Reactions of μ-Hydroxo-dicobalt(III) Complexes. Part VIII.[1] Kinetic Studies of the Bridge Cleavage of the μ-Hydroxo-bis[penta-amminecobalt(III)] Complex

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The kinetics of bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex, $(NH_3)_5Co\cdot OH\cdot Co(NH_3)_5^{5+}$ [equation (i)] have been studied in aqueous perchloric acid solutions, I = 2·0M ($LiClO_4$), at 15—30 °C. For the

$$(NH_3)_5Co\cdot OH\cdot Co(NH_3)_5^{5+} + H^+ + H_2O \longrightarrow 2Co(NH_3)_5H_2O^{3+} \qquad \text{(i)}$$

range of hydrogen-ion concentration investigated (10^{-4}—2·0M), first-order rate constants, k_{obs}, show the dependence (ii) on [H^+]. At 25 °C: $k_1 = (5{\cdot}37 \pm 0{\cdot}07) \times 10^{-3}$ l mol^{-1} s^{-1}, $\Delta H_1^‡ = 12{\cdot}0 \pm 0{\cdot}8$ kcal mol^{-1}, $\Delta S_1^‡ =$

$$k_{obs} = k_1[H^+] + k_2 \qquad \text{(ii)}$$

$-28{\cdot}7 \pm 2{\cdot}7$ cal K^{-1} mol^{-1}; and $k_2 = (7{\cdot}58 \pm 0{\cdot}10) \times 10^{-3}$ s^{-1}, $\Delta H_2^‡ = 20{\cdot}1 \pm 0{\cdot}70$ kcal mol^{-1}, $\Delta S_2^‡ = -1{\cdot}0 \pm 2{\cdot}2$ cal K^{-1} mol^{-1}. In the presence of thiocyanate ions (0·06—0·80M), k_{obs} can be expressed as in (iii),

$$k_{obs} = a[H^+] + b + c[H^+][NCS^-] \qquad \text{(iii)}$$

where a and b are *ca.* 15% smaller than k_1 and k_2 due to ion-pairing. At 25 °C and I = 2·0M ($LiClO_4$): $c = 0{\cdot}137 \pm 0{\cdot}003$ l^2 mol^{-2} s^{-1}, $\Delta H_c^‡ = 10{\cdot}9 \pm 0{\cdot}6$ kcal mol^{-1}, and $\Delta S_c^‡ = -25{\cdot}8 \pm 2{\cdot}2$ cal K^{-1} mol^{-1}. The thiocyanate-dependent path yields equal amounts of the complexes $Co(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5H_2O^{3+}$ as primary products.

HYDROXO-BRIDGE-CLEAVAGE reactions of the di- and tri-μ-hydroxo-cobalt(III) complexes $(NH_3)_4Co\cdot\mu(OH,OH)\cdot Co(NH_3)_4^{4+}$ (ref. 2), $(en)_2Co\cdot\mu(OH,OH)\cdot Co(en)_2^{4+}$ (en = ethylenediamine) (refs. 3—5), $(C_2O_4)_2Co\cdot\mu(OH,OH)\cdot Co(C_2O_4)_2^{4-}$ (ref. 6), and $(NH_3)_3Co\cdot\mu(OH,OH,OH)\cdot Co(NH_3)_3^{3+}$ (ref. 7) in aqueous acid solutions (generally perchloric acid) have been studied previously. Mononuclear complexes are formed and the rates of reaction are dependent on hydrogen-ion concentration. Details of hydroxo-bridge-cleavage reactions of the μ-amido-μ-hydroxo-complex $(NH_3)_4Co\cdot\mu(NH_2,OH)\cdot Co(NH_3)_4^{4+}$, in the presence of a variety of anions, have been reported in previous papers in this series.[8] An essential difference from studies with complexes having only hydroxo-bridges is that the amido-bridge (which has no site for protonation) is inert and a binuclear structure is retained. Siebert and Feuerhake[9] have prepared the μ-hydroxo-complex $(NH_3)_5Co\cdot OH\cdot Co(NH_3)_5^{5+}$ and we now report a detailed kinetic study of the bridge cleavage of this complex. Hydroxo-bridge cleavage of the analogous dichromium(III) complex $(NH_3)_5Cr\cdot OH\cdot Cr(NH_3)_5^{5+}$ has been studied[10] and found to be independent of hydrogen-ion concentration.

