Reactions of \( \beta \)-cis-(diaqua)(triethylenetetramine)cobalt(III) with sulphur(IV) in aqueous medium: A thermal and photochemical study

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The initial fast reaction of SO\(_2\) with \( \beta \)-[Co(trien) (OH)(OH\(_2\))]\(^+\) yields the O-bonded sulphito complex, \( \beta \)-[Co(trien) (OH\(_2\)) (OSO\(_2\)-O)]\(^+\) for which \( k = (4.76 \pm 0.25) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\), \( \Delta H^\circ = 42.1 \pm 5.1 \text{ kJ mol}^{-1}\), \( \Delta S^\circ = 43 \pm 17 \text{ J K}^{-1} \text{ mol}^{-1}\) at 25°C and \( I = 1.0 \text{ mol dm}^{-3}\). The O-sulphito complex undergoes \( \text{H}^+\)-catalysed aquation with \( k = (1.1 \pm 0.2) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) (25°C, \( I = 1.0 \text{ mol dm}^{-3}\)). These data are consistent with the rate limiting addition of SO\(_2\) to Co\(^{III}\)-OH and breakage of S-O bond in the formation and aquation of the O-sulphito complex respectively. The O-sulphito complex undergoes intramolecular electron transfer and ligand linkage isomerisation, Co-OSO\(_2\) \( \rightarrow \) Co-SO\(_2\) for which \( k_{\text{cis}} = (0.28 \pm 0.03) \times 10^9 \text{ s}^{-1}\), \( \Delta H^\circ = 76 \pm 12 \text{ kJ mol}^{-1}\), \( \Delta S^\circ = 81 \pm 39 \text{ J K}^{-1} \text{ mol}^{-1}\) and \( k_{\text{trans}} = (0.44 \pm 0.12) \times 10^7 \text{ s}^{-1}\), \( \Delta H^\circ = 57 \pm 7 \text{ kJ mol}^{-1}\), \( \Delta S^\circ = -138 \pm 24 \text{ J K}^{-1} \text{ mol}^{-1}\) respectively. The \( \beta \)-cis-[Co(trien)(OH)(SO\(_2\)-S)]\(^+\) has been isolated in the solid state and characterised.

We have a long standing interest on the reactions of sulphur(IV) with redox active transition metal ions and their complexes due to their relevance to atmospheric and environmental chemistry. In continuation of our earlier work \(^2\) we present here a study of the reaction of sulphur(IV) with \( \beta \)-cis-(diaqua)(trien)cobalt(III) (trien = triethylenetetramine) in aqueous medium. The purpose of undertaking this hitherto unreported study was to examine the effect of this tetradeionate amine ligand on the kinetics of the formation of the sulphito cobalt(III) species (both O- and S- bonded isomers) and the corresponding redox reaction between the reactants. The possibility of the rearrangement of the trien skeleton in the [(aqua)Co(trien)(SO\(_2\)-S)]\(^+\) under the trans-activating influence of the S-bonded sulphite was an additional consideration.

Materials and Methods

Preparation of complexes

The \( \beta \)-cis (carbonato)(trien)cobalt(III) perchlorate monohydrate was prepared by the method of Sargeson \( et\) al. \(^3\) and purity checked by analysis of cobalt. The corresponding diaqua complex was generated \textit{in situ} by acidifying the aqueous suspension of the carbonato complex with dilute HClO\(_4\), warming the solution and flushing with N\(_2\) to get rid of dissolved CO\(_2\). The acidified stock solution of the diaqua complex (0.1 mol dm\(^{-3}\)) was stored at 5°C in a refrigerator and used for kinetic study. Several such preparations of the diaqua complex showed identical kinetic behaviour. The UV-visible spectrum of the diaqua complex was in satisfactory agreement with the published data.\(^4\)

The (aqua)(sulphito)(trien)cobalt(III) perchlorate was prepared as follows: \( \beta \)-cis [Co(trien)CO\(_3\)](ClO\(_4\)) (1.9 g, 0.005 mol) was dissolved in 25 cm\(^3\) water acidified with HClO\(_4\) (pH = 2). Dissolved CO\(_2\) was allowed to escape. Na\(_2\)SO\(_4\) (1.26 g, 0.01 mol) was added and pH was adjusted to 6. The solution immediately turned deep brown indicating the formation of the O-bonded sulphito complex. When this solution was set aside overnight, it turned yellowish brown which is indicative of the formation of the S-bonded sulphito complex. This transformation was accelerated by warming the mixture. Finally the desired complex was obtained as a yellow brown solid by adding NaClO\(_4\) to the reaction mixture and scratching the sides of the container. The solid isolated by filtration on a glass sintered funnel was recrystallised from warm 0.01 mol dm\(^{-3}\) HClO\(_4\) solution by adding NaClO\(_4\) and cooling in an ice bath. It was washed successively with cold water, ethanol and diethyl
ether, air dried and stored over silica gel being protected from light. Anal. Found: Co, 14.3; C, 17.95; N, 13.3; H, 4.85. Calc. for \([\text{(trien)Co(OH)}_2(\text{SO}_3)\text{ClO}_4] \): Co, 14.6; C, 17.9; N, 13.9; H, 4.97%. \( \lambda_{max} \) nm \((\varepsilon, \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})\): 442 (185), 270 (15,675) (pH 2). The UV-visible spectrum of this complex was similar to those of S-bonded sulphito complexes of cobalt(III)\(^5\).

