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Thermal and photochemical reactions of bis(diamine)(sulfito)-cobalt(III) complexes: effect of chelate-ring size

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The kinetics of formation of *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^+$ (tn = 1,3-diaminopropane), its acid-catalysed aquation to the parent diaqua complex, anation of *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$ by N_3^-, NCS^-, SO_3^{2-}–HSO_3^-, anation of *trans*-$[Co(tn)_2(OH)(SO_3\text{-}S)]$ by SO_3^{2-} and acid-catalysed aquation of *trans*-$[Co(tn)_2(SO_3\text{-}S)_2]^-$ to the corresponding (aqua)(sulfito-*S*) complex were investigated and the results compared with analogous data for the corresponding 1,2-diaminoethane (en) complexes. Expanding the chelate-ring size from five to six had virtually no effect on the rate of formation of the sulfito-*O* complex, but retarded its acid-catalysed aquation. The latter effect was attributed to a p*K* perturbation; intramolecular hydrogen bonding between the co-ordinated H_2O and sulfite in *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^+$ hindered the protonation pre-equilibrium of the sulfito-*O* complex involved in the acid-catalysed aquation. This is further supported by the fact that there was no ring-size effect on the acid-catalysed aquation of *trans*-$[Co(L{-}L)_2(OH_2)(OSO_2)]^+$ (L–L = tn or en). The strong labilising action due to chelate-ring expansion is remarkably attenuated by the *trans* effect of S-bonded sulfite as observed in the anation of *trans*-$[Co(L{-}L)_2(OH_2/OH)(SO_3\text{-}S)]^{+/0}$. However, *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$ was found to be prone to intramolecular electron transfer between Co^{III} and S^{IV} under thermal conditions unlike its en analogue, further reflecting the ring-size effect. Flash photolysis of *trans*-$[Co(L{-}L)_2(OH_2)(SO_3\text{-}S)]^+$ (L–L = en or tn) generated the transient *trans*-$[Co(L{-}L)_2(OH_2)(OSO_2)]^+$. The photochemical ligand isomerisation of both complexes ($Co^{III}{-}SO_3^+ \longrightarrow Co^{III}{-}OSO_2^+$) also occurred at comparable rates [$k_{iso} = (4.1 \pm 0.8) \times 10^4$ and $(3.2 \pm 1.3) \times 10^4\ s^{-1}$ at 25 °C for the en and tn complexes respectively]. Steady-state photolysis at 254 nm indicated that *trans*-$[Co(en)_2(OH_2)(SO_3\text{-}S)]^+$ underwent photoaquation and photoreduction. Strikingly photoreduction could not be detected for this complex at pH > 8.

The O- and S-bonded sulfito complexes of cobalt(III) differ remarkably in their reactivities.[1–11] While the O-bonded species, $Co^{III}{-}OSO_2^+$, is formed by the addition of SO_2 to the $Co^{III}{-}OH$ bond,[1–4] the corresponding S-bonded isomers result either by isomerisation of the former[4–6] and/or direct replacement of co-ordinated H_2O (OH^-) in $Co^{III}{-}OH_2(OH)$ species by (-S-)-SO_3^{2-}.[8–10] The instability of the $Co^{III}{-}OSO_2^+$ species to redox, isomerisation and facile acid-catalysed SO_2 elimination[2–4,10,12] is an impediment to the isolation of such species in the solid state for full characterisation. In fact no such species have been characterised in the solid state as yet. On the other hand the S-bonded sulfito complexes which are relatively more inert to redox decomposition have been well characterised in the solid state. Both the kinetic *trans* effect[9,13,15] and the structural *trans* effect[15–17] which are believed to originate from electronic factors are significant features of S-bonded sulfito complexes. However, in comparision to the *trans*-labilising effect of sulfite in S-bonded sulfitocobalt(III) species, the corresponding effect in O-sulfito complexes is not well documented. In a preceding paper from our laboratory[12] it was evident that the possibility of the *cis*-labilising effect of O-bonded sulfite in *cis*-$[Co(en)_2B(OSO_2\text{-}O)]^+$ (en = 1,2-diaminoethane, B = amine ligand) cannot be ruled out. Now the questions to address are as follows: (*i*) how does the cobalt(III) centre respond to the kinetic *trans* effect of S-bonded sulfite with regard to ligand substitution, and redox (by S-bonded sulfite) when the chelate ring is expanded?; (*ii*) what is the effect of the chelate-ring size on the reversible formation of $Co^{III}{-}OSO_2^+$ and its isomerisation to $Co^{III}{-}SO_3^+$?

In order to elucidate these aspects we have chosen 1,3-diaminopropane (tn) and 1,2-diaminoethane as the chelating ligands and investigated the reactions of *cis/trans*-$[Co(diamine)_2(OH_2)(OSO_2\text{-}O)/(SO_3\text{-}S)]^+$ and trans-$[Co(tn)_2(SO_3\text{-}S)_2]^-$ as a sequel to our earlier work.

Experimental

Preparation of complexes

The complex *cis*-$[Co(tn)_2(CO_3)]ClO_4$ was prepared as reported;[18] *cis*-$[Co(tn)_2(OH_2)_2]^{3+}$ was generated *in situ* by acidifying the solution of the carbonato complex, dissolved CO_2 being expelled by bubbling N_2. The solution of the aqua complex ($[complex]_T = 0.05$ mol dm^{-3}, pH 2) was stored at 10 °C in a refrigerator {λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 508 (56) and 358 (69); lit., 510 (62), 360 (78),[19] 505 (55.2), 362 (67.7)[18] for *cis*-$[Co(tn)_2(OH_2)_2]^{3+}$}.

The complex *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]ClO_4$ was prepared from *cis*-$[Co(tn)_2(CO_3)]ClO_4$ (0.01 mol) and $NaHSO_3$ (0.011 mol). The aqueous solution of the mixture (50 cm^3) was set aside overnight at room temperature (30 °C). On adding $NaClO_4$ a yellowish brown solid crystallised. It was filtered on a glass sintered funnel, washed with ethanol and air dried. The sample was recrystallised from warm water (50 °C) by adding a small amount of $NaClO_4$, filtered off, washed with ethanol, diethyl ether and stored over fused calcium chloride in a desiccator taking care to avoid exposure to light (Found: C, 16.2; H, 5.4; Co, 13.0; N, 12.2. Calc. C, 16.3; H, 5.9; Co, 13.4; N, 12.7%) for $[Co(tn)_2(OH_2)(SO_3)]ClO_4{\cdot}2H_2O$ [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 475 (180), 280 (11 000) and 225 (10 800)]. IR spectrum (KBr): 3450, 3230, 3280 (O–H and N–H stretching); 1635, 1605, 1590 cm^{-1} (N–H and O–H bending) due to the presence of H_2O and the primary amino group of tn;[20] 1050, 1070, 1100, 1115, 1130 and 1150 cm^{-1} (co-ordinated H_2O), 1100–800 (sulfite),[15,20,21] 1100–1050 (free ClO_4^-);[20] strong bands at 960, 900 and 645 cm^{-1} {*cf.* *trans*-$[Co(en)_2(OH_2)(SO_3\text{-}S)]^+$[21] and other S-bonded sulfitocobalt(III) complexes[15,21]}. Na[*trans*-$Co(tn)_2(SO_3\text{-}S)_2]{\cdot}3H_2O$ was prepared from *trans*-$[Co(tn)_2Cl_2]Cl$ and Na_2SO_3 by warming (50 °C) an aqueous solution (50 cm^3) of the dichloro complex (0.01 mol) with Na_2SO_3 (0.025 mol).

The complex precipitated as a yellowish brown solid on cooling. It was recrystallised from water on adding a small amount of Na_2SO_3 (Found: C, 16.0; H, 5.7; Co, 13.1; N, 12.5. Calc. C, 16.2; H, 5.85; Co, 13.3; N, 12.6%). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 465 (250); 325 (5600) and 280 (12 700).

trans-$[Co(en)_2(OH_2)(SO_3\text{-}S)]ClO_4\cdot H_2O$ was prepared as described by Baldwin[22] and its purity checked by cobalt analysis and spectral parameters [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 466 (160), 274 (1.6×10^4); lit., 466 (159),[13] 465 (162)[22]].

Materials and methods

Analar grade reagents were used for kinetic study; $NaClO_4$ was used to adjust the ionic strength. The sodium content of a stock solution of $NaClO_4$ was estimated by an ion exchange/alkalimetric procedure using Dowex 50 W-X8 resin in the H^+ form. Sodium μ-oxo-tetraoxodisulfate, $Na_2S_2O_5$, was used as the source of S^{IV}. This salt dissociates rapidly in aqueous medium to produce an equilibrium mixture of SO_2, HSO_3^- and SO_3^{2-}. Sodium sulfite was used in anation studies in alkaline media.

The UV/VIS spectra were recorded on a JASCO 7800 spectrophotometer. Absorbance measurements were also made using a Beckman DU spectrophotometer. The IR spectra were recorded on a Perkin-Elmer 177 spectrophotometer. The pH measurements were done with an ELICO model LI 120 digital pH meter equipped with a combined glass-Ag–AgCl, Cl^- (2 mol dm^{-3} NaCl) electrode CL 51. The meter was standardised with NBS buffers of pH 4.01, 6.86 and 9.2.

The analysis (C, H, N) and IR spectral measurements were done at the Indian Association for the Cultivation of Science, Calcutta and Central Drug Research Institute, Lucknow, India.

Kinetics

The formation of *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^+$, anation of *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$ and acid-catalysed aquation of *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^+$ and *trans*-$[Co(tn)_2(SO_3\text{-}S)_2]^-$ were studied by the stopped-flow technique using a HITECH SF 51 stopped-flow spectrophotometer interfaced with an APPLE IIGS personal computer. The flow module, the drive syringes, and the observation chamber were thermostatted to the desired temperature by circulating water from a C-85D thermostat through a FC200 cooler (HITECH, UK). All rate measurements were carried out under pseudo-first-order conditions and absorbance *vs.* time curves (displayed as voltage output as a function of time) were single exponentials characteristic of first-order kinetics. The formation of the sulfito-*O* complex was studied in HSO_3^-–SO_3^{2-} buffer. The O-bonded sulfito complex *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^+$ was generated *in situ* by mixing the diaqua complex and sulfite buffer together and adjusting the pH to 6.2. It was stored at 10 °C in an ice–water bath to minimise decomposition before transferring to one of the drive syringes of the stopped flow equipment to study its acid-catalysed decomposition. Further details of the experimental procedures have been given in our earlier papers.[2,12] At least seven replicate measurements were made for each run to calculate k_{obs} and $\sigma(k_{obs})$. All other calculations were performed on an IBM compatible 486 personal computer using weighted least-squares programs. The dependent variable was weighted inversely as its variance ($w = 1/\sigma^2$).