RESULTS

Bridge Cleavage in Perchlorate Ion Solutions.—The reaction was studied by conventional spectrophotometry by following the decrease in absorption at the 529 nm peak of the μ-hydroxo-bis[penta-amminecobalt(III)] complex (ε = 174 l mol^{-1} cm^{-1}). At pH ⩽ 4 final spectra corresponded to the formation of 2 moles of the complex penta-ammineaquocobalt(III) ($\lambda_{max.}$ 490, ε 47·5; $\lambda_{max.}$ 345 nm, ε 44·6 l mol^{-1} cm^{-1}).[11] First-order plots of log ($OD_t - OD_\infty$) against time were linear to *ca.* 95% completion, and from the gradients (k_{obs}/2·303) values of the rate constant k_{obs} were evaluated. These were dependent on [H^+] but were independent of the initial concentration of complex over the range ($2{\cdot}8 \times 10^{-4}$—$2{\cdot}4 \times 10^{-3}$M) investigated. The nitrate salt of the complex, $[(NH_3)_5Co\cdot OH\cdot Co(NH_3)_5](NO_3)_5$, was used and it was necessary therefore to check the effect of nitrate ion on the reaction. From the data in Table 1, [NO_3^-] = 0—0·5M, it is clear that no dependence on nitrate ion is observed. A sample of bromide salt, $[(NH_3)_5Co\cdot OH\cdot Co(NH_3)_5]Br_5,H_2O$, was also prepared and this gave identical kinetic behaviour.

TABLE 1

Effect of nitrate ions on k_{obs} for bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex at 25 °C, [H^+] = 0·2M, and I = 2·0M ($NaClO_4$). The concentration of complex (nitrate salt) was $6{\cdot}8 \times 10^{-4}$M except where otherwise stated

[NO_3^-] M	10^3k_{obs} s^{-1}
0	6·85
0·1	6·81
0·2	7·20
0·3	6·31
0·4	6·80 [a]
0·5	6·48 [a]

[a] [Complex] = $2{\cdot}8 \times 10^{-4}$M.

The dependence of k_{obs} on hydrogen-ion concentration was investigated initially in a series of runs at 25 °C, in which the ionic strength was adjusted to I = 2·0M with sodium perchlorate (Table 2). As previously reported[12]

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[1] Part VII, R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1426.

[2] A. B. Hoffman and H. Taube, *Inorg. Chem.*, 1968, **7**, 903.

[3] S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 735.

[4] A. A. El-Awady and Z. Z. Hugus, *Inorg. Chem.*, 1971, **10**, 1415.

[5] M. M. DeMaine and J. B. Hunt, *Inorg. Chem.*, 1971, **10**, 2106.

[6] Lee Hin-Fat and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1971, 2589.

[7] M. Linhard and H. Siebert, *Z. anorg. Chem.*, 1969, **364**, 24.

[8] Further studies in the presence of selenate, phosphate, and bromide ions will appear in subsequent parts of this series.

[9] H. Siebert and H. Feuerhake, *Chem. Ber.*, 1969, **102**, 2951.

[10] D. W. Hoppenjans and J. B. Hunt, *Inorg. Chem.*, 1969, **8**, 505.

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

[12] J. D. Ellis, K. L. Scott, R. K. Wharton, and A. G. Sykes, *Inorg. Chem.*, 1972, **11**, 2565.

the data give a good fit to (1). There is no obvious explan-

$$10^3k_{obs} = 0{\cdot}99[H^+]^2 + 4{\cdot}32[H^+] + 5{\cdot}95 \qquad (1)$$

ation of a dependence on $[H^+]^2$ in terms of protonation of the complex and since this dependence is not observed when the ionic strength is adjusted with lithium perchlorate (see below), it is attributed to a medium effect. Other medium effects of this kind have been observed previously.[13] Replacement of hydrogen ions by lithium rather than sodium ions is preferred since the activity coefficients of H^+ and Li^+ are more similar.[14] The ionic strength was therefore adjusted to $I = 2{\cdot}0$M with lithium perchlorate in all subsequent runs. Rate constants obtained over the range $[H^+] = 10^{-4}$—2·0M (Table 3) gave a good fit to (2), where k_1

$$k_{obs} = k_1[H^+] + k_2 \qquad (2)$$

corresponds to the gradient and k_2 to the intercept in Figure 1. Values of the rate constants k_1 and k_2 (Table 4) were obtained by a non-linear least-squares treatment, each data point being given a weighting factor of unity.[15] Runs at 30 °C with $[H^+] > 1{\cdot}0$M were too fast to follow by conventional spectrophotometry. From the temperature dependence, log (k/T) against $1/T$, $\Delta H_1^‡ = 12{\cdot}0 \pm 0{\cdot}8$ kcal mol⁻¹, $\Delta S_1^‡ = -28{\cdot}7 \pm 2{\cdot}7$ cal K⁻¹ mol⁻¹, $\Delta H_2^‡ = 20{\cdot}1 \pm 0{\cdot}7$ kcal mol⁻¹, and $\Delta S_2^‡ = -1{\cdot}0 \pm 2{\cdot}2$ cal K⁻¹ mol⁻¹.

