Kinetics and Mechanisms of the Reduction of μ-Amido-μ-superoxo- and μ-Amido-μ-peroxo-bis[bis(ethylenediamine)cobalt(III)] Complexes by Sulphite, Nitrite, and Arsenite in Aqueous Solutions: Evidence for Bonded and Non-bonded Activated Complexes in the Reduction of Dioxygen-bridged Complexes

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The μ-amido-μ-superoxo-complex $(en)_2Co{\cdot}\mu(NH_2,O_2){\cdot}Co(en)_2^{4+}$ and the μ-amido-μ-peroxo-complex $(en)_2Co{\cdot}\mu(NH_2,O_2){\cdot}Co(en)_2^{3+}$ both react with sulphite ions to give the μ-amido-μ-sulphato-complex $(en)_2Co{\cdot}\mu(NH_2,SO_4){\cdot}Co(en)_2^{3+}$. The μ-amido-μ-superoxo-reaction proceeds with the intermediate formation of the μ-amido-μ-peroxo-complex and the sulphite radical. Stoicheiometries at pH 1—3 are (complex:sulphite) 2:3 for the superoxo- and 1:1 for the peroxo-complex, and rate laws are of the form k_s[superoxo][SO_3^{2-}] and k_p[peroxo][H_2SO_3] respectively, where $k_s = 3{\cdot}80(\pm0{\cdot}07) \times 10^4$ l mol^{-1} s^{-1} and $k_p = 55{\cdot}4(\pm6{\cdot}1)$ l mol^{-1} s^{-1}, both at 1·4 °C and $I = 1{\cdot}0$M ($LiClO_4$). The protonated μ-peroxo-complex may be the reactive species in the latter, in which case the rate law can be expressed in an alternative form. The complexes also react with nitrite ions to give the μ-amido-μ-nitrito-complex $(en)_2Co{\cdot}\mu(NH_2,NO_2){\cdot}Co(en)_2^{4+}$. With arsenite ions a different reaction path is operative, and the product is the μ-amido-μ-hydroxo-complex, $(en)_2Co{\cdot}(NH_2,OH){\cdot}Co(en)_2^{4+}$.

REACTIONS of molecular oxygen bonded to metals are important processes in the chemistry of living organisms and any insight into the mechanism of the stepwise reduction of oxygen ($O_2 \longrightarrow O_2^- \longrightarrow O_2^{2-}$, *etc.*) is highly relevant. We report in this study the reactions of the μ-amido-μ-peroxo- and μ-amido-μ-superoxo-dicobalt(III) complexes with sulphite, nitrite, and arsenite ions respectively, and consider different mechanisms which are apparent. One unprotonated and two singly protonated forms of the μ-peroxo-complex are present in solution. The μ-superoxo-complex does not protonate.

RESULTS

Stoicheiometries.—The stoicheiometries of the reactions of the μ-superoxo- and μ-peroxo-complexes with sulphite ion were determined at pH 1 and 3. The reaction of the μ-superoxo-complex with sulphite at pH *ca.* 3 involves an intermediate and the colour of solutions changes from green to brown and then to red. The reaction is sensitive to air and it was considered preferable to use triply distilled water. Runs at pH 3·1 in the presence of oxygen gave varying degrees of intermediate colour changes depending on the method of mixing of solutions (sulphite added to complex or *vice-versa*), and this was especially noted at low (*ca.* 2 : 1) concentrations of sulphite and superoxo-complex, and/or with excess of complex, when high values of the stoicheiometry (*ca.* 2 : 1) were obtained. Such inconsistencies in spectrophotometric changes and experimentally determined stoicheiometries were removed when air-free techniques were used and when solutions were prepared in triply distilled water. The anomalous behaviour was assigned to the presence of the sulphite radical, HSO_3, which is known to react with dissolved oxygen.[1] At low pH values no intermediate colour was observed in the μ-superoxo-reaction, and HSO_3 radicals are consumed rapidly by the μ-peroxo-complex. It was not necessary to use strictly air-free techniques under these conditions. No intermediate was apparent in the reaction with the μ-peroxo-complex which is not sensitive to the presence of oxygen. An iodometric method was used to determine the excess of sulphite ion in reactant solutions, the pH of which was controlled, where necessary, using acetate buffer. Results obtained with these various precautions are summarised in Table 1. For all conditions under which the stoicheiometry was determined the final spectrum of the solution showed a maximum absorption at λ 523 nm, ε 372 ± 2 l mol^{-1} cm^{-1}, which is a characteristic of the μ-amido-μ-sulphato-complex (Figure 1).

TABLE 1

The stoicheiometries of the reactions of the superoxo- and peroxo-complexes with sulphite ions as determined iodometrically

Complex	pH	10^4[complex] M	10^3[S^{IV}] M	Stoicheiometry [a]
Peroxo	1·1	9·17	9·2	1·07 [b]
Superoxo	1·1	8·98	9·2	1·59 [b]
Peroxo	3·1	11·0	9·2	1·09 [b]
Superoxo	3·1	9·5	9·2	1·54 [b]
Superoxo	3·1	14·6	5·18	1·58 [c]

[a] Number of mol of sulphite consumed per mol of complex. [b] Room temperature. Singly distilled water used. [c] Triply distilled water, and air-free solutions; temperature 0 °C.