Steady-state photolysis

The continuous photolysis experiments were carried out at 254 nm, with a T/M5/594 110 W low-pressure mercury-vapour lamp from Thermal Syndicate (UK). All solutions were flushed with purified N_2 prior to being irradiated. Solutions (3.5 cm^3) of *trans*-$[Co(L\text{–}L)_2(OH_2)(SO_3\text{-}S)]^+$ (L–L = tn or en) were irradiated in a rectangular long-necked quartz cell of 1.0 cm path length placed in an aluminium block (10 × 10 × 10 cm) with a rectangular slot to allow passage of the incident beam. The irradiation chamber was thermostatted to 35.0 ± 0.2 °C by circulating water from a constant-temperature water-bath. An optical bench fitted with sliding stands for mounting two quartz lenses (focal length 6.5 cm, diameter 4.0 cm) was used to concentrate radiations on the window of the thermostatted cell holder containing the reaction cell. The position of the lamp also mounted on the bench was adjusted so that the lamp axis was perpendicular to the axis of the lenses and parallel to the axis of the cell. The lamp output was monitored before and after each experiment by ferrioxalate actinometry.[23,24] The yield of Fe^{2+} was estimated spectrophotometrically as tris(1,10-phenanthroline)iron(II) ($\varepsilon = 1.11 \times 10^4$ dm^3 mol^{-1} cm^{-1} at 510 nm). The quantum yield[24] of Fe^{2+} was 1.25 and the intensity of radiation was 0.275×10^{16} quanta s^{-1}.

The concentrations of the sulfito-*S* complexes were 5.0×10^{-5} mol dm^{-3} for spectral kinetic studies and 5.0×10^{-4} mol dm^{-3} for cobalt(II) yield measurements. The pH in the ranges 1–3, 3.72–5.72 and 7.01–9.1 was controlled by $HClO_4$, $MeCO_2^-$–$MeCO_2H$ and tris(hydroxymethyl)methylamine (tris) buffer respectively. The cobalt(II) yield was monitored spectrophotometrically as $[Co(NCS)_4]^{2-}$ ($\varepsilon = 2.0 \times 10^3$ dm^3 mol^{-1} cm^{-1} at 625 nm) by Kitson's method.[25] The percentage transmission of 254 nm radiation by the reaction mixture ($[\text{complex}]_T = 5.0 \times 10^{-4}$ mol dm^{-3}, $\varepsilon = 6.73 \times 10^3$ dm^3 mol^{-1} cm^{-1} at 254 nm) was virtually zero. The quantum yield of Co^{2+} [$\varphi(Co^{2+})$] was calculated from the cobalt(II) yield considering that incident radiation was absorbed completely by the reaction mixture. The UV spectra of the reaction mixture irradiated for a given length of time were recorded to get kinetic information (see Discussion).

Flash photolysis

The flash photolysis of *trans*-$[Co(L\text{–}L)_2(OH_2)(SO_3\text{-}S)]^+$ (L–L = en or tn) was performed in an optical quartz cell of 10 cm path length. Solutions were deaerated by N_2 prior to irradiation. For uniform illumination two air-filled quartz lamps were placed on the two sides of the cell. The lamps were fired with 8 μF storage condensers charged at 8–10 kV. A steady light from a 150 W xenon-arc lamp (XBO 150 W Osram) was used as the analysing beam. The collimated light beam after passing through the photolysed solution and a grating monochromator (Monospek 600, M/s Rank Hilger, UK) was made to fall on an IP 28 photomultiplier. The output of the photomultiplier after amplification in a cathode follower circuit was recorded in a fast rise Gould digital oscilloscope model 4050 (UK). The calibration factor for the gain of the cathode follower coupled with the vertical response of the oscilloscope was determined by switching into the cathode follower circuit a calibrated voltage pulse from a pulse generator. Condensers were initially charged by a 0–10 000 V d.c. power supply. For firing the lamps an extended trigger-mode circuit was used. A pulse from a 16 μF, 300 V condenser, operated with a pulse switch was amplified with the help of a high-tension automobile coil and fed directly to the trigger wire of the flash lamp. A pulse from the same circuit was also used for triggering the oscilloscope simultaneously. The flash lamps were connected in series for synchronous firing. The steady photocurrent generated from the analysing light beam was stored as a voltage drop across a resistance on the storage oscilloscope and then transferred to graph paper with the help of an Epson H180 printer. In the present set-up the flash energy used for excitation was 250 J (1/e time = 25 μs).

The transient had an absorption maximum around 330 nm at which the parent compound also absorbed strongly. Hence the monitoring wavelength was chosen as 390 nm at which the transient had a substantially large absorbance compared to that of the parent compound and the final products. Typical growth and decay curves of the transient are shown in Figs. 1 and 2. The exponentials were analysed by the first-order kinetics

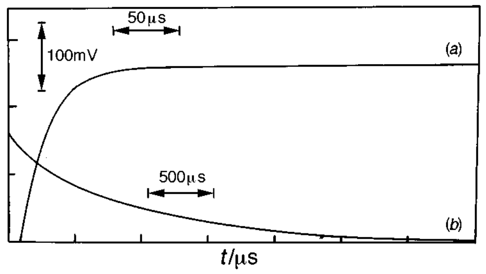


Fig. 1 (*a*) Formation and (*b*) decay of the transient in the flash photolysis of *trans*-$[Co(en)_2(OH_2)(SO_3\text{-}S)]^+$ at 25 °C and pH 3.7

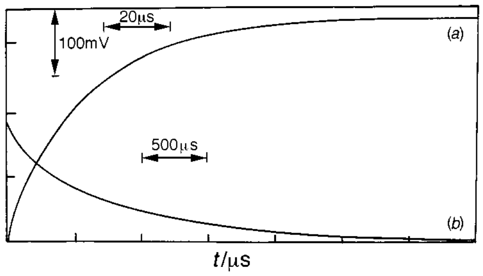


Fig. 2 (*a*) Formation and (*b*) decay of the transient in the flash photolysis of *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$ at 25 °C and pH 3.7

relationship $A_t - A_\infty = (A_0 - A_\infty)\exp(-k_{obs}t)$ to get the pseudo-first-order rate constants.

p*K* Measurements

A solution of *cis*-$[Co(tn)_2(OH_2)_2]^{3+}$ ($[complex]_T = 2.0 \times 10^{-3}$, $[HClO_4] = 2.0 \times 10^{-4}$, $I = 1.0$ mol dm^{-3}) was titrated potentiometrically with 0.100 mol dm^{-3} NaOH. The pH data were converted into $p[H^+]$ by using a calibration curve as described by Martell and Motekaitis.[26] At 25.0 °C, $I = 1.0$ mol dm^{-3} we obtained 4.53 ± 0.02 and 9.2 ± 0.02 as the values of the first and second p*K* of the diaqua complex respectively. Fowless and Stranks[19] reported p*K* values for $[Co(tn)_2(OH_2)_2]^{3+}$ of 4.75 and 7.45 ($I = 1.0$ mol dm^{-3}, 22 °C). However, they suggested that these data represent only average values due to the rapid (seconds) *trans-cis* isomerisation of the diaqua and aquahydroxo cations. They estimated $pK_1 = 6.0$ and $pK_2 = 8.4$ for *cis*-$[Co(tn)_2(OH_2)_2]^{3+}$ ($I = 1.0$ mol dm^{-3}, 25 °C) by analogy with those for the *cis*-$[Co(en)_2(OH_2)_2]^{3+}$.

The *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$ was potentiometrically titrated ($[complex] = 5.0 \times 10^{-3}$, $I = 1.0$ mol dm^{-3}) with 0.17 mol dm^{-3} NaOH. We obtained 9.67 ± 0.02 (25.0 °C) as the p*K* of the co-ordinated aqua ligand which may be compared with that of *trans*-$[Co(en)_2(OH_2)(SO_3\text{-}S)]^+$ ($pK = 9.45$, 1.0 mol dm^{-3}, 25.0 °C).[9]

Results

Formation of *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^+$

Addition of *cis*-$[Co(tn)_2(OH_2)_2]^{3+}$ to HSO_3^-–SO_3^{2-} buffer (pH 6.2) resulted in an instantaneous colour change with an intense band around 330 nm and a broad and weak band at 500 nm [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 335 (1100) and 510 (105)]. The reaction mixture on acidification without much delay (within 60 s) generated the spectrum of the diaqua complex. This is characteristic of the formation of the O-bonded sulfito complex.[1–4,12] The formation of the sulfito-*O* complex, *cis*-$[Co(tn)_2(OH_2)(OSO_2)]^+$, was studied with $[\text{aqua complex}]_T = (2.0\text{–}4.0) \times 10^{-4}$ and $0.01 \leqslant [S^{IV}]_T/\text{mol dm}^{-3} \leqslant 0.06$ in sulfite buffer ($5.3 \leqslant pH \leqslant 6.50$) at $10.0 \leqslant T/°C \leqslant 25.0$ and $I = 1.0$ mol dm^{-3}. The rate constants are collected in Table 1. Previous studies have shown that the rapid formation of the sulfito-*O* complex is due to the addition of SO_2 to the Co^{III}–OH bond.[1–4,12] Plots of k_{obs} *versus* $[S^{IV}]_T$ at constant pH (5.85 ± 0.05, 6.2 ± 0.1, and 6.2 ± 0.1 at 10, 20 and 25 °C respectively) were non-linear with vanishing intercept on the k_{obs} axis (see Fig. 3) indicating that S^{IV} in excess retards the reaction and the reverse reaction (*i.e.* aquation of the sulfito-*O* complex) is not significant under the experimental conditions. This trend is in keeping with the formation of unreactive ion pair of the diaqua complex with SO_3^{2-}.[4] Accordingly the observed rate constant is given by equation (1) where k_1, k_{-1} denote the rate constants