TABLE 2

Rate constants (k_{obs}) for bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex at 25 °C and $I = 2{\cdot}0$M ($NaClO_4$). The concentration of complex (nitrate salt) was $6{\cdot}8 \times 10^{-4}$M

$[H^+]$ / M	10^3k_{obs} [a] / s⁻¹
0·01	6·02 (2)
0·2	6·85
0·5	8·31 [b]
1·0	11·35 (2)
1·0	11·30 [c]
1·2	12·56
1·4	13·70
1·6	15·32
1·8	17·12
2·0	18·50 [d] (2)

[a] Figures in parentheses indicate the number of runs which have been averaged. [b] Bromide salt used. [c] [Complex] = $2{\cdot}4 \times 10^{-3}$M. [d] [Complex] = $1{\cdot}4 \times 10^{-3}$M in one run.

TABLE 3

Rate constants (k_{obs}) for bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex, $I = 2{\cdot}0$M ($LiClO_4$). The concentration of complex (nitrate salt) was $6{\cdot}8 \times 10^{-4}$M

Temp. / °C	$[H^+]$ / M	10^3k_{obs} / s⁻¹
15·0	0·01	2·05
	0·4	3·49
	1·0	4·96
	1·6	6·80
	2·0	7·37
20·0	0·01	4·14
	0·4	5·93
	1·0	7·85
	1·6	10·2
	2·0	11·2
25·0	0·0001	7·56
	0·001	7·69
	0·01	7·57 [a]
	0·2	8·79
	1·0	12·9 [a]
	1·6	16·1 [a]
	1·8	17·1
	2·0	18·5 [a]
30·0 [b]	0·01	13·5 [a]
	0·2	14·9 [a]
	0·4	16·5
	0·6	18·1
	1·0	21·2

[a] Average of two runs. [b] Runs at $[H^+] > 1{\cdot}0$M too fast to follow using SP 500 spectrophotometer.

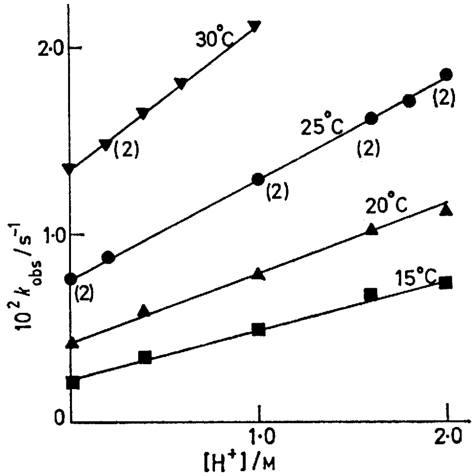

FIGURE 1 Dependence of k_{obs} on $[H^+]$ for the hydroxo-bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex, $I = 2{\cdot}0$M ($LiClO_4$). Figures in parentheses indicate the number of runs which have been averaged

TABLE 4

Summary of rate constants k_1 and k_2 for bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex, $I = 2{\cdot}0$M ($LiClO_4$)

Temp. / °C	10^3k_1 / l mol⁻¹ s⁻¹	10^3k_2 / s⁻¹
15·0	2·69 ± 0·16	2·24 ± 0·20
20·0	3·57 ± 0·14	4·30 ± 0·18
25·0	5·37 ± 0·07	7·58 ± 0·10
30·0	7·80 ± 0·03	13·37 ± 0·02

Bridge Cleavage in the Presence of Thiocyanate Ions.—Bridge cleavage of the μ-hydroxo-complex was faster in the presence of thiocyanate ions and the spectrum of the products indicated formation of substantial amounts of the penta-ammineisothiocyanatocobalt(III) complex (Figure 2). It is concluded that the additional reaction path (3) is

$$(NH_3)_5Co{\cdot}OH{\cdot}Co(NH_3)_5^{5+} + H^+ + NCS^- \longrightarrow Co(NH_3)_5H_2O^{3+} + Co(NH_3)_5NCS^{2+} \qquad (3)$$

effective. The dependence of the reaction on the thiocyanate-ion (Figure 3) and hydrogen-ion concentration (Figure 4) was investigated. Rate constants k_{obs} (Table 5) gave a good fit to (4). The variation of $[H^+]$ in these

$$k_{obs} = a[H^+] + b + c[H^+][NCS^-] \qquad (4)$$

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[13] See for example, J. Doyle and A. G. Sykes, *J. Chem. Soc.* (*A*), 1967, 795; R. Davies and A. G. Sykes, *ibid.*, 1968, 2831; J. C. Templeton and E. L. King, *J. Amer. Chem. Soc.*, 1971, **93**, 7160; and C. Lavallee and T. W. Newton, *Inorg. Chem.*, 1972, **11**, 2616.

