ); (4)  $trans-[Cr(Salen)(OH_2)_2]^+$  ( $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ); and (5)  $trans-[Cr(Salen)(OH_2)_2]^+$  ( $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) +  $[S^{IV}]$  ( $0.10 \text{ mol dm}^{-3}$ ).



**Figure 2**  $k_{obs}/s^{-1}$  vs.  $[S^{IV}]_T/\text{mol dm}^{-3}$  plots for the formation of  $trans-[Cr(Salen)(OH_2)(OSO_2-O)]^-$  at pH = 6.6.

excess  $[S^{IV}]$  indicated that the formation of the sulfite complex was virtually complete under these conditions.

The plots of  $k_{obs}$  vs.  $[S^{IV}]_T$  at constant pH (see Fig. 2) are linear with vanishing intercept on the rate axis. This further substantiates that the reverse reaction (i.e., the equation of the sulfite complex) is insignificant under the experimental conditions of pH and excess  $[S^{IV}]_T$  (see Table II). Assuming that  $SO_3^{2-}$ ,  $HSO_3^-$  and the diaqua complex are the reactive species,



$k_{obs}$  is given by eq. (6)

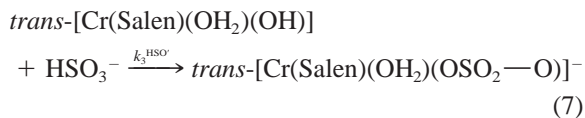
$$k_{obs} = (k_3^{HSO}f_2 + k_3^{SO}f_3)f_4[S^{IV}]_T \quad (6)$$

where

$$\begin{aligned} f_1 &= [H^+]^2 / \{ [H^+]^2 + K_1[H^+] + K_1K_2 \} \\ f_2 &= K_1[H^+] / \{ [H^+]^2 + K_1[H^+] + K_1K_2 \} \\ f_3 &= K_1K_2 / \{ [H^+]^2 + K_1[H^+] + K_1K_2 \} \\ f_4 &= [H^+] / \{ [H^+] + K_3 \} \end{aligned}$$

In eq. (6)  $k_3^{\text{HSO}}$  and  $k_3^{\text{SO}}$  denote the rate constants for the anation of  $[\text{Cr}(\text{Salen})(\text{OH}_2)_2]^+$  by  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$ ,  $K_1$ ,  $K_2$ , and  $K_3$  stand for the acid dissociation constants of  $\text{SO}_2$ ,  $\text{HSO}_3^-$ , and the diaqua complex, respectively. Values of  $\text{p}K_i$ ,  $\Delta H_i^\circ$  for the acid dissociation equilibria of  $\text{SO}_2$  are 1.91, 16.7 kJ mol $^{-1}$ , and 7.18, 12.5 kJ mol $^{-1}$  for  $i = 1, 2$  at 25°C and  $I = 0$ , respectively [23]. These data were temperature corrected and then ionic strength corrected using the activity coefficient expression:  $\log \gamma_z = -AZ^2(1^{1/2}/(1 + 1^{1/2}) - 0.21)$ . Values of  $\text{p}K_1$ ,  $\text{p}K_2$  turned out as 1.92, 6.75; 1.80, 6.64; 1.66, 6.52; and 1.53, 6.39 at 15.0°C, 20.0°C, 25.0°C, and 30.0°C ( $I = 0.3 \text{ mol dm}^{-3}$ ), respectively;  $\text{p}K_3$  was virtually temperature independent in the range 15.0–30.0°C ( $\text{p}K_3 = 7.52 \pm 0.05$ ). The values of  $f_i s(i = 1-4)$  were calculated and the rate constants were fitted to eq. (6) by a least-squares program;  $k_{\text{obs}}$  was weighted inversely as its variance. The calculated values of  $k_3^{\text{HSO}}$  and  $k_3^{\text{SO}}$  are  $798 \pm 97$ ,  $-233 \pm 82$  (15°C);  $1130 \pm 65$ ,  $-198 \pm 26$  (20°C);  $780 \pm 120$ ,  $76 \pm 132$  (25°C); and  $2450 \pm 120$ ,  $-235 \pm 47$  (30°C) dm $^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively. Note that the calculated values of  $k_3^{\text{SO}}$  are either negative or statistically insignificant.

Considering  $\text{HSO}_3^-$  as the reactive  $\text{S}^{\text{IV}}$  species and  $[\text{Cr}(\text{Salen})(\text{OH}_2)_2]^+$  and  $[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OH})]$  as the reactive  $\text{Cr}^{\text{III}}$  species (see eqs. (4) and (7))

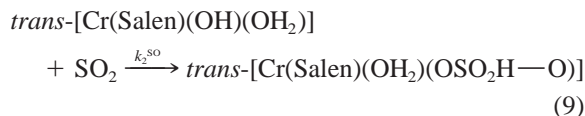


$k_{\text{obs}}$  is given by eq. (8):

$$k_{\text{obs}} = (k_3^{\text{HSO}} + k_3^{\text{HSO}'}K_3/[\text{H}^+])f_4f_2[\text{S}^{\text{IV}}]_{\text{T}} \quad (8)$$

The rate constants fitted to eq. (8) yielded the values of  $10^{-2}k_3^{\text{HSO}}(10^{-3}k_3^{\text{HSO}'})/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  as  $7.9 \pm 0.9$  ( $-1.4 \pm 0.6$ ),  $11.3 \pm 0.6$  ( $-1.6 \pm 0.2$ ),  $15.7 \pm 0.9$

( $-2.0 \pm 0.3$ ), and  $24.5 \pm 1.2$  ( $-3.3 \pm 0.6$ ) at 15.0°C, 20.0°C, 25.0°C, and 30.0°C, respectively. Again  $k_3^{\text{HSO}'}$  (see eq. (8)) turns out negative. Evidently the formation of sulfito complex must occur via any one of the reactions shown in eqs. (4), (5), or (7) but not via any two of these reactions simultaneously. However, the reaction of  $\text{HSO}_3^-$  with the diaqua complex is stoichiometrically equivalent to the reaction of  $\text{SO}_2$  with the (aqua)(hydroxo) complex (see eq. (9)).



