An Intermediate in the Reaction between *trans*-Aquabis(ethylenediamine)sulphitocobalt(III) and Sulphite Ion in Aqueous Solution

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At 25 °C, pH 7.1, and I = 1.00 mol dm^{-3}, the substitution reaction of *trans*-$[Co(en)_2(OH_2)(SO_3)]^+$ by $[SO_3]^{2-}$ proceeds *via* the *O*-bonded intermediate *trans*-$[Co(en)_2(OSO_2)(SO_3)]^-$ as follows:

$$[Co(en)_2(OH_2)(SO_3)]^+ + [SO_3]^{2-} \overset{K_{IP}}{\rightleftharpoons} \underset{\text{ion pair}}{\{[Co(en)_2(OH_2)(SO_3)][SO_3]\}^-}$$

$$\{[Co(en)_2(OH_2)(SO_3)][SO_3]\}^- \xrightarrow{k_1'} [Co(en)_2(OSO_2)(SO_3)]^- + H_2O$$

$$[Co(en)_2(OSO_2)(SO_3)]^- \xrightarrow{k_2} [Co(en)_2(SO_3)_2]^-$$

The values of K_{IP}, k_1'(lim.), and k_2 are 30 ±1 dm^3 mol^{-1}, 20 ±1 s^{-1}, and 59 ±7 s^{-1}.

THE rapid substitution reactions of cobalt(III) complexes containing a sulphite ligand have been studied extensively.[1-4] It has been established that substitution occurs at the position *trans* to the sulphite group which is *S*-bonded[5,6] and it has been suggested that substitution occurs *via* either[3,4] S_N1(lim.) or S_N1(IP) mechanisms.

In a previous paper we showed that in substitution reactions of *trans*-$[Co(en)_2(OH_2)(SO_3)]^+$ (en = ethylenediamine) with cyanometallates to form[4] binuclear complexes, the values of $k_{obs.}$, the first-order rate constants for the substitution reactions, were directly proportional to the concentrations of the cyanometallates. However, it has been shown[3] that in the substitution of $[Co(en)_2(OH_2)(SO_3)]^+$ by $[SO_3]^{2-}$ the rate of this reaction, $-d[Co(en)_2(OH_2)(SO_3)^+]/dt$, becomes independent of the concentration of $[SO_3]^{2-}$ at high concentrations of this substituent, and under these conditions the values of the observed first-order rate constants are smaller than those for the substitution by, for example,[4] $[Fe^{II}(CN)_5(NO)]^{2-}$ which has the same net charge as $[SO_3]^{2-}$, at comparable concentrations of the two substituents. Sulphite ion has shown a similar anomaly in its substitution reactions[2] with *trans*-$[Co(Hdmg)_2(OH_2)(SO_3)]^-$ [Hdmg = dimethylglyoximate(1−)] compared to other substituents.

These observations suggest a special mechanism for the substitution reactions of $[SO_3]^{2-}$, and with this possibility in mind we have re-examined the reaction of $[Co(en)_2(OH_2)(SO_3)]^+$ with $[SO_3]^{2-}$.

EXPERIMENTAL

The complex *trans*-$[Co(en)_2(OH_2)(SO_3)][ClO_4]\cdot H_2O$ was prepared as previously[7] described. All the other chemicals used were of AnalaR grade with the exception of Li[SCN] (Hopkin and Williams, reagent grade) which was recrystallised three times from water. Doubly distilled water was used in all the kinetic experiments. Solutions of $Na[ClO_4]$ and $Li[ClO_4]$, which were used to maintain constant ionic strength, were standardised using the method described previously.

With the exception of several runs at pH 8.1 where 'trizma base' [tris(hydroxymethyl)methylammonium chloride (B.D.H. Laboratory Grade)] buffer was used, the pH of reaction mixtures was varied by altering the relative concentrations of $[HSO_3]^-$ and $[SO_3]^{2-}$ by the addition of $HClO_4$. The pH was measured using a pH meter standardised against phthalate and borate buffers. Solutions of $Na_2[SO_3]\cdot 7H_2O$ were prepared by weight. Changes in optical density with time during reactions were followed using a Durrum D-110 stopped-flow spectrophotometer, and the spectra of reactants and products were obtained using a Unicam SP 800 recording spectrophotometer.

