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Kinetics and mechanism of formation, acid catalysed aquation, reversible anation and photochemical reaction of *trans*-(aqua)(sulfito-*S*)[*N*,*N*′-ethylenebis(salicylidiniminato)]cobaltate(III) in aqueous media †

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The reaction of *trans*-[Co(salen)(OH_2)OH] with SO_2 yields *trans*-[Co(salen)(OH_2)(SO_3-*S*)]$^-$ (*S*-bonded isomer) for which the rate and activation parameters at 25 °C (I = 0.3 mol dm^{-3}) are $k^{SO_2} = (5.9 \pm 0.1) \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $\Delta H^‡ = 66 \pm 4$ kJ mol^{-1} and $\Delta S^‡ = 183 \pm 14$ J K^{-1} mol^{-1}. One possibility for the S^{IV} substitution is that Co–S bond formation is concerted with Co–O bond breaking. An alternative mechanism, involving a fast equilibrium between SO_2 and *trans*-[Co(salen)(OH_2)OH] forming an *O*-bonded sulfito species which then undergoes sulfite ligand linkage isomerisation, is also possible. An estimated value of the isomerisation rate constant for the *trans*-[Co(salen)(OH_2)(OSO_2H)] at 25 °C is *ca.* 10^6 s^{-1}. The *trans*-[Co(salen)(OH_2)(SO_3-*S*)]$^-$ (p$K = 10.1 \pm 0.1$ at 25 °C, I = 0.3 mol dm^{-3}) undergoes acid catalysed aquation to yield the parent diaqua complex and S^{IV} with $k_H = 29.5 \pm 1.1$ dm^3 mol^{-1} s^{-1}, $\Delta H^‡ = 72 \pm 3$ kJ mol^{-1}, $\Delta S^‡ = 24 \pm 9$ J K^{-1} mol^{-1} at 25 °C (I = 0.3 mol dm^{-3}). Steady state photolysis (254 nm) of *trans*-[Co(salen)(OH_2)(SO_3-*S*)]$^-$ resulted in the reduction of Co^{III}. The redox rate constant and $\varphi(Co^{2+})$ decreased with increasing pH. Attempts to detect an *O*-bonded sulfito complex as a transient in the conventional flash photolysis of this aqua-sulfito complex proved unsuccessful.

The aqua ligand replacement reactions of *trans*-[Co(salen)(OH_2/OH)(OH_2)]$^{+/0}$ with imidazole and that of the corresponding aqua-sulfito complex with N_3^-, NCS^-, imidazole, and S^{IV} in a large excess of the entering ligands have been studied at 25 °C. A comparison of the rate constants with the analogous data for *trans*-[Co(AA)$_2$(OH_2)(SO_3-*S*)]$^+$ (AA = 1,2-diaminoethane; 1,3-diaminopropane) clearly shows that the kinetic *trans*-effect of the S-bonded sulfite is substantially attenuated in *trans*-[Co(salen)(OH_2)(SO_3-*S*)]$^-$.

The study reported herein is an outcome of our long standing interest in the reactions of S^{IV} with transition metal ions and their complexes.[1,2] In recent times, there has been great upsurge of interest in the study of the reactions of SO_2, owing to its impact on environmental pollution. Also S^{IV} offers interesting chemistry with regard to its participation in non-metal redox,[3] redox and substitution reactions involving *O*- and *S*-bonded sulfito metal complexes.[1–9] The oxidation of SO_2 to SO_3^{2-} is catalysed by transition metal ions and their complexes.[10–12] The formation of S-bonded sulfito complexes in the sulfite substitution reactions of *cis*-[Co(AA)$_2$(OH_2)$_2$]$^{3+}$ (AA = 1,10-phenanthroline, 2,2′-bipyridyl) without intervention of the *O*-bonded sulfito species has been reported.[13] We have also shown that [(tetren)CoOH]$^{2+}$ (tetren = tetraethylenepentamine) undergoes sulfite substitution in basic media (pH > 10) to yield the corresponding *S*-bonded sulfito complex.[14] In acidic or neutral media, however, SO_2 addition to $Co^{III}OH$ prevails to generate the *O*-sulfito species, [(tetren)CoOSO$_2$]$^+$.[15] The formation of *trans*-[Mn(salen)(OH_2)(SO_3-*S*)]$^-$ from the corresponding diaqua complex[2a] has been shown to involve direct substitution of one of the aqua ligands by HSO_3^- or SO_3^{2-}. Like SO_3^{2-} and HSO_3^-, SO_2 is also known to form a S-bonded sulfur dioxide complex of ruthenium(II).[16] Thus, ambiguities exist regarding the mechanisms of formation of sulfito complexes due to the fact that various paths, such as SO_2 addition to M–OH^{n+} or direct replacement of coordinated H_2O by the O- and S-end of SO_3^{2-} or HSO_3^-, or the *S*-end of SO_2, leading to *O*- and *S*-bonded sulfito species, can be envisaged. The possibility of observing an *O*-bonded sulfito species is, however, linked to the relative speed of its formation and isomerisation to the *S*-bonded isomer.

In this work, we report a kinetic investigation of the reactions of S^{IV} with *trans*-[Co(salen)(OH_2)$_2$]$^+$. The cobalt(III) substrate shows exceptional lability to substitution of the aqua ligands[17–20] due to the presence of the delocalised π-electron frame. Our objectives were to examine the effects of the salen ligand on the rates of sulfite substitution at Co^{III}, electron transfer between S^{IV} and the metal centre, and to elucidate further the mechanism of formation of *O*- and *S*-bonded sulfito complexes. Relevant data for *trans*-[M(salen)(OH_2)$_2$]$^+$ (M = Cr^{III}, Mn^{III})[21,2a] are available for comparison. In order to throw more light on the mechanism of reaction, and the kinetic *trans*-effect of the S-bonded sulfite in *trans*-[Co(salen)(X)(SO_3-*S*)]$^{n-}$ (X = H_2O, OH^-, or any other anionic or neutral ligand) we have also investigated the kinetics of the aqua ligand substitution of *trans*-[Co(salen)(OH_2)$_2$]$^+$ by imidazole (im) and of *trans*-[Co(salen)(OH_2)(SO_3-*S*)]$^-$ by N_3^-, NCS^-, S^{IV} and imidazole respectively which, to the best of our knowledge, have not been previously reported.

Experimental

Preparation of complexes

trans-[Co(salen)(OH_2)$_2$]ClO_4·H_2O[22] was prepared by a published method and the purity checked by elemental analysis.

trans-[Co(salen)(OH_2)(SO_3)]Na was prepared as follows: an aqueous solution (30 cm^3) of *trans*-[Co(salen)(OH_2)$_2$]ClO_4·H_2O (1 mmol) was treated with Na_2SO_3 (3 mmol) and the mixture at pH *ca.* 6 was set aside overnight in the dark at room

† Electronic supplementary information (ESI) available: rate constants for the reaction of *trans*-[Co(salen)(OH_2)$_2$]$^+$ with S^{IV}. See http://www.rsc.org/suppdata/dt/a9/a909562d/

temperature. The desired complex precipitated as a brown solid, which was isolated by filtration on a glass sintered funnel, washed successively with cold ethanol and diethyl ether and stored over silica gel in a desiccator, avoiding exposure to light (yield *ca.* 60%). Anal. calcd. for Na[Co(salen)(OH_2)(SO_3)]: C, 43.0; H, 3.58; N, 6.27; S, 7.11; Co, 13.2; Na, 5.15. Found: C, 42.1; H, 3.67; N, 6.18; S, 7.70; Co, 12.9; Na, 5.12%. λ_{max}/nm (ε/M^{-1} cm^{-1}): 310 (7900), 390 (4245) at pH 6.0. The IR spectra (KBr phase) shows bands at 3445 and 1641 cm^{-1} assignable to coordinated H_2O. Bands at 983 and 619 cm^{-1} are characteristics of *S*-bonded sulfite.[1,23–25] Furthermore, multiplet band structures in the range 1641–1448 cm^{-1} are also characteristic of the coordinated salen.

Materials and methods

Analar reagents were used for kinetic studies. Solutions were prepared in doubly distilled water, the second distillation being made from alkaline $KMnO_4$ in an all-glass distillation apparatus. Sodium μ-oxo-tetraoxodisulfate, $Na_2S_2O_5$, was the source of sulfur(IV). This salt is very stable in the solid state but hydrolyses rapidly in aqueous media to an equilibrium mixture of SO_3^{2-}–HSO_3^-–SO_2. A fresh solution of S^{IV} was prepared just before commencing the kinetic experiments. $NaClO_4$ used to adjust ionic strength was prepared from Na_2CO_3 and $HClO_4$ and estimated by a combined ion-exchange and alkalimetric procedure. Dowex 50W X-8 resin (H^+ form) was used for ion exchange experiments. The pH of the stock sodium perchlorate solution was adjusted to 6.