The results obtained are in accordance with overall reactions (1) and (2). The stoicheiometries for the μ-superoxo-reaction (Table 1) are in slight excess of 1·5 : 1. We have considered the possibility that this may be due to contributions from the reaction $2HSO_3 \longrightarrow H_2S_2O_6$. If this is effective and the only reaction of HSO_3, the stoicheiometry would become 2 : 1. Attempts to determine $S_2O_6^{2-}$ by the procedure in ref. 2 indicated <2% formation of $S_2O_6^{2-}$.

$$2\mu(NH_2,O_2^-) + 3SO_3^{2-} + 2H^+ \longrightarrow 2\mu(NH_2,SO_4^{2-}) + SO_4^{2-} + H_2O \quad (1)$$

$$\mu(NH_2,O_2^{2-}) + SO_3^{2-} + 2H^+ \longrightarrow \mu(NH_2,SO_4^{2-}) + H_2O \quad (2)$$

Kinetics of the Reaction of the μ-Amido-μ-peroxo-complex with Sulphite.—At pH <2 the reaction is too fast to study by conventional means even at 0 °C. Scan spectra of the reaction at *ca.* 0 °C, pH 3·4, I = 1·0M ($LiClO_4$) with excess of sulphite gave well defined isosbestics at λ 505 and 572 nm as predicted for the formation of the μ-amido-μ-sulphato-complex. The kinetics were studied spectrophotometrically at λ 523 nm and 1·4 °C, I = 1·0M ($LiClO_4$), with pH in the range 3—4. Plots of absorbance (O.D.) readings log(O.D.$_\infty$ − O.D.$_t$) against time were linear to >70% and first-order rate constants, k_{obs}, obtained from gradients (×2·303) are as summarised in Table 2. Some runs at 25 °C are also included. Rate constants k_{obs} are first order in total sulphite concentration [S^{V}] (Figure 2),

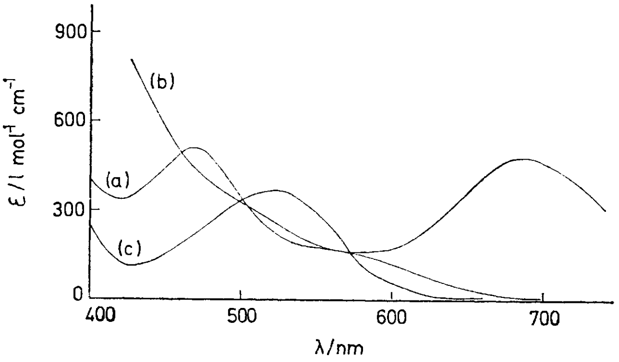

FIGURE 1 Visible absorption spectra of dicobalt(III) complexes; (a) μ-amido-μ-superoxo-complex at pH 3; (b) μ-amido-μ-peroxo-complex at pH 3; (c) μ-amido-μ-sulphato-complex in 0·1M $HClO_4$

TABLE 2

Pseudo-first-order rate constants, k_{obs}, for the reaction of μ-amido-μ-peroxo-complex with sulphite ions, I = 1·0M ($LiClO_4$); λ 523 nm

Temp. °C	10^4[peroxo] M	10^3[S^{IV}] M	10^4[H+] [a] M	10^4k_{obs} s^{-1}
1·4	2·20	2·25	1·12 [b]	2·4
	2·20	4·50	1·12	4·2
	0·89	5·60	1·12	5·5
	3·40	5·60	1·12	5·7
	1·80	1·65	3·31 [c]	4·3
	1·50	2·89	3·31	8·0
	1·50	4·27	3·31	10·6
	1·60	5·00	3·31	13·6
	1·80	5·86	3·31	17·3
	1·50	1·65	7·08 [d]	8·1
	1·70	2·25	7·08	9·7
	1·50	2·47	7·08	13·1
	1·60	3·80	7·08	19·0
	1·80	1·43	11·22 [e]	11·7
	1·70	2·11	11·22	19·3
	1·80	2·50	11·22	20·3
25	1·72	2·10	2·88	36·0
	1·72	4·20	2·88	79·5
	1·72	6·00	2·88	111·0
	1·72	7·00	2·88	129·0

[a] pH maintained constant in run using acetate buffer. [b] pH 3·95. [c] pH 3·48. [d] pH 3·15. [e] pH 2·95.

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[1] See for example N. Uri, *Chem. Rev.*, 1952, **50**, 439.

[2] W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 1957, 447.

and first order in $[H^+]$ (Figure 3), and the full rate dependence can therefore be expressed as in (3).

$$\text{Rate} = k_{obs}[\text{peroxo}] = k[\text{peroxo}][S^{IV}][H^+] \qquad (3)$$

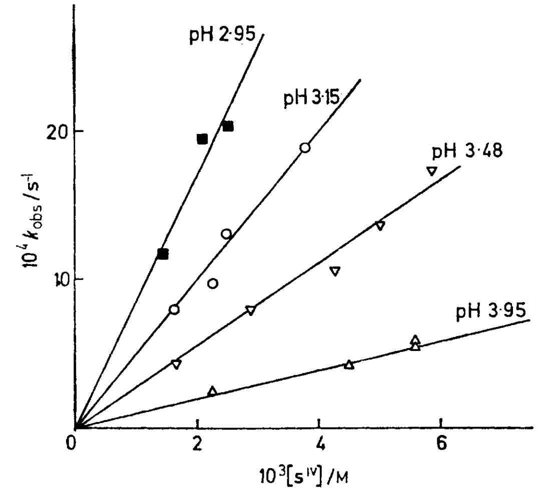

FIGURE 2 Dependence of k_{obs} on $[S^{IV}]$ for the reaction of the μ-amido-μ-peroxo-complex with sulphite ions at 1·4 °C, I = 1·0M ($LiClO_4$)