RESULTS

Plots of $\ln(A_\infty - A_t)$ against time for kinetic data obtained at 400 and 430 nm showed slight curvature (Figure 1) and optical densities obtained at 480 nm, where the absorption coefficients of $[Co(en)_2(OH_2)(SO_3)]^+$ and $[Co(en)_2(SO_3)_2]^-$ are the same, at first increased and then decreased with time (Figure 2). These observations are consistent with the formation of an intermediate species of higher absorption coefficient at 480 nm than either the reactant or product. As a result the optical density against time data obtained at all the three wavelengths were analysed by a curve-fitting computer program[8] written for the reaction sequence (1) under conditions

$$[Co(en)_2(OH_2)(SO_3)]^+ + [SO_3]^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Intermediate} \xrightarrow{k_2} [Co(en)_2(SO_3)_2]^- \quad (1)$$

where $[SO_3{}^{2-}] \gg [Co(en)_2(OH_2)(SO_3)^+]$, and the optimised values of k_1, k_{-1}, k_2, and ε (the absorption coefficient of the intermediate) were obtained. The validity of each set of results was assessed using the following criteria. In more than 95% of all the runs k_{-1} was less than 1% of the corresponding value of k_2. When k_{-1} was greater than this, the complete set of results for the parameters was excluded from our calculations of the average values of these constants. The concentration limits for the 5% of runs rejected were within those for the other 95%.

Since in our experiments $[SO_3{}^{2-}] \gg [Co(en)_2(OH_2)(SO_3)^+]$, the pseudo-first-order rate constant k_1' was obtained from

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[1] J. Halpern, R. A. Palmer, and L. M. Blakeley, *J. Amer. Chem. Soc.*, 1966, **88**, 2877.

[2] H. G. Tsaing and W. K. Wilmarth, *Inorg. Chem.*, 1968, **7**, 2535.

[3] D. R. Stranks and J. K. Yandell, *Inorg. Chem.*, 1970, **9**, 751.

[4] K. L. Scott, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1975, 1339.

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[6] E. N. Maslen, C. L. Raston, A. H. White, and J. K. Yandell, *J.C.S. Dalton*, 1975, 327.

[7] K. L. Scott, R. S. Murray, W. C. E. Higginson, and S-W. Foong, *J.C.S. Dalton*, 1973, 2335.

[8] J. R. Chipperfield, A. Hayter, and D. E. Webster, *J.C.S. Dalton*, 1975, 2048.

the relation $k_1' = k_1[SO_3^{2-}]$. It has been shown[9] that expression (2), where $t_{max.}$ corresponds to the time taken

$$t_{max.} = (\ln k_2/k_1')(k_2 - k_1') \qquad (2)$$

for the concentration of the intermediate to reach a maximum (*i.e.* maximum absorbance at 480 nm), is valid provided k_{-1} can be neglected, and where calculated values of $t_{max.}$ using the experimental values of k_1' and k_{-1} deviated from the experimental value of $t_{max.}$ by more than ±10% these results were also rejected from further calculations to obtain average values of the rate constants. Approximately 80% of our results at pH 7.1 satisfied the above criteria and a slightly lower percentage acceptance of results occurred for data at the other pH values. For the results at pH 8.1 the absorbances at infinite time were difficult to estimate due to a minor side reaction that occurred at this pH only. Therefore we used only the data obtained at 480 nm at this pH.

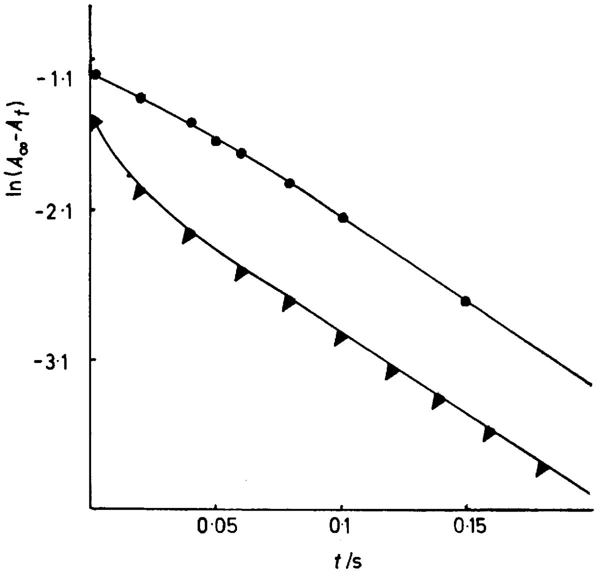

FIGURE 1 Plots of $\ln(A_\infty - A_t)$ against time for kinetic data obtained at 400 (▲) and 430 nm (●), 25 °C, $I = 1.00$ mol dm^{-3}, and pH 5.9. $[Co(en)_2(OH_2)(SO_3)^+] = 1.1 \times 10^{-3}$ and $[Na_2SO_3] = 7.3 \times 10^{-2}$ mol dm^{-3}