[14] A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, 1962, **66**, 1065.

[15] Los Alamos Report LA 2367 (1959) and Addenda by R. H. Moore and R. K. Zeigler. We are grateful to Dr. T. W. Newton for sending us details of this program and to Dr. P. Gans for helpful comments.

experiments was limited to low values since, in the absence of complex and with $[H^+] > 1{\cdot}0$M, thiocyanate ion solutions assume an initial brown colouration and eventually, on leaving overnight, yellow needle-shaped crystals are obtained. The nature of these reactions is uncertain.

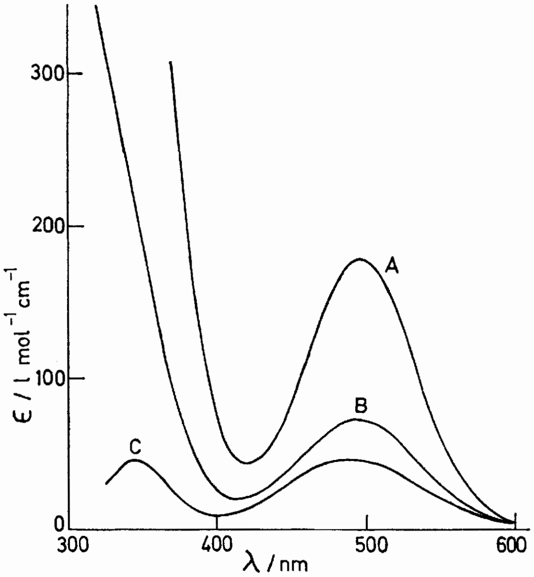

FIGURE 2 Spectra of the complexes $Co(NH_3)_5NCS^{2+}$ (A) and $Co(NH_3)_5H_2O^{3+}$ (C), and that of the solution obtained on cleavage of the hydroxo-bridge of $(NH_3)_5Co{\cdot}OH{\cdot}Co(NH_3)_5^{5+}$ (B) at 25 °C, $[NCS^-] = 0{\cdot}2$M, $[H^+] = 0{\cdot}5$M, and $I = 2{\cdot}0$M ($LiClO_4$)

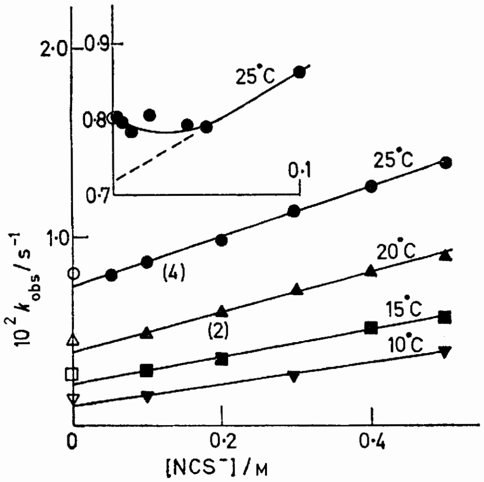

FIGURE 3 Dependence of rate constants on thiocyanate ion concentration for the hydroxo-bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex, $[H^+] = 0{\cdot}1$M, $I = 2{\cdot}0$M ($LiClO_4$). Points obtained in absence of thiocyanate are indicated and the effect of small concentrations of thiocyanate ions at 25 °C is shown in the inset. The number of runs averaged is indicated in parentheses

The intercepts in Figure 4, corresponding to b, are *ca.* 15% lower than values of k_2 from Figure 1, hence our use of different terminology. A discrepancy of similar magnitude is observed between a and k_1. For the conditions of $[H^+]$ and $[NCS^-]$ investigated, a makes a relatively small contribution to k_{obs} and values evaluated are not as accurate as b and c. Values of a, b, and c were obtained using a non-linear least-squares program with weighting factors of (i) unity and (ii) $1/k_{obs}^2$.[15] Slightly better resolution (*i.e.* smaller standard deviations) was obtained using the $1/k_{obs}^2$ weighting factor and values of the activation parameters for a and b were in better agreement with those previously determined for k_1 and k_2 respectively. Values of the rate constants a, b, and c (Table 6) quoted and their corresponding activation parameters (Table 7) are those obtained using method (ii).