The corresponding \( O \)-bonded sulphito complex could not be isolated in the solid state in spite of our best efforts.

Reagents and chemicals

Analar grade chemicals were used for kinetic study. Sodium \( \mu \)-oxo-tetraoxodisulphate \((\text{Na}_2\text{S}_2\text{O}_5)\) was used as the source of sulphite. This salt dissociates rapidly in aqueous medium to produce an equilibrium mixture of \( \text{SO}_4^{2-} / \text{HSO}_5^- / \text{SO}_3^{2-} \). \( \text{NaClO}_4 \) used for ionic strength adjustment was prepared from \( \text{Na}_2\text{CO}_3 \) and \( \text{HoCl}_4 \). \( \text{NaClO}_4 \) was used for ionic strength adjustment as the source of sulphite. This salt dissociates rapidly in aqueous medium to produce an equilibrium mixture of \( \text{SO}_4^{2-} / \text{HSO}_5^- / \text{SO}_3^{2-} \). The elemental analysis was done at Indian Association for the Cultivation of Science, Calcutta and Central Drug Research Institute, Lucknow. All solutions were prepared in doubly distilled water, the second distillation being made in an all glass apparatus over alkaline \( \text{KMnO}_4 \).

Instrumentation

The UV-visible spectra were recorded on a JASCO 7800 spectrophotometer using matched 1 cm quartz cells. The I.R. spectra was recorded on a Paragon 500 F. T. I. R. spectrometer. The \( ^1 \text{H} \) NMR spectrum was recorded on a 300 MHz Bruker FT NMR spectrometer in \( \text{D}_2\text{O} \) medium at RSIC, Chandigarh. The \( \text{pH} \) measurements were done with ELICO digital \( \text{pH} \) meter LI 120 equipped with a glass-Ag/AgCl, CI (2 mol dm\(^{-3}\) NaCl) combined electrode CL 51; the \( \text{pH} \) data were converted to \( \text{pH}^+ \) by calibrating the meter readings against standard solutions of \( \text{HClO}_4 \) as described earlier\(^6\). The elemental analysis was done at Indian Association for the Cultivation of Science, Calcutta and Central Drug Research Institute, Lucknow. The steady state and conventional flash photolysis experiments were conducted at the Centre for Ultra Fast Research in the Department of Chemistry, University of Chennai.

Kinetics

The formation of the \( O \)-bonded sulphito complex was studied using a SF 51 stopped flow spectrophotometer (HITECH, U K) with an on line APPLE II GS P C. The experimental details are given in our earlier work\(^7\). The relatively slow reactions were monitored spectrophotometrically. The redox reaction was monitored by measuring Co(II) yield as \( \text{Co(NCS)}_2 \) at 625 nm \((\varepsilon = 1780 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \) at 625 nm for \( \text{Co(NCS)}_2 \). The concentration of the complex in the reaction mixture was \( 2.0 \times 10^{-3} \text{ mol dm}^{-3} \). Aliquot of the reaction mixture (2.0 cm\(^3\)) withdrawn at regular time intervals, was treated with \( \text{NH}_4\text{NCS}, \text{acetone} \) and \( \text{HCl} \) and volume was made up to \( 10 \text{ cm}^3 \) for cobalt(II) analysis\(^7\). All rate measurements were made under pseudo-first order conditions. The formation of the \( O \)-sulphito complex as well as the redox reaction obeyed first order kinetics. The rate constants reported from stopped flow runs are average of five replicate runs and the errors quoted are standard deviations. The time dependence of the absorbance for Co(II) yield followed the relationship: \( A_t = C \times [1- \exp(-k_{obs} t)] \) (see results and discussion part) where \( A_t \) is the absorbance due to \( \text{Co(NCS)}_2 \) at time \( t \) and \( C \) is constant \( (C = A_0) \) and \( k_{obs} \) is the observed pseudo-first order rate constant. The values of \( A_0 \) indicated that at the most 60% of \( \text{[Co}^{III}] \) was reduced to Co(II) in the range of \( \text{pH} = 3.1 - 4.4 \) (30°C - 45°C). All other calculations were made on an IBM compatible 486 P. C. using a weighted least squares program. The dependent variable was weighted inversely as its variance.