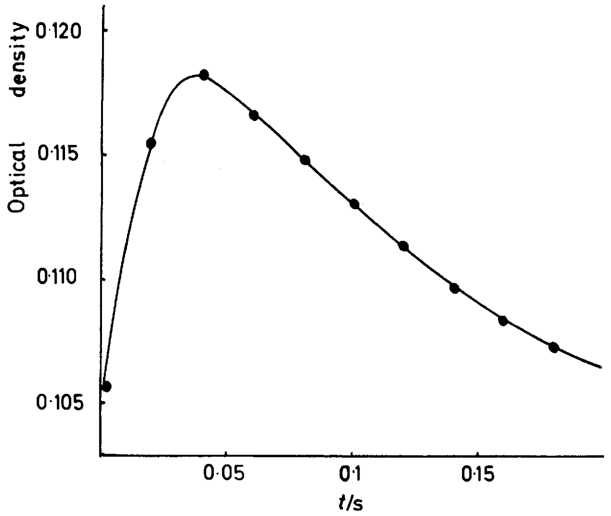

FIGURE 2 Variation of optical density with time for data obtained at 480 nm, 25 °C, $I = 1.00$ mol dm^{-3}, and pH 7.1 $[Co(en)_2(OH_2)(SO_3)^+] = 9.6 \times 10^{-4}$ and $[Na_2SO_3] = 3.7 \times 10^{-2}$ mol dm^{-3}

Values of k_1' at each concentration of sulphite ion are given in Table 1, and the average values of k_2, which were found to be independent of sulphite-ion concentration (Figure 3), are 59 ± 5, 59 ± 7, and 64 ± 8 s^{-1} respectively at pH 8.1, 7.1, and 5.9. Good agreement was obtained between observed and calculated optical densities using the above values of k_1' and k_2 and the corresponding values of the absorption coefficients of the intermediate for all the experimental data including those from experiments which were not used in the determination of the average values of these parameters: for example the average deviation between computed and experimental optical densities did not exceed 6.5% for more than 99% of all the runs and in 95% of our experiments the average deviation was less than 5%. Included in Table 1 are values of k_1' and k_2 obtained under identical experimental conditions from measurements at 480, 430, and 400 nm, and it can be seen that the values of the rate constants are independent of the wavelength used.

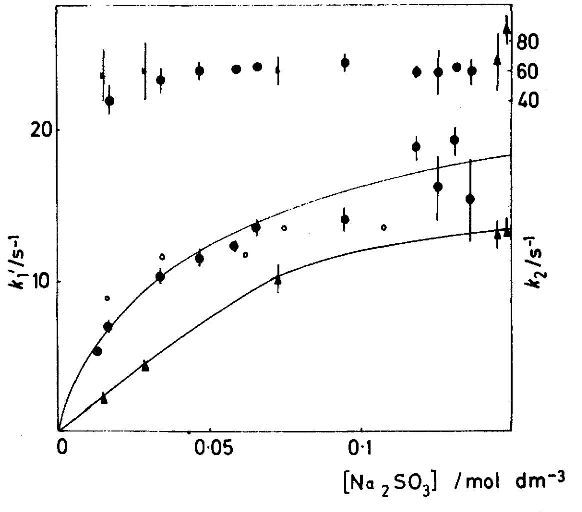

FIGURE 3 Variation of k_1' and k_2 with $[SO_3^{2-}]_T$ at 25 °C and $I = 1.00$ mol dm^{-3}: pH 5.9 (▲) and 7.1 (●); (○), data from ref. 3 (pH 8.1)

Included in Figure 3 is a plot of k_1' against $[SO_3^{2-}]$ for the data at pH 7.1 and 5.9, and the corresponding results obtained by Stranks and Yandell[3] are included for comparison.