Accordingly  $k_{\text{obs}}$  is given by eq. (10)

$$k_{\text{obs}} = k_2^{\text{SO}}(1 - f_4)f_1[\text{S}^{\text{IV}}]_{\text{T}} \quad (10)$$

The values of  $k_2^{\text{SO}}$  were also calculated using eq. (10). The values of the rate parameters,  $k_3^{\text{HSO}}$ ,  $k_3^{\text{SO}}$ ,  $k_3^{\text{HSO}'}$ , and  $k_2^{\text{SO}}$  (assuming that the sulfito complex is formed via any one path only) and the associated activation-parameters are collected in Table IV.

It is worth noting that the calculated values of  $k_3^{\text{HSO}}$  are greater than (or comparable with) the values of  $k_3^{\text{SO}}$ . Reverse trend is expected from the electrostatic grounds for dissociative interchange ( $I_d$ ) mechanism involving diffusion controlled ion-pairing of the reactants. The calculated values of  $k_3^{\text{HSO}}$  and  $k_3^{\text{SO}}$  may be contrasted with the values of the anation rate constants of  $[\text{Cr}(\text{Salen})(\text{OH}_2)_2]^+$  with  $\text{NCS}^-$ ,  $\text{N}_3^-$ , pyridine-3-carboxylate ( $N$ -coordination), imidazole (imH) and pyridine(py) which fall within a narrow range,  $0.15\text{--}0.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (30°C,  $I = 1.0 \text{ mol dm}^{-3}$ ) [19]. In such cases it is believed that ion-pair dissociative interchange mechanism operates.

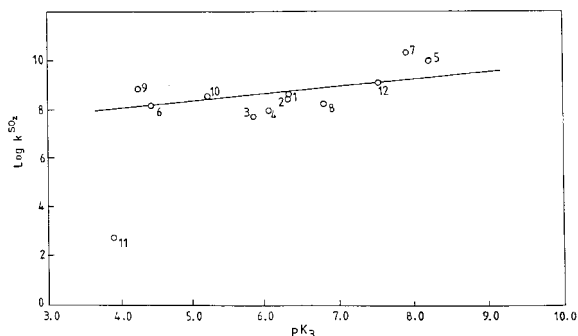
The calculated value of  $k_2^{\text{SO}}$  compare satisfactorily with those for the  $\text{SO}_2$  addition reaction of  $(\text{NH}_3)_5\text{CrOH}^{2+}$  ( $2.9 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 25°C,  $I = 1.0 \text{ mol dm}^{-3}$ ) [8] and several other (hydroxo)-

**Table IV** Rate and Activation Parameters for the Formation of  $[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2\text{—O})]^+$ <sup>a</sup>

Temp., °C	$10^{-2}k_3^{\text{HSO}}$ <sup>b</sup>	$10^{-2}k_3^{\text{SO}}$ <sup>b</sup>	$10^{-8}k_2^{\text{SO}}$ <sup>b</sup>	$10^{-3}k_3^{\text{HSO}}$ <sup>b</sup>
15.0	$5.8 \pm 1.5$	$6.1 \pm 3.0$	$2.4 \pm 0.6$	$3.7 \pm 1.8$
20.0	$8.9 \pm 1.7$	$7.4 \pm 3.0$	$4.9 \pm 0.9$	$5.0 \pm 2.4$
25.0	$12.3 \pm 2.1$	$8.0 \pm 2.9$	$9.2 \pm 1.6$	$8.4 \pm 3.1$
30.0	$18.8 \pm 2.7$	$8.6 \pm 3.5$	$19.1 \pm 2.6$	$11.0 \pm 4.0$
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$54 \pm 2$	$15 \pm 3$	$98 \pm 3$	$52 \pm 5$
$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	$-5 \pm 8$	$-140 \pm 11$	$256 \pm 8$	$5 \pm 16$

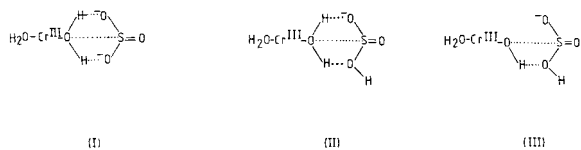
<sup>a</sup>  $I = 0.3 \text{ mol dm}^{-3}$

<sup>b</sup> Unit: dm $^3 \text{ mol}^{-1} \text{ s}^{-1}$ ;  $k_3^{\text{HSO}}$ ,  $k_3^{\text{SO}}$  are the rate constants for the reaction of  $[\text{Cr}(\text{Salen})(\text{OH}_2)_2]^+$  with  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$ , respectively;  $k_2^{\text{SO}}$  and  $k_3^{\text{HSO}'}$  are the rate constants for the reaction of  $[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OH})]$  with  $\text{SO}_2$  and  $\text{HSO}_3^-$ , respectively.

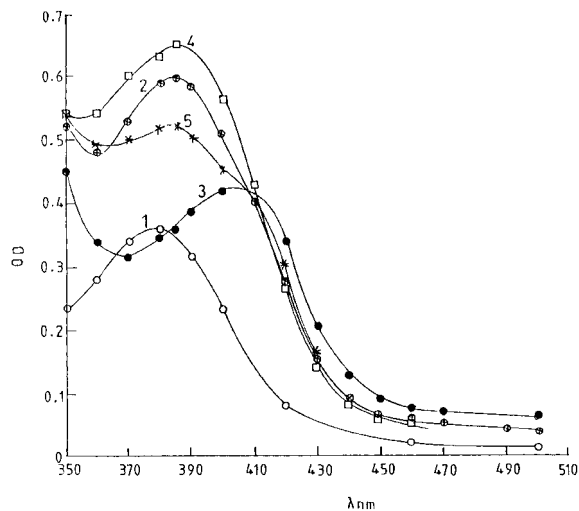


**Figure 3**  $\log k^{\text{SO}_2}$  vs.  $pK_3$  plot at 25°C. (1)  $\text{Co}(\text{NH}_3)_5\text{OH}$ , (2)  $\text{Co}(\text{treden})\text{OH}^{2+}$ , (3)  $\text{Co}(\text{tren})(\text{OH}_2)(\text{OH})^{2+}$ , (4) *cis*- $\text{Co}(\text{en})_2(\text{OH}_2)(\text{OH})^{2+}$ , (5) *cis*- $\text{Co}(\text{en})_2(\text{OH}_2)^+$ , (6) *trans*- $\text{Co}(\text{en})_2(\text{OH}_2)(\text{OH})^{2+}$ , (7) *trans*- $\text{Co}(\text{en})_2(\text{OH}_2)$ , (8)  $\text{Rh}(\text{NH}_3)_5\text{OH}^{2+}$ , (9)  $\text{Pt}(\text{NH}_3)_5\text{OH}^{3+}$ , (10)  $\text{Cr}(\text{NH}_3)_5\text{OH}^{2+}$ , (11)  $\text{Cr}(\text{OH}_2)_5(\text{OH})^{2+}$ , and (12) *trans*- $\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OH})$ .