Steady state photolysis

Steady state photolysis experiments at 254 nm were carried out using a low pressure mercury vapour pen-ray lamp (Ultraviolet Products, U S A). The sample solution was taken 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 Ferroxylate actinometry as described in our earlier work\(^5\). The concentration of the sulphito complex, \( \text{[trien} \text{Co(OH)}_2(\text{SO}_3^-)]^+ \), was \( 1.0 \times 10^{-3} \text{ mol dm}^{-3} \). The spectral kinetic study was monitored at 480 nm. The \( \text{pH} \) in the ranges 1 - 3, 3.98 - 6.1 and at > 6.1 was controlled by \( \text{HClO}_4, \text{MeCO}_2 \text{H} \) and \( \text{MeCO}_2 \text{H} \) buffer and tris buffer respectively. The Co(II) yield was monitored spectrophotometrically as \( \text{[Co(NCS)}_2]^2 \) by Kitson's method\(^7\) and the quantum yield of Co(II) was calculated as described in our earlier work\(^5\).
Flash photolysis

Conventional flash photolysis experiments were carried out using 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 10KV using a 200J, 1 mF capacitor bank. The power of the capacitor was fed by a high voltage power supply unit. A 12V, 100W quartz tungsten iodine lamp (Phillips, Holland) was used as the source of monitoring beam. The desired wavelength 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, and then displayed on a Scopex 486 oscilloscope and recorded using a CR-550 Y-T recorder. For detecting low intensity signals, a 25 MHz IE-567 transient digitizing oscilloscope was used. The typical growth and decay curves of the transient are shown in Figs 1 and 2. The exponentials were analysed by the first order kinetics relationship: \[ A(t) = A_0 \exp(-k_\text{obs} t) \] to get the pseudo-first order rate constants, where the \( A_0 \)'s denote the output signal (in mV) at the respective times.

\( pK's \) of \( \beta\text{-cis-}[\text{Co(trien)}(\text{OH}_2)_2]^{1+} \) and \( \beta\text{-cis-}[\text{Co(trien)}(\text{OH})(\text{SO}_2\text{-S})]^+ \)

The aqua complexes (5.0 \( \times \) 10\(^{-3} \), and 2.0 \( \times \) 10\(^{-2} \)) for the diaqua and aqua-sulphito complexes respectively, were titrated pH-metrically against NaOH (0.100 or 0.154 mol dm\(^{-3} \)). The pH data in the range 3.4 - 11.7 were analysed for the possible equilibria (1) and (2) for the diaqua complex:

\[
\begin{align*}
\text{(trien)Co(OH)}_2^{1+} & \Leftrightarrow \text{(trien)Co(OH)}_2^{2+} + \text{H}^+ \quad (1) \\
\text{(trien)Co(OH)(OH)}_2^{1+} & \Leftrightarrow \text{(trien)Co(OH)}_2^{2+} + \text{H}^+ \quad (2)
\end{align*}
\]

We obtained \( pK_1 = 5.1 \pm 0.1 \) and \( pK_1 + pK_2 = 15.5 \pm 0.2 \) at 25°C. For the (aqua)(sulphito) complex, the corresponding equilibrium constant (see Eq 3), \( pK_3 \) was 9.0 \( \pm \) 0.1 (25°C, \( I = 1.0 \) mol dm\(^{-3} \)). The value of \( pK_3 \) is in satisfactory agreement with the published data (\( pK_3 = 5.3 \) at 20°C).

\[
\begin{align*}
\text{K}_3 & = \frac{[\text{trien}][\text{Co(OH)}_2(\text{SO}_2\text{-S})]}{[\text{trien}][\text{Co(OH)}(\text{SO}_2\text{-S})]} \quad (3)
\end{align*}
\]

Results and Discussion

Characterisation of O- and S- bonded (aqua)(sulphito)(trien)cobalt(III) complexes

An instantaneous reaction occurs when the diaqua complex is added to sulphite buffer. The absorption
maxima of the diaqua complex \( \lambda_{\text{max}}, \text{nm} (\epsilon, \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}) : 488 (113), 358 (83) \) are replaced by a broad maximum at 512 nm and an intense maximum at 330 nm with \( \epsilon = 141 \) and 1192 dm\(^3\)mol\(^{-1}\)cm\(^{-1}\) [pH = 5.47, \([\text{S}^\text{IV}]_T = 0.05, [\text{complex}]_T = (0.5 - 2.0) \times 10^{-2} \text{mol dm}^{-3} \). This is typical of the formation of the O-bonded sulphito complex. The repetitive spectral scans further indicate that these \( \lambda_{\text{max}} \) shift to 442 and 270 nm with \( \epsilon \) values 185 and 16000 dm\(^3\)mol\(^{-1}\)cm\(^{-1}\) at these wave lengths respectively which agree with spectral parameters of the (aqua)(S-bonded sulphito) complex (see Experimental Section). Figure 3 depicts such changes in the wave length range 400 - 600 nm. This is typical of the transformation of the O-sulphito complex to its S-bonded analogue. At pH \( \geq 5 \) reduction of cobalt(III) by \( \text{S}^\text{IV} \) is not significant as indicated by the Co(II) test. However, when this reaction was carried out at pH 3, there was positive test for Co(II) and reduction could be accelerated by heating the reaction mixture. Evidently the fast formation of the O-sulphito complex is followed by the slow ligand isomerisation and redox processes.