For the ion-pair mechanism to be discussed later it can be shown that equation (3) is applicable. Plots of $(k_1')^{-1}$

$$k_1' = \frac{k_1'(\text{lim.})K_{IP}[SO_3^{2-}]}{1 + K_{IP}[SO_3^{2-}]} \qquad (3)$$

against $[SO_3^{2-}]^{-1}$ were linear and the gradients and intercepts were found by least-squares calculations to be $(3.0 \pm 0.2) \times 10^{-3}$ mol dm^{-3} s^{-1} and $(3.0 \pm 0.3) \times 10^{-2}$ s, $(1.67 \pm 0.03) \times 10^{-3}$ mol dm^{-3} s^{-1}, and $(5.0 \pm 0.1) \times 10^{-2}$ s, and $(5.7 \pm 0.2) \times 10^{-3}$ mol dm^{-3} s^{-1} and $(3.0 \pm 0.6) \times 10^{-2}$ s at pH 8.1, 7.1, and 5.9 respectively. The respective values

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[9] S. Glasstone, 'Textbook of Physical Chemistry,' Macmillan, 1962, p. 1077.

of k_1'(lim.), the limiting values of k_1' at high concentrations of sulphite [where k_1'(lim.) = intercept^{-1} and K_{IP} = (intercept) (gradient)$^{-1}$ in the later discussion] are 33 ± 3, 20 ± 1, and 33 ± 5 s^{-1}. Stranks and Yandell obtained a value of k_1'(lim.) of 13.4 s^{-1} derived from first-order plots of spectrophotometric data at 432 nm and pH 8.1;. their lower value is probably due to contributions to the gradients of these plots of the slight curvature shown in Figure 1.

TABLE 1

Kinetics of formation and isomerism of the intermediate[a] in the reaction between $[Co(en)_2(OH_2)(SO_3)]^+$ and $[SO_3]^{2-}$ at 25.0 °C

pH	$10^4[Co(en)_2(OH_2)(SO_3)^+]$ / mol dm^{-3}	$[SO_3^{2-}]_T$ [b] / mol dm^{-3}	k_1' / s^{-1}	k_2 / s^{-1}	Number of runs
8.1 [c]	9	0.037	9.1 ± 0.1	49 ± 3	3
c	9	0.074	13.5 ± 1.3	59 ± 6	6
c, d	9	0.136	19.6 ± 2.2	64 ± 6	5
c	9	0.147	20.4 ± 1.0	62 ± 6	5
7.1	10	0.013	5.3 ± 0.1	42 ± 2	3
	10	0.017	7.0 ± 0.3	41 ± 10	11
	10	0.034	10.4 ± 0.4	54 ± 8	12
	10	0.047	11.5 ± 0.4	59 ± 6	10
	10	0.059	12.3 ± 0.3	60 ± 1	6
	10	0.066	13.5 ± 0.5	62 ± 2	6
	10	0.095	14.1 ± 0.9	65 ± 6	8
	10	0.119	18.8 ± 0.8	58 ± 2	4
	20	0.126	18.3 ± 2.9	64 ± 6	9
	10	0.126	16.3 ± 2.3	60 ± 15	10
	8	0.126	16.5 ± 1.6	66 ± 6	10
	5	0.126	17.5 ± 1.8	61 ± 6	10
	3	0.126	18.3 ± 1.3	55 ± 5	4
	10	0.132	19.3 ± 0.9	61 ± 1	3
e	10	0.137	15.2 ± 2.7	57 ± 5	12
	10	0.137	15.2 ± 2.7	62 ± 12	11
f	10	0.137	14.5 ± 0.1	73 ± 7	9
g	10	0.137	16.4 ± 0.3	50 ± 11	5
c	10	0.137	16.7 ± 3.4	26 ± 8	8
h	10	0.172	15.4 ± 2.8	67 ± 12	8
5.9	11	0.015	2.4 ± 0.1	57 ± 17	5
	11	0.029	4.5 ± 0.1	60 ± 19	9
	11	0.073	10.1 ± 0.9	60 ± 10	3
	11	0.146	13.1 ± 0.9	67 ± 20	8
	11	0.149	13.6 ± 0.4	88 ± 10	8

[a] The absorption coefficients of the intermediate were found to be 1 060 ± 85, 260 ± 30, and 320 ± 40 dm^3 mol^{-1} cm^{-1} at 400, 430, and 480 nm respectively. [b] $[SO_3^{2-}]_T = [SO_3^{2-}] + [HSO_3^-]$. [c] Optical densities were recorded at 480 nm only. Except where otherwise specified, all the other kinetic data were obtained from combined results at 400, 430, and 480 nm. [d] Solution contained tris(hydroxymethyl)aminomethane buffer (0.4 mol dm^{-3}). [e] Oxygen excluded. [f] Measurements at 400 nm. [g] Measurements at 430 nm. [h] Ionic strength = 1.13 mol dm^{-3}. In all other cases I = 1.00 mol dm^{-3}.