The pH measurements were made with an ELICO digital pH meter LI 120 using a glass-Ag/AgCl, Cl^- (2 mol dm^{-3} NaCl) combined electrode CL 51. The performance of the pH meter was checked by standard buffers of pH 4.01, 6.86 and 9.2. The pH data were converted into p[H^+] by a calibration curve (p[H^+] = − log[H^+] = pH − *A*)[26] constructed from the measured pH values of a set of solutions of $HClO_4$ ($2.0 \times 10^{-3} - 2.0 \times 10^{-8}$ mol dm^{-3} adjusted to the desired ionic strength) against 0.05 mol dm^{-3} potassium hydrogenphthalate (pH 4.01 at 25 °C) as reference and the p[H^+] of the acid solutions calculated using appropriate values of the ionic product of water (pK_W = 14.24, 13.87 and 13.69 at 10.0, 20.0 and 25 °C, respectively, $I = 0.3$ mol dm^{-3}).[27] At 10–25 °C the pH calibration factor *A* was 0.10 ± 0.02. UV–visible spectra were recorded on JASCO 7800 or Perkin-Elmer lambda 20 spectrophotometers using 1 cm matched quartz cells. The IR spectra were recorded on a Perkin-Elmer Paragon 500 FTIR spectrometer. ^1H NMR spectra were recorded on a Varian 300 MHz FT NMR spectrometer in D_2O. The C H N analysis was carried out at the Central Drug Research Institute, Lucknow, India. Cobalt was estimated as described in our earlier work.[28] Na was estimated by atomic absorption spectrometry using a Perkin-Elmer 3100 atomic absorption spectrometer. Sulfur in the sulfito complex was oxidised by ammoniacal H_2O_2 solution and estimated gravimetrically as $BaSO_4$.[29]

Steady state photolysis and conventional flash photolysis studies were carried out at the Centre for Ultrafast Kinetics Research, University of Chennai, India. The rapid scan spectral measurements were made on an SF 61 stopped flow spectrophotometer with rapid scan accessory and IS_2 software suite (HITECH, UK) at the Tata Institute of Fundamental Research, Mumbai, India. The thermal decomposition of *trans*-[Co(salen)(OH_2)(SO_3-*S*)]Na was studied by a Shimadzu DT50 thermal analyser. The temperature calibration was carried out using pure indium metal (mp 156.63 °C). The performance of the equipment was further checked by a thermal study of the dehydration of $CuSO_4 \cdot 5H_2O$.

Thermal study of *trans*-[Co(salen)(OH_2)(SO_3-*S*)]Na

20 mg of the sample was thermally decomposed in static air in the range of temperatures 30–500 °C at a heating rate of 5 °C min^{-1}. The DTA and TG curves (see Fig. 1) show an endothermic peak around 90–110 °C, corresponding to *ca.* 5% weight loss. Two other very pronounced exothermic peaks are associated with *ca.* 20% and *ca.* 75% weight losses at 210–230 and 260–280 °C, respectively. These correspond to the overall reactions as depicted below, for which the % weight losses are *ca.* 4.0 (−H_2O), 18.4 [−(H_2O + SO_2)] and 74.4 (final weight loss leading to Co_2O_3 + Na_2O as residue), respectively.

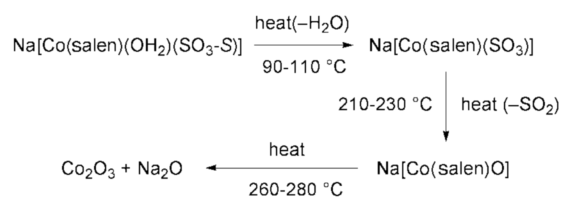


Table 1 Calculated values of $k^{SO_2\,a,b}$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$

Temp./°C	$10^{-10}k^{SO_2}$/dm^3 mol^{-1} $s^{-1\,c}$	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
10.0	1.41 ± 0.05	66.0 ± 4.2	183 ± 14
15.0	2.06 ± 0.06		
20.0	3.63 ± 0.05		
25.0	5.94 ± 0.10		

[a] [Co(salen)$_2$(OH_2)$_2^+$]$_T$ = (2.0 − 5.0) × 10^{-4}, $0.01 \le$ [S^{IV}]$_T$/mol dm^{-3} ≤ 0.05, $2.09 \le pH \le 8.51$, $I = 0.3$ mol dm^{-3}; $\lambda = 420$ nm. [b] −log[H^+] = pH − 0.1. [c] Based on the values of pK_1(pK_2): 1.47 (6.47), 1.52 (6.51), 1.57 (6.54) and 1.62 (6.59) at 10, 15, 20, and 25 °C ($I = 0.3$ mol dm^{-3}), respectively (ref. 34*a*, p. 78); pK_3 = 8.6 (10–25 °C).

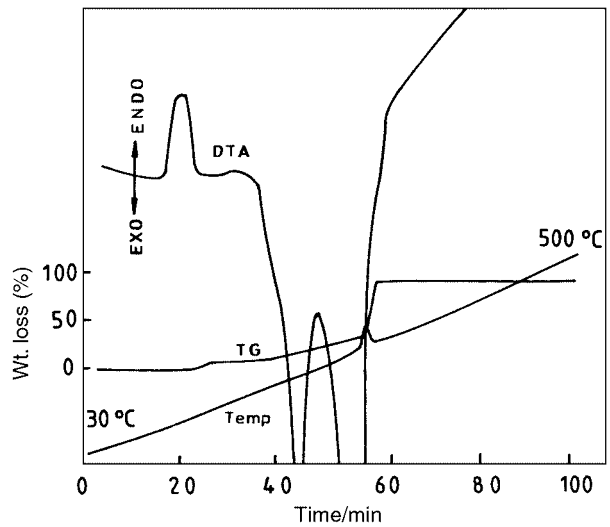


Fig. 1 DTA and TG curves for the thermal decomposition of *trans*-[Co(salen)(OH_2)(SO_3-*S*)]Na.

Kinetics

The kinetics of formation of the sulfito complex of *trans*-[Co(salen)(OH_2)$_2$]$^+$ was investigated under pseudo-first order conditions at $10.0 \le T$/°C ≤ 25.0 ($I = 0.3$ mol dm^{-3}) with [complex]$_T$ = (2–4) × 10^{-4}, $0.005 \le$ [S^{IV}]$_T$/mol dm^{-3} ≤ 0.05 and pH 2.2–8.5. Sodium chloroacetate–chloroacetic acid and trishydroxymethylaminomethane–$HClO_4$ were used as buffers in the pH ranges 2.2–4.0 and 7.2–8.5, respectively. In the pH range 4.0–7.2 self-buffered sulfite was used. The reactions were monitored by a HITECH model SF 51 stopped flow spectrophotometer at 420 nm. The acid catalysed aquation of the sulfito complex, *trans*-[Co(salen)(OH_2)(SO_3)]$^-$ was monitored at 340 nm. The absorbance–time curves were strictly single exponentials, characteristic of first order kinetics. At least seven replicate measurements were made for each run to calculate k_{obs} and $\sigma(k_{obs})$ which are collected in Table 1.†

The kinetics of the aqua ligand replacement reactions of *trans*-[Co(salen)(OH$_2$)$_2$]$^+$ and *trans*-[Co(salen)(OH$_2$)(SO$_3$-*S*)]$^-$ were studied by stopped flow techniques at 25 °C under pseudo-first order conditions. Relevant data are collected in Tables 2 and 3.

All slow reactions were monitored spectrophotometrically. The cell compartment was thermostatted to the desired temperature.

All calculations were performed on an IBM compatible 486 PC, using a weighted least squares program. The dependent variable was weighted as the inverse of its variance.

Steady state photolysis

The continuous photolysis experiments at 254 nm were carried out using a low pressure mercury vapour pen-ray lamp (Ultraviolet Products, USA). The sample solution was contained in a 1 cm quartz cuvette covered with a teflon cap. The cuvette was placed near the pen-ray lamp during photolysis. The lamp output was monitored by ferrioxalate actinometry as described in our earlier work.[1] The intensity of light was 3.084×10^{15} quanta s^{-1}. The concentration of the sulfito complex, *trans*-[Co(salen)(OH$_2$)(SO$_3$-*S*)]$^-$, was 1.0×10^{-3} mol dm^{-3}. The pH in the range 4–6 was controlled by $MeCO_2^- - MeCO_2H$ buffer and beyond 7 by tris buffer. The Co(II) yield was monitored spectrophotometrically as $[Co(NCS)_4]^{2-}$ by Kitson's method[30] and the quantum yield of Co^{2+} [$\varphi(Co^{2+})$] was calculated as described in our earlier work.[1] The values of $\varphi(Co^{2+})$ and k_{obs} for photo reduction at 25 °C are collected in Table 4. The successive spectral scans of the photolysed solutions are also presented in Fig. 2. Photoreduction without build up of any intermediate is indicated.

Flash photolysis

The conventional flash photolysis experiments were carried out using an Applied Photophysics KN 020 model flash kinetic spectrometer, which consisted of two LR-16 flash lamps filled with Xenon. The sample cell (made of quartz and of inner diameter 10 mm, optical path length 104 mm) was placed at the centre of the flash cavity, in between the flash lamps, and the lamps were fired at 10 kV using a 200 J, 1 mF capacitor bank. The capacitor was fed by a high voltage power supply unit. A 12 V, 100 W quartz tungsten iodine lamp (Phillips, Holland) was used as the source of the monitoring beam. The desired wave length of the analysing beam was chosen by using a Czerny-Turner M-300 high radiance monochromator. The detecting system was a R-926 Hammamatsu photomultiplier tube with a sensitivity range of 300–800 nm. The output signal from the PMT was fed to the photometric control unit which provided signal amplification and offset control. The signal from the photometric control unit was stored in a Datalab DL-905 transient digitizer, then displayed on a Scopex 486 oscilloscope and recorded using a CR-550 Y-T recorder. Our attempts to detect a transient in the range 390–500 nm proved unsuccessful.