The \( \beta \)-arrangement of trien around Co(III) is likely to be unaffected during the fast conversion of the diaqua complex to the (aqua)(O-sulphito) complex. However, the ligand isomerisation is slow and S-bonded sulphite is known to exert strong \textit{trans}-activating influence. It is, however, important to note that the \(^1\text{H} \) NMR spectrum of the S-bonded (aqua)(sulphito)(trien)cobalt(III) displayed three groups of signals at \( \delta(\text{ppm}) 2.28 - 2.67, 2.88 - 3.03, \) and 3.06 - 3.27 with complex splitting pattern (see Fig. 4). This is characteristic of the three (-CH\(_2\)-CH\(_2\)-) units in the \textit{cis}-\( \beta \) arrangement of trien in ([Co(trien)(OH\(_2\))(SO\(_3\)-S)]\(^+\)). We further suggest that out of the two \textit{cis}-\( \beta \) isomers (excluding the arrangement of the trien skeleton dictated by the spatial orientation of the N-H proton of the planar sec-N-H), the one with S-SO\(_2\) \textit{trans} to the primary amine group is very unlikely as this would lead to the opening up of the terminal CH\(_2\)-CH\(_2\)-NH\(_2\) arm due to the \textit{trans}-effect of the S-bonded sulphite. Our results are compatible with retention of the gross structure of the complex in the transformation as shown in Scheme 1.

![Fig. 4 1H NMR spectrum of β-cis-(trien)Co(OH\(_2\))(SO\(_3\)-S)\(^+\) in D\(_2\)O.](attachment:image)

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**Fig. 3** Repetitive spectral scans for \( \beta \)-cis-[Co(trien)(OH\(_2\))]\(^+\) (4.0 \times 10^{-3} \text{mol dm}^{-3}) + \text{S}^\text{IV} (0.05 \text{mol dm}^{-3}) \) at pH = 5.28 at 25°C. (1) 2 min, (2) 7 min, (3) 12 min, (4) 17 min, (5) 35 min, (6) 52 min, (7) 67 min, (8) 82 min, (9) 157 min.
Equilibrium constant for the formation of O-sulphito complex

The initial rapid equilibrium between the diaqua complex and $S^\text{VI}$ was studied spectrophotometrically at 25°C and $I = 1.0 \text{ mol dm}^{-3}$. The absorbances of the reaction mixtures (at 380 nm) were measured within 60 s of mixing the reactants to avoid complications due to secondary reactions as mentioned earlier. The absorbance data were collected at a fixed total $[\text{Co}^{III}]_\text{T}$ ($= 5.0 \times 10^{-4} \text{ mol dm}^{-3}$) and varying $[S^\text{VI}]_\text{T}$ ($0 \leq [S^\text{VI}]_\text{T} / \text{mol dm}^{-3} \leq 0.08$) and $\text{pH } (3.18 \leq \text{pH} \leq 5.07)$. In terms of the equilibria shown below, the absorbance ($A_{\text{obs}}$) for a fixed total concentration of the aqua complex under varying pH and $[S^\text{VI}]_\text{T}$ (see Table 1), may be expressed by Eq (4),

$$Q = \frac{A_{\text{obs}}}{(\text{trien})\text{Co(OH)}_2(\text{OH}^+)^+ + \text{SO}_4^- \Leftrightarrow (\text{trien})\text{Co(OH)}_2(\text{OSO}_2^-\text{O})^+ + \text{H}^+}$$

$$K_i = \frac{[S^\text{VI}]_\text{T}}{[\text{SO}_4^\text{II}^- + \text{H}^+ \Leftrightarrow \text{HSO}_4^-; \text{HSO}_4^- + \text{H}^+ \Leftrightarrow \text{SO}_2^-]}$$

$$A_{\text{obs}} = \frac{[S^\text{VI}]_\text{T}}{1 + K_i[H^+] + K_i[H^+] + K_i[H^+] + K_i[H^+]} \cdots \cdots (4)$$

where $A_{\text{obs}} = A_{\text{obs}}$ at $[S^\text{VI}]_\text{T} = 0$, and $A^*$ for complete conversion of the aqua complex to the mono-O-sulphito complex, $(\text{trien})\text{Co(OH)}_2(\text{OSO}_2^-\text{O})^+$ respectively and $K_i$ is the acid dissociation constant of the diaqua complex (see Eq 1). The fraction $f_i (= [H^+]^2/[H^+ + K_i[H^+] + K_i[H^+]])$ denoting the fraction of $[S^\text{VI}]_\text{T}$, as $[SO_2^-]$ could be calculated using the known values of the acid dissociation constants of $SO_2^-$ (see foot note d of Table 1). The absorbance changes in the range 0.079 - 0.893 were monitored. Data fitted to Eq (4) using a constant weighting factor (w = 1.0) for all data points yielded $A^* = 34.7 \pm 4.7$, and $Q = 41.8 \pm 6.1$ with a reasonably good fit as indicated by the matching of $A_{\text{obs}}$ with $A_{\text{cal}}$ (see Table 1).