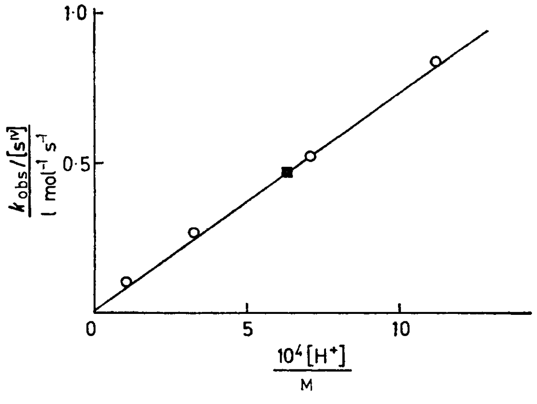

FIGURE 3 Dependence of $k_{obs}/[S^{IV}]$ on $[H^+]$ for the reaction of the μ-amido-μ-peroxo-complex with sulphite ions at 1·4 °C, I = 1·0M ($LiClO_4$). Values of $k_{obs}/[S^{IV}]$ were obtained from gradients of plots of k_{obs} *vs.* $[S^{IV}]$, determined by an unweighted least-squares treatment, where intercepts were always negligibly small. Points marked (○) are for the μ-amido-μ-peroxo-complex and the point marked (■) is for the second stage of the reaction of the the μ-amido-μ-superoxo-complex at pH 3·2

The predominant species in reactant solutions at pH 3—4 are the unprotonated (B) form of the μ-amido-μ-peroxo-complex[3] (95—99%) and the ion HSO_3^- (*ca.* 100%). Equations (4)—(8) define the concentrations of possible reactant species. The complex (BH) is the protonated form of (B), (AH) is the hydroperoxo-form [an isomer of (BH)], and C_0 is the total concentration of complex. At 1·4 °C, I = 0·245M ($NaClO_4$), the acid dissociation constant K_1 for (BH) is 0·067 mol l^{-1}, and the equilibrium constant K_2 for the isomerisation (BH) $\rightleftharpoons$ (AH) is 2·27 (ref. 3). The constant K_1, but possibly not K_2, may vary with ionic strength. Values of K' and K'' at 25 °C and I = 1·0M ($NaClO_4$) are 2·19 × 10^6 l mol^{-1} and 23·5 l mol^{-1}, ref. 4. The temperature dependence of K' and K'' has not, however, been studied. Thermodynamic enthalpies of reaction $\Delta H_0'$ and $\Delta H_0''$ corresponding to K' and K'' have been determined with $I \longrightarrow 0$ by several workers, and empirically it is generally found that values ($I \longrightarrow 0$) for the protonation of oxo-anions do not greatly differ from those at I = 1·0M if the ionic strength is adjusted with $NaClO_4$ or $LiClO_4$.[5] Values of $\Delta H_0'$ and $\Delta H_0''$ are 2·9 kcal mol^{-1} and 3·9 kcal mol^{-1} both at 25 °C, $I \longrightarrow 0$. Using these values estimates of K' and K'' at 1·4 °C, I = 1·0M ($LiClO_4$), can be made. These are $K' \simeq 1{\cdot}45 \times 10^6$ l mol^{-1} and $K'' \simeq 13{\cdot}2$ l mol^{-1}, which values are believed to be accurate to better than an order of magnitude.

$$K' = [HSO_3^-]/[H^+][SO_3^{2-}] \qquad (4)$$

$$K'' = [H_2SO_3]/[HSO_3^-][H^+] \qquad (5)$$

$$[AH] = [H^+]K_2C_0/(K_2[H^+] + K_1 + [H^+]) \qquad (6)$$

$$[BH] = [H^+]C_0/(K_2[H^+] + K_1 + [H^+]) \qquad (7)$$

$$[B] = K_1C_0/(K_2[H^+] + K_1 + [H^+]) \qquad (8)$$

For the pH range 3—4, assuming that the reactive species are (B) and H_2SO_3, equation (9) applies:

$$\text{Rate} = k_p[\text{peroxo}][H_2SO_3] = k_pK''[\text{peroxo}][HSO_3^-][H^+] \qquad (9)$$

Equation (10) then follows,

$$\frac{k_{obs}}{[HSO_3^-]} = k[H^+] = k_pK''[H^+] \qquad (10)$$

since $[HSO_3^-]$ is equal to the total sulphite concentration at the pH studied. From an unweighted least-squares treatment the gradient in Figure 3 has a value of 731(±81) l^2 mol^{-2} s^{-1} and an intercept 0·01(±0·04) l mol^{-1} s^{-1}. We conclude that within experimental error there is no $[H^+]$-independent pathway, and that k_p = 55·4(±6·1) l mol^{-1} s^{-1} at 1·4 °C, using the estimated value of K''.

The kinetic data are also fitted by assuming that the (BH) form is reacting with HSO_3^- thus:

$$k_{obs}[\text{peroxo}] = k_{BH}[BH][HSO_3^-] = k_{BH}\frac{[H^+]}{K_1}[\text{peroxo}][HSO_3^-] \qquad (11)$$

and

$$\frac{k_{obs}}{[HSO_3^-]} = \frac{k_{BH}}{K_1}[H^+] \qquad (12)$$

In this case the gradient (Figure 3) gives k_{BH}/K_1, and since K_1 at 1·4 °C is 0·067 mol l^{-1}, k_{BH} = 49·0(±5·4) l mol^{-1} s^{-1}.

Participation of (AH) in the reaction can be ruled out since the product would be the μ-amido-μ-hydroxo-complex.

Products of the μ-Amido-μ-superoxo-complex with Sulphite.—Air-free techniques and triply distilled water were used. When a buffered solution of the μ-amido-μ-superoxo-complex was mixed with a buffered solution of sulphite ions, with concentrations in the ratio 1 : 1 at pH 3, all the superoxo-complex was rapidly consumed, as indicated by the disappearance of the absorption maximum at λ 687 nm. When an excess of sulphite (1·5 : 1) was used,

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[3] M. Mori and J. A. Weil, *J. Amer. Chem. Soc.*, 1967, **89**, 3732.

[4] M. Frydman, G. Nilsson, T. Rengemo, and L. G. Sillen, *Acta Chem. Scand.*, 1958, **12**, 878.