TABLE 5

Pseudo-first-order rate constants (k_{obs}) for hydroxo-bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex in the presence of thiocyanate ions, $I = 2{\cdot}0$M ($LiClO_4$). The concentration of complex (nitrate salt) was $6{\cdot}8 \times 10^{-4}$M and the number of runs which have been averaged is indicated in parentheses

Temp. / °C	$[H^+]$ / M	$[NCS^-]$ / M	10^3k_{obs} / s^{-1}
10·0	0·05	0·10	1·28
	0·05	0·20	1·65
	0·10	0·10	1·48
	0·10	0·30	2·62
	0·10	0·50	3·96
	0·10	0·80	5·24
	0·30	0·10	2·99
	0·30	0·20	4·34
	0·50	0·10	4·48
	0·50	0·20	6·10
15·0	0·05	0·10	2·39
	0·05	0·20	2·75
	0·10	0·10	2·84
	0·10	0·20	3·46
	0·10	0·40	5·07
	0·10	0·50	5·64
	0·30	0·10	4·71
	0·30	0·20	7·10
	0·50	0·10	6·64
	0·50	0·20	10·64
20·0	0·05	0·10	4·34
	0·05	0·20	4·61
	0·10	0·10	4·82
	0·10	0·20	5·89(2)
	0·10	0·30	7·08
	0·10	0·40	8·06
	0·10	0·50	8·97
	0·20	0·10	6·34
	0·30	0·10	7·83
	0·30	0·20	11·25
	0·40	0·10	8·84
	0·50	0·10	10·05
	0·50	0·20	15·24
25·0	0·05	0·10	7·38
	0·05	0·20	8·21
	0·10	0·001	8·05
	0·10	0·005	7·96
	0·10	0·01	7·83
	0·10	0·02	8·07
	0·10	0·04	7·92
	0·10	0·05	7·90
	0·10	0·10	8·62(4)
	0·10	0·20	9·80
	0·10	0·30	11·33
	0·10	0·40	12·71
	0·10	0·50	13·89
	0·20	0·10	10·38
	0·30	0·10	12·63
	0·30	0·20	17·37
	0·50	0·10	16·58
	0·50	0·20	24·60

Visible spectra of reacted solutions were examined in detail for a number of runs and amounts of the products $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5NCS^{2+}$ were determined at 492 nm using $\varepsilon = 46$ and 181 l mol⁻¹ cm⁻¹ respectively. The ratio of the products, $R = [Co(NH_3)_5H_2O^{3+}] : [Co(NH_3)_5NCS^{2+}]$, can be expressed as in (5). A graph of R against

$$R = \frac{2(a[H^+] + b)}{c[H^+]} \cdot \frac{1}{[NCS^-]} + 1 \qquad (5)$$

$[NCS^-]^{-1}$ at 25 °C and $[H^+] = 0{\cdot}1$M (Figure 5) gave satisfactory linearity and from the gradient we were able to evaluate $2(a[H^+] + b)/c[H^+]$ as 1·09 mol l^{-1}. The value obtained from the rate constants (Table 6) is 1·05 mol l^{-1}.

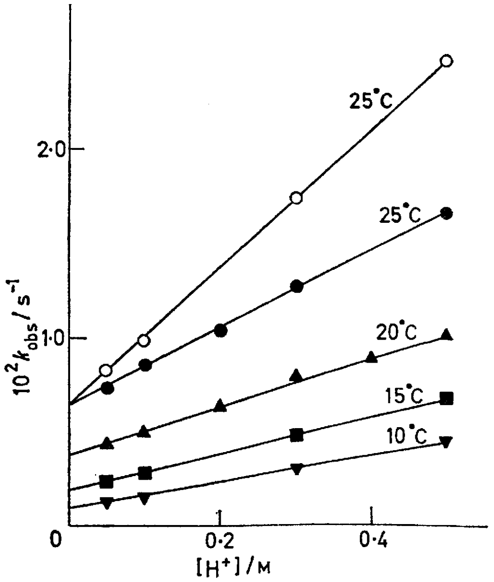

FIGURE 4 Dependence of rate constants on $[H^+]$ for hydroxo-bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex in the presence of thiocyanate ions, $I = 2{\cdot}0$M ($LiClO_4$). $[NCS^-] = 0{\cdot}1$ (full symbols) and 0·2M (○)