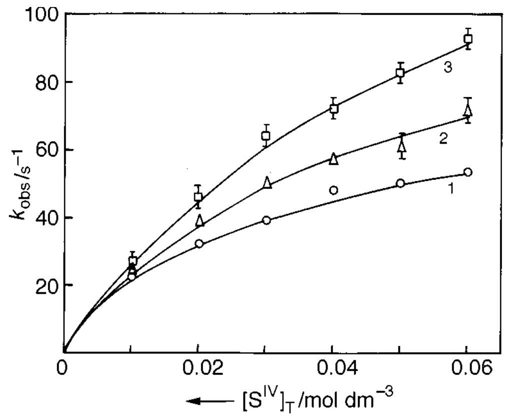


Fig. 3 Plots of k_{obs}/s^{-1} *versus* $[S^{IV}]_T$ for the formation of *cis*-$[Co(tn)_2(OH_2)(OSO_2)]^+$ at 10 (pH 5.85 ± 0.05) (1), 20 °C (pH 6.2 ± 0.10) (2) and 25.0 °C (pH 6.2 ± 0.1) (3)

$$k_{obs} = k_1 f_1[S^{IV}]_T/\{1 + K_3^{-1}[H^+] + K_3^{-1}Q[H^+]f_3[S^{IV}]_T\} + k_{-1}[H^+] \quad (1)$$

of formation and H^+-catalysed aquation of *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^+$, f_1, f_3 are the fractions of $[S^{IV}]_T$ as SO_2 and SO_3^{2-}, K_3 and Q are the acid dissociation constant of *cis*-$[Co(tn)_2(OH_2)_2]^{2+}$ and association constant of its ion pair with SO_3^{2-} respectively [see equations (2)–(4)]. Considering the acid

$$cis\text{-}[Co(tn)_2(OH_2)(OH)]^{2+} + SO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis\text{-}[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^+ + H^+ \quad (2)$$

$$cis\text{-}[Co(tn)_2(OH_2)_2]^{3+} \overset{K_3}{\rightleftharpoons} cis\text{-}[Co(tn)_2(OH_2)(OH)]^{2+} + H^+ \quad (3)$$

$$cis\text{-}[Co(tn)_2(OH_2)_2]^{3+} + SO_3^{2-} \overset{Q}{\rightleftharpoons} \{cis\text{-}[Co(tn)_2(OH_2)_2]^{3+},SO_3^{2-}\} \quad (4)$$

dissociation equilibria (5) and (6) of S^{IV}, the fractions f_1 and f_3 are given by equations (7) and (8) where K_1, K_2 are the acid

$$SO_2 + H_2O \overset{K_1}{\rightleftharpoons} HSO_3^- + H^+ \quad (5)$$

$$HSO_3^- \overset{K_2}{\rightleftharpoons} SO_3^{2-} + H^+ \quad (6)$$

$$f_1 = [H^+]^2/([H^+]^2 + K_1[H^+] + K_1K_2) \quad (7)$$

$$f_3 = K_1K_2/([H^+]^2 + K_1[H^+] + K_1K_2) \quad (8)$$

dissociation constants of SO_2 and HSO_3^- respectively. Preliminary calculations showed that dimerisation of HSO_3^- ($2HSO_3^- \rightleftharpoons S_2O_7^{2-} + H_2O$; $Q_D = 0.088$ dm^3 mol^{-1} at $I = 1.0$ mol dm^{-3}, 25 °C)[27] was not significant under the experimental conditions of pH and $[S^{IV}]_T$.

The term $k_{-1}[H^+]$ was neglected and the rate constants at essentially constant pH and varying $[S^{IV}]_T$ (see Table 1) were used to calculate Q from the plots of k_{obs}^{-1} *versus* $[S^{IV}]_T^{-1}$. Using $pK_3 = 6.0$ and the known values of pK_1, pK_2 (see footnote

Table 1 Rate constants for the formation of *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^{+}$ [a]

T/°C	$[S^{IV}]_T$/mol dm^{-3}	pH	k_{obs}/s^{-1}	$k_{calc}{}^{b}$/s^{-1}	$[S^{IV}]_T$/mol dm^{-3}	pH	k_{obs}/s^{-1}	$k_{calc}{}^{b}$/s^{-1}
10.0 ± 0.1	0.010	5.74	23 ± 1	23	0.04	6.51	11 ± 1	10
	0.020	5.86	32 ± 1	32	0.04	6.27	19 ± 1	19
	0.030	5.85	39 ± 2	41	0.04	6.08	34 ± 2	30
	0.040	5.81	48 ± 2	52	0.04	5.90	45 ± 2	44
	0.050	5.76	51 ± 5	64	0.04	5.72	72 ± 5	62
	0.060	5.90	54 ± 2	52	0.04	5.61	82 ± 3	76
					0.04	5.44	97 ± 4	98
20.0 ± 0.1	0.010	6.13	22 ± 1	23	0.04	6.57	21 ± 1	19
	0.020	6.16	39 ± 1	38	0.04	6.42	26 ± 1	30
	0.030	6.19	51 ± 1	47	0.04	6.30	41 ± 1	43
	0.040	6.17	58 ± 2	60	0.04	6.28	46 ± 1	45
	0.050	6.27	62 ± 3	54	0.04	6.19	57 ± 2	57
	0.060	6.19	72 ± 4	73	0.04	5.95	101 ± 3	102
	0.040	6.70	12 ± 1	12	0.04	5.87	118 ± 7	121
25.0 ± 0.1	0.010	6.01	26 ± 1	31	0.04	6.51	25 ± 1	26
	0.020	6.10	46 ± 2	46	0.04	6.41	36 ± 1	35
	0.030	6.10	64 ± 3	62	0.04	6.31	49 ± 1	46
	0.040	6.10	72 ± 1	75	0.04	6.22	58 ± 1	57
	0.050	6.10	83 ± 3	85	0.04	6.12	75 ± 2	72
	0.060	6.18	93 ± 3	79	0.04	5.85	128 ± 7	124
	0.040	6.75	16 ± 1	13	0.04	5.72	183 ± 17	155

10^{-7} k_1/dm^3 mol^{-1} s^{-1}: 9.3 ± 2.3 (10), 11.6 ± 1.7 (20), 13.7 ± 3.4 (25 °C) [c]
10^{-5} $K_3{}^{-1}$/dm^3 mol^{-1}: 8.1 ± 2.7 (10), 5.4 ± 1.6 (20); 10.6 ± 4.1 (25 °C) [c]

[a] $\lambda = 330$ nm, $[Co(tn)_2(OH_2)_2{}^{3+}]_T = (2\text{–}6) \times 10^{-4}$, $I = 1.0$ mol dm^{-3}. [b] Calculated [see equation (1)] using best-fit values of k_1, $K_3{}^{-1}$ and Q; values of Q/dm^3 mol^{-1} are 185, 118 and 87 at 10, 20 and 25 °C respectively; values of pK_1 are 1.74 (10), 1.85 (20) and 1.92 (25 °C); pK_2 is 6.3 (10–25 °C) (refs. 4 and 10). [c] Values of $\Sigma[(k_{calc} - k_{obs})/\sigma(k_{obs})]^2$: 29 (10), 54 (20) and 96 (25 °C).

Table 2 Rate constants for the acid-catalysed aquation of *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^{+}$

$k_{obs}{}^{a}$/s^{-1} (pH)			
10.0	15.0	20.0	25.0 °C
22 ± 1 (2.85)	24 ± 1 (3.05)	42 ± 1 (3.38)	35 ± 1 (3.75)
29 ± 1 (2.83)	29 ± 1 (3.02)	65 ± 2 (3.03)	39 ± 1 (3.70)
35 ± 1 (2.67)	39 ± 1 (2.89)	60 ± 1 (3.00)	42 ± 2 (3.66)
38 ± 2 (2.63)	40 ± 1 (2.85)	67 ± 2 (2.99)	63 ± 1 (3.33)
55 ± 2 (2.59)	44 ± 1 (2.83)	75 ± 2 (2.93)	87 ± 2 (3.05)
58 ± 1 (2.50)	49 ± 1 (2.79)	99 ± 2 (2.82)	105 ± 3 (2.96)
62 ± 1 (2.49)	62 ± 2 (2.75)	103 ± 3 (2.75)	111 ± 5 (2.92)
76 ± 1 (2.40)	71 ± 3 (2.65)	—	152 ± 4 (2.73)
85 ± 3 (2.35)	85 ± 2 (2.59)	—	—

10^{-4} $k_{-1}{}^{b}$/dm^3 mol^{-1} s^{-1} 1.8 ± 0.2 (10), 3.1 ± 0.2 (15), 6.9 ± 1.4 (20), 13.6 ± 5.1 (25 °C)
$\Delta H^{\ddagger}$/kJ mol^{-1} 86 ± 10, $\Delta S^{\ddagger}$/J K^{-1} mol^{-1} 141 ± 36

[a] $\lambda = 330$ nm, $[\text{aqua complex}]_T = 6.0 \times 10^{-4}$, $[S^{IV}]_T = 3.0 \times 10^{-3}$, $I = 1.0$ mol dm^{-3}; values of pH in parentheses. [b] Based on the values of 10^{-7} k_1/dm^3 mol^{-1} s^{-1}, 10^{-5} $K_3{}^{-1}$/dm^3 mol^{-1} and Q/dm^3 mol^{-1}: 9.3, 8.1, 182 (10); 10.0, 6.0, 150 (15); 11.6, 5.4, 110 (20); 13.7, 10.6, 86 (25 °C) respectively; values of pK_1 (1.79 at 15 °C) and pK_2 are given in footnote *b* of Table 1.

b of Table 1) we obtained the Q values (2.3 ± 1.2) × 10^2, (1.2 ± 0.3) × 10^2 and (0.87 ± 0.17) × 10^2 dm^3 mol^{-1} at 10, 20 and 25 °C respectively from the intercepts and gradients of such plots. All rate constants at a given temperature were then fitted by equation (1) (with the $k_{-1}[H^+]$ term neglected) by varying k_1, $K_3{}^{-1}$ and $K_3{}^{-1}Q$ and minimising $\Sigma[(k_{calc} - k_{obs})/\sigma(k_{obs})]^2$. The calculated values of k_1 and $K_3{}^{-1}$ and Q (see footnote *b* of Table 1) are collected in Table 1.

Acid-catalysed aquation of *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^{+}$

The acid-catalysed aquation of *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^{+}$ was studied in the range $2.35 \leqslant \text{pH} \leqslant 3.75$ ($ClCH_2CO_2{}^{-}$–$ClCH_2CO_2H$ buffer) at $10.0 \leqslant T/°C \leqslant 25.0$ and the rate constants are collected in Table 2. The rate constant (k_{obs}) was insensitive to variation of the concentrations of the buffer components when the pH was held fixed. The reaction was reversible. The values of k_1, $K_3{}^{-1}$ and Q being known from the formation study (see footnote *b* of Table 2), k_{-1} was calculated from the k_{obs} data using equation (1). Values of k_{-1} are also collected in Table 2.