[5] *Chem. Soc. Special Publ.* No. 17, 1964; No. 25, 1971.

the same intermediate spectrum was obtained, but subsequently a slower reaction occurred resulting in the formation of the μ-amido-μ-sulphato-complex. When reactants were mixed with excess of μ-amido-μ-superoxo-complex, and with increasing [SO_3^{2-}] up to 1 : 1 amounts, the resulting scan spectra showed good isosbestics at λ 582(±1), 492(±1), and 444(±2) nm, indicating that an intermediate is formed rapidly and quantitatively on addition of sulphite. Iodometric titrations showed that 1 mol of sulphite was consumed per mol of complex and the intermediate spectrum corresponds to a mixture of the μ-amido-μ-peroxo- and μ-amido-μ-sulphato-species. This was confirmed by comparing the behaviour of a 1 : 1 mixture of sulphite and μ-amido-μ-superoxo-complex, pH 3, on a cation-exchange column, with that of an equimolar mixture of pure μ-amido-μ-peroxo- and μ-amido-μ-sulphato-complexes. The solutions containing *ca.* 10^{-5} mol of binuclear complex were loaded separately onto two 8 cm × 3 cm^2 columns of Dowex 50W-X2 resin in the hydrogen form cooled to 0 °C, and elution was started with a solution of 1M-$NaClO_4$ containing 10^{-3}M-$HClO_4$. Both columns immediately showed a red band moving very slowly down the column, and leaving a red-brown portion at the top. Elution was somewhat faster with 2M-$NaClO_4$/10^{-3}M-$HClO_4$, but separation was not efficient enough to enable quantitative estimation of the components. Only two coloured bands were observed initially, but after 8 h of elution, there appeared a further red band above the existing brown and red bands. The first band was eluted with 3M-$NaClO_4$/10^{-3}M-$HClO_4$ and its spectrum showed that the μ-amido-μ-sulphato-species had significantly aquated to the μ-amido-μ-hydroxo-complex ($\lambda_{max.}$ *ca.* 505 nm). The spectrum of the first band from the reactant column showed similar characteristics. All the remaining complex on the column was eventually aquated in the same way. A further experiment was carried out using two 6 cm × 5 cm^2 columns of Dowex 50W-X2 resin, 2 × 10^{-4} mol of complex, and adding 2 × 10^{-4} mol and 10^{-4} mol of sulphite in separate solutions. These solutions were loaded at 0 °C and eluted with increasing concentrations of $NaClO_4$/10^{-3}M-$HClO_4$. The first 200 ml of eluant from each column was collected to determine any free sulphate ion produced initially. From four separate determinations the amount of sulphur determined as barium sulphate was *ca.* 50% of the amount of sulphur(IV) added initially. An allowance was made for sulphate impurity in AnalaR sodium sulphite which contained only 85(±2)% of the expected amount of sulphur(IV). The accuracy and reproducibility could not be further improved. The experiments clearly indicate that the intermediate produced at pH >3 is the μ-amido-μ-peroxo-complex (brown band). The μ-amido-μ-sulphato-complex (red band) and free sulphate ions are also formed.

The suggestion that the μ-amido-μ-peroxo-complex is formed was confirmed by observing the kinetics of the intermediate with sulphite ions. The intermediate was formed in the manner described above, using air-free solutions and a 1 : 1 ratio of reactants. Further amounts of buffered Na_2SO_3/$LiClO_4$ solution were then syringed into the solution in a thermostatted 4-cm cell to start the run and the absorbance changes observed at λ 450 nm. Runs were carried out under pseudo-first-order conditions at 1·4 °C and I = 1·0M ($LiClO_4$), and plots of log(O.D.$_t$ − O.D.$_\infty$) against time were linear to *ca.* 85%. The results are summarised in Table 3, and rate constants, k_{obs}, show a first-order dependence on [S^{IV}]. A value for k_{obs}/[S^{IV}] was evaluated from the gradient of a plot of k_{obs} against [S^{IV}] using a least-squares treatment, where the intercept was insignificantly small. This value fits very well on a plot of k_{obs}/[S^{IV}] against [H^+] for the μ-amido-μ-peroxo-reaction (Figure 3). It is concluded, therefore, that the reaction observed is that of the μ-amido-μ-peroxo-complex which is formed in 1 : 1 amounts along with the μ-amido-μ-sulphato-complex.

TABLE 3

Pseudo-first-order rate constants k_{obs}, for the reaction of μ-amido-μ-superoxo-complex with sulphite ions at I = 1·0M ($LiClO_4$), pH 3·2 (acetate buffer), λ = 450 nm

Temp. °C	10^4[superoxo] mol l^{-1}	10^3[S^{IV}] mol l^{-1}	10^4k_{obs} s^{-1}
1·4	2·8	1·30	7·61
	2·8	1·95	8·80
	2·8	3·24	15·30

Kinetics of the Reaction of the μ-Amido-μ-superoxo-complex with Sulphite.—Scan spectra were recorded for the reaction at [H^+] = 0·1M, I = 1·0M ($LiClO_4$), and 0 °C. Isosbestics were observed at λ 577 nm and 498(±1) nm which are in satisfactory agreement with those predicted for the conversion of μ-amido-μ-superoxo- into the μ-amido-μ-sulphato-complex (Figure 1). The kinetics of reaction at 1·4 °C, I = 1·0M ($LiClO_4$), were followed spectrophotometrically at λ 687 nm, which is the maximum for the superoxo-complex, with [H^+] in the range 0·04—0·20M. Under these conditions with sulphite in greater than ten-fold excess it was not necessary to use air-free conditions or triply distilled water since the reaction of sulphite radicals with dissolved oxygen and other trace impurities does not interfere with the kinetics. Plots of log(O.D.$_\infty$ − O.D.$_t$) against time were linear to *ca.* 85% and pseudo-first-order rate constants, k'_{obs}, are summarised in Table 4. A first-order dependence on [S^{IV}] and an inverse dependence on [H^+] is observed.