Table 1 - Absorbance data for the initial rapid equilibrium between $(\text{trien})\text{Co(OH)}_2(\text{OSO}_2^-\text{O})^+$ and $S^\text{VI}$

<table>
<thead>
<tr>
<th>pH b</th>
<th>$[S^\text{VI}]_\text{T}$ (mol dm$^{-3}$)</th>
<th>obs $A^*$</th>
<th>cal $A^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.18</td>
<td>0.005</td>
<td>0.260</td>
<td>0.178</td>
</tr>
<tr>
<td>3.20</td>
<td>0.010</td>
<td>0.305</td>
<td>0.262</td>
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<td>3.25</td>
<td>0.020</td>
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<td>0.395</td>
</tr>
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<td>3.30</td>
<td>0.030</td>
<td>0.490</td>
<td>0.493</td>
</tr>
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<td>3.35</td>
<td>0.040</td>
<td>0.525</td>
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</tr>
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<td>3.40</td>
<td>0.050</td>
<td>0.580</td>
<td>0.543</td>
</tr>
<tr>
<td>3.45</td>
<td>0.070</td>
<td>0.689</td>
<td>0.696</td>
</tr>
<tr>
<td>3.60</td>
<td>0.080</td>
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</tr>
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</tr>
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</tr>
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<td>0.160</td>
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<tr>
<td>4.60</td>
<td>0.180</td>
<td>0.996</td>
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*25°C, $[\text{Co}^{III}]_T = 5.0 \times 10^{-4}$, $I = 1.0$ mol dm$^{-3}$; $b$ $[\text{H}^+] = \text{pH} - 0.1$; $c$ $\lambda = 380$ nm, cell path = 1 cm, $A^* = 0.078 \pm 0.001$ in the range pH studied. $d$ see Eq (4). $A_{\text{cal}}$ values are based on $pK_i = 1.92$, $pK_i = 6.3$ and $pK_i = 5.1$; $\Sigma [A_{\text{cal}} - A_{\text{obs}}]^2$ = 0.065 for 24 data points.

Formation of $\beta$-cis-$(\text{trien})\text{Co(OH)}_2(\text{OSO}_2^-\text{O})^+$

The rate constants at 15.0 - 30°C, 0.01 $\leq [S^\text{VI}]_T / \text{mol dm}^{-3} \leq 0.08$, 6.0 $\leq \text{pH} \leq 7.0$ ($I = 1.0$ mol dm$^{-3}$) are collected in Table 2. In this pH range, the diaqua complex ($pK_i = 5.1$) will exist predominantly as the (aqua)(hydroxo) species while the $S^\text{VI}$ will be distributed as the equilibrium mixture of $SO_2^-$, $HSO_4^-$, and $SO_3^2$'. Preliminary calculation showed that the dimerisation of $HSO_3^-$ to disulphite ($2HSO_3^- = S_2O_4^{2-} + H_2O$; $Q_{10} = 0.088$ dm$^{-1}$, $I = 1.0$ mol dm$^{-3}$) is not significant. The fast formation of the $O$-bonded sulphito complex, as stated earlier, is due to the reaction of $SO_2^-$ with the (aqua-hydroxo) species (see Eq. 5):

$$k_i \cdot (\text{trien})\text{Co(OH)}_2(\text{OH}^-)^+ + \text{SO}_2^- \Leftrightarrow (\text{trien})\text{Co(OH)}_2(\text{OSO}_2^-\text{O})^+ + \text{H}^+ \cdots \cdots (5)$$

for which...
The value of \( k_r \) is comparable to that for
\[
 t[(tren)Co(OH)_{3}](OH)_{1}^{+} \text{ (tren} = \beta, \beta', \beta'' \text{ triamino triethylamine, } k_r = (5.3 \pm 0.4) \times 10^7 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1} \text{ at } 25^\circ \text{C, } I = 1.0 \text{ mol dm}^{-3})^{10} \text{ but is lower by a factor of 3 - 10 for several other hydroxo(amine)cobalt(III) species (see data collected in Table 11 of ref 5). This difference largely rests on relatively higher value of activation enthalpy for the trien complex the effect of which is not adequately compensated by the substantially large value of activation...}

\( k_{\text{so}} = k_r[S^0]/(H^+ + K_r + [H^+] \text{)} \) \( \cdots (6) \)

Data fitted to Eq. (6) yielded statistically insignificant value of \( k_r \). Hence the term, \( k_r[H^+] \), was neglected in the final calculation. A constant value of \( pK_r \) (5.1) was chosen; \( k_r \) values were however, not significantly sensitive to the variation of \( pK_r \) (as \( K_r/[H^+] \) is greater than 7). The calculated values of \( k_r \) and the associated activation parameters are collected in Table 2.
entropy. It is, however, evident that $\Delta S^e$ value for the formation of the O-sulphito complexes increases in tune with the increasing value of $\Delta H^e$. This is attributed to the usual compensation effect owing to the solvation requirements of the initial state and transition state of the reaction when the intimate mechanism is unperturbed. It is further worth noting that the (diaqua)(trien)cobalt(III) did not undergo substitution of the aqua ligand by SO$_3^-$ while El-Awady et al. reported such a reaction for the corresponding tren complex.