Anation of *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^{+}$

Anation of the *trans*-aqua(sulfito-*S*) complex by NCS^- and $N_3{}^-$ was studied in absence of any buffer and in $N_3{}^-$–HN_3 buffer respectively. The rate constants (k_{obs}) collected in Table 3 satisfactorily obeyed equation (9) in the range of $[L^-]_T$ used,

$$k_{obs} = k_f[L^-] + k_r \qquad (9)$$

where $[L^-] = [NCS^-]_T$ or $[N_3{}^-]_T/(1.0 + K_d[H^+]^{-1})$ (K_d [28] is the acid dissociation constant of N_3H, see footnote *d* of Table 3) and k_f and k_r denote the anation rate constant of the aqua complex and dissociation rate constant of the anated product respectively, see equation (10). The sulfite substitution reaction

$$trans\text{-}[Co(tn)_2(OH_2)(SO_3\text{-}S)]^{+} + L^{-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} trans\text{-}[Co(tn)_2L(SO_3\text{-}S)] + H_2O \qquad (10)$$

at $[OH^-]_T = 0.02$ mol dm^{-3} ($I = 1.0$ mol dm^{-3}) also obeyed (see Table 4) equation (9) in the range $0.01 \leqslant [SO_3{}^{2-}]_T$/mol dm^{-3} $\leqslant 0.20$. Under this condition the reaction is represented as in equation (11). The anation by S^{IV} was also studied at

$$trans\text{-}[Co(tn)_2(OH)(SO_3\text{-}S)] + SO_3{}^{2-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} trans\text{-}[Co(tn)_2(SO_3\text{-}S)_2]^{-} + OH^{-} \qquad (11)$$

$0.01 \leqslant [S^{IV}]_T$/mol dm^{-3} $\leqslant 0.1$ and pH 6.2 ± 0.1. The rate constant, k_{obs} (see Table 5) increased with $[S^{IV}]_T$ tending to a saturation limit in accord with equation (12). This is consistent with

$$k_{obs} = a[S^{IV}]_T/(1.0 + b[S^{IV}]_T) \qquad (12)$$

an ion-pair dissociative interchange mechanism as shown in Scheme 1 for which *a* and *b* of equation (12) are given by expressions (13) and (14) where $1 - f_3$ is the fraction of S^{IV} as

$$\begin{array}{lll}
\textit{trans}\text{-}[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+ + SO_3^{2-} & \xrightleftharpoons{Q_{ip}^{SO_3}} & \{\textit{trans}\text{-}[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+,SO_3^{2-}\} \\
\qquad\qquad\qquad\qquad\qquad + & & \qquad\text{Ion pair 1} \\
\qquad\qquad\qquad\qquad\qquad H^+ & & \\
\qquad\qquad\qquad\qquad\qquad \Updownarrow & & \\
\textit{trans}\text{-}[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+ + HSO_3^- & \xrightleftharpoons{Q_{ip}^{HSO_3}} & \{\textit{trans}\text{-}[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+,HSO_3^-\} \\
 & & \qquad\text{Ion pair 2}
\end{array}$$

$$\begin{array}{ll}
\text{Ion pair 1} \xrightarrow{k_{1ip}} & \\
 & \textit{trans}\text{-}[Co(tn)_2(SO_3\text{-}S)_2]^- \\
\text{Ion pair 2} \xrightarrow[-H^+]{k_{2ip}} &
\end{array}$$

Scheme 1

$$\begin{array}{l}
\textit{trans}\text{-}[Co(tn)_2(SO_3\text{-}S)_2]^- \xrightarrow[H_2O]{k_0} \textit{trans}\text{-}[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+ + SO_3^{2-} \\
\qquad + \\
\qquad H^+ \\
\quad H_2O \downarrow k_H \\
\textit{trans}\text{-}[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+ \\
\qquad + \\
\qquad HSO_3^-
\end{array}$$

Scheme 2

$$\begin{array}{l}
\textit{trans}\text{-}[Co(tn)_2(OH_2)(SO_3)]^+ \xrightarrow{k_{red}} [Co(tn)_2(OH_2)_2]^{2+} + SO_3^{\bullet -} \\
\qquad\qquad + \\
\qquad\qquad SO_3^{\bullet -} \\
\qquad\qquad \downarrow \text{fast} \\
[Co(tn)_2(OH_2)_2]^{2+} + SO_4^{2-} + SO_2
\end{array}$$

Scheme 3

$$a = [k_{1ip}Q_{ip}^{SO_3}f_3 + k_{2ip}Q^{HSO_3}(1 - f_3)] \qquad (13)$$

$$b = Q_{ip}^{SO_3}f_3 + Q_{ip}^{HSO_3}(1 - f_3) \qquad (14)$$

HSO_3^-. Note $[S^{IV}]_T = [HSO_3^-] + [SO_3^{2-}]$ as $[SO_2]$ is negligible at pH 6.2 and $f_3 = 0.442$. Data were fitted by equation (12). The values of *a* and *b* are given in Table 5.

Acid-catalysed aquation of *trans*-$[Co(tn)_2(SO_3\text{-}S)_2]^-$

The aquation of the *trans*-disulfito complex is acid catalysed. The product was identified spectrophotometrically to be the *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$. The observed rate constants in the range pH 2.96–4.52 (see Table 6) obeyed equation (15)

$$k_{obs} = k_0 + k_H[H^+] \qquad (15)$$

satisfactorily in conformity with the operation of spontaneous and acid-catalysed paths (Scheme 2). Values of k_0 and k_H calculated using equation (15) are collected in Table 6.

Reduction of *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$

The complex *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$ undergoes slow internal reduction under thermal conditions unlike its ethanediamine analogue. The rate of reduction was monitored by estimating Co^{II}. The values of 10^5k_{obs} were 3.1 ± 0.5, 4.0 ± 1.0 and 7.5 ± 0.7 s^{-1} at 40.0, 45.0 and 50.0 °C respectively (pH 2.64–3.80, $I = 1.0$ mol dm^{-3}). Reduction of the cobalt(III) substrate by the $SO_3^{\bullet -}$ radical (see below) was assumed to be fast as the reaction followed first-order kinetics (Scheme 3). This is also consistent with previous studies of related systems.[12,29] The activation enthalpy and entropy for reduction calculated from the temperature dependence of k_{red} ($k_{red} = k_{obs}/2$) are 74 ± 11 kJ mol^{-1} and −102 ± 35 J K^{-1} mol^{-1} respectively.

Steady-state photolysis

The photoinduced reduction of *trans*-$[Co(en)_2(OH_2)(SO_3\text{-}S)]^+$ was studied at 35 °C. The quantum yield $[\varphi(Co^{2+})]$ and the rates of cobalt(II) formation were measured at $1 \leqslant pH \leqslant 8.01$. The $\varphi(Co^{2+})$ showed a decreasing trend with increasing duration of irradiation and obeyed the relationship $\varphi_t(Co^{2+}) = \varphi_0(Co^{2+}) - bt$. The quantum yield of Co^{II} at zero time $[\varphi_0(Co^{2+})]$ was pH dependent (see Table 7). Formation of Co^{II} could not be detected at $pH \geqslant 8$ (Tris buffer). The observed rate constants for photoreduction of this complex (see Table 8) were calculated from the first-order relationship, $k_{obs} = (1/t)\ \ln\ [a/(a - x)]$ where $a = [complex]_T = 5.0 \times 10^{-4}$ mol dm^{-3}, $x = [Co^{II}]$ produced at time *t* (Kitson's method).[25] Repetitive spectral scans of the photolyte during the steady-state photolysis of the aqua(sulfito-*S*) complexes at pH 2 (0.01 mol dm^{-3} $HClO_4$) and 7.01 (Tris buffer) displayed time-dependent decay of the absorption peak of *trans*-$[Co(L\text{–}L)_2(OH_2)(SO_3\text{-}S)]^+$ (λ_{max} 274 and 277 nm for L–L = en and tn respectively, see Fig. 4). The variation in absorbance with time at these peak wavelengths obeyed first-order kinetics and k_{obs} at $pH\ 1 \leqslant pH \leqslant 7$ averaged to (7.4 ± 0.7) × 10^{-3} s^{-1} and (5.4 ± 0.9) × 10^{-3} s^{-1} (35 °C) for 1,2-diaminoethane and 1,3-diaminopropane complexes respectively. Deviation from first-order kinetics was evident at $pH \geqslant 8$ beyond three half-lives. The decay of the 274 (277) nm peak with time might be due to photoinduced aquation and reduction of the sulfito-*S* complexes, the latter being less significant at least for the 1,2-diaminoethane complex as indicated by the quantum yield and rate data for cobalt(II) formation (see Table 8). The spectra of the photolyte at different pH (1–8) and time intervals for the 1,2-diaminoethane complex were compared with those of the authentic samples of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$, SO_3^{2-}, HSO_3^- and $S_2O_6^{2-}$ under comparable conditions of pH and concentrations of the sulfito-*S* complex (5 × 10^{-5} mol dm^{-3}). The peak of the photolysed product at 225 nm corresponds to that of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$. The spectra of the photolysed products for *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$ (pH 1–8, $[complex]_T = 5.0 \times 10^{-5}$ mol dm^{-3}) also displayed λ_{max} in the range 225–235 nm which was pH sensitive presumably due to *cis-trans* isomer distribution in the product $[Co(tn)_2(OH_2)_2]^{3+}$ and its aquahydroxo analogue.

The spectral growth at 242 nm during the steady-state photolysis of *trans*-$[Co(en)_2(OH_2)(SO_3\text{-}S)]^+$ was monitored for limited runs at pH 7, 8 and 9 (Tris buffer) which yielded $k_{obs} = (4.6 \pm 0.9) \times 10^{-3}$ s^{-1} (average). The value of the ratio $k_{obs}^{274}\!:k_{obs}^{242} = 1.6 \pm 0.3\!:\!1$ for this complex indicated that the kinetic processes monitored at these two wavelengths are most likely the same.