Ion-exchange separation of the products was carried out using Dowex(H^+) 50X 2—400 and 50X 12—400 resins, details as in the Experimental section. Two fractions were eluted in both cases. The first band (orange in colour) was identified spectrophotometrically as the complex $Co(NH_3)_5NCS^{2+}$, and the second (red) band gave a spectrum identical with that for $Co(NH_3)_5H_2O^{3+}$. There was no visible or spectrophotometric evidence for any other reaction product and we were unable to observe any purple band corresponding to the complex $Co(NH_3)_5SCN^{2+}$ containing *S*-bonded thiocyanate ion.[16] The separation of the complexes took *ca.* 3 days; the half-life for the rearrangement of the *S*-bonded thiocyanato-complex has been reported to be *ca.* 9 days at 25 °C.[16]

TABLE 6

Summary of rate constants obtained for hydroxo-bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex in the presence of thiocyanate ions, $I = 2{\cdot}0$M ($LiClO_4$)

Temp. / °C	10^3a / l mol^{-1} s^{-1}	10^3b / s^{-1}	$10c$ / l^2 mol^{-2} s^{-1}
10·0	0·53 ± 0·63	1·03 ± 0·26	0·53 ± 0·02
15·0	2·52 ± 0·39	1·90 ± 0·09	0·71 ± 0·02
20·0	3·24 ± 0·73	3·58 ± 0·36	1·02 ± 0·03
25·0	7·12 ± 0·66	6·45 ± 0·10	1·37 ± 0·03

TABLE 7

Summary of activation parameters from log (k/T) against $1/T$ dependences for hydroxo-bridge cleavage of the μ-hydroxo-bis[penta-amminecobalt(III)] complex in the presence of thiocyanate ions, $I = 2{\cdot}0$M ($LiClO_4$)

Rate constant	$\Delta H^‡$ / kcal mol^{-1}	$\Delta S^‡$ / cal K^{-1} mol^{-1}
a	17·7 ± 3·7	−9·2 ± 12·7
b	20·5 ± 0·5	0·1 ± 1·6
c	10·9 ± 0·6	−25·8 ± 2·2

Preliminary experiments indicated an enhancement in the rate of the bridge-cleavage process in the presence of chloride ions. This was not investigated further owing to the insoluble nature of the μ-hydroxo-complex in such solutions.

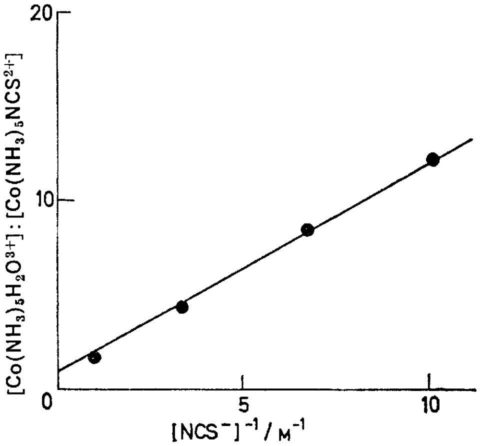

FIGURE 5 Dependence of the product ratio $[Co(NH_3)_5H_2O^{3+}] : [Co(NH_3)_5NCS^{2+}]$, as determined spectrophotometrically at 492 nm, on thiocyanate-ion concentration [equation (5)] $[H^+] = 0{\cdot}1$M, $I = 2{\cdot}0$M ($LiClO_4$)

DISCUSSION

The existence of a term, k_1, first order in hydrogen-ion concentration in the hydroxo-bridge-cleavage reaction of the μ-hydroxo-bis[penta-amminecobalt(III)] complex [equation (2)] has been firmly established by working over a wide range of $[H^+]$ (10^{-4}—2·0M). Earlier results,[9] which indicated no H^+ dependence, can readily be explained in view of the range of hydrogen-ion concentration (5×10^{-4}—5×10^{-2}M) investigated in that study. At such low concentrations there is no significant contribution to k_{obs} from the k_1 term in (2). The low value of the enthalpy of activation for k_1 ($\Delta H_1^‡ = 12{\cdot}0$ kcal mol^{-1}) is noted (assuming prior protonation of the hydroxo-bridge, k_1 is a composite term, *i.e.* $k_1 = K_pk_1'$ where K_p is the protonation constant and k_1' the rate constant for bridge cleavage of the aquo-complex). This is consistent with the weak bridging properties of a water molecule. In other words protonation of the hydroxo-bridge weakens the bonding of the oxygen atom to the two cobalt centres, and energy requirements for bridge cleavage are considerably reduced.