TABLE 4

Pseudo-first-order rate constants, k'_{obs}, for the reaction of the μ-amido-μ-superoxo-complex with sulphite ions at I = 1·0M ($LiClO_4$); λ = 687 nm

Temp. °C	10^1[H^+] [a] M	10^4[superoxo] M	10^3[S^{IV}] M	$10^4k'_{obs}$ s^{-1}	10^{-5} F [b] l^2 mol^{-2} s^{-1}
1·4	0·35	1·4	3·47	17·90	10·93
	0·37	1·4	2·00	9·10	9·85
	0·73	1·4	4·86	8·50	4·97
	0·75	1·4	3·38	5·90	5·03
	0·77	1·4	2·00	3·27	4·78
	1·11	5·5	5·55	5·19	3·34
	1·11	1·4	5·55	5·08	3·27
	1·14	1·4	3·87	3·80	3·56
	1·16	1·4	2·58	2·41	3·42
	1·17	1·4	2·00	1·60	2·95
	1·18	0·7	0·99	0·99	3·72
	1·50	1·4	6·20	4·01	2·79
	1·51	1·4	5·23	3·19	2·65
	1·57	1·4	2·00	1·08	2·40
	1·89	1·4	6·70	2·46	1·86
	1·90	1·4	6·10	2·11	1·75
	1·92	1·4	4·50	1·64	1·87
	1·93	1·4	3·99	1·59	2·05
	1·95	1·4	2·90	1·03	1·84
	1·97	1·4	2·00	0·70	1·82
	1·98	0·7	1·00	0·27	1·42

[a] Corrected for consumption of H^+ by SO_3^{2-} ions in forming H_2SO_3/HSO_3^- according to equations (4) and (5). [b] $F = k'_{obs}\,(K' + K'K''[H^+])/[S^{IV}]$.

The variation of k'_{obs} with $[S^{IV}]$ and $[H^+]$ can be accounted for if the only reactive path is the reaction of SO_3^{2-} with the μ-superoxo-complex. All three sulphite species have to be taken into account [see equation (13)],

$$[S^{IV}] = [SO_3^{2-}] + [HSO_3^-] + [H_2SO_3] \qquad (13)$$

hence equation (14) is obtained:

$$[SO_3^{2-}] = [S^{IV}]/(1 + K'[H^+] + K'K''[H^+]^2) \qquad (14)$$

The rate law is as in equation (15)

$$\text{Rate} = k'_{obs}[\text{superoxo}] = k_S[\text{superoxo}][SO_3^{2-}] \qquad (15)$$

and since $(K'[H^+] + K'K''[H^+]^2) \gg 1$ the $[H^+]$ dependence of k'_{obs} is given by equation (16):

$$\frac{k'_{obs}}{[S^{IV}]}(K' + K'K''[H^+]) = k_S[H^+]^{-1} \qquad (16)$$

Figure 4 is a plot of the left-hand side of this equation (F) against $[H^+]^{-1}$.

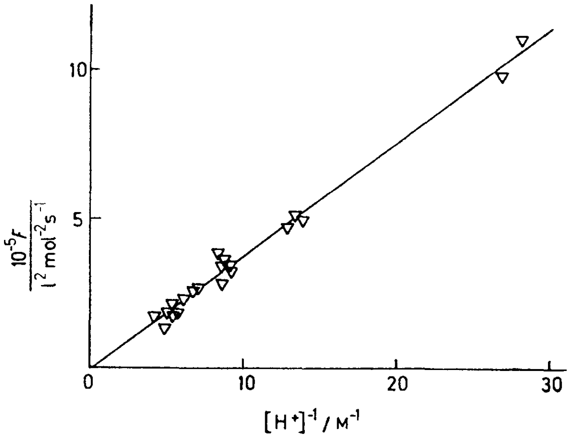

FIGURE 4 Dependence of F [the left-hand side of equation (16)] on $[H^+]^{-1}$ for the reaction of the μ-amido-μ-superoxo-complex with sulphite ions at 1·4 °C, I = 1·0M ($LiClO_4$)

In calculating $[H^+]$ for any particular run it was necessary to correct for the formation of H_2SO_3 and HSO_3^- since the sulphite was introduced in the form of sodium sulphite. It can be seen that the experimental data give a good fit to equation (16). The gradient gives a value for k_S equal to 3·80(±0·07) × 10^4 l mol^{-1} s^{-1} determined using an unweighted least-squares treatment. An intercept of 0·5(±1) × 10^2 l mol^{-1} s^{-1} suggests that within experimental error there is no detectable contribution from an $[H^+]$-independent pathway.

Reactions of μ-Amido-μ-peroxo- and μ-Amido-μ-superoxo-complexes with Nitrite.—At pH *ca.* 6 and 0 °C the reaction of the μ-amido-μ-superoxo-complex with excess of nitrite is rapid and complete in <30 s. Quantitative formation of the μ-amido-μ-peroxo-complex is observed, which is not itself reduced by nitrite at this pH at room temperature or at 50 °C, during a period of several hours. At $[HClO_4]$ = 0·36M the reaction is slower with the formation of the μ-amido-μ-nitrito-complex spectrum ($\lambda_{max.}$ 472 nm, ε 272 l mol^{-1} cm^{-1})[6] requiring *ca.* 10 min for completion. There was no evidence for intermediate formation of the μ-amido-μ-peroxo-complex which under these conditions of high $[H^+]$ is presumably reacting rapidly with nitrite. At $[HClO_4]$ = 0·1M the reaction was faster and complete in *ca.* 5 min indicating that the rate-determining step involving the μ-amido-μ-superoxo-complex and nitrite has an inverse dependence in $[H^+]$. A scan spectrum of a solution of the μ-amido-μ-peroxo-complex with an excess of nitrite ions at pH 3·49 and at ice temperature showed a slow reaction with the formation of the μ-amido-μ-nitrito-complex ($\lambda_{max.}$ 472 nm, ε 280 l mol^{-1} cm^{-1}) reaching completion in a period of several hours. The lack of reaction at pH 6 suggests that HNO_2 and/or a protonated form of the complex is involved. At pH <1, oxidation of the μ-amido-μ-peroxo-complex by HNO_2 becomes comparable to the reaction of NO_2^- with the μ-amido-μ-superoxo-complex.