Flash photolysis

Flash photolysis of *trans*-$[Co(L\text{–}L)_2(OH_2)(SO_3\text{-}S)]^+$ clearly indicated the formation and decay of a transient irrespective of the diamine, L–L (en, tn) [see Figs. 1(*a*), 1(*b*) and 2(*a*), 2(*b*)]. A similar observation has been made in the case of $[Co(tetren)(SO_3\text{-}S)]^+$ (tetren = tetraethylenepentamine).[30] The initial rapid reaction for which absorbance at 390 nm increased with time was reconciled with photoinduced isomerisation of the S-bonded sulfito complex to its O-bonded analogue. The tran-

Table 3 Rate constants for anation of *trans*-[Co(tn)$_2$(OH$_2$)(SO$_3$-*S*)]$^+$ by N$_3^-$ and (NCS$^-$)[a]

T/°C	L	[L$^-$]$_T$/mol dm^{-3}	k_{obs}/s^{-1} (pH)[b]	[L$^-$]$_T$/mol dm^{-3}	k_{obs}/s^{-1} (pH)[b]
10.0 ± 0.1	N$_3^-$	0.01	9.4 ± 0.2 (4.27)	0.02	22 ± 1 (4.70)
		0.03	35 ± 1 (4.88)	0.04	54 ± 1 (5.41)
		0.05	77 ± 3 (5.41)	0.07	86 ± 3 (5.58)
		0.08	95 ± 2 (5.62)	0.10	117 ± 4 (5.65)
15.0 ± 0.1		0.01	13.8 ± 0.5 (4.17)	0.02	32 ± 1 (4.65)
		0.03	51 ± 2 (4.78)	0.04	77 ± 2 (5.40)
		0.05	97 ± 5 (5.45)	0.07	138 ± 3 (5.60)
		0.08	164 ± 6 (5.65)	0.10	201 ± 5 (5.67)
20.0 ± 0.1		0.007	13.0 ± 0.4 (3.58)	0.009	14.7 ± 0.6 (3.81)
		0.01	23 ± 1 (4.03)	0.02	52 ± 1 (4.62)
		0.03	84 ± 2 (4.92)	0.04	115 ± 3 (5.12)
		0.05	133 ± 6 (5.26)	0.07	222 ± 13 (5.44)
		0.08	248 ± 15 (5.54)		
25.0 ± 0.1		0.007	25 ± 1 (3.67)	0.009	29 ± 1 (3.92)
		0.01	37 ± 1 (4.23)	0.02	85 ± 2 (4.66)
		0.03	129 ± 6 (4.91)		
10^{-3} k_f/[c,d] 1.28 ± 0.05 (10), 2.00 ± 0.02 (15), 3.12 ± 0.11 (20), 4.94 ± 0.21 (25 °C)					
k_r[c,d] 3.0 ± 0.7 (10), 5.1 ± 0.5 (15), 10.1 ± 0.7 (20), 18.0 ± 1.0 (25 °C)					
10.0 ± 0.1	NCS$^-$	0.007	7.1 ± 0.2	0.009	9.5 ± 0.2
		0.010	10.4 ± 0.3	0.020	21 ± 1
		0.030	36 ± 1	0.040	47 ± 3
		0.050	60 ± 3	0.070	71 ± 2
		0.080	91 ± 4	0.10	105 ± 5
15.0 ± 0.1		0.007	13.2 ± 0.4	0.009	16.2 ± 1.0
		0.010	19.6 ± 0.4	0.020	36 ± 1
		0.030	56 ± 2	0.040	64 ± 1
		0.050	83 ± 2	0.070	125 ± 5
20.0 ± 0.1		0.007	25 ± 1	0.009	28 ± 1
		0.010	29 ± 1	0.020	56 ± 1
		0.030	91 ± 1	0.040	105 ± 2
		0.050	130 ± 5		
25.0 ± 0.1		0.007	36 ± 1	0.009	39 ± 1
		0.010	43 ± 2	0.020	94 ± 3
		0.030	138 ± 7	0.040	165 ± 8
		0.050	209 ± 8		
10^{-3} k_f/[c] 1.07 ± 0.03 (10), 1.60 ± 0.05 (15), 2.73 ± 0.15 (20), 4.18 ± 0.26 (25 °C)					
k_r[c] 0.2 ± 0.3 (10), 2.7 ± 0.8 (15), 3.8 ± 2.9 (20), 4.1 ± 2.8 (25 °C)					

[a] $I = 0.5$, [complex]$_T$ = 1.0×10^{-3} mol dm^{-3}; λ/nm = 473 (N$_3^-$), 455 (NCS$^-$). [b] pH Values for N$_3^-$ are given in parentheses; pH = 7.4–7.8 for NCS$^-$. [c] Units of k_f and k_r are dm^3 mol^{-1} s^{-1} and s^{-1} respectively. [d] Based on pK_d(HN$_3$) = 4.26, 4.30, 4.34 and 4.38 at 10.0, 15.0, 20.0 and 25.0 °C respectively; values of pK_d(HN$_3$) at 10–20 °C were calculated using $\Delta H° = -13.0$ kJ mol^{-1} and pK_{HN_3} = 4.38 at 25 °C ($I = 0.5$ mol dm^{-3}).[28]

Table 4 Rate constants for the anation of *trans*-[Co(tn)$_2$(OH$_2$)(SO$_3$-*S*)]$^+$ by sulfite

	k_{obs}[a]/s^{-1}			
[S^{IV}]$_T$/mol dm^{-3}	10.0	15.0	20.0	25.0 °C
	(6.20 ± 0.03)[b]	(6.09 ± 0.05)[b]	(6.29 ± 0.06)[b]	(6.24 ± 0.08)[b]
0.010	6.8 ± 0.1	13.6 ± 0.3	17.6 ± 0.4	25 ± 1
0.020	11.8 ± 0.4	22 ± 1	33 ± 1	46 ± 1
0.030	17.2 ± 0.5	27 ± 1	48 ± 3	71 ± 3
0.040	20 ± 1	34 ± 1	57 ± 2	88 ± 2
0.050	27 ± 1	43 ± 1	67 ± 1	99 ± 2
0.060	30 ± 1	46 ± 1	77 ± 2	108 ± 2
0.070	33 ± 1	49 ± 1	81 ± 2	117 ± 6
0.080	35 ± 1	52 ± 1	85 ± 2	141 ± 5
0.090	37 ± 1			
0.10	37 ± 1			
10^{-2} a[c]/dm^3 mol^{-1} s^{-1}	7.39 ± 0.15	15.7 ± 0.7	19.6 ± 0.4	27.6 ± 1.3
b[c]/dm^3 mol^{-1}	9.3 ± 0.7	18.2 ± 2.1	9.9 ± 0.7	7.8 ± 1.4
k_{ip}[d]/s^{-1}	79 ± 6	86 ± 11	198 ± 15	354 ± 66

$\Delta H^{\ddagger}$[e]/kJ mol^{-1} 64 ± 13, $\Delta S^{\ddagger}$[e]/J K^{-1} mol^{-1} 18 ± 46

[a] $I = 0.5$, [complex]$_T$ = 2.0×10^{-4} mol dm^{-3}; λ = 350 nm. [b] pH values (HSO$_3^-$–SO$_3^{2-}$ buffer). [c] $k_{obs} = a[S^{IV}]_T/(1 + b[S^{IV}]_T)$. [d] Based on $k_{1ip} = k_{2ip} = k_{ip}$ [see equation (13)]. [e] From the temperature dependence of k_{ip}.

sient, *trans*-[Co(L–L)$_2$(OH$_2$)(OSO$_2$-*O*)]$^+$, had a long life at pH ≈ 7 (>2000 μs). Values of k_{iso} (25 °C) at pH 3–7 collected in Table 9 reflect that ligand isomerisation is essentially pH independent.

The decay of the transient also obeyed first-order kinetics. The process is, however, acid catalysed as expected for the sulfito-*O* complex. For the reactions shown in Scheme 5, k_{obs} is given by equation (16). The values of k_{obs} are collected in Table

$$k_{obs} = k_H K_H[H^+]/(1.0 + K_H[H^+]) \qquad (16)$$

Table 5 Rate constants for anation of *trans*-[Co(tn)$_2$(OH)(SO$_3$-*S*)] by sulfite

	k_{obs}[a]/s^{-1}			
[SO$_3$$^{2-}$]$_T$/mol dm^{-3}	10.0	20.0	25.0	30.0 °C
0.010	0.350 ± 0.004	1.00 ± 0.03	1.80 ± 0.03	—
0.015	0.380 ± 0.004	1.30 ± 0.01	1.90 ± 0.02	—
0.020	0.450 ± 0.004	1.35 ± 0.01	2.20 ± 0.02	—
0.030	0.480 ± 0.007	1.43 ± 0.01	2.30 ± 0.01	3.6 ± 0.1
0.040	0.560 ± 0.006	1.70 ± 0.05	2.70 ± 0.02	3.9 ± 0.1
0.050	0.680 ± 0.007	1.90 ± 0.02	3.40 ± 0.08	—
0.080	0.880 ± 0.005	2.60 ± 0.06	4.30 ± 0.06	6.5 ± 0.1
0.100	1.00 ± 0.02	3.00 ± 0.03	5.1 ± 0.1	8.4 ± 0.2
0.150	1.30 ± 0.03	4.10 ± 0.04	7.1 ± 0.2	11.4 ± 0.2
0.200	1.70 ± 0.01	5.6 ± 0.1	9.8 ± 0.2	15.0 ± 0.5
k_f[b]/dm^3 mol^{-1} s^{-1}	7.2 ± 0.2	20.8 ± 1.1	36.0 ± 3.0	66.2 ± 2.7
k_r[b]/s^{-1}	0.286 ± 0.009	0.90 ± 0.043	1.30 ± 0.09	1.4 ± 0.2
k_f'[c]/s^{-1}	0.144 ± 0.004	0.42 ± 0.02	0.72 ± 0.06	1.32 ± 0.05

$\Delta H^‡$/ kJ mol^{-1} 76 ± 2[d] (68.4 ± 7.0)[e] [76 ± 2],[f] $\Delta S^‡$/J K^{-1} mol^{-1} 40 ± 6[d] (−13 ± 24)[e] [7 ± 6][f]

[a] $I = 0.5$, [complex]$_T$ = 2.0 × 10^{-4}, [NaOH]$_T$ = 0.020 mol dm^{-3}; $\lambda = 350$ nm. [b] $k_{obs} = k_f[SO_3^{2-}]_T + k_r$. [c] $k_f' = k_2k_1/k_{-1}$ [see equation (17)]. [d] From k_f. [e] From k_r. [f] From k_f'.

Table 6 Rate and activation parameters for the acid-catalysed aquation of *trans*-[Co(tn)$_2$(SO$_3$-*S*)$_2$]$^-$ [a]

T (±0.1)/°C	pH	k_{obs}/s^{-1}	pH	k_{obs}/s^{-1}	pH	k_{obs}/s^{-1}
10.0	4.52	1.50 ± 0.05	4.22	2.50 ± 0.07	4.07	3.40 ± 0.03
	3.99	4.00 ± 0.05	3.97	3.70 ± 0.02	3.82	5.10 ± 0.20
	3.79	5.40 ± 0.08	3.71	5.80 ± 0.07	3.61	6.70 ± 0.04
	3.53	8.20 ± 0.05	3.50	8.50 ± 0.10	3.23	18.6 ± 0.2
	3.00	31.3 ± 0.7	3.14	21.9 ± 0.6	3.09	25.7 ± 0.7
	3.28	13.4 ± 0.7	3.10	30.1 ± 0.6	2.96	42.7 ± 0.8
15.0	4.67	2.10 ± 0.09	4.33	2.90 ± 0.07	4.01	4.80 ± 0.06
	3.85	6.00 ± 0.04	3.80	7.40 ± 0.10	3.77	7.80 ± 0.02
	3.69	9.40 ± 0.10	3.67	9.80 ± 0.03	3.61	10.5 ± 0.2
	3.54	12.5 ± 0.2	3.51	13.9 ± 0.4	3.48	14.9 ± 0.2
	3.22	33.9 ± 1.1	3.05	41.9 ± 1.5	2.96	52.3 ± 1.3
	2.92	61.7 ± 1.0	2.81	82.7 ± 2.1	2.57	115 ± 2
20.0	4.85	2.40 ± 0.06	4.55	3.70 ± 0.07	4.42	4.40 ± 0.10
	4.09	8.40 ± 0.05	3.98	10.4 ± 0.3	3.92	13.7 ± 0.3
	3.81	15.3 ± 0.8	3.73	16.9 ± 0.2	3.69	19.3 ± 0.6
	3.61	22.0 ± 0.7	3.51	24.5 ± 0.7	3.48	26.9 ± 0.4
	3.14	46.0 ± 0.4	3.03	61.1 ± 0.7	2.87	76.8 ± 1.1
	2.67	151 ± 5	2.58	212 ± 5		
25.0	4.72	4.40 ± 0.10	4.52	6.70 ± 0.08	4.26	8.90 ± 0.20
	4.01	14.5 ± 0.7	3.87	16.6 ± 0.6	3.85	23.5 ± 0.7
	3.78	26.8 ± 0.4	3.69	28.2 ± 0.3	3.58	31.8 ± 0.4
	3.51	25.4 ± 0.4	3.45	42.3 ± 1.4	3.43	45.2 ± 0.7
	3.05	71.5 ± 0.8	2.98	131 ± 4	2.96	156 ± 3
	2.61	258 ± 11				

	k_0/s^{-1}	10^{-4} k_H/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
10.0	−0.6 ± 0.8	3.44 ± 0.16	53 ± 4[b]	28 ± 16[b]
15.0	1.1 ± 1.2	4.57 ± 0.15		
20.0	0.8 ± 2.6	7.29 ± 0.27		
25.0	5.2 ± 4.0	10.7 ± 0.5		