Table 2 Rate constants for the reaction of imidazole (im) with *trans*-[Co(salen)(OH$_2$)$_2$]$^{+\,a}$

pH	10^2[HClO$_4$]$_T$/ mol dm^{-3}	10^2[im]$_T$/ mol dm^{-3}	10^2k_{obs}/s^{-1}
5.99	2.57	3.00	1.03 ± 0.06
5.92	3.43	4.00	1.44 ± 0.06
6.12	4.29	5.00	2.37 ± 0.09
6.01	5.15	6.00	2.79 ± 0.09
6.28	6.00	7.00	3.24 ± 0.08
6.21	6.86	8.00	3.45 ± 0.08
6.99	5.00	10.0	19.0 ± 0.8
7.33	4.00	10.0	20.5 ± 0.8
7.57	3.00	10.0	24.4 ± 0.7
7.89	2.00	10.0	31 ± 1
8.01	1.50	12.0	37 ± 1
8.20	1.00	10.0	34 ± 1
8.17	1.50	15.0	50 ± 1
8.18	2.00	20.0	71 ± 2
8.17	2.50	25.0	82 ± 2
8.18	3.00	30.0	99 ± 2

k_1/dm^3 mol^{-1} s^{-1} 2.87 ± 0.11; k_2/dm^3 mol^{-1} s^{-1} 3.78 ± 0.08. [a] [Complex]$_T$ = 5.0×10^{-4}, I = 0.5 mol dm^{-3}, T = 25.0 ± 0.1 °C, λ = 400 nm.

Table 4 Rate constant (k_{obs}) and $\varphi(Co^{2+})$ for photo reduction of *trans*-[Co(salen)(OH$_2$)(SO$_3$-*S*)]$^{-\,a}$

pH	10^4k_{obs}/s$^{-1\,b}$	$\varphi(Co^{2+})$
4.01	7.0	0.32
4.31	7.2	0.37
4.58	8.3	0.38
4.76	8.0	0.35
5.01	6.7	0.27
5.46	6.0	0.28
5.89	6.2	0.29
6.83	0.41 [c]	0.042 [c]
8.01 [d]	—	0.00

[a] [Complex]$_T$ = 1.0×10^{-3}, I = 0.3 mol dm^{-3}, 25 °C. [b] $k_{obs} = (1/t)\ln [Co^{III}]_T/([Co^{III}]_T - [Co^{II}])$; k_{obs} was calculated from Co^{II} yield at 25–30 min of irradiation (60–70% of reduction for most of the runs). [c] From *ca.* 7% reduction (30 min). [d] Co^{II} was undetectable after 30 min of irradiation.

Table 3 Rate constants for reversible anation of *trans*-[Co(salen)(OH$_2$)(SO$_3$-*S*)]$^{-\,a}$

$$trans\text{-}[Co(salen)(OH_2)(SO_3 - S)]^- + X^{n-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} trans\text{-}[co(Salen)(X)(SO_3 - S)]^{(n+1)-}$$

[X^{n-}]$_T$/ mol dm^{-3}	k_{obs}/s$^{-1\,b}$ X^{n-} = NCS$^-$	N$_3^-$	imidazole (im)	S^{IV}
0.05	0.99 ± 0.04	0.84 ± 0.04	1.42 ± 0.10	0.52 ± 0.02
0.10	1.22 ± 0.09	1.05 ± 0.08	2.09 ± 0.10	0.75 ± 0.03
0.15	1.68 ± 0.10	1.30 ± 0.10	2.37 ± 0.11	0.86 ± 0.03
0.20	1.97 ± 0.13	1.52 ± 0.10	3.57 ± 0.11	1.04 ± 0.05
0.25	2.17 ± 0.14	1.88 ± 0.10	4.25 ± 0.13	1.24 ± 0.06
0.30	2.78 ± 0.10	2.24 ± 0.17	4.88 ± 0.20	1.44 ± 0.07
k_f/dm^3 mol^{-1} s^{-1}	6.8 ± 0.4	5.1 ± 0.3	17.6 ± 0.3 [c]	3.3 ± 0.3
k_r/s^{-1}	0.63 ± 0.05	0.57 ± 0.03	0.69 ± 0.04	0.36 ± 0.04

[a] [Complex]$_T$ = 1.0×10^{-4}, I = 0.5 mol dm^{-3}, 25.0 °C: λ/nm = 340 (NCS$^-$, N$_3^-$, imidazole), 320 (S^{IV}). [b] pH 6.67 ± 0.08 (NCS$^-$), 6.43 ± 0.04 (N$_3^-$), 6.99 ± 0.12 (imidazole), 6.73 ± 0.13 (S^{IV}). [c] Based on $k_{obs} = k_f[im] + k_r$; [im] = [im]$_T$ − [HClO$_4$]; [HClO$_4$] = [im]$_T$/5.

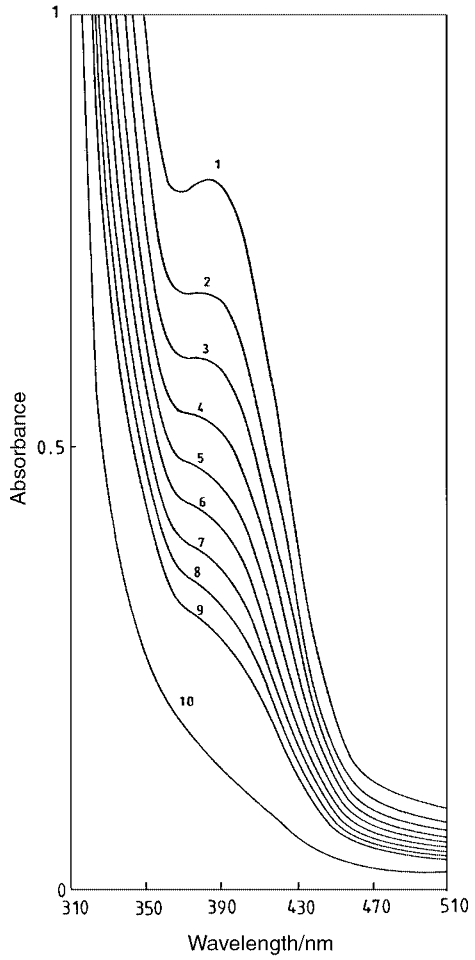


Fig. 2 Successive spectral scans of photolysed solutions of *trans*-[Co(salen)(OH$_2$)(SO$_3$-*S*)]$^-$ at 25 °C. Absorbance decreases with time. [Complex]$_T$ = 2.0 × 10^{-4} mol^{-3}, pH 6.2.

p*K* of *trans*-[Co(salen)(OH$_2$)$_2$]$^+$ and *trans*-[Co(salen)(OH$_2$)(SO$_3$)]$^-$

The p*K* measurements were made by pH titration. Aliquots (100 cm^3) of complex solutions of 5.0 × 10^{-4} mol dm^{-3} (I = 0.3 mol dm^{-3}) were pH titrated with 0.05 mol dm^{-3} NaOH at 25.0 °C. We obtained $K_3 = (1.6 \pm 0.4) \times 10^{-9}$ and $K_4 = (7.9 \pm 1.6) \times 10^{-11}$ mol dm^{-3} for the acid dissociation constants of the diaqua and the aqua-sulfito complexes, respectively (see eqn. 1 and 2). For the diaqua complex, K_3 was also calculated

$$trans\text{-}[Co(salen)(OH_2)_2]^+ \underset{}{\overset{K_3}{\rightleftharpoons}} trans\text{-}[Co(salen)(OH_2)(OH)] + H^+ \quad (1)$$

$$trans\text{-}[Co(salen)(OH_2)(SO_3\text{-}S)]^- \underset{}{\overset{K_4}{\rightleftharpoons}} trans\text{-}[Co(salen)(OH)(SO_3\text{-}S)]^{2-} + H^+ \quad (2)$$

from the pH dependence of its absorbance (λ = 400 nm, $5.0 \le pH \le 10.2$, I = 0.3 mol dm^{-3}); the solutions of the diaqua complex of a fixed total concentration ([complex]$_T$ = 2.0 × 10^{-4} mol dm^{-3}) were adjusted to the desired pH with NaOH. For equilibrium 1, K_3 was calculated from the relationships, $K_3 = x[H^+]/(a - x)$, where $x = a(A_{obs} - A')/(A'' - A')$, a = [diaqua complex]$_T$, x = [aqua-hydroxo], A', A'', and A_{obs} denoted the absorbances of the complex as a diaqua complex, an aqua-hydroxo complex and an equilibrium mixture of the two respectively. The values of 10^9 K_3 were 3.4 ± 1.5, 2.3 ± 1.0, 2.7 ± 1.5 and 2.4 ± 0.8 mol dm^{-3} at 10, 15, 20 and 25 °C (I = 0.3 mol dm^{-3}), respectively. The acid dissociation of *trans*-[Co(salen)(OH$_2$)(OH)] was not observed below pH *ca.* 10. However,