(amine)cobalt(III) substrates [2, 4–7]; it is  $10^6$  times higher than for the analogous reaction of  $\text{Cr}(\text{OH}_2)_5(\text{OH})^{2+}$  ( $k_2^{\text{SO}_2} = 440 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 25°C,  $I = 1.0 \text{ mol dm}^{-3}$ ) [9]. This difference for the two  $\text{Cr}^{\text{III}}\text{OH}$  species is too large to be accounted for by the difference in  $pK$  of the aqua complexes (5.2 and 3.88 for  $[(\text{NH}_3)_5\text{CrOH}]^{3+}$  and  $[\text{Cr}(\text{OH}_2)_6]^{3+}$  at 25°C,  $I = 1.0 \text{ mol dm}^{-3}$ , respectively) [9]. A reasonably good Bronsted correlation ( $\log k_2^{\text{SO}_2}$  vs.  $pK_3$  plot, see Fig.3) with slope  $0.4 \pm 0.1$  for a series of aqua complexes of Co(III), Cr(III), Rh(III), and Pt(IV) inclusive of *trans*- $[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OH})]$  is indicative of the fact that  $\text{SO}_2$  addition to  $\text{M}^{\text{III}}-\text{OH}$  bond responds to the variation of basicity of the coordinated hydroxide. However, the large deviation of the data point for  $[\text{Cr}(\text{OH}_2)(\text{OH})]^{2+}$  presumably reflects difference in mechanism. The Bronsted correlation is consistent with the  $\text{SO}_2$  addition to  $\text{Cr}^{\text{III}}-\text{OH}$  in the present case; the activation parameters ( $\Delta H^\ddagger = 98 \pm 3 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 256 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$ ) for this process are unusually high. The large positive value of  $\Delta S^\ddagger$  for such a mechanism might indicate substantial solvent structure breaking influence of the dipolar transition state (t. s.) relative to the solvated initial states of the reactants. The activation enthalpy consequently increased due to disorder in the solvation cell of the transition state (presumably due to hydrogen bond breaking in the solvation cell of the transition state). This infact

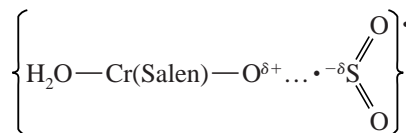


**Figure 4** Hydrogen bonded intermediates/transition states.



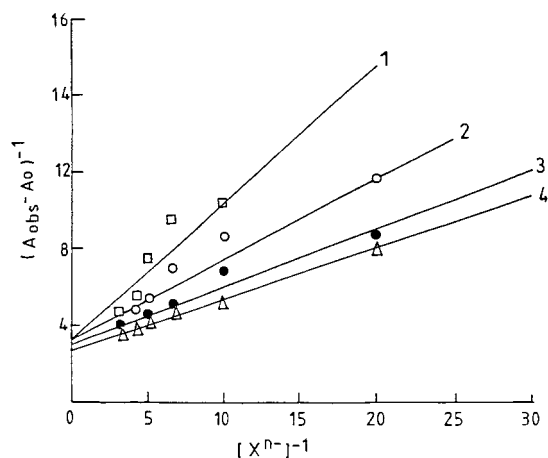
**Figure 5** Spectra of *trans*- $[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2-\text{O})]^-$  (in situ generated) in the presence and absence of  $\text{X}^{n-}$  ( $= \text{N}_3^-$ ,  $\text{NCS}^-$ , pyridine, and imidazole) at  $\text{pH} = 6.7 \pm 0.1$ ,  $[\text{Cr}(\text{Salen})(\text{OH}_2)_2^+]_{\text{T}} = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{S}^{\text{IV}}]_{\text{T}} = 0.05 \text{ mol dm}^{-3}$ , and  $[\text{X}^{n-}] = 0$  (1),  $0.2 \text{ mol dm}^{-3}$  (2–5) [ $\text{X}^{n-} = \text{N}_3^-$  (2), imidazole (3),  $\text{NCS}^-$  (4), and pyridine (5)].

reflects the variation of the solvation components of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  in a mutually compensatory manner.



(proposed structure of the transition state)

This may be contrasted with comparatively low values of  $\Delta H^\ddagger$  and almost zero values of  $\Delta S^\ddagger$  for the reactions



**Figure 6**  $(A_{\text{obs}} - A_0)^{-1}$  vs.  $[\text{X}^{n-}]^{-1}/\text{dm}^3 \text{ mol}^{-1}$  plots:  $\text{NCS}^-$  (1),  $\text{N}_3^-$  (2), pyridine (3), and midazole (4).

of  $[\text{Cr}(\text{Salen})(\text{OH}_2)_2]^+$  and the corresponding (aqua)(hydroxo) analogue with  $\text{HSO}_3^-$  (see Table IV). Furthermore the very low value of  $\Delta H^\ddagger$  and large negative value of  $\Delta S^\ddagger$  for the reaction of  $[\text{Cr}(\text{Salen})(\text{OH}_2)_2]^+$  with  $\text{SO}_3^{2-}$  clearly depicts an associative transition state. The striking features of the reaction mechanism is the involvement of hydrogen bonds between the  $\text{Cr}^{\text{III}}$  substrate and  $\text{S}^{\text{IV}}$  species,  $\text{HSO}_3^-$ , and  $\text{SO}_3^{2-}$  (see Fig. 4). The transition state involving  $\text{Cr}^{\text{III}}-\text{O} \cdots \text{S}^{\text{IV}}$  bond formation assisted by

hydrogen bond reorganization demands substantially less activation enthalpy and entropy as compared to the same for the conventional  $\text{I}_d$  process. Hydrogen bonded transition states have been proposed in the oxoanion complexation involving  $[(\text{NH}_3)_5\text{MOH}_2]^{3+}/\text{HCrO}_4^-$  ( $\text{M} = \text{Co}^{\text{III}}, \text{Cr}^{\text{III}}$ ) [1],  $[(\text{NH}_3)_5\text{CoOH}_2]^{3+}/\text{succinate}^{2-}$  [24],  $[\text{Co}(\text{NH}_3)_5\text{OH}_2]^{3+}/\text{MoO}_4^{2-}$  [25],  $[(\text{NH}_3)_5\text{CrOH}_2]^{3+}/\text{IO}_3^-$  [26];  $[(\text{NH}_3)_5\text{CoOH}_2]^{3+}/\text{AsO}_4^{3-}$  [27];  $[\text{Co}(\text{tn})_2(\text{OH}_2)]^{3+}/\text{SeO}_3^{2-}$  [28].