With the data obtained in this study it is possible to make comparison of the ease of cleavage of a hydroxo-bridge in mono-, di-, and tri-bridged dicobalt(III)

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[16] D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 655.

complexes (Table 8). The equilibrium between the tri-μ-hydroxo-bis[triamminecobalt(III) complex and that of di-μ-hydroxo-bis[triammineaquocobalt(III)] ($K = 53$ l mol^{-1} at 20 °C) is known to be rapid,[7] but rate constants have not been determined. Rate constants for the corresponding equilibrium involving the μ-amido-di-μ-hydroxo-bis[triamminecobalt(III)] complex ($K = 66$ l mol^{-1} at 25 °C) have been measured [17] and, in view of the similarity of the equilibrium constants K for the bridge-cleavage process, similar rate constants are anticipated for bridge cleavage in the two complexes. The hydrogen-ion dependences for dissociation of the di-μ-hydroxo-bis[bis(ethylenediamine)cobalt(III)] and di-μ-hydroxo-bis[tetra-amminecobalt(III)] complexes are more complicated.[12] Hoffman and Taube, in their study of the Cr^{2+} and Eu^{2+} reductions of the second of these complexes,[2] observed a term independent of reductant and dependent on [H$^+$] which is believed to correspond to cleavage of one of the bridges, where the reductant subsequently scavenges the bisaquo-product.

TABLE 8

Comparison of rate constants (25 °C) for hydroxo-bridge cleavage of some binuclear cobalt(III) ammine complexes

Complex	$\frac{k_1}{\text{l mol}^{-1}\ \text{s}^{-1}}$	$\frac{k_2}{\text{s}^{-1}}$	Ref.
$(NH_3)_5Co{\cdot}OH{\cdot}Co(NH_3)_5^{5+}$	$5{\cdot}37 \times 10^{-3}$	$7{\cdot}58 \times 10^{-3}$	This work
$(NH_3)_4Co{\cdot}\mu(OH,OH){\cdot}Co(NH_3)_4^{4+}$	$1{\cdot}2 \times 10^{-3}$ [a]	Not detected	2
$(NH_3)_4Co{\cdot}\mu(NH_2,OH){\cdot}Co(NH_3)_3^{4+}$	$7{\cdot}9 \times 10^{-5}$ [a]	Not detected	*b*
$(NH_3)_3(H_2O)Co{\cdot}\mu(OH,OH){\cdot}Co(H_2O)(NH_3)_3^{4+}$	$3{\cdot}5 \times 10^{-5}$ [c]	Not detected	7
$(NH_3)_3Co{\cdot}\mu(OH,OH,OH){\cdot}Co(NH_3)_3^{3+}$	Fast	Not detected	7
$(NH_3)_3Co{\cdot}\mu(NH_2,OH,OH){\cdot}Co(NH_3)_3^{3+}$	30	Not detected	17

[a] From Cr^{2+} studies; Cr^{2+} scavenges the bisaquo-product at a rate independent of [Cr^{2+}]. [b] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1991. [c] Cleavage of second hydroxo-bridge in studies on the tri-μ-hydroxo-bis[triamminecobalt(III)] complex.

TABLE 9

Comparison of rate constants k_1 and k_2 [as defined in equation (2)] for the cleavage of hydroxo- and oxo-bridges of binuclear complexes at 25 °C

	$\frac{k_1}{\text{l mol}^{-1}\ \text{s}^{-1}}$	$\frac{k_2}{\text{s}^{-1}}$	Ref.
$(NH_3)_5Cr{\cdot}OH{\cdot}Cr(NH_3)_5^{5+}$		$7{\cdot}6 \times 10^{-4}$	10
$(H_2O)_5Cr{\cdot}OH{\cdot}Cr(H_2O)_5^{5+}$		$1{\cdot}5 \times 10^{-6}$	20
$(en)_2Cr{\cdot}\mu(OH,OH){\cdot}Cr(en)_2^{4+}$		$4{\cdot}9 \times 10^{-5}$ (40 °C)	21
$(phen)_2Cr{\cdot}\mu(OH,OH){\cdot}Cr(phen)_2^{4+}$	$1{\cdot}0 \times 10^{-4}$		22
$Fe{\cdot}\mu(OH,OH){\cdot}Fe^{4+}$	3·33	0·42	19
$V{\cdot}\mu(OH,OH){\cdot}V^{4+}$	1·54	0·03	*a*
$Cr{-}O{-}Np{-}O^{4+}$		$2{\cdot}3 \times 10^{-6}$	*b*
$Cr{-}O{-}V^{4+}$	0·645	0·018	*c*
$(EDTA)Fe{-}O{-}Fe(EDTA)^{4-}$	$5{\cdot}0 \times 10^{8}$	1·2	*d*
$(HEDTA)Fe{-}O{-}Fe(HEDTA)^{2-}$	$3{\cdot}0 \times 10^{6}$	4·0	*d*
$(cdta)Fe{-}O{-}Fe(cdta)^{4-}$ [e]	*ca.* 10^{10}	9	*d*