TABLE 2

Kinetic data for the substitution reactions of $[Co(en)_2(OH_2)(SO_3)]^+$ (1.2 × 10^{-3} mol dm^{-3}) with $[SCN]^-$ at 25 °C and I = 1.00 mol dm^{-3}

$10^2[SCN^-]$ / mol dm^{-3}	$k_{obs.}$ / s^{-1}
50	148 ± 13
30	83 ± 4
15.0	41 ± 2
10.0	28 ± 0.7
5.0	14.7 ± 0.2
1.00	3.1 ± 0.1
0.50	1.40 ± 0.3

In order to confirm that the direct dependence of the first-order rate constant on the concentration of the substitution reactions of $[Co(en)_2(OH_2)(SO_3)]^+$ by species other than sulphite was a general phenomenon, some runs were carried out with thiocyanate ion. These results, which show a direct dependence of $k_{obs.}$, the first-order rate constant, on the concentration of thiocyanate ion, are given in Table 2. From these data the second-order rate constant for the substitution of $[Co(en)_2(OH_2)(SO_3)]^+$ by $[SCN]^-$ was found to be 294 ± 5 dm^3 mol^{-1} s^{-1} at 25 °C and I = 1.0 mol dm^{-3} compared with the corresponding rate constant for the substitution by $[Fe^{II}(CN)_6]^{4-}$ of 7 450 dm^3 mol^{-1} s^{-1}.[4]

DISCUSSION

For the reaction scheme described in (1), under conditions where $[SO_3^{2-}] \gg [Co(en)_2(OH_2)(SO_3)^+]$, it was not possible to decide unambiguously[9] from our experiments which of the rate constants, k_1' or k_2, refers to the first and second stages of the reaction respectively, although this would be possible if independent estimates of k_1' or k_2 could be obtained. Although we were unable to obtain these, we feel that the inversion of the values of k_1' and k_2 in Table 1 would be unsatisfactory since this would require the rate of the first step of the reaction to be dependent on the concentration of $[Co(en)_2(OH_2)(SO_3)]^+$ and independent of the concentration of sulphite ion, and such a reaction would be expected to be important in the substitution reactions of $[Co(en)_2(OH_2)(SO_3)]^+$ by other substituents. However, in the reactions[4] with $[SCN]^-$ and $[Fe^{II}(CN)_6]^{4-}$ at high concentrations of substituent the overall first-order rate constants for the substitution reactions exceed the average value of k_2 under the same experimental conditions.

We suggest that the intermediate species formed in the reaction between $[Co(en)_2(OH_2)(SO_3)]^+$ and $[SO_3]^{2-}$ is the linkage isomer $[Co(en)_2(OSO_2)(SO_3)]^-$ where the incoming sulphite is *O*-bonded. Although the *S*-bonded isomers are believed [2,3] to be more stable, *O*-bonded intermediates have been suggested previously in substitution [2,10] and redox [11] reactions. When the data are interpreted in this way, the values of k_2 in the Table refer to the internal isomerisation of $[Co(en)_2(OSO_2)(SO_3)]^-$ to $[Co(en)_2(SO_3)_2]^-$ which, as expected, is independent of the total concentration of the sulphite ion (Figure 3).

The most important difference between the substitution reactions of $[Co(en)_2(OH_2)(SO_3)]^+$ by $[SO_3]^{2-}$ and other substituents such as $[Fe^{II}(CN)_6]^{4-}$ and $[SCN]^-$ is that the former reaction attains a limiting rate, $-d[Co(en)_2(OH_2)(SO_3)^+]/dt$, at high concentrations of sulphite ion. It has been suggested previously that the substitution by $[SO_3]^{2-}$ occurs by a S_N1(lim.) mechanism, (4) and (5), where the rate-determining step is the loss of a water ligand.

$$[Co(en)_2(OH_2)(SO_3)]^+ \rightleftharpoons [Co(en)_2(SO_3)]^+ + H_2O \quad (4)$$

$$[Co(en)_2(SO_3)]^+ + [SO_3]^{2-} \longrightarrow [Co(en)_2(SO_3)_2]^- \quad (5)$$