To summarise, the reaction of nitrite ions with the two complexes appears qualitatively similar to that of sulphite, in that the μ-amido-μ-superoxo-complex reacts with the unprotonated reductant, NO_2^-, and μ-amido-μ-peroxo-complex requires protons in the activated complex.

Reactions of the μ-Amido-μ-peroxo- and μ-Amido-μ-superoxo-complexes with Arsenite.—Two solutions of the μ-amido-μ-superoxo-bis[bis(ethylenediamine)cobalt(III)] complex containing an excess of arsenite ions, at pH 1 and 3·1 respectively, showed no change in spectrum at room temperature during *ca.* 24 h. A 6·4 × 10^{-4}M-solution of the μ-amido-μ-peroxo-complex at pH 1 reacted with an excess of arsenite (4·7 × 10^{-2}M) to give the μ-amido-μ-hydroxo-complex ($\lambda_{max.}$ 509 nm, ε 180 l mol^{-1} cm^{-1}).[7] At room temperature the reaction reached completion in 2 h. At pH 3 the reaction was incomplete after 20 h and this reaction could not be distinguished from the decomposition of the μ-amido-μ-peroxo-complex which is known to yield the same product.[8] Thus it appears that only the μ-amido-μ-peroxo-complex reacts with arsenite ions and then only when the pH is sufficiently low. No evidence for μ-arsenato-products was obtained, and such binuclear cobalt(III) complexes have not as yet been identified.

Other Reactions.—Solutions of the μ-amido-μ-superoxo- and μ-amido-μ-peroxo-complexes at pH 3 and pH 1 were mixed with an excess of acetaldehyde at room temperature. No spectrophotometric changes were observed during 4 days other than those expected for decomposition of the μ-amido-μ-peroxo-complex.

DISCUSSION

The reaction of the μ-amido-μ-peroxo-complex with sulphite has been shown to proceed directly to the μ-amido-μ-sulphato-complex without the intermediate formation of the μ-amido-μ-hydroxo-complex. The reaction is most likely between H_2SO_3 (which is more precisely SO_2,xH_2O)[9] and the unprotonated form of the μ-amido-μ-peroxo-complex (B), as shown in (17). It is necessary to invoke an intermediate, *e.g.* (I), which undergoes a rapid intramolecular reaction to give the μ-amido-μ-sulphato-complex. Contribution from a reaction path involving BH and HSO_3^- cannot be excluded.

The reaction of the μ-amido-μ-superoxo-complex

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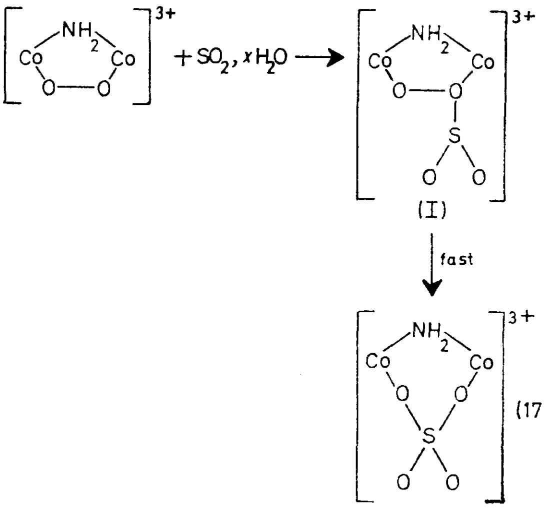
[6] K. Garbett and R. D. Gillard, *J. Chem. Soc.* (*A*), 1968, 1725.

[7] M. B. Stevenson and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 2979.

[8] R. Davies and A. G. Sykes, *J. Chem. Soc.* (*A*), 1968, 2840.

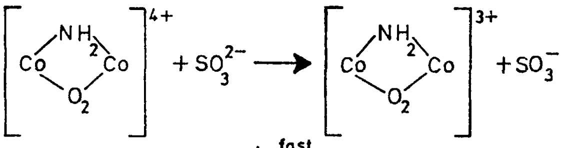
[9] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley, London, 1972, p. 447.

proceeds with intermediate formation of the μ-peroxo-complex and HSO_3. A possible scheme suggested by



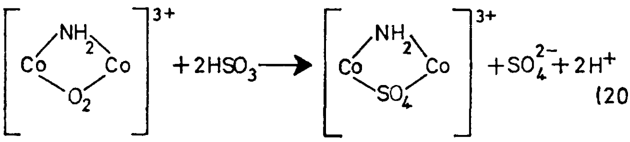
(17)

our observations is as in (18) to (20). This is able to account for the intermediate formation of 1 : 1 amounts



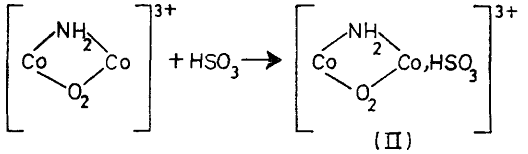
(18)

$$SO_3^- + H^+ \underset{}{\overset{fast}{\rightleftharpoons}} HSO_3 \qquad (19)$$