Due to small difference in  $\text{pK}$  of  $\text{HSO}_3^-$  and *trans-*

**Table III** Rate Constants for the Formation of  $[\text{XCr}(\text{Salen})(\text{OSO}_2-\text{O})]^{(n+1)-}$  at  $30.0 \pm 0.1^\circ\text{C}$  and  $\text{I} \pm 0.5 \text{ mol dm}^{-3\text{a}}$

$[\text{X}]_{\text{T}}/\text{mol dm}^{-3}$	$10^2 k_{\text{obs}}/\text{s}^{-1}$					
	$\text{X} = \text{N}_3^-$					
	$(6.35 \pm 0.06)^{\text{b}}$	$(6.75 \pm 0.06)^{\text{b}}$	$(7.20 \pm 0.04)^{\text{b}}$	$(7.57 \pm 0.04)^{\text{b}}$	$(6.33 \pm 0.05)^{\text{c}}$	
0.050	$3.0 \pm 0.1$		$8.9 \pm 0.3$	$10.2 \pm 0.4$	$3.0 \pm 0.1$	
0.10	$3.7 \pm 0.1$	$6.1 \pm 0.3$	$10.4 \pm 0.4$	$12.4 \pm 0.4$	$3.7 \pm 0.3$	
0.15	$4.5 \pm 0.1$	$6.8 \pm 0.3$	$11.4 \pm 0.4$	$14.4 \pm 0.9$	$4.2 \pm 0.2$	
0.20	$5.8 \pm 0.2$	$7.7 \pm 0.4$	$12.6 \pm 0.3$	$16.6 \pm 0.4$	$5.3 \pm 0.2$	
0.25	$6.4 \pm 0.3$	$8.8 \pm 0.3$	$13.7 \pm 0.4$	$18.7 \pm 0.9$	$6.2 \pm 0.3$	
0.30	$7.3 \pm 0.3$	$9.2 \pm 0.3$	$15.2 \pm 0.4$	$20.5 \pm 0.7$	$7.23 \pm 0.7$	
	$\text{X} = \text{NCS}^-$					
	$(6.69 \pm 0.02)^{\text{b}}$	$(7.01 \pm 0.02)^{\text{b}}$	$(7.23 \pm 0.04)^{\text{b}}$	$(7.51 \pm 0.04)^{\text{b}}$	$(6.71 \pm 0.03)^{\text{c}}$	$(6.72 \pm 0.02)^{\text{d}}$
0.075	$2.0 \pm 0.3$	$3.3 \pm 0.2$	$4.6 \pm 0.2$	$7.8 \pm 0.2$	$2.1 \pm 0.1$	$2.0 \pm 0.2$
0.10	$2.1 \pm 0.2$	$3.5 \pm 0.2$	$5.2 \pm 0.5$	$8.2 \pm 0.2$	$2.3 \pm 0.2$	$2.3 \pm 0.2$
0.15	$2.8 \pm 0.2$	$4.6 \pm 0.2$	$6.5 \pm 0.2$	$10.2 \pm 0.2$	$2.8 \pm 0.2$	$2.7 \pm 0.2$
0.175	—	$5.3 \pm 0.3$	$7.0 \pm 0.3$	$11.3 \pm 0.3$	—	—
0.20	$3.6 \pm 0.2$	$5.8 \pm 0.3$	$7.6 \pm 0.3$	$13.2 \pm 0.2$	$3.7 \pm 0.2$	$3.5 \pm 0.4$
0.225	—	$6.0 \pm 0.3$	$8.4 \pm 0.3$	$13.8 \pm 0.3$	—	—
0.25	$4.5 \pm 0.3$	$6.2 \pm 0.3$	$9.2 \pm 0.2$	$15.1 \pm 0.3$	$4.1 \pm 0.2$	$4.6 \pm 0.3$
	$\text{X} = \text{imH}$					
	$(6.42 \pm 0.05)^{\text{b}}$	$(6.73 \pm 0.03)^{\text{b}}$	$(7.16 \pm 0.06)^{\text{b}}$	$(7.55 \pm 0.05)^{\text{b}}$	$(7.08 \pm 0.05)^{\text{d}}$	$(7.16 \pm 0.05)^{\text{c}}$
0.075	$2.2 \pm 0.1$	$4.1 \pm 0.1$	$7.1 \pm 0.1$	$9.4 \pm 0.5$	$4.9 \pm 0.2$	$6.7 \pm 0.3$
0.10	$2.6 \pm 0.1$	$4.4 \pm 0.1$	$7.6 \pm 0.5$	$10.4 \pm 1.6$	$5.1 \pm 0.1$	$6.9 \pm 0.3$
0.15	$3.3 \pm 0.1$	$5.2 \pm 0.1$	$8.2 \pm 0.3$	$12.1 \pm 1.1$	$7.1 \pm 0.1$	$7.3 \pm 0.4$
0.20	$4.0 \pm 0.1$	$6.2 \pm 0.1$	$9.0 \pm 0.7$	$14.2 \pm 0.7$	$8.2 \pm 0.1$	$7.8 \pm 0.1$
0.25	$4.7 \pm 0.1$	$6.8 \pm 0.2$	$9.8 \pm 0.7$	$16.7 \pm 0.5$	$10.5 \pm 0.5$	$8.9 \pm 0.3$
0.30	$5.5 \pm 0.1$	$7.6 \pm 0.1$	$11.3 \pm 0.6$	$18.8 \pm 1.4$	$11.9 \pm 0.8$	$10.2 \pm 0.3$
	$\text{X} = \text{py}$					
	$(6.15 \pm 0.05)^{\text{b}}$	$(6.85 \pm 0.07)^{\text{b}}$	$(7.17 \pm 0.04)^{\text{b}}$	$(7.53 \pm 0.04)^{\text{b}}$	$(6.86 \pm 0.04)^{\text{c}}$	$(6.16 \pm 0.06)^{\text{c}}$
0.050	$4.2 \pm 0.6$	$13.0 \pm 0.1$	$20.3 \pm 0.6$	$38.1 \pm 2.0$	$13.2 \pm 0.4$	$4.3 \pm 0.1$
0.10	$5.4 \pm 0.2$	$18.3 \pm 0.7$	$29.2 \pm 0.7$	$51.6 \pm 1.4$	$18.4 \pm 0.4$	$5.4 \pm 0.2$
0.15	$6.2 \pm 0.6$	$23.4 \pm 0.4$	$38.4 \pm 0.3$	$70.2 \pm 3.0$	$23.7 \pm 1.0$	$6.1 \pm 0.3$
0.20	$7.3 \pm 0.2$	$29.9 \pm 0.5$	$47.0 \pm 0.6$	$87.7 \pm 3.5$	$30.5 \pm 1.2$	$7.3 \pm 0.3$
0.25	$8.5 \pm 0.7$	$35.1 \pm 0.4$	$59.9 \pm 0.4$	$102 \pm 3$	$34.7 \pm 0.9$	$8.4 \pm 0.3$
0.30	$9.4 \pm 0.8$	$40.1 \pm 0.4$	$70.9 \pm 1.4$	$123 \pm 5$	$39.9 \pm 2.0$	$9.3 \pm 0.2$