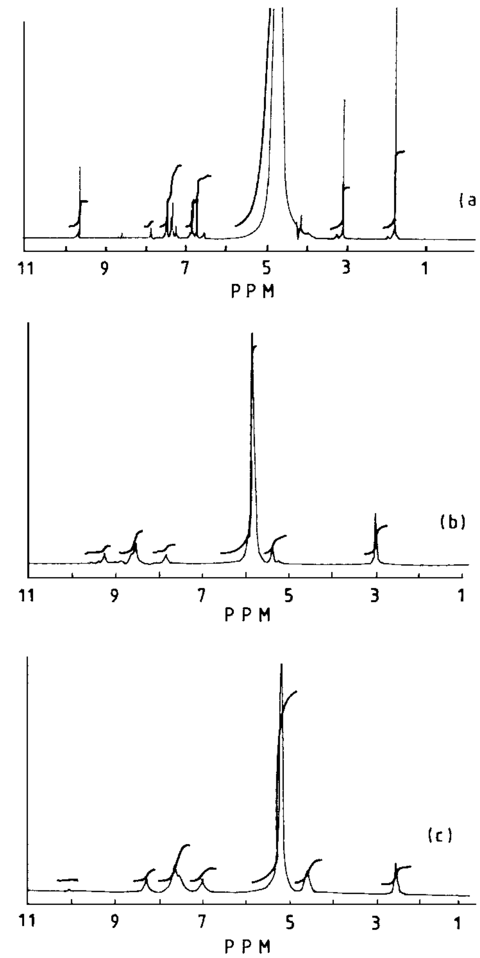


Fig. 3 ^{1}H NMR spectra of *trans*-[Co(salen)(OH$_2$)(SO$_3$-*S*)]$^-$ in D$_2$O at pH 2 (a), 7 (b) and 11(c) (pH adjusted with HClO$_4$ and NaOH).

the formation of the dihydroxo complex, *trans*-[Co(salen)(OH)$_2$]$^-$, at pH *ca.* 13 has been reported by Costa *et al.*[17]

Results

Preliminary observations

trans-[Co(salen)(OH$_2$)$_2$]$^+$ displays absorption maxima at 250 and 380 nm, with molar extinction coefficients 2200 and 2940 M^{-1} cm^{-1}, respectively. In the presence of S^{IV}, these bands appear at 310 and 390 nm. Both the positions and intensities of the new bands agree with those for an authentic sample of *trans*-[Co(salen)(OH$_2$)(SO$_3$-*S*)]$^-$ [λ_{max}/nm (ε/M^{-1} cm^{-1}): 310 (7900), 390 (4245)]. Furthermore, the spectral changes of the diaqua complex in the presence of S^{IV} were instantaneous. The acid catalysed aquation of the sulfito complex also generated the spectrum of the corresponding diaqua complex. A test for Co^{II} by Kitson's method[30] in the reaction of the diaqua complex with sulfite under wide pH conditions (pH 2.0–8.5) and extended time period at 20–40 °C was negative, thus indicating that this cobalt(III) substrate is substantially inert to reduction by S^{IV} under thermal conditions.

The ^{1}H NMR spectra of *trans*-[Co(salen)(OH$_2$)(SO$_3$-*S*)]$^-$ at pH 2, 7 and 11 are presented in Fig. 3(a–c). At pH 2, the complex undergoes fast aquation (see below) to yield *trans*-[Co(salen)(OH$_2$)$_2$]$^+$; signals at δ 1.83 (singlet, CH$_2$CH$_2$), 9.87 (singlet, 2HC=N), 3.13 (singlet, H$_2$O), and 6.75–7.5 (aromatic protons) are observed. At pH 7 and 11, the complex is stable to aquation/base hydrolysis but exists as (aqua)(sulfito) and (hydroxo)(sulfito) species, respectively, for which the aliphatic CH$_2$ protons appear at δ 1.97 and 1.91. The intensity of signal due to the azomethine proton (δ 9.95 and 10.0 at pH 7 and 11, respectively) is considerably reduced due to exchange

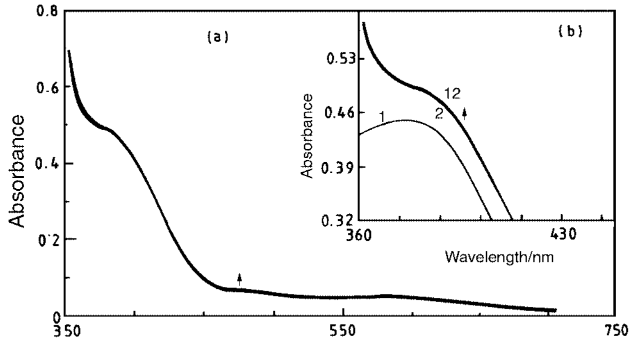


Fig. 4 Rapid scan spectra of *trans*-[Co(salen)(OH_2)$_2$]$^+$ + S^{IV} at 25 °C. [Complex]$_T$ = 1.0 × 10^{-4} + [S^{IV}]$_T$ = 0.02 mol dm^{-3}(pH 6.39, self buffered). (a) number of scans = 96, total time = 0.120 s; (b) inset: curve 1 for complex alone; curves 2–12 for the reaction mixture in 0.12 s; Δt = 0.012 s between successive runs.

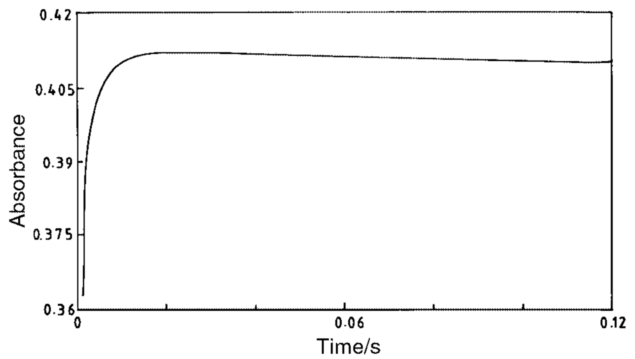


Fig. 5 Absorbance *vs.* time plot for a stopped flow run at 400 nm; conditions the same as for Fig. 4.

with D and the aromatic protons are also well resolved (δ 6.74–8.13). The H_2O signal shows substantial shifts in neutral and alkaline media with considerable broadening.

Formation of *trans*-[Co(salen)(OH_2)(SO_3)]$^-$

The rapid scan spectra of a mixture of *trans*-[Co(salen)(OH_2)$_2$]$^+$ (1.0 × 10^{-4} mol dm^{-3}) and S^{IV} (0.02 mol dm^{-3}) at pH 6.39 is displayed in Fig. 4(a). In all, 96 scans during 0.120 s (Δt = 1.25 ms between successive scans) were collected in the wave length range 350–700 nm, which are further amplified in Fig. 4(b) in the range 360–410 nm (12 scans, Δt = 10 ms between successive scans). Fig. 5 displays the stopped flow trace of the same reaction mixture over 0.120 s at 400 nm. In none of these is any transient evident within the stopped flow timescale. Thus, the stopped flow kinetics and rapid scan spectroscopy are consistent with the formation of a single product. A k_{obs} *vs.* pH plot at constant [S^{IV}]$_T$ (0.02 mol dm^{-3}) [see Fig. 6(a)] indicates that the observed rate constant is virtually insensitive to pH in the range 2.5–5.5 and then decreases steadily with increasing of pH. Note that k_{obs} at 25 °C *decreased 100 fold* when [SO_3^{2-}] *increased 5000 fold*. Evidently SO_3^{2-} can not be considered to be a reactive species under these conditions. Also, the possibility that HSO_3^- and the aqua-hydroxo complex are the reacting partners can be excluded as fast prototopic equilibrium within the preassembled ion-pair {*trans*-[Co(salen)(OH_2)(OH)] + HSO_3^- $\Longleftrightarrow$ *trans*-[Co(salen)(OH_2)$_2$]$^+$ + SO_3^{2-}} prior to the rate limiting step will make it essentially indistinguishable from the diaqua complex + SO_3^{2-} reaction. The k_{obs} *vs.* [S^{IV}]$_T$ plot at constant pH [see Fig. 6(b)] is also linear, with a zero intercept on the k_{obs} axis indicating that the reverse reaction (*i.e.* the aquation of the product sulfito complex) is not significant at pH > 2 in excess [S^{IV}]$_T$. This is further supported by an independent rate study of the acid catalysed aquation of the *S*-sulfito complex (see below). In addition to this, our recent study of the reactions

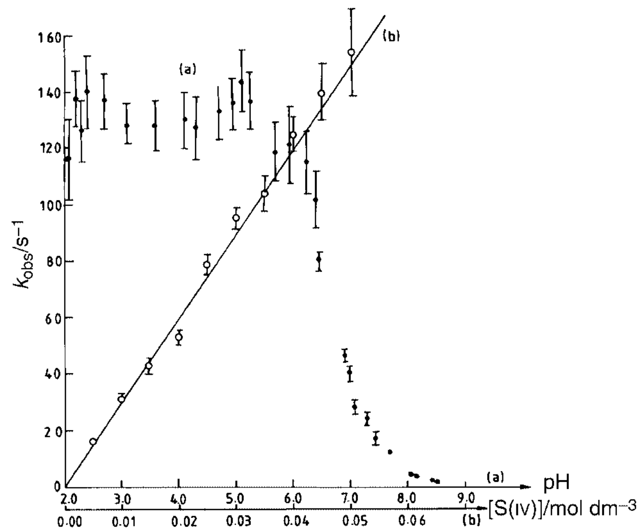


Fig. 6 (a) k_{obs}/s^{-1} *vs.* pH plot at [S^{IV}]$_T$ = 0.02 mol dm^{-3} and (b) k_{obs} *vs.* [S^{IV}]$_T$/mol dm^{-3} plot at pH 6.6 for the formation of *trans*-[Co(salen)(OH_2)(SO_3-*S*)]$^-$ at 25.0 °C.