[a] $I = 1.0$, [complex]$_T$ = 2.0 × 10^{-4} mol dm^{-3}, $\lambda = 325$ nm; MeCO$_2$$^-$–MeCO$_2$H (pH 4.85–3.71), ClCH$_2CO_2$$^-$–ClCH$_2CO_2$H (pH 3.61–2.61). [b] For acid-catalysed path (k_H).

$$\begin{tikzcd}
\textit{trans}\text{-}[\mathrm{Co(L{-}L)_2(OH_2)(SO_3\text{-}}S)]^+ \arrow[r, "h\nu", "\text{fast}"'] & \textit{trans}\text{-}[\mathrm{Co(L{-}L)_2(OH_2)(SO_3\text{-}}S)]^{+*} \arrow[d, "k_{iso}"] \\
 & \textit{trans}\text{-}[\mathrm{Co(L{-}L)_2(OH_2)(OSO_2\text{-}}O)]^+
\end{tikzcd}$$

Scheme 4

$$\begin{tikzcd}
\textit{trans}\text{-}[\mathrm{Co(L{-}L)_2(OH_2)(OSO_2\text{-}}O)]^+ + \mathrm{H}^+ \arrow[r, shift left, "K_H"] & \textit{trans}\text{-}[\mathrm{Co(L{-}L)_2(OH_2)(OSO_2H\text{-}}O)]^{2+} \arrow[l, shift left] \arrow[d, "k_H"] \\
 & \textit{trans}\text{-}[\mathrm{Co(L{-}L)_2(OH_2)(OH)}]^{2+} + \mathrm{SO_2}
\end{tikzcd}$$

Scheme 5

10. The values of k_H and K_H (see Table 10) were calculated from the intercepts and gradients of plots of k_{obs}^{-1} *versus* [H$^+$]$^{-1}$.

Dogliotti and Hayon[31,32] reported the formation of SO$_3$$^{\bullet -}$ in the photolysis of Na$_2$SO$_3$ (10^{-2} mol dm^{-3}) and Na$_2$S$_2$O$_6$ (0.1 mol dm^{-3}) which has an absorption maximum at 275 nm. They also reported fast decay of SO$_3$$^{\bullet -}$ by a second-order process. The SO$_3$$^{\bullet -}$ radical formed in the photolysis of the sulfito complexes did not interfere in the present study with the formation and decay of the transient, *trans*-[Co(L–L)$_2$(OH$_2$)(OSO$_2$-*O*)]$^+$; SO$_3$$^{\bullet -}$ produced in the photolysis of the sulfito-*S* complex was, however, rapidly scavenged by the complex yielding Co^{II} and SO$_4$$^{2-}$ and SO$_3$$^{2-}$ {*trans*-[Co(L–L)$_2$(OH$_2$)(SO$_3$-*S*)]$^+$ +

Table 7 Quantum yield of Co^{2+} as a function of pH, $\lambda = 254$ nm, 35.0 ± 0.1 °C

pH	$\varphi_0(Co^{2+})$	pH	$\varphi_0(Co^{2+})$
1.0	0.18 ± 0.013	5.72	0.34 ± 0.038
3.0	0.36 ± 0.008	7.01	0.19 ± 0.017
3.72	0.37 ± 0.018	⩾8.0	Co^{2+} could not be detected
4.72	0.40 ± 0.035		

Table 8 Rate constants for photoreduction of *trans*-$[Co(en)_2(OH_2)(SO_3\text{-}S)]^{+}$ [a]

pH [b]	$10^4\ k_{obs}/s^{-1}$	pH [b]	$10^4\ k_{obs}/s^{-1}$
1.0	4.2 ± 0.1	5.72	8.4 ± 0.9
3.0	9.2 ± 0.9	7.01	3.0 ± 0.9
3.72	11.0 ± 1.0	8.01	no reduction
4.72	10.4 ± 0.9		

[a] $[complex]_T = 5.0 \times 10^{-4}$ mol dm^{-3}, $\lambda = 254$ nm, 35.0 ± 0.2 °C. [b] pH 1 and 3 maintained by 0.1 and 0.001 mol dm^{-3} $HClO_4$ respectively; 3.72–5.72 by $MeCO_2H$–$MeCO_2Na$ buffer; 7.01–8.01 by Tris buffer.

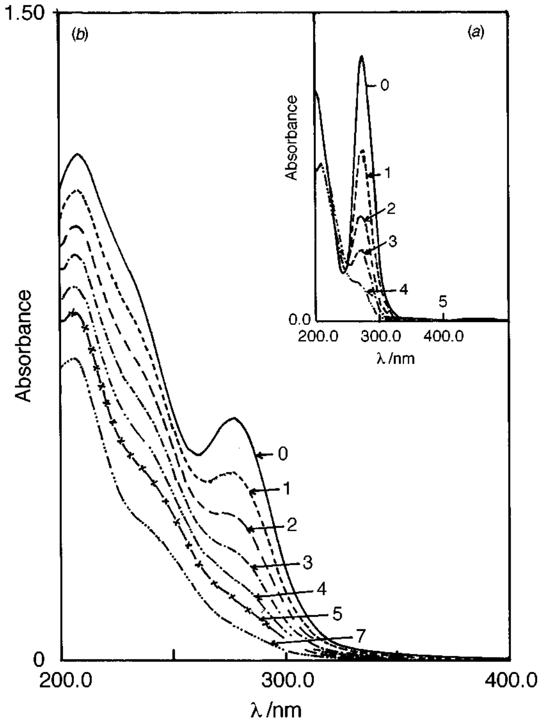


Fig. 4 Spectral scans during photolysis of *trans*-$[Co(L\text{–}L)_2(OH_2)(SO_3\text{-}S)]^{+}$; $[complex]_T = 5 \times 10^{-5}$, $[HClO_4]_T = 0.010$ mol dm^{-3}, L–L = 1,2-diaminoethane (*a*) or 1,3-diaminopropane (*b*); numbers 0–7 denote the duration of irradiation in minutes

$SO_3^{\bullet -} \longrightarrow [Co(L\text{–}L)_2]^{2+} + SO_4^{2-} + SO_3^{2-} + 2H^{+}\}$ as has been reported in the thermal redox reactions of (sulfito-*O*) cobalt(III) complexes.[11,12,21,29]

Discussion

The rate and activation parameters for the formation and acid-catalysed aquation of some O-bonded sulfito complexes of cobalt(III) are compared in Table 11. It may be noted that the *cis/trans*-$[Co(en)_2(OH_2)(OH)]^{2+}$ and *cis*-$[Co(tn)_2(OH_2)(OH)]^{2+}$ complexes react with SO_2 virtually at the same rate, thus indicating that the steric and electronic effects due to chelate-ring expansion do not affect the kinetics of formation of O-bonded sulfito complexes. Further the rate comparison shows that k_1 is little sensitive to the nature of the non-labile ligands with regard to the number of chelate rings and the stereochemistry of the cobalt(III) substrates. This is understandable as the reaction involves addition of SO_2 to the Co^{III}–OH bond.[1] The $SO_2(OH)^-$ ion is reported to have a long S–OH bond.[35] Thus the lack of a significant dependence of k_1 on the steric and electronic effects of the ligands bound to cobalt(III) might indicate that the bond between Co^{III}–OH and SO_2 $[Co^{III}\text{–}(H)O \cdots SO_2]$ is long enough in the transition state to be influenced by the non-labile ligands bound to the cobalt(III) centre. The variation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (see Table 11) with the nature of the non-labile ligands is, however, a reflection of the solvation requirements of the initial and transition states.

Table 9 Rate constants for the formation of the transient in the flash photolysis of *trans*-$[Co(L\text{–}L)_2(OH_2)(SO_3\text{-}S)]^{+}$ at 25.0 °C

	$10^{-4}\ k_{obs}/s^{-1}$	
pH *	L–L = en	tn
3.0	5.2	4.1, 5.5
3.7	3.8, 3.4, 4.7	3.7
4.0		2.1
4.7	3.4	2.8
≈7.0		2.5, 1.7
Average	4.1 ± 0.8	3.2 ± 1.3

* pH 3.7–4.7 ($MeCO_2^-$–$MeCO_2H$), ≈7 (no buffer), 3 (0.001 mol dm^{-3} $HClO_4$).

Table 10 Rate constants for the decay of the transient generated in the flash photolysis of *trans*-$[Co(L\text{–}L)_2(OH_2)(SO_3\text{-}S)]^{+}$ at 25.0 °C and $I = 0.3$ mol dm^{-3}

	$10^{-3}\ k_{obs}/s^{-1}$	
pH *	L–L = en	tn
3.0	5.1	5.3, 4.7, 4.5
3.7	1.1, 1.5	1.3
4.0		1.2
4.7	0.41	0.63
$10^{-3}\ k_H/s^{-1}$	1.8 ± 0.3	3.7 ± 1.8
$10^{-4}\ K_H/dm^3\ mol^{-1}$	1.5 ± 0.4	1.0 ± 0.5

* See footnote to Table 9.