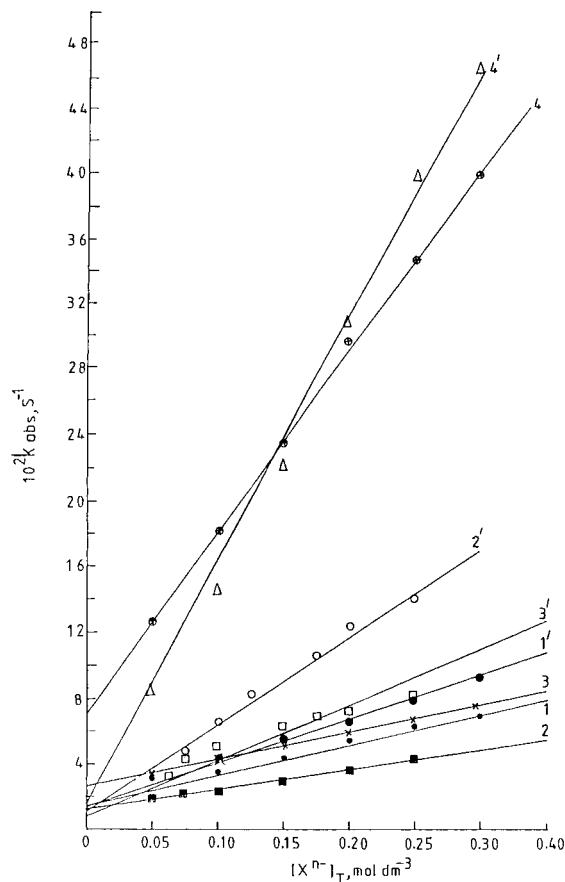
<sup>a</sup> Values given in parentheses denote  $\text{pH}$ .  $[\text{S}^{\text{IV}}]_{\text{T}}/\text{mol dm}^{-3}$  were held fixed at:

<sup>b</sup> 0.05;

<sup>c</sup> 0.075; and

<sup>d</sup> 0.025 for runs with varying  $[\text{X}^{\text{n-}}]_{\text{T}}$ .





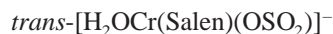
**Figure 7**  $10^2 k_{\text{obs}}/\text{s}^{-1}$  vs.  $[X^{n-}]_{\text{T}}/\text{mol dm}^{-3}$  plots for anation of  $\text{trans-}[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2\text{-O})]^-$  and  $\text{trans-}[\text{Cr}(\text{Salen})(\text{OH}_2)_2]^+$  by  $\text{N}_3^-$  (1,1', pH = 6.4),  $\text{NCS}^-$  (2,2', pH = 6.7), imidazole (3,3', pH = 6.8), and pyridine (4,4', pH = 6.7); the primed numbers (1'–4') are for the diaqua complex.

$[\text{Cr}(\text{Salen})(\text{OH}_2)_2]^+$ , it is likely that intermediate I will pass over to III in a fast proton transfer step to generate the nucleophile,  $\text{Cr}^{\text{III}}\text{-OH}$ . However, the required proton flight through H-bond reorganization in II is less likely considering the fact that  $\text{p}K_1$  of  $\text{SO}_2$  is ca. 6 unit lower than the  $\text{p}K$  of the diaqua complex. Also it is likely that the  $\text{S}^{\text{IV}}$  centre in I (i.e., the sulfite ion-pair) is far less electrophilic than the same in III. The coordinated hydroxide in (aqua)(hydroxo) complex is also a stronger nucleophile than coordinated  $\text{H}_2\text{O}$  in the diaqua complex. Considering these aspects it also appears that the alternative path of sulfite complex formation may involve  $\text{trans-}[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OH})]$  and  $\text{HSO}_3^-$  (intermediate III). However, the calculated value of the rate constant for this path is at least 1000 fold higher than the same reported for the reaction of  $\text{HSO}_3^-$  with  $[\text{Cr}(\text{OH}_2)_5(\text{OH})]^{2+}$  and at least 10 fold higher than the same for the reaction of  $\text{HSO}_3^-$

with  $[\text{Pt}(\text{NH}_3)_5\text{OH}]^{3+}$  despite the fact that coulombic interactions are distinctly more favourable for the latter two cases in comparison to the former. This unusual trend leads us to suggest that the reaction of  $[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OH})]$  with  $\text{HSO}_3^-$  does not compete effectively with the relatively much faster reaction of  $\text{SO}_2$  with the hydroxo complex.

**Anation of  $\text{trans-}[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2)]^-$ :** In the presence of the excess of  $\text{N}_3^-$ ,  $\text{NCS}^-$ , py, and imH, the spectrum of the aqua-sulfite complex,  $\text{trans-}[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2\text{-O})]^-$  (in situ-generated) is modified as shown in Figure 5. The broad maxima shown at 385 ( $\text{N}_3^-$ ,  $\text{NCS}^-$ , py), and 400 nm (imH) are indicative of the formation of  $\text{trans-}[\text{XCr}(\text{Salen})(\text{OSO}_2\text{-O})]^{(n+1)-}$ . The anated products,  $\text{trans-}[\text{XCr}(\text{Salen})(\text{OSO}_2\text{-O})]^{(n+1)-}$ , have been isolated in the solid state as their sodium salts (see experimental section).