From the values of the equilibrium constant $'Q'$ and $k_p$, we calculated the $H^+$-catalysed SO$_3^-$ elimination rate constant for the O-sulphito complex ($k = k_p/Q$) as (1.1 ± 0.2) x 10$^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ (25°C, I = 1.0 mol dm$^{-3}$) which may be compared with those for cis-[N$_4$Co(OH)$_2$(OSO$_3^-$-O)]$^+$ (10$^9$$k = 1.5$, 4.1, 0.75, 0.14 dm$^3$ mol$^{-1}$ s$^{-1}$ at 25°C, I = 1.0 mol dm$^{-3}$ for N$_4$ = tren, tetren, (1,2 diaminopropane), (1,3 diaminopropane)(see data collected in Table 11 of ref 5)). The variation of $k_p$ with the cobalt(III) substrates is a consequence of the solvation demand of the substrates as the mechanism of the reaction involves a transition state in which S-O bond breaking is envisaged.

**Steady state photolysis**

The photoinduced electron transfer between Co$^{III}$ and S$^{IV}$ centres in (trien)Co(OH)$_2$(SO$_3^-$-S)$^+$ was studied at 25°C. The quantum yield of Co$^0$, $\phi$(Co$^{II}$), at 1.2 ≤ pH ≤ 8.52 collected in Table 3 shows a decreasing trend with the increase in pH. There was no redox reaction at pH ≥ 8.52. The S-bonded aqua sulphito complex is highly stable to any of the thermal reactions such as redox, aquation and Co$^{III}$ - SO$_3^-$ → Co$^{II}$ - OSO$_3^-$ isomerisation. The observed trend is similar to what has been reported by us for the trans- bis (diamine) Co(OH)$_2$(SO$_3^-$) complexes.

The spectral behaviour (200 - 600 nm) of the (aqua)sulphito complex during photolysis is presented in Fig 5. There is no evidence of the formation of any long lived intermediate in the time scale of measurement. However, the steady decrease of absorbance at all wave lengths is a consequence of the photo induced redox reaction.

$$\text{hv} \rightarrow \text{Co}^{III}-(\text{trien})(\text{OH})(\text{SO}_3^->\text{S}^->\text{S}^2-+\text{Co}^{II}\text{products})$$

The kinetics was followed at 480 nm and the rate constants were calculated by fitting the absorbance - time data to $A_t - A_0 = (A_0 - A_\infty)\exp(-k_{obs}t)$ in the range of pH 2.88 - 5.70. At pH 6.1 and 7.01, less than 40% of the reaction could be monitored and $k_{obs}$ data were calculated using appropriate $A_\infty$ value judged from those at lower pH. Reduction could not be observed spectrally at pH 8.23 thus supporting the observed zero value of $\phi$(Co$^{II}$) at this pH. The rate constants (see Table 3) are comparable to those for the trans-(en)$_2$Co(OH)$_2$(SO$_3^-$- S)$^+$. The contrasting feature of (trien)$_2$Co(OH)$_2$(SO$_3^-$-S)$^+$ with trans-(en)$_2$Co(OH)$_2$(SO$_3^-$-S)$^+$ was that $k_{obs}$ for the

<table>
<thead>
<tr>
<th>pH</th>
<th>$10^3k_{obs}$ (s)$^{-1}$</th>
<th>pH</th>
<th>$\phi$(Co$^{II}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.28</td>
<td>9.9 ± 0.4</td>
<td>1.28</td>
<td>0.40</td>
</tr>
<tr>
<td>3.17</td>
<td>8.6 ± 0.4</td>
<td>3.95</td>
<td>0.39</td>
</tr>
<tr>
<td>3.95</td>
<td>6.2 ± 0.7</td>
<td>3.95</td>
<td>0.39</td>
</tr>
<tr>
<td>5.10</td>
<td>5.3 ± 0.6</td>
<td>5.10</td>
<td>0.34</td>
</tr>
<tr>
<td>5.70</td>
<td>3.9 ± 0.2</td>
<td>5.70</td>
<td>0.32</td>
</tr>
<tr>
<td>6.10</td>
<td>1.0 ± 0.2</td>
<td>6.10</td>
<td>0.21</td>
</tr>
<tr>
<td>7.01</td>
<td>0.56 ± 0.14</td>
<td>7.01</td>
<td>0.20</td>
</tr>
<tr>
<td>8.23</td>
<td>no reduction</td>
<td>8.23</td>
<td>Co$^2$ could not be detected</td>
</tr>
</tbody>
</table>

*λ = 480 nm, [complex]$_0$ = 1.0 x 10$^{-3}$, $I$ = 1.0 mol dm$^{-3}$, *b* λ = 254 nm, ionic strength not adjusted.
former showed a steady decrease with increase in pH while for the latter it maximised around pH 4. Also it is important to note that the trien complex, particularly at higher pH, is more resistant to photo-reduction as compared to its (en)_2 analogue. This is due to the rigidity inflicted by the multidentate ligand to attain the transition state for electron transfer.

**Flash photolysis**

Flash photolysis of (trim)Co(OH)₂(SO₂⁻S)⁺ clearly indicated the formation and decay of a transient which was monitored at 390nm (see Figs 1 and 2). At pH 6.09 and 8.01 we obtained $k_{obs} = 4.9 \pm 0.1$ and $2.7 \pm 0.1$ s⁻¹ (25°C) respectively for the formation of the transient. These values are at least 1000 fold smaller than the rate constants for the photoinduced linkage isomerisation of the coordinated sulphite in trans-Co(AA)₂(OH)₂(SO₂⁻S)⁻ $\{k_{obs} = (4.1 \pm 0.5) \times 10^4$ and $(3.2 \pm 1.3) \times 10^4$ s⁻¹ at 25°C for AA = 1.2 diaminoethane and 1.3-diaminopropane respectively\}. Similar behaviour was present in the presence of air and in argon saturated solution.