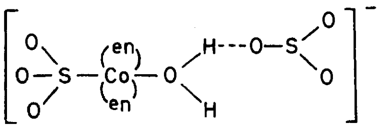
An alternative S_N1(IP) scheme, (6)—(8), has been proposed for the substitution by cyanometallates.[4]

$$[Co(en)_2(OH_2)(SO_3)]^+ + X^{n-} \xrightleftharpoons{K_{IP}(X^{n-})} \{[Co(en)_2(OH_2)(SO_3)][X]\}^{(1-n)+} \quad (6)$$

$$\{[Co(en)_2(OH_2)(SO_3)][X]\}^{(1-n)+} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \{[Co(en)_2(SO_3)][X]\}^{(1-n)+} + H_2O \quad (7)$$

$$\{[Co(en)_2(SO_3)][X]\}^{(1-n)+} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} [Co(en)_2(SO_3)X]^{(1-n)+} \quad (8)$$

The substitution reactions of $[Co(en)_2(OH_2)(SO_3)]^+$ can be rationalised by the former [S_N1(lim.)] mechanism for substitution by sulphite only if the reactions of substituents other than sulphite occur with some assistance from the incoming group. Alternatively we suggest that all the substituents react *via* the S_N1(IP) scheme, with the sulphite ion occupying a preferred position in the second co-ordination sphere, due perhaps to hydrogen bonding, whereas the positions of ion pairing by substituents such as cyanometallates and thiocyanate ion are less restricted. Provided the position of ion pairing for sulphite ion relative to the other substituents is more remote from the aqua-ligand, a correspondingly lower value of k_8/k_{-7} might be expected [$k_1' = K_{IP}k_7k_8(k_{-7} + k_8)^{-1}$]. However, we note that our results do not exclude the possibility that ion pairing occurs between the aqua-ligand and the sulphite ion, which might result in a reduction in the rate of cleavage of the cobalt–oxygen bond of the water ligand.



Values of K_{IP} of 10 ± 3, 30 ± 1, and 5 ± 1 $dm^3\ mol^{-1}$ were obtained from the data at pH 8.1, 7.1, and 5.9 respectively. The value at pH 8.1 is lower than expected on the basis of the results at pH 7.1. However, we feel that the latter data are more reliable for the reasons already stated. The lower value of K_{IP} at pH 5.9 is consistent with a lower value of $K_{IP}(HSO_3^-)$ compared to $K_{IP}(SO_3^{2-})$ which is expected due to the lower charge of the former. (At pH 5.9 *ca.* 75% of the total sulphite species exist as $[HSO_3]^-$.[12]) From the data at pH 7.1 and 5.9 we estimate $K_{IP}(SO_3^{2-})$ to be *ca.* 35 $dm^3\ mol^{-1}$; unfortunately our data were not sufficiently accurate to give an estimate of $K_{IP}(HSO_3^-)$. This value for $K_{IP}(SO_3^{2-})$ is higher than that predicted [4] for the more highly charged $[Fe^{II}(CN)_6]^{4-}$, and this difference may reflect the contribution to the stability of the $\{[Co(en)_2(OH_2)(SO_3)][SO_3]\}^-$ ion pair by hydrogen bonding. Such bonding has been suggested [6] between the sulphito-ligand and the hydrogen atoms of the ethylenediamine ligands in solid $[Co(en)_2(OH_2)(SO_3)][ClO_4]\cdot H_2O$.

We conclude that it is not necessary to postulate a special mechanism, (9), for the formation of the intermediate which does not involve breakage [2,10] of the cobalt–oxygen bond

$$[Co(en)_2(^*OH_2)(SO_3)]^+ + [SO_3]^{2-} \longrightarrow [Co(en)_2(^*OSO_2)(SO_3)]^- + H_2O \quad (9)$$

since the limiting value of k_1' at high concentrations of sulphite ion is much less than the observed first-order rate constants for the substitution by $[Fe^{II}(CN)_5(NO)]^{2-}$, which has the same charge as $[SO_3]^{2-}$, at comparable concentrations of the substituents. However, the substitution reaction of *trans*-$[Co(en)_2(OH_2)(OH)]^{2+}$ by $[SO_3]^{2-}$ is known [10] to be more rapid than the solvent-exchange reaction and we intend investigating this and related reactions in the future.

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