The anation reaction is reversible (see eq. (11)).



The observed absorbances of the mixtures of the aqua-sulfite complex (in situ generated) and  $[X^{n-}]_{\text{T}}$  at 400 nm (pH = 6.5) were used to compute the forward equilibrium constant,  $K_e$  from the relationship shown in eq. (12):

$$(A_{\text{obs}} - A_0)^{-1} = [(\epsilon_2 - \epsilon_1)a]^{-1} + [(\epsilon_2 - \epsilon_1)aK_e]^{-1}[X^{n-}]^{-1} \quad (12)$$

where  $A_{\text{obs}} = \epsilon_2 [\text{XCr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2\text{-O})]^{-(n+1)} + \epsilon_1 [\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2\text{-O})]^-$ ,  $A_0 = A_{\text{obs}}$  at  $[X^{n-}]_{\text{T}} = 0$ , and  $a = [\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2\text{-O})]_{\text{T}} (= 4.0 \times 10^{-4} \text{ mol dm}^{-3})$ . The complex concentration was held fixed and  $[X^{n-}]_{\text{T}}$  was varied in the range 0.05–0.30  $\text{mol dm}^{-3}$ . It was further assumed that the diaqua complex was completely converted to the aqua-sulfite complex under the experimental conditions (i.e., pH = 6.5 and  $[\text{S}^{\text{IV}}]_{\text{T}} = 0.04 \text{ mol dm}^{-3}$ ). The aqua-sulfite complex is not significantly protonated at this pH. The protonation of  $X^{n-}$  was also taken into account ( $[X^{n-}] = [X^{n-}]_{\text{T}}/(1.0 + [\text{H}^+]/K_d^{\text{HX}})$  ( $\text{p}K_d^{\text{HX}} = 6.89, 5.37,$  and  $4.60$  for  $\text{imH}^+$ ,  $\text{pyH}^+$ , and  $\text{N}_3\text{H}$ , respectively, at  $30^\circ\text{C}$ ,  $I = 0.5 \text{ mol dm}^{-3}$  [29]). The plots of  $(A_{\text{obs}} - A_0)^{-1}$  vs.  $[X^{n-}]^{-1}$  (see Fig. 6) yielded values of  $K_e/\text{dm}^3 \text{ mol}^{-1}$  as  $7.2 \pm 1.4, 11.2 \pm 1.0, 10.5 \pm 1.2,$  and  $6.4 \pm 1.0$  ( $I = 0.5 \text{ mol dm}^{-3}, 25.0^\circ\text{C}$ ) for  $X = \text{N}_3^-, \text{imH}, \text{Py},$  and  $\text{NCS}^-$ , respectively.

The observed rate constants ( $k_{\text{obs}}$ ) for the anation reaction of  $\text{trans-}[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2\text{-O})]^-$  are collected in Table III. The  $k_{\text{obs}}$  vs.  $[X^{n-}]_{\text{T}}$  plots at a given

**Table V** Calculated Rate and Equilibrium Parameters of Anation of  $\text{Trans}-[(\text{OH}_2)\text{Cr}(\text{Salen})(\text{OSO}_2)]^-$  by  $\text{X}^{n-}$  at  $I = 0.5 \text{ mol dm}^{-3}$ ,  $30^\circ\text{C}^a$ 

$\text{X}^{n-}$	$10^2 k_1^b$ ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )	$10^8 k_2 K_d$ ( $\text{s}^{-1}$ )	$1/K_e$ ( $\text{mol dm}^{-3}$ )	$10^2 k_{-1}^b$ ( $\text{s}^{-1}$ )
$\text{N}_3^-$	$13.8 \pm 1.5$	$1.09 \pm 0.11$	$0.147 \pm 0.028$	$2.0 \pm 0.4$
imH	$29.2 \pm 4.3$	$0.82 \pm 0.13$	$0.086 \pm 0.018$	$2.5 \pm 0.6$
py	$17.2 \pm 2.3$	$11.0 \pm 0.6$	$0.080 \pm 0.018$	$1.4 \pm 0.3$
$\text{NCS}^-$	$6.50 \pm 0.31$	$1.16 \pm 0.03$	$0.092 \pm 0.007$	$0.6 \pm 0.05$

<sup>a</sup> Values  $K_d^{\text{HX}}$  used for calculation are 4.61, 6.89, and 5.37 for  $\text{N}_3\text{H}$ ,  $\text{imH}_2^+$ , and  $\text{pyH}^+$ , respectively,  $\text{NCS}^-$  is not protonated under the experimental conditions.