The decay of the transient occurred at a longer time scale (see Fig. 2). The decay curve at 390 nm yielded $k_{obs} = 1.03 \pm 0.07$ s⁻¹ and $4.3 \pm 0.13 \times 10^2$ s⁻¹ at pH = 6.10 and 8.01 respectively (25°C, $I = 1.0$ mol dm⁻³ argon saturated solution) from which we calculate $k_{ll} = k_{obs}/[H⁺] = 1.0 \times 10^6$ and $3.5 \times 10^5$ dm³ mol⁻¹ s⁻¹ respectively. These values agree satisfactorily with the acid catalysed SO₂ elimination rate constant for the O-sulphito complex calculated from its formation rate constant and the equilibrium data as mentioned above. A higher value of $k_{ll}$ at pH 8.01 might be indicative of the contribution of the base catalysed hydrolysis. Thus we are led to believe that the flash photolysis of the S-bonded sulphito complex generated O-sulphito complex as the transient which underwent acid catalysed decomposition to SO₂ and the corresponding aqua-hydroxo complex.

The very large difference in the photochemical linkage isomerisation of the S-sulphito complexes might be due to the flexibility of the diamine skeleton in comparison to the rigidity of the trien frame as also the stereochemical consequence. However, further work needs to be done to understand this aspect.

---

**Table 4 - Rate data for the thermal redox and isomerisation of β-cis-trimCo(OH)₂(SO₂⁻S)⁺ collected by Co⁹ assay.**

<table>
<thead>
<tr>
<th>Temp/°C (± 0.1°C)</th>
<th>pH</th>
<th>[S⁻³]</th>
<th>$10^6k_{obs}$ (s⁻¹)</th>
<th>$A_\infty$ (obs)</th>
<th>$10^6k_{eq}$ (s⁻¹)</th>
<th>$10^6k_{ll}$ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.0</td>
<td>3.10</td>
<td>0.050</td>
<td>0.87 ± 0.06</td>
<td>0.424</td>
<td>0.28 ± 0.03</td>
<td>0.44 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>3.10</td>
<td>0.10</td>
<td>0.84 ± 0.10</td>
<td>0.436</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.31</td>
<td>0.050</td>
<td>1.14 ± 0.12</td>
<td>0.397</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.61</td>
<td>0.10</td>
<td>1.17 ± 0.17</td>
<td>0.348</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.0</td>
<td>3.74</td>
<td>0.050</td>
<td>1.62 ± 0.17</td>
<td>0.421</td>
<td>0.38 ± 0.14</td>
<td>0.74 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>3.80</td>
<td>0.10</td>
<td>1.60 ± 0.20</td>
<td>0.455</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.69</td>
<td>0.050</td>
<td>1.39 ± 0.31</td>
<td>0.222</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.45</td>
<td>0.10</td>
<td>1.36 ± 0.14</td>
<td>0.313</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>3.65</td>
<td>0.050</td>
<td>3.02 ± 0.19</td>
<td>0.534</td>
<td>0.86 ± 0.30</td>
<td>1.10 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>3.82</td>
<td>0.10</td>
<td>3.31 ± 0.29</td>
<td>0.472</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.57</td>
<td>0.050</td>
<td>2.34 ± 0.30</td>
<td>0.329</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.55</td>
<td>0.10</td>
<td>2.44 ± 0.24</td>
<td>0.272</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45.0</td>
<td>3.53</td>
<td>0.050</td>
<td>4.85 ± 0.36</td>
<td>0.500</td>
<td>1.10 ± 0.5</td>
<td>1.34 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>3.75</td>
<td>0.10</td>
<td>4.18 ± 0.56</td>
<td>0.472</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.51</td>
<td>0.050</td>
<td>2.25 ± 0.66</td>
<td>0.338</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.42</td>
<td>0.10</td>
<td>2.65 ± 0.66</td>
<td>0.344</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Δ$H$(kJ mol⁻¹) 76 ± 12 57 ± 7
Δ$S$(J K⁻¹ mol⁻¹) -81 ± 39 -138 ± 24

$I = 1.0$ mol dm⁻³; $p[H⁺] = pH - 0.1$; $A_\infty = 0.712$
Thermal redox and isomerisation reactions of the O-sulphito complex

The in situ generated O-sulphito complex, \([\text{[trien} \text{Co(OH)}_2(\text{OSO}_2)\text{-}O])^+\), underwent two slow thermal reactions depending upon the pH conditions. At pH \(<4.5\) internal redox and linkage isomerisation of the O-bonded sulphite were competitive. The S-bonded sulphito complex, \([\text{[trien} \text{Co(OH)}_2(\text{SO}_2)^-\text{S}]^+\), was also found to be inert to internal redox as well as reduction of the cobalt(III) centre in the presence of excess \(\text{S}^{\text{IV}}\).