This is, however, not the case in the acid-catalysed aquation path. Using the data of Dasgupta and Harris[33] we find $k_{-1}^{en}/k_{-1}^{tn} = 42$ (10 °C) for the *cis*-$[Co(L\text{–}L)_2(OH_2)(OSO_2\text{-}O)]^{+}$ (L–L = en or tn) complexes. This may be contrasted with the comparable values of the rate constant for aquation of *cis*-$[Co(L\text{–}L)_2(OH_2)(OSeO_2H)]^{2+}$ complexes ($k_{aq}/s^{-1} = 0.16$ and 0.18 at 25 °C, $I = 1.0$ mol dm^{-3} for L–L = en and tn respectively) which involves Se–O bond cleavage.[19] The acid-catalysed aquation rate constants for the *trans* complexes reported in this work are comparable ($k_{-1}^{tn}/k_{-1}^{en} = 1.4 \pm 0.5$ at 25 °C, $I = 0.3$ mol dm^{-3} see Table 11). Also it is worth noting that the rate constant for aquation of *trans*-$[Co(L\text{–}L)_2(OH_2)(OSeO_2H)]^{2+}$ shows marginal variation with chelate size ($k_{aq}^{tn}/k_{aq}^{en} = 3$ at 25 °C).[19]

The value of k_{-1} for *trans*-$[Co(en)_2(OH_2)(OSO_2\text{-}O)]^{+}$ reported by El-Awady and Harris[36] from stopped-flow measurements on the *in situ* generated sulfito-*O* complex ($I = 1.0$ mol dm^{-3}, 25 °C, $[S^{IV}]_T$ in excess of the aqua complex) is ≈700 times smaller than the same reported by us in this work (by flash photolysis). The large difference cannot be accounted for by an ionic strength effect. However, our values of k_{-1} for *trans*-$[Co(L\text{–}L)_2(OH_2)(OSO_2\text{-}O)]^{+}$ complexes compare well with those for similar complexes listed in Table 11. The value of k_{-1} for *trans*-$[Co(en)_2(OH_2)(OSO_2\text{-}O)]^{+}$ obtained by extrapolation of the data of El-Awady and Harris[36] (3.3×10^4 dm^3 mol^{-1} s^{-1}, 25 °C, $I = 1.0$ mol dm^{-3}) compares with the rate constant for the acid-catalysed aquation of *trans*-$[Co(en)_2(SO_3\text{-}S)_2]^{+}$ ($k_H = 1.5 \times 10^4$ dm^3 mol^{-1} s^{-1}, 25.0 °C, $I = 1.0$ mol dm^{-3}).[12] El-Awady and Harris observed biphasic kinetics for the acid-catalysed aquation of the *in situ* generated disulfito complex *trans*-$[Co(en)_2(OSO_2\text{-}O)_2]^{-}$ in excess of sulfite. Their value for

Table 11 Comparative listing of rate and activation parameters for the formation and acid-catalysed aquation of some O-bonded sulfito complexes of cobalt(III) at 25.0 °C and $I = 1.0$ mol dm^{-3}

Complex[a]	$10^{-8}\ k_1$/dm^3 mol^{-1} s^{-1}	$10^{-6}\ k_{-1}$/dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	Ref.
$[Co(NH_3)_5(OH)]^{2+}$	4.7 ± 0.3		41 ± 1	59 ± 2	29
cis-$[Co(en)_2(OH_2)(OH)]^{2+}$	1.05 ± 0.05		25 ± 1	−7 ± 1	33
trans-$[Co(en)_2(OH_2)(OH)]^{2+}$	1.4		27 ± 8	−46 ± 24	36
cis-$[Co(tn)_2(OH_2)(OH)]^{2+}$	1.4 ± 0.3		15 ± 2	−39 ± 9	This work
$[Co(tren)(OH_2)(OH)]^{2+}$	0.53 ± 0.04		19 ± 1	−33 ± 3	3
(αβS)$[Co(tetren)(OH)]^{2+}$	3.3 ± 0.3		−2 ± 4	−88 ± 15	4
cis-$[Co(en)_2(NH_3)OH]^{2+}$	4.7 ± 0.4		46 ± 4	77 ± 15	12
cis-$[Co(en)_2(MeNH_2)(OH)]^{2+}$	2.4 ± 0.3		47 ± 4	72 ± 14	12
cis-$[Co(en)_2(EtNH_2)(OH)]^{2+}$	4.8 ± 0.5		53 ± 6	98 ± 21	12
cis-$[Co(en)_2(PhCH_2NH_2)(OH)]^{2+}$	2.5 ± 0.2		55 ± 1	101 ± 5	12
cis-$[Co(en)_2(C_6H_{11}NH_2)(OH)]^{2+}$	2.0 ± 0.1		51 ± 8	85 ± 28	12
cis-$[Co(en)_2(Him)(OH)]^{2+}$	0.77 ± 0.03		32 ± 1	13 ± 4	2
trans-$[Co(NH_3)_4(CN)(OH)]^{+}$	1.04 ± 0.07		41 ± 6	50 ± 20	5
$[Co(NH_3)_5(OSO_2)]^{+}$		2.2 ± 0.4[b]			29
cis-$[Co(en)_2(OH_2)(OSO_2)]^{+}$		0.75[b]			33
cis-$[Co(tn)_2(OH_2)(OSO_2)]^{+}$		0.14 ± 0.05	86 ± 10	141 ± 36	This work
trans-$[Co(en)_2(OH_2)(OSO_2)]^{+}$		0.033[c]	114[d]	223[d]	36
		26 ± 6			This work
trans-$[Co(tn)_2(OH_2)(OSO_2)]^{+}$		36 ± 10			This work
$[Co(tren)(OH_2)(OSO_2)]^{+}$		1.5 ± 0.2	46 ± 3	29 ± 2	3
(αβS)$[Co(tetren)(OSO_2)]^{+}$		4 ± 1[c]	58.6 ± 0.4	79 ± 1	4
cis-$[Co(en)_2(NH_3)(OSO_2)]^{+}$		17.2 ± 1.5	66 ± 6	114 ± 21	12
cis-$[Co(en)_2(MeNH_2)(OSO_2)]^{+}$		11.8 ± 1.9	48 ± 4	51 ± 14	12
cis-$[Co(en)_2(EtNH_2)(OSO_2)]^{+}$		9.1 ± 1.0	78 ± 12	152 ± 42	12
cis-$[Co(en)_2(PhCH_2NH_2)(OSO_2)]^{+}$		1.7 ± 0.4	49 ± 7	40 ± 26	12
cis-$[Co(en)_2(C_6H_{11}NH_2)(OSO_2)]^{+}$		3.0 ± 0.3	60 ± 13	77 ± 47	12
cis-$[Co(en)_2(Him)(OSO_2)]^{+}$		2.7 ± 0.3	58 ± 3	72 ± 9	2
trans-$[Co(NH_3)_4(CN)(OSO_2)]^{+}$		2.5 ± 0.3	61 ± 1	83 ± 4	5

[a] Him = Imidazole. [b] At 10 °C. [c] Extrapolated value. [d] Recalculated from the values of the rate constant k_{-2}' at 10 and 15 °C (see Table VI of ref. 36).

the rate constant of acid-catalysed aquation of the disulfito complex to the corresponding (aqua)(monosulfito) intermediate (4.8×10^6 dm^3 mol^{-1} s^{-1} at 15 °C, $I = 1.0$ mol dm^{-3}) also compares with the rate constant for *trans*-$[Co(en)_2(OH_2)(OSO_2\text{-}O)]^+$ obtained in the present work. They also reported that the disulfito complex underwent partial ligand isomerisation and internal redox reaction. Considering the method of generation of the disulfito-*O* complex and the usual time allowed by them before stopped-flow kinetics measurements were taken, the isomerisation of the initially formed disulfito-*O* complex to its S-bonded form cannot be completely ruled out. The discrepancy between the two sets of rate data for *trans*-$[Co(en)_2(OH_2)(OSO_2\text{-}O)]^+$ might be due to the fact that the disulfito complex used by El-Awady and Harris was a mixture of *trans*-$[Co(en)_2(SO_3\text{-}S)_2]^-$ and *trans*-$[Co(en)_2(OH_2)(OSO_2\text{-}O)]^+$.

The comparison thus shows that, unlike the *cis* complexes, chelate-ring expansion does not lead to significant rate acceleration in the acid-catalysed aquation of the *trans*-$[Co(L\text{–}L)_2(OH_2)(OSO_2\text{-}O)]^+$ complexes. A similar effect was observed in the photochemical isomerisation of the *trans*-$[Co(L\text{–}L)_2(OH_2)(SO_3\text{-}S)]^+$ complexes. Since the mechanism is the same, the observed retardation for the *cis* complexes is attributed to the effect of the chelate-ring size on the fast protonation equilibrium preceding the rate-limiting step. The expansion of the chelate ring from a five- to a six-membered one results in an expansion of the N–Co–N bond angle.[34,37,38] Note that the N–Co–N bond angles in $[Co(tren)(CO_3)]^+$ (five-membered chelate) [tren = tris(2-aminoethyl)amine] is rigidly fixed at 87° while the same in $[Co(trpn)(CO_3)]^+$ (six-membered chelate) [trpn = tris(3-aminopropyl)amine] opposite to the carbonate ligand is flexible and expands to 100°.[38] This distortion is likely to bring the co-ordinated H_2O and SO_3^{2-} much closer in the tn complex for a relatively tighter hydrogen bond. In consequence, the protonation constant (K_H) of the sulfito-*O* complex is decreased causing rate retardation ($k_{-1} = k_H K_H$) for *cis*-$[Co(tn)_2(OH_2)(OSO_2\text{-}O)]^+$ relative to its ethanediamine analogue. It may be noted that the steric retardation observed in the acid-catalysed SO_2-elimination reactions of *cis*-$[Co(en)_2(RNH_2)(OSO_2)]^+$ (R = H, Me, Et, $PhCH_2$ or C_6H_{11}) (see Table 11) is explicable in terms of the unfavourable steric effect on the protonation equilibria of such complexes. The large value of $\Delta H^\ddagger$ and substantially large positive value of $\Delta S^\ddagger$ for the acid-catalysed aquation of the tn complex (see Table 3) might be indicative of substantial entropy gain and enthalpy demand in the protonation of the internally hydrogen-bonded form of the sulfito-*O* complex.