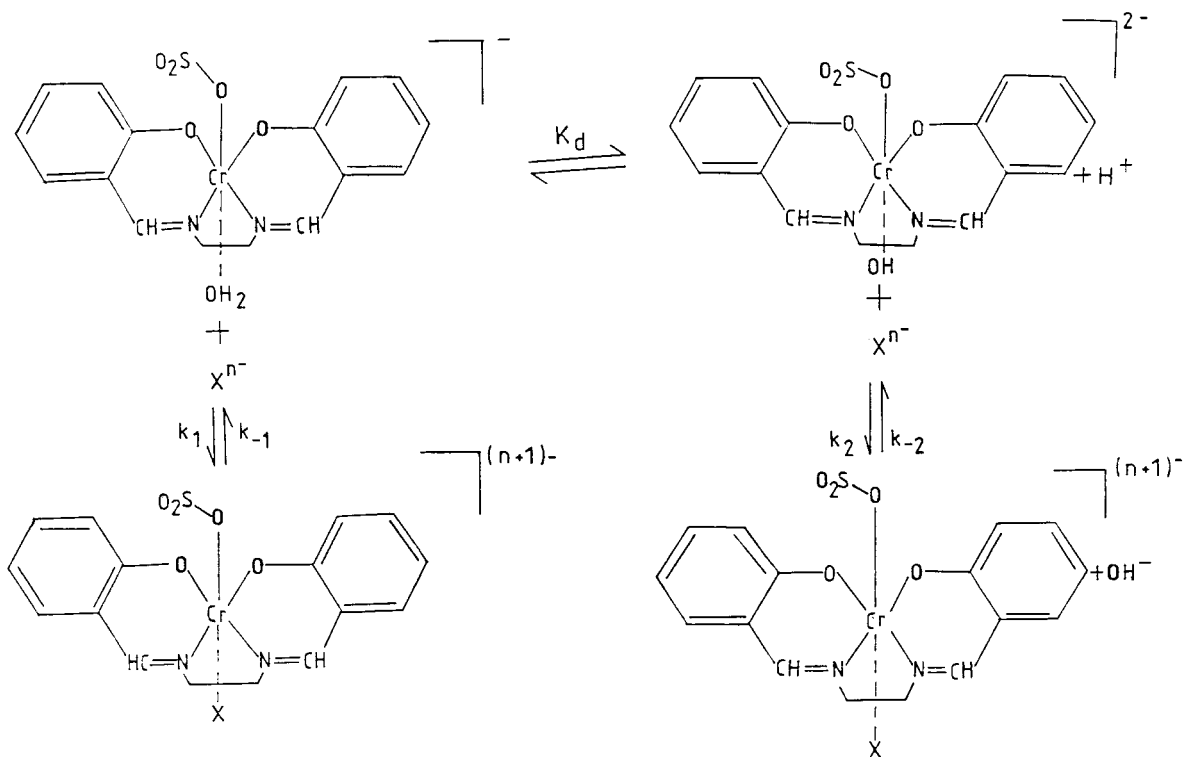
<sup>b</sup>  $k_{-1} = k_1/K_e$ .  $10^2 k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  ( $10^2 k_{-1}/\text{s}^{-1}$ ):  $21 \pm 2$  ( $0.8 \pm 0.2$ )( $\text{N}_3^-$ );  $53 \pm 30$ (0.75)(imH);  $21 \pm 10$ ( $0.21 \pm 0.4$ )(py); and  $15 \pm 4$ ( $1.0 \pm 0.4$ )( $\text{NCS}^-$ ) for the reversible anation of  $\text{trans}-[\text{Cr}(\text{Salen})(\text{OH}_2)]^+$  at  $30.0^\circ\text{C}$  and  $I = 1.0 \text{ mol dm}^{-3}$  (ref. [19]).

pH for the aqua sulfito and diaqua complexes (see Fig. 7) show that  $\text{S}^{\text{IV}}$  retards the reaction. Note that the anation involves  $\text{trans}-[\text{OH}_2\text{Cr}(\text{Salen})(\text{OH}_2)]^+$  and  $\text{trans}-[\text{OHCr}(\text{Salen})(\text{OH}_2)]^0$  in absence of  $\text{S}^{\text{IV}}$ , while  $\text{trans}-[\text{OH}_2\text{Cr}(\text{Salen})(\text{OSO}_2-\text{O})]^-$  and  $\text{trans}-[\text{OHCr}(\text{Salen})(\text{OSO}_2-\text{O})]^{2-}$  are the anating  $\text{Cr}^{\text{III}}$  species in the presence of  $\text{S}^{\text{IV}}$  (see Scheme I). It is thus evident that the reaction  $\text{trans}-[\text{OHCr}(\text{Salen})(\text{OH}_2)]^0 + \text{X} \rightarrow \text{trans}-[\text{OHCr}(\text{Salen})\text{X}]^0$  is more facile than the reaction  $\text{trans}-[\text{OHCr}(\text{Salen})(\text{OSO}_2-\text{O})]^{2-} + \text{X} \rightarrow \text{trans}-[\text{XCr}(\text{Salen})(\text{OSO}_2-\text{O})]^- + \text{OH}^-$ . Further analysis of data (see later) shows that (aqua)sulfito complex undergoes relatively faster an-

ation with the neutral ligands than the diaqua complex. The  $k_{\text{obs}}$  data at a given pH and  $[\text{X}^{n-}]_{\text{T}}$  and under varying concentrations of  $[\text{S}^{\text{IV}}]$  (0.025, 0.05, and  $0.075 \text{ mol dm}^{-3}$ , see Table III) are virtually independent of  $[\text{S}^{\text{IV}}]_{\text{T}}$ . It may be further noted that eq. (13) is

$$k_{\text{obs}} = k_f^{\text{app}}[\text{X}^{n-}] + k_r^{\text{app}} \quad (13)$$

valid at each pH (see Fig. 7). The intercepts and gradients of the plots of  $k_{\text{obs}}$  vs.  $[\text{X}^{n-}]$  (after correcting for the protonation of  $\text{X}^{n-}$ ) show inverse  $[\text{H}^+]$  dependence. These observations are consistent with the reaction Scheme I given below.

**Scheme I** Anation of  $\text{trans}-[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2-\text{O})]^-$  by  $\text{X}^{n-}$ ;  $\text{X}^{n-} = \text{N}_3^-$ ,  $\text{NCS}^-$ , imH, py

for which

$$k_{\text{obs}} = k_f^{\text{app}} \{ [X^{n-}]_T / (1.0 + [H^+] / K_d^{\text{HX}} + K_e^{-1}) \} \quad (14)$$

where

$$k_f^{\text{app}} = k_1 + k_2 K_d / [H^+] \quad (15)$$

Equation (15) assumes  $K_d/[H^+] \ll 1$  under the experimental pH conditions where  $K_d$  is the acid dissociation constant of the aqua-sulfite complex. Equation (13) is transformed to eq. (14) by expressing  $k_r^{\text{app}}$  in terms of  $k_f^{\text{app}}$  and  $K_e$ . Values of  $k_1$ ,  $k_2 K_d$ , and  $K_e^{-1}$  were used as adjustable parameters and the rate constants were fitted to eq. (14) by a weighted least-squares program ( $k_{\text{obs}}$  was weighted inversely as its variance). The calculated values of these parameters are collected in Table V. The values of  $K_e^{-1}$  calculated from the rate data are in satisfactory agreement with those obtained from the equilibrium measurements further substantiating the reaction Scheme I.