The significantly slow substitution of the aqua ligand of this S-sulphito complex by \(\text{N}_3\) as evidenced from the spectral measurements confirms its cis geometry (i.e., \(\text{OH}_2\) cis to the \(\text{SO}_2\)). It may be noted that \(\text{SO}_4\) was the sole product of \(\text{S}^{\text{IV}}\) oxidation thus indicating that \(\text{SO}_3\) generated in the electron transfer process is rapidly oxidised to \(\text{SO}_4\) by the cobalt(III) species. In the range of pH 3.1 - 4.45 Co\(^{\text{III}}\) yield was \(<60\%\) of [Co\(^{\text{III}}\)]\(_T\). Similar observation was made for the cis-(aqua)(amine)Cobalt(III)-\(\text{S}^{\text{IV}}\) reactions\(^{11}\). Scheme 2 is proposed to depict the sequence of reactions at a constant pH where redox and isomerisation reactions are competitive.

\[
\begin{align*}
\text{Co}^{\text{II}} \text{ product} + \text{SO}_4^{2-} & \quad \text{(slow)} \\
\text{cis}\text{-}[\text{trien} \text{Co(OH)}_2\text{OH}^+ + \text{SO}_2] \Leftrightarrow \text{cis}\text{-}[\text{trien} \text{Co(OH)}_2(\text{OSO}_2)^- + \text{H}^+] \\
\text{fast} & \\
\text{Co}^{\text{II}} + \text{SO}_4^{2-} & \rightarrow \text{Co}^{\text{II}} \text{ product} + \text{SO}_4^{2-} \\
\text{H}_2\text{O}
\end{align*}
\]

Scheme 2 - Redox and isomerisation of the O-bonded sulphito complex

Accordingly the [Co\(^{\text{III}}\)] yield is given by Eq. (7)

\[
[\text{Co}^{\text{III}}] = \left(\frac{2k_{\text{red}}}{k_{\text{obs}}}\right) G \text{[Co}^{\text{III}}]\text{[1 - exp(-}k_{\text{obs}}t)] \quad \text{(7)}
\]

where

\[
k_{\text{obs}} = 2k_{\text{red}} + k_{\text{iso}}, \quad \text{and}
\]

\[
G = \frac{Qf[\text{S}^{\text{IV}}]_T / [\text{H}^+]}{1 + [\text{H}^+] / K_s + Qf[\text{S}^{\text{IV}}]_T / [\text{H}^+]},
\]

the coefficient(2) of \(k_{\text{red}}\) stands for the stoichiometry of the redox reaction and [Co\(^{\text{III}}\)]\(_T\) denotes the total initial concentration of Co\(^{\text{III}}\); all other terms have their usual meaning. Equation (7) can be translated in to absorbance (A) for Co\(^{\text{II}}\) as shown in Eq. (8)

\[
A = A_{\text{obs}} [1 - \exp(-k_{\text{obs}}t)] \quad \text{(8)}
\]

where \(A_{\text{obs}} = (2k_{\text{red}}/k_{\text{obs}}) G A_{\text{e}}\cdot A_{\text{e}}\) being the value of absorbance for complete reduction of Co\(^{\text{III}}\). The rate constants for the redox reaction monitored by Co\(^{\text{II}}\) assay are collected in Table 4. The calculated values of \(2k_{\text{red}} G = (A_{\text{obs}} k_{\text{obs}} / A_{\text{e}})\) (see Table 4) appear to be independent of \([\text{S}^{\text{IV}}]_T\) indicating thereby that the values of \(G\) are close to 1. A sample calculation of the data at 35°C using \(Q = 42, pK_1 = 1.96, pK_2 = 3, pK_3 = 5.1\) confirms this (ca. \(G = 0.771, 0.869, 0.848\) and 0.946). Also using values of \(Q\) in the range 42 - 100 resulted in the insensitivity of \(2k_{\text{red}}\) (= \(8.0 \pm 0.6 - 6.6 \pm 0.3\) x \(10^5\) s\(^{-1}\)) at 30°C. Judging from the weighted residuals, the value of \(Q\) at 30°C is likely to be 80. The values of \(k_{\text{red}}\) were thus calculated assuming \(G = 1.0\) at all temperatures. The values of \(k_{\text{red}}\) and \(k_{\text{iso}}\) (= \(k_{\text{obs}} - 2k_{\text{red}}\)) are collected in Table 4. The isomerisation of the O-sulphito complex to its S-bonded analogue is relatively more facile than its redox transition. This is understandable in terms of greater energy demand for the reorganisation of bonds to attain the transition state for the electron transfer. Accordingly the activation enthalpy for the redox process is relatively higher than the same for the isomerisation process. Similar observations have been reported on related systems\(^{11,12}\). The large negative value of activation entropy for the ligand linkage isomerisation must be linked with a strongly ordered transition state for this process which might, in conjunction with the low value of the activation enthalpy (see Table 4), reflect a associative (concerted) process in which Co-S bond formation has advanced significantly prior to the stretching of the Co-O bond to the limit of breaking.

Acknowledgement

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References

   (b) Dash A C, Jena K C & Das A, Indian J Chem Sec A (a companion paper)