of *trans*-[Mn(salen)(OH_2)$_2$]$^+$ with S^{IV} under almost identical experimental conditions showed that both HSO_3^- and SO_3^{2-} substitute the aqua ligand to yield *trans*-[Mn(salen)(OH_2)(SO_3-*S*)]$^-$ with $k^{HSO_3^-} < k^{SO_3^{2-}}$.[2a] The observed trend in the reactivity of the *trans*-[Co(salen)(OH_2)$_2$]$^+$ with S^{IV} over the extended pH range is, however, similar to what has been reported earlier for the SO_2 addition reactions of several (hydroxo)(amine)cobalt(III) complexes which generate the *O*-sulfito complex beyond any doubt.[1,2b,d,15,31–33] The *O*-sulfito cobalt(III) complexes, however, undergo fast acid catalysed aquation. It is, therefore, compelling to consider that the the reactive species are SO_2 and *trans*-[Co(salen)(OH_2)(OH)] and the resulting product is, however, the *S*-sulfito complex, *trans*-[Co(salen)(OH_2)(SO_3-*S*)]$^-$ (see eqn. 3). Details of the mechanistic aspects of this process are discussed in a later section.

$$trans\text{-}[(OH_2)Co(salen)OH] + SO_2 \xrightarrow{k^{SO_2}} trans\text{-}[(OH_2)Co(salen)(SO_3\text{-}S)]^- + H^+ \quad (3)$$

Accordingly, k_{obs} is given by eqn. 4 where $f_1 = [H^+]^2/D$,

$$k_{obs} = k^{SO_2} f_1 f_4 [S^{IV}]_T \quad (4)$$

$D = ([H^+]^2 + K_1[H^+] + K_1K_2)$, and $f_4 = K_3/([H^+] + K_3)$. Values of pK_1 and pK_2 (K_1 and K_2 are the acid dissociation constants of $SO_2\cdot H_2O$ and HSO_3^-, respectively) at the experimental temperatures and ionic strengths were calculated from the available data[34a] (see footnote *c*, Table 1). The acid dissociation constant of the diaqua complex (K_3) is temperature insensitive; its mean value (spectrophotometric data) at 10–25 °C is (2.5 ± 0.1) × 10^{-9} mol dm^{-3} (pK_3 = 8.60 ± 0.02). The value of pK_3 shows that $f_4 \approx 1$ in the pH range 2–7. A constant value of pK_3 (8.6) was used and the rate constants were fitted to eqn. 4. The values of k^{SO_2} are collected in Table 1. The validity of eqn. 4 is further indicated by the straight line plots of k_{obs} *versus* f_1f_4[S^{IV}]$_T$ with zero intercept on the k_{obs} axis (see Fig. 7).

Reaction of *trans*-[Co(salen)(OH_2)$_2$]$^+$ with S^{IV} at pH 10.2

The repetitive spectral scans for S^{IV} + diaqua complex at pH 10.2 (borate buffer) display a sudden increase of absorbance at several wavelengths, followed by a slow increase of absorbance at 310 nm with isosbestic points at 355 and 380 nm (see Fig. 8). The formation of the *S*-sulfito complex is indicated. Similar behaviour was also exhibited with higher [S^{IV}]$_T$ and at pH 8.51, 9.31 and 9.81. There was no buffer effect at constant pH. The pseudo-first order rate constants (k_{obs}) for this change at several

Table 5 Rate constants of anation of *trans*-[Co(salen)(OH_2)OH] by SO_3^{2-} [a]

pH [b]	[S^{IV}]/mol dm^{-3}	10^3k_{obs}/s^{-1}	$10^3k^{SO_2}f_1f_4[S^{IV}]_T$/s^{-1}	$10^2k^{SO_3^{2-}}$/dm^3 mol^{-1} s^{-1} [c]
10.06	0.005	0.92 ± 0.04	0.59	6.5
10.16	0.010	1.57 ± 0.05	0.72	8.5
10.12	0.010	1.74 ± 0.12	0.83	9.1
10.21	0.010	1.40 ± 0.05	0.57	8.3
10.09	0.015	2.13 ± 0.06	1.50	4.2
10.16	0.015	1.89 ± 0.03	1.08	5.4
10.19	0.015	2.16 ± 0.04	0.94	8.1
10.13	0.020	2.80 ± 0.29	1.66	5.7
10.10	0.025	3.49 ± 0.21	2.38	4.4
10.21	0.030	3.02 ± 0.15	1.72	4.3

[a] $[\text{Complex}]_T = (1.2 - 1.6) \times 10^{-4}$, $I = 0.3$ mol dm^{-3}, 25 °C, $\lambda = 310$ nm. [b] Borate buffer, $-\log[H^+] = \text{pH} - 0.1$. [c] $(k_{obs} - k^{SO_2}f_1f_4[S^{IV}]_T)/[SO_3^{2-}]$.

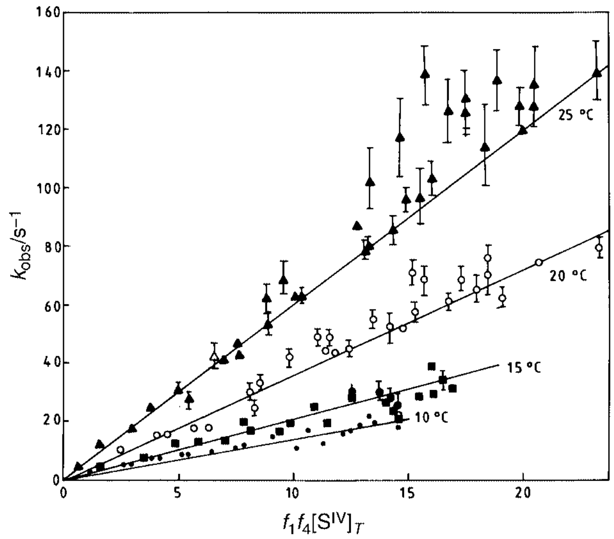


Fig. 7 k_{obs}/s^{-1} *vs.* $f_1f_4[S^{IV}]_T$ plots at 10.0, 15.0, 20.0 and 25.0 °C.

$[S^{IV}]_T$ and pH 10.06–10.21 (25 °C, $I = 0.3$ mol dm^{-3}) are collected in Table 5. Under the experimental conditions, the predominant S^{IV} species is SO_3^{2-} and 94% of the cobalt(III) substrate will exist as *trans*-[Co(salen)(OH_2)(OH)]. [SO_2] (=$f_1[S^{IV}]_T$) ranges from *ca.* 4.79×10^{-15} to 19.9×10^{-15} mol dm^{-3}. However, the high value of k^{SO_2} results in a significant contribution from the reaction of SO_2 with the aqua-hydroxo complex (see Table 5) to the overall rate of formation of the sulfito complex. A correction was, therefore, applied and the rate constant of the anation of the aqua-hydroxo complex by SO_3^{2-} (see eqn. 5) was then calculated $\{k^{SO_3^{2-}} = (k_{obs} - k^{SO_2} f_1f_4[S^{IV}]_T)/[SO_3^{2-}]\}$. The average value of k^{SO_3} turned out to be $(6.4 \pm 1.9) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} at 25 °C and $I = 0.3$ mol dm^{-3} (see Table 5).

$$\textit{trans}\text{-[Co(salen)(OH}_2\text{)(OH)]} + SO_3^{2-} \xrightarrow{k^{SO_3^{2-}}} \textit{trans}\text{-[Co(salen)(OH)(SO}_3\text{-}S\text{)]}^{2-} \quad (5)$$

Aquation of *trans*-[Co(salen)(OH_2)(SO_3-*S*)]$^+$

The aquation of *trans*-[Co(salen)(OH_2)(SO_3-*S*)]$^-$ is moderately acid catalysed. The k_{obs} values at $0.04 \le [H^+]/\text{mol dm}^{-3} \le 0.3$, $10.0 \le T/\,°C \le 25.0$ ($I = 0.3$ mol dm^{-3}) (see Fig. 9) show linear dependence with [H^+] and, when fitted to the relationship $k_{obs} = k_0 + k_H[H^+]$, yielded either negative or statistically insignificant values of k_0 indicating that the sulfito complex undergoes aquation exclusively *via* the H^+-catalysed path (see eqn. 6).

$$\textit{trans}\text{-[Co(salen)(OH}_2\text{)(SO}_3\text{)]}^+ + H^+ \xrightarrow{k_H} \textit{trans}\text{-[Co(salen)(OH}_2\text{)}_2\text{]}^+ + HSO_3^- \quad (6)$$

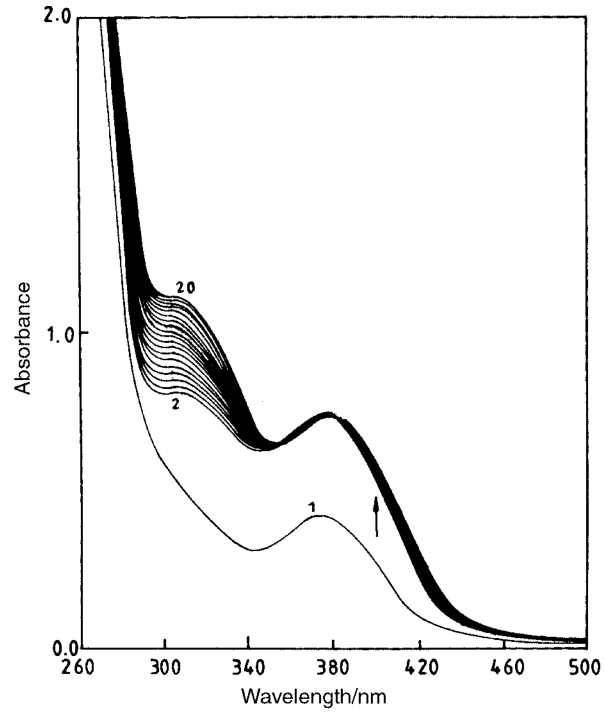


Fig. 8 Successive spectral scans for the reaction of *trans*-[Co(salen)-(OH_2)$_2$]$^+$ with S^{IV} at pH 10.18 (borate buffer) at 25 °C. $[\text{Complex}]_T = 1.207 \times 10^{-4}$, $[S^{IV}]_T = 0.005$ mol dm^{-3}; curve 1 for the diaqua complex (pH 10.1) in absence of S^{IV}; curves 2–20 for the reaction mixture with $\Delta t = 2$ min between successive scans.