The values of  $k_1$  and  $k_2 K_d$  show little dependence on the nature of  $X^{n-}$ . The acid dissociation constant ( $K_d$ ) of the aqua-sulfite complex is likely to be less than that of the aqua-hydroxo complex. From this consideration  $k_2/k_1 < 10^{-3}$  is a reasonable estimate. This reflects the relative labilizing effect of the coordinated sulfite on the  $\text{Cr}^{\text{III}}-\text{OH}_2$  and  $\text{Cr}^{\text{III}}-\text{OH}$  bonds in  $\text{trans-Cr}(\text{Salen})(\text{OH}_2/\text{OH})(\text{OSO}_2-\text{O})^{-/2-}$ . Using the symmetry number corrected values of  $k_1$  for  $\text{trans}[\text{Cr}(\text{Salen})(\text{OH}_2)_2]^+$  (i.e.,  $k_1/2$ ) (see footnote b of Table V) and neglecting ionic strength effect, we obtain  $k_{-1}(\text{S}^{\text{IV}})/k_{-1}(\text{H}_2\text{O}) = 1.1$  (imH), 0.9 ( $\text{NCS}^-$ ), 1.3 ( $\text{N}_3^-$ ), and 1.6 (py) as the relative rate profile of anation of the (aqua)(sulfite) and (diaqua) complexes. The lack of incoming ligand dependence in the anation of the (aqua)(sulfite) complex strongly supports  $I_d$  mechanism for the aqua-sulfite complex.

The dissociation rate constant,  $k_{-1} (= k_1 K_e^{-1})$ , see Table V) shows a weak ligand dependence and follows the sequence  $\text{NCS}^- < \text{py} \text{ ca. imH} \text{ ca. } \text{N}_3^-$ . Using the data of Ramasami et al. [19] we calculate  $k_{-1}(\text{S}^{\text{IV}})/k_{-1}(\text{H}_2\text{O}) = 3.3$  (imH), ca. 0.6 ( $\text{NCS}^-$ ), 2.5 ( $\text{N}_3^-$ ), and 6.7 (py) which reflect the labilizing action of coordinated  $\text{H}_2\text{O}$  and  $\text{SO}_3^{2-}$  (O—bonded). This small rate variation can be understood in terms of the dissociative interchange mechanism.

Thus, we conclude that the  $\text{trans}[\text{Cr}(\text{Salen})(\text{OH}_2)(\text{OSO}_2-\text{O})]^-$  is formed by the  $\text{SO}_2$  addition to the  $\text{Cr}^{\text{III}}-\text{OH}$ . The O-sulfite complex does not isomerise to its S-bonded analogue and does not exert

any significant labilizing effect on the ligand bonded *trans* to itself in  $\text{trans}[\text{XCr}(\text{Salen})(\text{OSO}_2-\text{O})]^{n-}$  where  $\text{X} = \text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{NCS}^-$ ,  $\text{N}_3^-$ , Py, and imH.

We acknowledge the assistance rendered by the Central Drug Research Institute, Lucknow and Regional Research Laboratory, Bhubaneswar for elemental analysis and infrared spectral measurements. This work was supported by a research grant from the Department of Science and Technology, New Delhi.

## BIBLIOGRAPHY

1. M. R. Grace and P. A. Treglon, *Inorg. Chem.*, **31**, 4524 (1992) and references cited therein.
2. A. C. Dash, A. A. El-Awady, and G. M. Harris, *Inorg. Chem.*, **20**, 3160 (1981).
3. R. van Eldik, J. Jouanne, and H. Kelm, *Inorg. Chem.*, **21**, 2818 (1982).
4. T. P. Dasgupta and G. M. Harris, *Inorg. Chem.*, **23**, 4399 (1984).
5. A. A. El-Awady and G. M. Harris, *Inorg. Chem.*, **25**, 1323 (1986).
6. A. N. Acharya and A. C. Dash, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **105**, 225 (1993).
7. A. C. Dash and K. C. Jena, *Transition Met. Chem.*, **22**, 141 (1997).
8. R. van Eldik, *Inorg. Chim. Acta.*, **42**, 49 (1980).
9. P. A. Moritzen, A. A. El-Awady, and G. M. Harris, *Inorg. Chem.*, **24**, 313 (1985).
10. K. C. Koshy and G. M. Harris, *Inorg. Chem.*, **22**, 2947 (1983).
11. V. K. Joshi, R. van Eldik, and G. M. Harris, *Inorg. Chem.*, **25**, 229 (1986).
12. A. C. Dash, A. N. Acharya, and A. K. Patnaik, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **107**, 533 (1995).
13. C. Brandt and R. van Eldik, *Chem. Rev.*, **95**, 119 (1995).
14. A. C. Dash, A. K. Patnaik, and N. Das, *Indian J. Chem., SecA*, **36**, 268 (1997).
15. G. Mahal and R. van Eldik, *Inorg. Chem.*, **26**, 2838 (1987).
16. P. Coggon, A. T. Mcphail, F. E. Mabbs, A. Richards, and A. S. Thornley, *J. Chem. Soc., Dalton Trans.*, 3296 (1970).
17. S. Yamada and K. Iwasaki, *Bull. Chem. Soc., Jpn.*, **42**, 1463 (1964).
18. S. Yamada and K. Iwasaki, *Inorg. Chim. Acta.*, **5**, 3 (1971).
19. D. R. Prasad, T. Ramasami, D. Ramaswamy, and M. Santappa, *Inorg. Chem.*, **21**, 850 (1981).
20. F. Lloret, M. Julve, M. Mollar, I. Castra, J. Latorre, J. Faus, X. Sloans, and I. M. Badarau, *J. Chem. Soc. Dalton Trans.*, 729 (1989).
21. C. N. R. Rao, *Chemical Application of Infra-red Spectroscopy*, Academic, New York, 1963, p. 344.

22. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 3rd ed., Longmans, London, 1961, p. 264.
23. A. E. Martell and R. M. Smith, *Critical Stability Constants*, Plenum, New York, vol. 4, 1976, p. 78.
24. A. C. Dash and M. S. Dash, *J. Coord. Chem.*, **10**, 79 (1980).
25. M. R. Grace and P. A. Treglon, *Polyhedron*, **10**, 2317 (1991).
26. Gy. Bazsa and H. Diebler, *React. Kinet. Catal. Lett.*, **2**, 217 (1975).
27. T. A. Beech, N. C. Lawrence, and S. F. Lincoln, *Aust. J. Chem.*, **26**, 1877 (1973).
28. A. D. Fowless and D. R. Stranks, *Inorg. Chem.*, **16**, 1276 (1977).
29. A. E. Martell and R. M. Smith, *Critical Stability Constants*, Plenum, New York, vol. 2, (1976) p. 165, p. 144; vol. 4, (1976) p. 45.