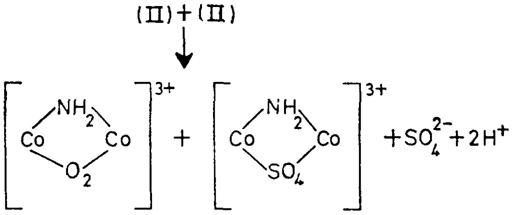
(20)

of the μ-amido-μ-peroxo- and μ-amido-μ-sulphato-complexes identified by spectrophotometric and ion-exchange techniques. Kinetic studies confirm the presence of the μ-amido-μ-peroxo-complex, and uncomplexed sulphate has also been detected. However a reaction step (20) is introduced involving two radical species and the μ-peroxo-complex which initially is present at low concentrations. An alternative is that the incipient μ-amido-μ-peroxo-complex and SO_3^-/HSO_3 formed in reactions (18) and (19) give some sort of adduct represented by formula (II), which then reacts



(21)

as in equation (22). Another alternative is that HSO_3 radicals reduce the μ-amido-μ-superoxo-complex to give an intermediate (directly or indirectly depending on whether the HSO_3 is able to bond to the superoxo-bridge prior to the redox process), which is then required



(22)

to react with sulphite to yield the μ-amido-μ-sulphato-product. We cannot rule out small contributions from a path involving:

$$2HSO_3 + H_2O \longrightarrow SO_4^{2-} + SO_3^{2-} + 4H^+ \qquad (23)$$

This cannot be a main path however since the μ-sulphato-complex is present at intermediate stages, *i.e.* in a 1 : 1 reaction, in equivalent or near equivalent amounts to the μ-peroxo-complex. Equation (23) would require a reaction of the μ-peroxo-complex with sulphite to be the only source of the μ-sulphato-product. It is useful at this point to compare the reaction of the single-bridged μ-superoxo-complex $(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5^{5+}$ with sulphite ion.[10] The rate constant for this reaction ($k_s = 6{\cdot}2 \times 10^4$ l mol^{-1} s^{-1} at 25 °C and $I = 0{\cdot}5$M) is of similar magnitude to that of the doubly bridged analogue ($k_s = 3{\cdot}8 \times 10^4$ l mol^{-1} s^{-1} at 1·4 °C and $I = 1{\cdot}0$M). It was shown that labelled oxygen from the O_2 bridge was present in both the complexed and uncomplexed sulphate fractions in reaction (24).

$$[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{5+} + 2SO_3^{2} \xrightarrow{H^+} [(NH_3)_5CoSO_4]^+ + SO_4^{2-} + Co^{2+} + 5NH_4^+ \qquad (24)$$

The mechanism may be similar to that for the doubly bridged complex, where the adduct which is formed as an intermediate in reaction (24) reacts further with sulphite. If the μ-peroxo-complex is formed as an intermediate it must undergo further rapid reaction since otherwise it would decompose to give Co^{2+} and molecular oxygen.[11,12] The reaction is best summarised as in (25) without attempting to specify the charge distribution or bonding in the intermediate.

$$[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{5+} \xrightarrow{SO_3^{2-}} [(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5,SO_3]^{3+}$$

$$\Big\downarrow {\scriptstyle H^+/SO_3^{2-}}$$

$$Co^{2+} + 5NH_4^+ + SO_4^{2-} + [Co(NH_3)_5SO_4]^+ \qquad (25)$$

The reaction of the μ-amido-μ-superoxo- and μ-amido-μ-peroxo-complexes with nitrite ion can be discussed in the same manner as that of sulphite. Thus an inverse [H^+] dependence is apparent in the reaction of the μ-amido-μ-peroxo-complex suggesting that NO_2^- is the reactant. Here again a radical species NO_2 is a

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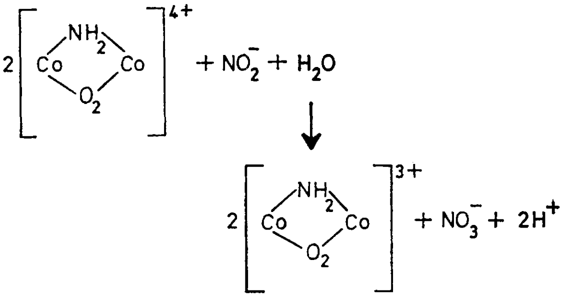
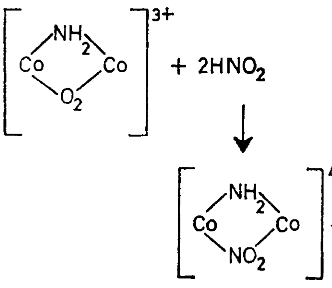
[10] R. Davies, A. K. E. Hagopian, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 623.

[11] R. Davies and A. G. Sykes, *J. Chem. Soc.* (*A*), 1968, 2831.

[12] A. B. Hoffman and H. Taube, *Inorg. Chem.*, 1968, **7**, 1971.

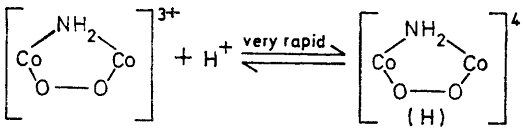
possible intermediate as has been noted previously for reactions of nitrite with one-equivalent oxidants.[13] It is reasonable to propose that reaction proceeds by a non-bonded activated complex since in this case the only intermediate is the μ-amido-μ-peroxo-complex as shown by the u.v. visible spectrum. The reaction is summarised in (26). The μ-amido-μ-peroxo-complex reacts with nitrite ions at low pH values, the reaction being catalysed by H^+ ions. The reaction is most likely between the (B) form and HNO_2 but contributions from BH and NO_2^- (or HNO_2) cannot be excluded. The only product of the reaction is the μ-amido-μ-nitrito-complex (27), and a stoicheiometry of 2 : 5 is implied therefore. There is no evidence for the formation of a nitrato-complex which would absorb at significantly longer wavelengths.[14] In the reaction of $(NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5^{5+}$ with nitrite ions[15] the stoicheiometry and products are similar to those for the reaction with sulphite [reaction (28)] and similar comments apply with regard to mechanism and possible intermediates.