The values of k_H(=$k_{obs}/[H^+]$), are 6.0 ± 0.2, 9.8 ± 0.1, 16.5 ± 1.0 and 29.5 ± 1.1 dm^3 mol^{-1} s^{-1} at 10.0, 15.0, 20.0 and 25.0 °C, respectively, which yield $\Delta H^‡ = 72 \pm 3$ kJ mol^{-1} and $\Delta S^‡ = 24 \pm 9$ J K^{-1} mol^{-1}. The values of k_H further substantiate that the aquation rate constant of the sulfito complex will not contribute significantly to k_{obs} for its formation at pH > 2 and in excess $[S^{IV}]_T$.

Formation of *trans*-[Co(salen)(OH_2)(im)]$^+$

In order to establish the mechanism, we studied the formation of the imidazole complex at 25.0 °C ($I = 0.5$ mol dm^{-3}). Rate constants (k_{obs}) collected in Table 2 fitted to eqn. 7 satisfactorily,

$$k_{obs} = (k_1 + k_2K_3/[H^+]) \times [\text{im}]_{free}/(1.0 + K_3/[H^+]) \quad (7)$$

indicating that the reverse reaction (aquation of the imidazole complex) was negligible. In eqn. 7, k_1 and k_2 denote the rate constants for the reaction of imidazole with *trans*-[Co(salen)(OH_2)$_2$]$^+$ and its aqua-hydroxo analogue respectively (see eqn. 8a,b). The concentration of free imidazole ([im]$_{free}$) was taken to be $[\text{im}]_T - [HClO_4]_T$.

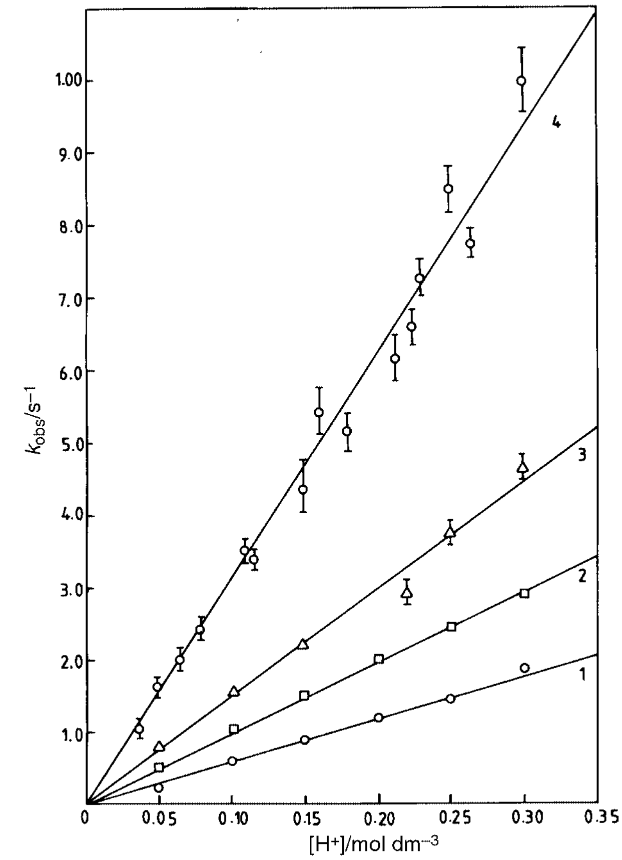


Fig. 9 k_{obs} *vs.* $[H^+]$ plot for the acid catalysed aquation of *trans*-$[Co(salen)(OH_2)(SO_3\text{-}S)]^+$ at 10.0 (1), 15.0 (2), 20.0 (3), and 25.0 °C (4), $I = 0.3$ mol dm^{-3}.

$$
\begin{array}{ccc}
trans\text{-}[Co(salen)(OH_2)_2]^+ + im & \xrightarrow{k_1} & trans\text{-}[Co(salen)(OH_2)(im)]^+ \quad (8a) \\
(-H^+)K_3 \Big\downarrow\Big\uparrow & & (-H^+) \Big\downarrow\Big\uparrow \\
trans\text{-}[Co(salen)(OH_2)(OH)] + im & \xrightarrow{k_2} & trans\text{-}[Co(salen)(im)(OH)] \quad (8b)
\end{array}
$$

The calculated values of k_1 and k_2 are also collected in Table 2.

Anation of *trans*-$[Co(salen)(OH_2)(SO_3\text{-}S)]^-$

In order to examine the kinetic *trans*-effect of the coordinated sulfite, we studied replacement of the aqua ligand by NCS^-, N_3^-, imidazole (im) and S^{IV}. The reaction is reversible but kinetically controlled as the k_{obs} (see Table 3) *versus* $[X]_T$ plots yielded excellent straight lines with positive intercepts on the rate axis and positive gradients. The pH conditions were such that the acid dissociation of the aqua ligand was insignificant. Correction of the protonation of $N_3^-[pK(N_3H) = 4.38$, 25 °C, $I = 0.5$ mol dm^{-3}][34a] was also negligible, while the concentration of free imidazole was taken to be $[im]_T - [HClO_4]$ [$pK(imH^+) = 7.03$ and 7.31 at $I = 0.16$ and 1.0 mol dm^{-3}, 25 °C].[34b] The S^{IV} anation was studied at pH = 6.73 ± 0.13 [$pK(HSO_3^-) = 6.48$, 25 °C, $I = 0.5$ mol dm^{-3} (ref. 11)] and both HSO_3^- and SO_3^{2-} may be the anating species. The observed rate constants for reaction 9 were analysed in terms of eqn. 10.

$$trans\text{-}[(OH_2)Co(SO_3\text{-}S)]^+ + X^{n-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} trans\text{-}[XCo(SO_3\text{-}S)]^{(n-1)-} \quad (9)$$

$$k_{obs} = k_f[X^{n-}] + k_r \quad (10)$$

The values of the anation rate constant (k_f) and the reverse rate constant (k_r) are collected in Table 3.

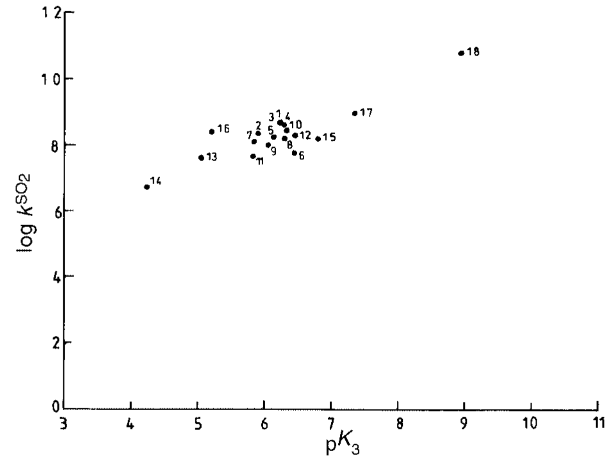


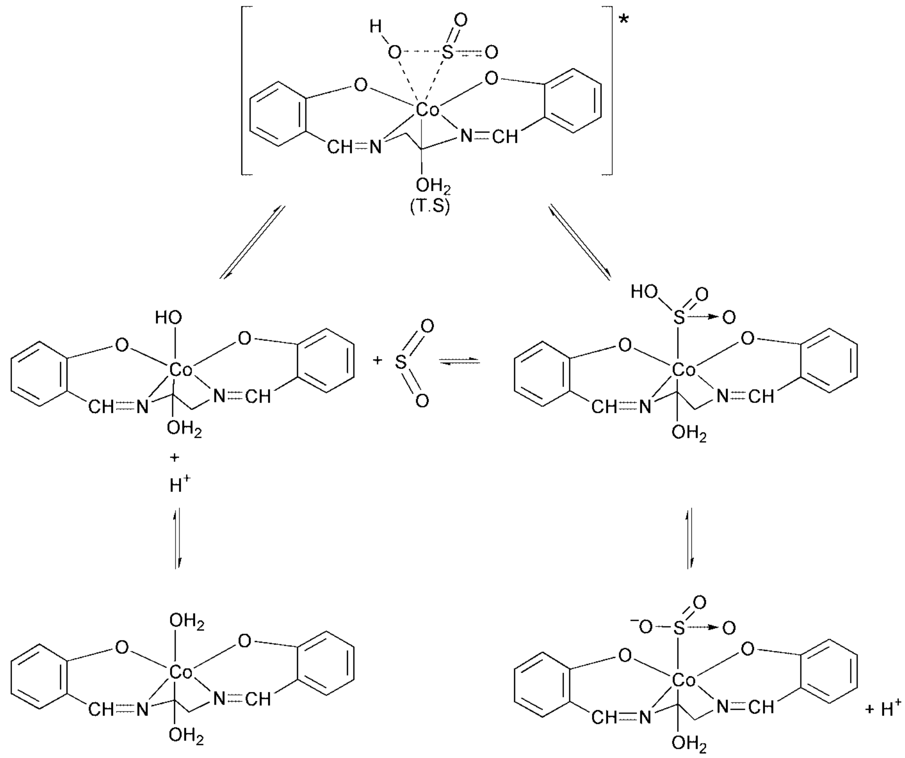
Fig. 10 log k^{SO_2} *versus* pK_3 plot at 25 °C for *cis*-$(en)_2Co(B)OH^{2+}$: B = NH_3 (1), $MeNH_2$ (2), $EtNH_2$ (3), $C_6H_5CH_2NH_2$ (4), $C_6H_{11}NH_2$ (5), imidazole (6), benzimidazole (7), *N*-Me-imidazole (8), OH_2 (9); $[(NH_3)_5CoOH]^{2+}$ (10); $[(tren)Co(OH_2)OH]^{2+}$ [tren = tris(2-aminoethyl)amine] (11); $[(tetren)CoOH]^{2+}$ (12); β-*cis*-$[(tren)Co(OH_2)OH]^{2+}$ (13); $[(NH_3)_5PtOH]^{3+}$ (14); $[(NH_3)_5RhOH]^{2+}$ (15); $[(NH_3)_5CrOH]^{2+}$ (16); *trans*-$[(salen)Cr(OH_2)OH]$ (17); and *trans*-$[(salen)Co(OH_2)OH]$ (18).