Rate constants for the anation of *trans*-$[Co(L\text{–}L)_2(OH_2)(SO_3\text{-}S)]^+$ (L–L = en or tn) by SCN^-, N_3^-, SO_3^{2-} and of *trans*-$[Co(L\text{–}L)_2(OH)(SO_3\text{-}S)]$ by SO_3^{2-} are presented in Table 12. All data are based on an ion-pair dissociative interchange mechanism. The rate constants for the ion pairs of *trans*-$[Co(tn)_2(OH_2)(SO_3\text{-}S)]^+$ with HSO_3^- and SO_3^{2-} are assumed to be independent of the charge of the ion pair (*i.e.* $k_{1ip} = k_{2ip}$) as water dissociation from the cobalt(III) centre is rate limiting. Values of $k_f^{tn}(L^{n-})/k_f^{en}(L^{n-})$ are 14 (NCS^-), 20 (N_3^-) and 4 (SO_3^{2-}) for the aqua complexes and 16 (SO_3^{2-}) for the hydroxo complexes at 25 °C. Complex *trans*-$[Co(tn)_2(OH)(SO_3\text{-}S)]$ being an uncharged species, sulfite substitution in an alkaline medium ($[OH^-] \geqslant 0.02$ mol dm^{-3}) would involve a D mechanism[9] as in Scheme 6. In accord with the D mechanism the linear dependence of k_{obs} on $[SO_3^{2-}]$ at constant $[OH^-]$ is consistent with equation (17) ($k_2[SO_3^{2-}] \ll k_{-1}[OH^-]$). A similar

$$k_{obs} = (k_1 k_2/k_{-1})[SO_3^{2-}][OH^-]^{-1} + k_{-2} \qquad (17)$$

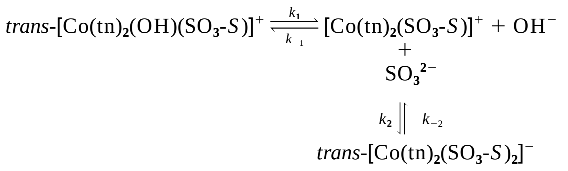
relationship was found to be valid for the anation of *trans*-$[Co(en)_2(OH)(SO_3\text{-}S)]$ by SO_3^{2-}.[9] Thus k_f and k_r are identified as $k_1 k_2/(k_{-1}[OH^-])$ and k_{-2} respectively. Hence a comparison of k_f and k_r values for 1,2-diaminoethane and 1,3-diaminopropane complexes under identical conditions is justified.

The interchange rate constants of the ion pairs {*trans*-$[Co(L\text{–}L)_2(OH_2)(SO_3\text{-}S)],SO_3^{2-}$}$^-$ yield $k_{ip}^{tn}/k_{ip}^{en} = 18$ (25 °C). The relative rates of spontaneous dissociation of L^{n-} from *trans*-$[Co(L\text{–}L)_2(L^{n-})(SO_3\text{-}S)]^{(1-n)-}$ [$k^{tn}/k^{en} = 43$ (NCS^-), 20

Table 12 Comparative listing of the rate and activation parameters for anation of *trans*-$[Co(L-L)_2(OH_2)(SO_3\text{-}S)]^+$ at 25.0 °C and $I = 1.0$ mol dm^{-3}

X^{n-}	L–L	$k_f/dm^3\ mol^{-1}\ s^{-1}$	$\Delta H^‡/kJ\ mol^{-1}$	$\Delta S^‡/J\ K^{-1}\ mol^{-1}$	k_r/s^{-1}	Ref.
trans-$[Co(L-L)_2(OH_2)(SO_3\text{-}S)]^+ + X^{n-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}}$ *trans*-$[Co(L-L)_2X(SO_3\text{-}S)]^{(n-1)-}$						
SCN^-	en	$(2.75 \pm 0.05) \times 10^2$ $(2.94 \pm 0.05) \times 10^{2a}$	47 ± 3	−39 ± 12	0.11	13
	tn	$(41.8 \pm 2.6) \times 10^2$	61 ± 3	28 ± 12	4.1 ± 2.8	This work
N_3^-	en	$(2.35 \pm 0.22) \times 10^2$			0.8 ± 0.4	13
	tn	$(49.4 \pm 2.1) \times 10^2$	61 ± 1	30 ± 4	18 ± 1	This work
SO_3^{2-}	en	6.0×10^{2a}				
	tn	$(27.6 \pm 1.3) \times 10^{2b}$				This work
	tn	$(3.5 \pm 0.6) \times 10^{2c}$	64 ± 13	18 ± 46		This work
	en	$20 \pm 1^{a,c}$				
	en	13.4^d	69 ± 2	66 ± 6		9
trans-$[Co(L-L)_2(OH)(SO_3\text{-}S)] + X^{n-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}}$ *trans*-$[Co(L-L)_2(SO_3\text{-}S)_2]^- + OH^-$						
SO_3^{2-}	en	2.2 ± 0.3			0.111	9
	en	0.044 ± 0.006^e				9
	tn	36 ± 3			1.3 ± 0.1	This work
	tn	0.76 ± 0.02^e	76 ± 2	7 ± 6		This work

[a] Ref. 39. [b] Value of *a* [see equation (13)]. [c] Interchange rate constant of the ion pair {*trans*-$[Co(L-L)_2(OH_2)(SO_3\text{-}S)]^+,SO_3^{2-}$}; unit s^{-1}. [d] Limiting rate constant for water dissociation from *trans*-$[Co(en)_2(OH_2)(SO_3\text{-}S)]^+$.[9] [e] Value of $k_f' = k_1k_2/k_{-1}$ [see equation (17)]; unit s^{-1}.



$$trans\text{-}[Co(tn)_2(OH)(SO_3\text{-}S)]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(tn)_2(SO_3\text{-}S)]^+ + OH^-$$
$$+\ SO_3^{2-}\ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}\ trans\text{-}[Co(tn)_2(SO_3\text{-}S)_2]^-$$

Scheme 6

(N_3^-), 12 (SO_3^{2-})] and the acid-catalysed dissociation of S-bonded sulfite from *trans*-$[Co(L-L)_2(SO_3\text{-}S)_2]^-$ [$k_H^{tn}/k_H^{en} = 7$; $10^{-4}\ k_H/dm^3\ mol^{-1}\ s^{-1} = 1.52 \pm 0.06$ (en),[12] 10.7 ± 0.5 (tn) at 25 °C, $I = 1.0$ mol dm^{-3}] also reflect a similar trend with respect to the chelate ring expansion. The substitution reactions of these (aqua or hydroxo)(sulfito-*S*) complexes are subject to the strong *trans* effect of the co-ordinated sulfite. Stranks and Yandell[9] proposed a D mechanism for the anation of *trans*-$[Co(en)_2(OH_2/OH)(SO_3\text{-}S)]^{+/0}$ by sulfite. However, the ion-pair dissociative interchange mechanism as mentioned above is essentially a D process for the ion pair considering the kinetic *trans* effect of the S-bonded sulfite. If this *trans* effect is assumed to be independent of the chelate-ring size, then the relative rates (k^{tn}/k^{en}) as mentioned above reflect the extra driving force for the tn complex due to the chelate-ring expansion. The observed rate acceleration due to the chelate-ring expansion upon dissociative ligand substitution at the cobalt(II) centre is rather small considering the remarkably faster aquation rate of *trans*-$[Co(tn)_2Cl_2]^+$ compared to that of its en analogue ($k_{aq}^{tn}/k_{aq}^{en} > 1000$ at 25 °C)[40] and the 1450 times faster isomerisation rate for *trans*-$[Co(tn)_2(OH_2)_2]^{3+}$ compared to that for *trans*-$[Co(en)_2(OH_2)_2]^{3+}$.[19] The kinetic *trans* effects of Cl^- and H_2O in these complexes are negligible in comparison to that of sulfite in the S-bonded sulfito complexes. Thus our data reflect that the rate-acceleration effect due to chelate-ring expansion is substantially reduced by the strong *trans* effect of the S-bonded sulfite. We suggest that the effect of chelate-ring expansion is minimised due to lengthening of the Co–X bond *trans* to the *S*-co-ordinated sulfite in the ground state (ground-state *trans* effect). There have been reports on the lengthening of the *trans*-Co^{III}-to-ligand bond in *trans*-$[Co(en)_2X(SO_3)]^{-(n-1)}$ [$X = SO_3^{2-}\text{-}S$ ($n = 2$), H_2O ($n = 0$) or Cl^- ($n = 1$)].[16,17]

The activation enthalpies and entropies for anation of the *trans*-(aqua)(sulfito-*S*) complexes (see Table 11) do not show substantial variation with the nature of the diamine. Small variations of these parameters appear to be mutually compensatory possibly due to the solvation effects. However, the activation parameters for the acid-catalysed aquation of *trans*-$[Co(L-L)_2(SO_3\text{-}S)_2]^-$ complexes [$\Delta H^‡/kJ\ mol^{-1}$ ($\Delta S^‡/J\ K^{-1}\ mol^{-1}$): 81 ± 2 (108 ± 5) and 53 ± 4 (28 ± 16) for L–L = en and tn respectively] are significantly decreased with increasing chelate-ring size.

The cobalt centre in *trans*-$[Co(en)_2(OH_2)(SO_3)]^+$ is inert to reduction by the S-bonded sulfite. Photochemical activation of this complex, however, results in both aquation and reduction of Co^{III}. In contrast, the corresponding tn complex undergoes facile intramolecular redox reaction as mentioned above under thermal conditions. This is also a manifestation of the relatively weaker stabilising effect of tn relative to that of en on the intramolecular electron-transfer process involving S^{IV} and Co^{III}, predominantly due to chelate-ring expansion.

Conclusion

We have tried to delineate the effect of chelate-ring size on the rates of formation and acid-catalysed aquation of O-bonded sulfito complexes of cobalt(III), *cis/trans*-$[Co(L-L)_2(OH_2)(OSO_2\text{-}O)]^+$, photochemical isomerisation, $Co^{III}\text{–}SO_3^+ \longrightarrow Co^{III}\text{–}SO_2^+$, substitution and redox reactions of *trans*-$[Co(L-L)_2(OH_2)(SO_3\text{-}S)]^+$, and acid-catalysed aquation of *trans*-$[Co(L-L)_2(SO_3\text{-}S)_2]^-$ using L–L = 1,2-diaminoethane or 1,3-diaminopropane. The rate constant for formation of the O-bonded sulfito complex from *cis/trans*-$[Co(L-L)_2(OH_2)(OH)]^{2+}$ is little affected by the chelate-ring size consistent with an associative mechanism involving addition of SO_2 to Co^{III}–OH. However, substantial rate retardation is observed in the acid-catalysed aquation of *cis*-$[Co(L-L)_2(OH_2)(OSO_2\text{-}O)]^+$ due to the chelate-ring expansion from five to six members. This is explained by intramolecular hydrogen bonding between O-bonded sulfite and the H_2O molecule co-ordinated to cobalt(III) which prevents protonation of the O-bonded sulfite, at least partly. The substitutional lability of the $Co^{III}\text{–}OH_2$ in *trans*-$[Co(L-L)_2(OH_2)(SO_3\text{-}S)]^+$ due to chelate-ring expansion is greatly attenuated by the *trans* effect of S-bonded sulfite. However, increasing the chelate-ring size from five to six enhanced the intramolecular electron-transfer rate between Co^{III} and S^{IV} in *trans*-$[Co(L-L)_2(OH_2)(SO_3\text{-}S)]^+$.

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