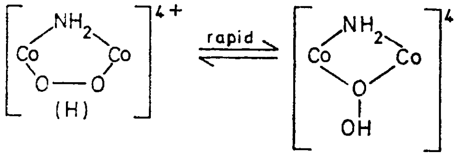

(26)



$$[(NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5]^{5+} + 2NO_2^- \xrightarrow{H^+} [Co(NH_3)_5NO_3]^{2+} + NO_3^- + Co^{2+} + 5NH_4^+ \quad (28)$$

The arsenite reduction of the μ-amido-μ-peroxo-complex is in sharp contrast to the reactions of sulphite and nitrite ions, in that the product is not an oxo-anion-bridged complex, and thus there is no evidence for bonding of the arsenite ion at any stage. In our view this is not surprising since there are no previous reports of arsenate bridging two cobalt(III) atoms. The reaction is catalysed by H^+ ions in the same manner as those of nitrite and sulphite, but since the μ-amido-μ-hydroxo-complex is produced we suggest that the (AH) form of the complex is involved in this instance. Chloride, bromide,[8] and iodide[16] have also been observed to react with (AH), with the formation of the μ-amido-μ-hydroxo-complex. The reaction sequence is, accordingly, as indicated in equations (29)—(31), where features of (29) and (30) have been discussed previously.[3,16]


(29)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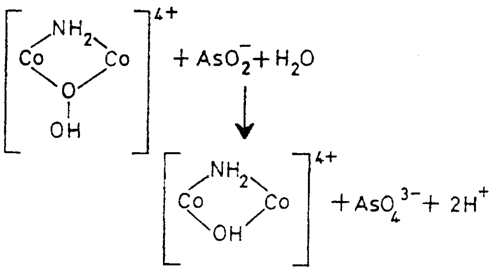
(31)

The observation that acetaldehyde is not oxidised by the μ-amido-μ-peroxo- or μ-amido-μ-superoxo-complexes at pH 1 and 3 suggests that the complexes may not be strong enough oxidants. Acetaldehyde would be expected to react most favourably with two-electron oxidants. The protonated hydroperoxo-complex (AH) is believed to be such an oxidant,[8,16] but no reaction is observed at pH 1 when (AH) is known to be present.

There are two over-riding features of the reactions of the μ-amido-μ-superoxo- and μ-amido-μ-peroxo-complexes with sulphite. These are (*a*) the superoxo-complex reacts preferentially with SO_3^{2-} whereas the peroxo-complex reacts preferentially with protonated sulphite, and (*b*) the sulphite is non-bonded (or outer sphere) in the reaction with the superoxo-complex, but bonded in the reaction with the peroxo-complex. These observations are supported in the less extensive studies with nitrite. A more comprehensive survey of other reactions of these two complexes in which these features are likewise apparent is to be found elsewhere.[17]

EXPERIMENTAL

Samples of the complexes μ-amido-μ-superoxo-bis[bis(ethylenediamine)cobalt(III)] nitrate dihydrate, the analogous complex with ammonia ligands, and μ-amido-μ-peroxo-bis[bis(ethylenediamine)cobalt(III)] bromide were

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[13] See for example G. Davies and K. Kustin, *Inorg. Chem.*, 1969, **8**, 484.

[14] See for example M. B. Stevenson, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1059.

[15] M. Green and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 3209.

[16] R. Davies, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1261.

[17] A. G. Sykes, *Chem. in Britain*, 1974, **10**, 170.

prepared as described previously.[18,3] A sample of μ-amido-μ-sulphato-bis[bis(ethylenediamine)cobalt(III)] bromide was also obtained by the procedures of Stevenson and Sykes.[7] Iodometric titrations to determine stoicheiometry were performed as follows. Deoxygenation of solutions was carried out using argon to improve reproducibility of results. Excess of 0·1N-iodine solution (B.D.H. 'CVS' volumetric solution) was diluted *ca.* ten-fold with water and acidified with perchloric acid so that $[H^+] \simeq 0{\cdot}05$M in the titration. The sulphite-containing solution was then added with the tip of the pipette under the solution and with swirling of the flask. The solution was immediately titrated with 0·1N-sodium thiosulphate solution (B.D.H. 'CVS' volumetric solution) to estimate the excess of iodine, using a 'Thyodene' indicator. Volumes and concentration were adjusted so that about half the iodine was consumed by the sulphite. For reactant solutions, blank experiments were carried out, using no complex, to estimate the loss of sulphite by aerial oxidation or loss of SO_2 vapour. This was usually found to be negligible at least at high pH. All solutions containing μ-amido-μ-superoxo-complex were kept in light-proof containers throughout handling and storage. All chemicals used were of AnalaR grade. Water for the experiments investigating the intermediate of the μ-amido-μ-superoxo-reaction was triply distilled from alkaline potassium permanganate and acidified potassium dichromate solutions. Lithium perchlorate was prepared by methods previously used in these laboratories. U.v.-visible spectrophotometric measurements were made using Unicam SP 500 and SP 800 instruments with thermostatted cell housings. Dowex 50W-X2 (100—200 mesh) resin was used for ion-exchange experiments, prepared in the hydrogen form and washed copiously with distilled water. The pH of buffered solutions was checked using a Radiometer pH meter (type M4d) and glass (type G202C) and calomel (type K401) electrodes, standardised with pH 3·1 and 4 buffers and found to agree with calculated values within 0·05 of a pH unit. The buffer solutions were prepared by mixing the required amounts of sodium acetate and perchloric acid solutions to give 0·2M-sodium acetate concentrations and corresponding amounts of perchloric acid.[19] Ionic strength was calculated assuming that acetic acid made no contribution.

We are grateful to the S.R.C. for the award of a Postdoctoral Fellowship (to C.-H. Y.) and postgraduate studentship (to J. D. E.).

[4/009 *Received, 3rd January,* 1974]

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[18] M. B. Stevenson and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 2293.

[19] A. I. Vogel, 'Quantitative Inorganic Analysis,' Longmans, London, 1960.