Discussion

The rate constants of anation of *trans*-$[Co(salen)(OH_2)_2]^+$ by $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ are 4.5×10^3 and 4.8×10^2 dm^3 mol^{-1} s^{-1} at 25.0 °C ($I = 0.5$ mol dm^{-3}),[20] respectively. The dissociation of the species, *trans*-$[Co(salen)(OH_2)(NCFe(CN)_5)]^{2-}$, to the parent reactants is also fast ($k = 1.5 \pm 0.2$ s^{-1} at 25 °C).[20] The activation enthalpies and entropies for the formation and dissociation of *trans*-$[Co(salen)(OH_2)(NCFe(CN)_5)]^{2-}$ are not unusually high ($\Delta H^\ddagger = 43 \pm 7, 52 \pm 8$ kJ mol^{-1}; $\Delta S^\ddagger = -52 \pm 22, -67 \pm 27$ J K^{-1} mol^{-1} for the formation and dissociation reactions respectively).[20] These data, as well as the formation rate constants of *trans*-$[Co(salen)(OH_2)(im)]^+$ (see Table 2), are suggestive of the fact that the rate constant of anation of *trans*-$[Co(salen)(OH_2)_2]^+$ by HSO_3^- and SO_3^{2-} must follow the sequence $k^{HSO_3^-} < k^{SO_3^{2-}}$ or $k^{HSO_3^-} \sim k^{SO_3^{2-}}$ if these ions replace the aqua ligand *via* A, I_a or D, I_d mechanisms. It is clear that the formation of the sulfito complex does not involve direct replacement of the aqua ligand at the cobalt(III) centre by S^{IV}.

The *O*-bonded sulfito cobalt(III) complexes are formed as transient intermediates in the reaction of S^{IV} with (aqua)(amine)cobalt(III) complexes. This involves addition of SO_2 to Co^{III}–OH and the reaction is fast ($k = 10^8$ dm^3 mol^{-1} s^{-1} at 25 °C) and generally associated with low activation enthalpy ($\Delta H^\ddagger = 20$–60 kJ mol^{-1}) (see Table 11 of ref. 1). However, the *O*-bonded sulfito complexes undergo fast acid catalysed aquation ($k = 10^6$ dm^3 mol^{-1} s^{-1} at 25 °C) and considerably slower ligand isomerisation ($Co^{III}OSO_2 \longrightarrow Co^{III}SO_3$; $k_{iso} \approx 10^{-4}$ s^{-1} at 25 °C).[2b,d,15,35]

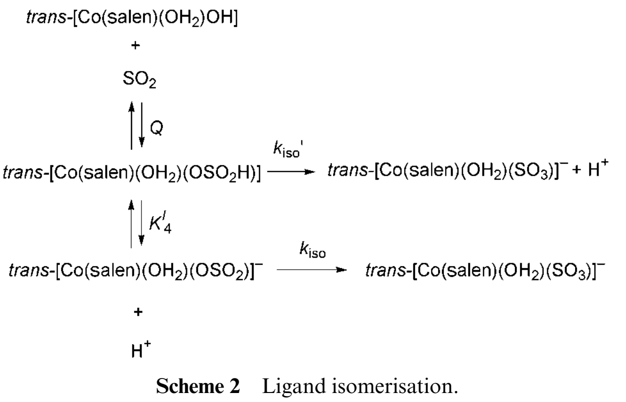
The calculated values of the rate constant for the reaction of SO_2 with *trans*-$[Co(salen)(OH_2)(OH)]$ are at the diffusion controlled limit and may be contrasted with those for the formation of *trans*-$[Cr(salen)(OH_2)(OSO_2\text{-}O)]^-$ [$k^{SO_2} = (9.2 \pm 1.6) \times 10^8$ dm^3 mol^{-1} s^{-1} at 25 °C, $I = 0.3$ mol dm^{-3}];[21] a higher value for the former is in keeping with the higher pK of the corresponding diaqua complex ($pK_3 = 7.35 \pm 0.05$ for *trans*-$[Cr(salen)(OH_2)_2]^+$ at 25 °C, $I = 0.3$ mol dm^{-3}).[21] This is amplified in the log k^{SO_2} *versus* pK_3 plot [log $k^{SO_2} = 0.58 \pm 0.09\, pK_3 + 3.9 \pm 0.7$ (corr. coeff. 0.89)] (see Fig. 10) for the formation of several M-OSO_2 species.[2(b,c,f),15,21,25,32,33,36–38] It is also important to note that there was no evidence for the formation of the *O*-sulfito complex in the range of pH 2–8. The activation parameters for the formation of the sulfito complex are also substantially



Scheme 1 Formation and acid catalysed aquation of *trans*-[Co(salen)(OH_2)(SO_3-*S*)]$^-$.

higher (see Table 1) which, in conjunction with the high value of the rate constant ($k_f > 10^{10}$ dm^3 mol^{-1} s^{-1} at 25 °C), can not be accommodated exclusively by a rate limiting process involving SO_2 addition to Co^{III}–OH followed by a much faster linkage isomerisation of the sulfite ligand in the present case. To account for these facts, we propose that the formation of the sulfito complex involves SO_2 addition to Co^{III}–OH which is concerted with Co^{III}–S bond formation as depicted in Scheme 1. The uncharged nature of the aqua-hydroxo complex, the labilising action of the coordinated salen and relatively greater nucleophilicity of S^{IV} centre (compared to O) play a dominant role in favouring the concertedness of this transformation. The high activation enthalpy and high positive activation entropy of the reaction (see Table 1) are explicable in terms of the energy demands and entropy gain in attaining a cyclic transition state. Noteworthy is the fact that the activation enthalpy for the formation of the sulfito complex is essentially the same as that for its acid catalysed aquation. This is in accord with a common transition state, as demanded by microscopic reversibility.

Another possibility worth considering may be the attainment of fast equilibrium between *trans*-[Co(salen)(OH_2)(OH)] and SO_2, generating the *O*-bonded sulfito complex, which undergoes ligand linkage isomerisation in a slow step (see Scheme 2).



Scheme 2 Ligand isomerisation.

Accordingly,

$$k_{obs} = (k_{iso}'Q + k_{iso}QK'_4/[H^+])f_4 f_1[S^{IV}]_T / \{1 + Qf_4 f_1[S^{IV}]_T(1 + K'_4/[H^+])\} \quad (11)$$

where f_1 and f_4 denote the fractions of $[S^{IV}]_T$ and $[\text{complex}]_T$ as SO_2 and hydroxo complex, respectively, as defined earlier, and K'_4 is the acid dissociation constant of the protonated *O*-sulfito complex. pK'_4 may be taken to be 4.0, considering the reported values for *trans*-[Co(AA)$_2$(OH_2)(OSO_2H)]$^{2+}$ $\{K'_4{}^{-1} = (1.5 \pm 0.4) \times 10^4$ and $(1.0 \pm 0.5) \times 10^4$ at 25 °C, $I = 0.3$ mol dm^{-3} for AA = 1,2-diaminoethane and 1,3-diaminopropane, respectively$\}$.[1] Then, a simple calculation shows that the values of $f_1 f_4[S^{IV}]_T(1.0 + K'_4/[H^+])$ at 25 °C for the pH and $[S^{IV}]_T$ used fall in the range 10^{-7} and 10^{-9}. Evidently, the value of Q must be $<10^5$ and $k_{iso}QK'_4/[H^+]$ much less than $k_{iso}'Q$ to account for the linearity of the plots of k_{obs} *versus* $[S^{IV}]_T$ (see Fig. 6b) and k_{obs} *versus* $f_1 f_4[S^{IV}]_T$ (see Fig. 7) respectively. A higher value of pK'_4 expected for *trans*-[Co(salen)(OH_2)(OSO_2H-*O*)], at least on electrostatic grounds, also yielded statistically insignificant values of Q and ($k_{iso}Q$) when data were fitted to eqn. 11. The stopped flow traces for kinetic runs also did not show base line shift (expected for the initial rapid equilibration of the *O*-sulfito complex if formed in detectable concentrations) followed by the exponential increase of absorbance with time. Thus eqn. 11 must reduce to $k_{obs} = k_{iso}'Qf_4 f_1[S^{IV}]_T$ and k^{SO_2} of eqn. 4 is identified as ($k_{iso}'Q$).

An optimised estimate of $Q = 10^5$ dm^3 mol^{-1} yields $k_{iso}' \approx 10^6$ s^{-1} at 25 °C (as $k_{iso}'Q = k^{SO_2}$). The very fast sulfite ligand linkage isomerisation of *trans*-[Co(salen)(OH_2)(OSO_2H-*O*)] has no parallel in the other (*O*-sulfito)(amine)cobalt(III) complexes, [ACo^{III}–OSO_2-*O*]$^+$ [A = N_5, or $N_4(OH_2)$; $k_{iso} \le 10^{-4}$ s^{-1} at 25 °C].[2b,d,15,35] In accord with this, the observed large positive $\Delta S^‡$ and $\Delta H^‡$ values (see Table 1) can then be reconciled with the contributions from both the rate and equilibrium steps ($\Delta X^‡ = \Delta X^‡(k_{iso}') + \delta X^0(Q)$, $X = H,S$). The dramatic rapidity of the linkage isomerisation for *trans*-[Co(salen)(H_2O)(OSO_2H-*O*)] can be understood in terms of: (i) a very weak electrostatic control of the low positive charge developed at the cobalt(III) centre in the transition state, (ii) involvement of

Table 6 Comparison of rate constants of reversible anation of *trans*-$[(OH_2)Co^{III}(A)(SO_3-S)]$

$$trans\text{-}[(OH_2)Co^{III}(A)(SO_3-S)] + X \underset{k_r}{\overset{k_f}{\rightleftharpoons}} trans\text{-}[XCo^{III}(A)(SO_3\text{-}S)]$$

	A =		
X	$(1,2\text{-diaminoethane})_2$	$(1,3\text{-diaminopropane})_2$	salen
k_f/dm^3 mol^{-1} s^{-1}			
N_3^-	$(2.35 \pm 0.22) \times 10^2$ [a]	$(4.94 \pm 0.21) \times 10^3$ [c]	5.1 ± 0.3 [d]
NCS^-	$(2.75 \pm 0.04) \times 10^2$ [a]	$(4.18 \pm 0.26) \times 10^3$ [c]	6.8 ± 0.4 [d]
SO_3^{2-}	$(2.2 \pm 1.1) \times 10^3$ [b]	$(2.76 \pm 0.13) \times 10^3$ [c]	3.3 ± 0.3 [d,e]
im	5.2 ± 0.3 [a]		17.6 ± 0.3 [d]
k_r/s^{-1}			
N_3^-	0.8 ± 0.4 [a]	18 ± 1 [c]	0.57 ± 0.03 [d]
NCS^-	0.11 ± 0.02 [a]	4.1 ± 2.8 [c]	0.63 ± 0.05 [d]
SO_3^{2-}	0.11 ± 0.01 [a]	1.3 ± 0.1 [c]	0.36 ± 0.04 [d]
im	0.02 ± 0.01 [a]	—	0.69 ± 0.04 [d]

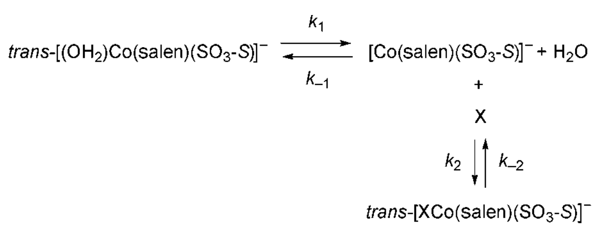
[a] 25 °C, $I = 1.0$ mol dm^{-3}, J. K. Yandell and L. H. Tomlins, *Aust. J. Chem.*, 1978, **31**, 561. [b] 25 °C, $I = 1.0$ mol dm^{-3}, calculated using the rate parameters reported by D. R. Stranks and J. K. Yandell, *Inorg. Chem.*, 1970, **9**, 751. [c] 25 °C, $I = 0.5$ mol dm^{-3}, ref. 1. [d] 25 °C, $I = 0.5$ mol dm^{-3}, this work. [e] Based on $k_f^{HSO_3^-} = k_f^{SO_3^{2-}}$.

intramolecular H^+-catalysis in the breakage of the Co–O bond (see Scheme 1), and (iii) the electron displacement properties of the salen moiety favouring an ion-pair like transition state.

Reactions of *trans*-$[Co(salen)(OH_2)_2]^+$ and *trans*-$[Co(salen)(OH_2)(SO_3\text{-}S)]^-$ with X^{n-}

A comparative listing of the rate constants of aqua ligand substitution reactions of some *trans*-$[(H_2O)Co^{III}A(SO_3\text{-}S)]$ complexes is presented in Table 6. For a given X (NCS^-, N_3^- and SO_3^{2-}), the salen complex reacts 600–1000 times slower than *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$ (tn = 1,3-diaminopropane) and at least 40–600 times slower than *trans*-$[Co(en)_2(OH_2)(SO_3\text{-}S)]^+$ (en = 1,2-diaminoethane). This can be at least partly reconciled with the electrostatic effect due to the difference in charges of the substrates and partly due to the rigidity of the coordinated salen. However, in the imidazole substitution reaction for which the electrostatic effect is likely to be insignificant, *trans*-$[Co(salen)(OH_2)(SO_3\text{-}S)]^-$ reacts 3.5 times faster than its $(en)_2$ analogue, thus reflecting an imidazole specific effect for the salen complex. A similar effect is also evident on comparing the k_r values of *trans*-$[Co^{III}(salen)X(SO_3\text{-}S)]$ with those of *trans*-$[Co^{III}(en)_2(X)(SO_3\text{-}S)]$. The tetradentate quasiaromatic salen skeleton in the salen complex compared to the saturated six-membered rings in *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$ has an attenuating effect on the *trans*-effect of *S*-bonded sulfite (see k_r values in Table 6). Further comparing the values of k_f for imidazole substitution of *trans*-$[Co(salen)(OH_2)_2]^+$ (**1**), *trans*-$[Co(salen)(OH_2)(OH)]$ (**2**), and *trans*-$[Co(salen)(OH_2)(SO_3\text{-}S)]^-$ (**3**) (k_f/dm^3 mol^{-1} s^{-1} = 2.87 ± 0.11 (**1**), 3.78 ± 0.08 (**2**) and 17.6 ± 0.3 (**3**) at 25 °C), it is evident that the *trans*-labilising effect of the S-bonded sulfite is only marginally stronger than that of OH^- or H_2O [SO_3^{2-} (*S*-bonded) > OH^- > OH_2]. This is again demonstrated by the relative anation rate constant of the aqua-sulfito- and aqua-hydroxo(salen)cobalt(III) complexes with SO_3^{2-} [k(aqua-SO_3)/k(aqua-OH) ≈ 50 at 25 °C].

The mechanism of anation of *trans*-$[Co(en)_2(OH_2)(SO_3\text{-}S)]^+$ has been suggested to be dissociative (D).[39] Insensitivity of the values of k_f and k_r to X is taken to be indicative of the operation of the D mechanism for the formation/dissociation of *trans*-$[Co(salen)X(SO_3\text{-}S)]^-$ for which (making a steady state approximation for the five coordinate intermediate) k_f and k_r are given by eqn. 12 and 13, respectively.



$$k_f = k_1k_2[X]/(k_{-1}[OH_2] + k_2[X]) \quad (12)$$

$$k_r = k_{-2}k_{-1}[OH_2]/(k_{-1}[OH_2] + k_2[X]) \quad (13)$$

The observed linearity of the k_{obs} *versus* [X] plot can only arise if $k_2[X] \ll k_{-1}[OH_2]$ is valid and, accordingly, k_f and k_r are given by $k_2k_1/(k_{-1}[OH_2])$ and k_{-2}, respectively. k_f does not display strong dependence on the entering ligand for the diaqua-, aqua-hydroxo-, and aqua-SO_3-*S*-(salen)cobalt(III) complexes. This strongly supports that the five-coordinate intermediate $[Co(salen)(SO_3\text{-}S)]^-$ has little selectivity/discrimination for the entering group. Also notable is the fact that the values of k_r ($=k_{-2}$) for N_3^-, NCS^- and im, for which Co–N bond breaking is envisaged, are comparable with each other. A lower value of k_r for SO_3^{2-} is consistent with Co–S bonding in the disulfito complex, *trans*-$[Co(salen)(SO_3\text{-}S)_2]^{3-}$.

Conclusion

We have shown that the reaction of *trans*-$[Co(salen)(OH_2)_2]^+$ with S^{IV} in the pH range 2–8.4 generated *trans*-$[Co(salen)(OH_2)(SO_3\text{-}S)]^-$. The results could be interpreted in terms of a mechanism involving *trans*-$[Co(salen)(OH_2)(OH)]$ and SO_2 in which Co–S formation is concerted with Co–O bond breaking. An alternative mechanism, equally acceptable on kinetic grounds, is the fast and reversible addition of SO_2 to *trans*-$[Co(salen)(OH_2)OH]$, generating the *O*-sulfito complex with a very small equilibrium constant for its formation which did not allow its detection; this is then followed by linkage isomerisation to its *S*-bonded analogue ($k_{iso} \approx 10^6$ s^{-1} at 25 °C for *trans*-$[Co(salen)(OSO_2H\text{-}O)]$). *trans*-$[Co(salen)(OH_2)(SO_3\text{-}S)]^-$ undergoes H^+-catalysed aquation, facile photoreduction in mild acidic media and reversible aqua ligand substitution with N_3^-, NCS^-, imidazole and SO_3^{2-}, essentially *via* a dissociative mechanism displaying a small *trans*-activation from the *S*-bonded sulfite.

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