[a] T. W. Newton and F. B. Baker, *Inorg. Chem.*, 1964, **3**, 569. [b] J. C. Sullivan, *J. Amer. Chem. Soc.*, 1962, **84**, 4256. [c] J. H. Espenson, *Inorg. Chem.*, 1965, **4**, 1533. [d] R. G. Wilkins and R. E. Yelin, *Inorg. Chem.*, 1969, **8**, 1470. [e] cdta = *trans*-1,2-Cyclohexanediaminetetra-acetate.

The behaviour of the mono-, di-, and tri-μ-hydroxo-complexes can be summarized as follows. Cleavage of the first bridge of a triply bridged complex is fast, of a doubly bridged complex slow, and of a singly bridged complex comparable or slightly faster than that of a doubly bridged complex. It is possible to account for the speed at which hydroxo-bridge cleavage occurs in triply bridged complexes in terms of strained ring structures.[18] However reformation of the third bridge from the corresponding bisaquo-complex is also rapid ($0{\cdot}415$ s^{-1} at 25 °C).[17] It is also apparent that reformation of the μ-amido-μ-hydroxo-complex from the corresponding bisaquo-complex and elimination of a water ligand from other μ-amido-complexes is rapid.[1,8] The intermolecular reformation of the μ-hydroxo-bis[penta-amminecobalt(III)] complex from mononuclear species was not observed and presumably requires much higher pH values. Also, since linear behaviour is observed in Figure 1, we can estimate $K_p < 0{\cdot}02$ l mol^{-1} for protonation of the hydroxo-bridge in μ-hydroxo-bis[penta-amminecobalt(III)]. From information available it would appear that the hydroxo-bridge-cleavage path independent of [H$^+$] plays a more significant role in the cleavage of the singly bridged complex. This observation seems reasonable since the presence of additional bridges will help to retain the binuclear structure and stretching of metal–OH bonds is less likely to lead to chemical change unless protonation also occurs.

Rate constants for the dissociation of a number of binuclear complexes of other metal ions are compared in Table 9. As pointed out previously,[19] dissociations of oxo-bridged binuclear complexes are much more dependent on hydrogen-ion concentration (ratio $k_1 : k_2$ larger)

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[17] Ref. 1; the reaction was studied at only 25 °C and the data are not extensive (7 runs).

[18] P. Andersen (*Acta Chem. Scand.*, 1967, **21**, 243) has determined the crystal structure of the tri-μ-hydroxo-bis[triammine-cobalt(III)] complex and reports an almost regular octahedral arrangement of ligands about each cobalt atom. The Co–Co distance of 2·28 Å is longer and the O–O distance shorter than might have been predicted.

[19] H. N. Po and N. Sutin, *Inorg. Chem.*, 1971, **10**, 428.

than are those of the di-μ-hydroxo-complexes. A second point to be made is that hydroxo-bridge cleavage of three μ-hydroxo-chromium(III) complexes [10,20,21] [but not of the complex $(phen)_2Cr\cdot\mu(OH,OH)\cdot Cr(phen)_2^{4+}$, ref. 22] is independent of $[H^+]$. A possible explanation is that hydroxo-bridges in the dichromium(III) complexes do not readily protonate due to electron shifts towards the chromium(III) ions which, compared with cobalt(III) and iron(III), have fewer *d* electrons. This is supported by the tendency of the μ-hydroxo-bridge of $(NH_3)_5Cr\cdot OH\cdot Cr(NH_3)_5^{5+}$ to lose a proton and form the oxo-complex $(NH_3)_5Cr\cdot O\cdot Cr(NH_3)_5^{4+}$ (pK_a 7·8).[23] Alternatively it could reflect increased S_N2 character in the bridge-cleavage reactions of the chromium(III) complexes. It has also been observed [10] that the chromium(III) complex $(NH_3)_5Cr\cdot OH\cdot Cr(NH_3)_5^{5+}$ readily loses an ammonia ligand (*rhodo* to *erythro* conversion) to give $(NH_3)_5Cr\cdot OH\cdot Cr(H_2O)(NH_3)_4^{5+}$. A much slower loss of ammonia has been observed in the case of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex.[1] There is no loss of ammonia in the case of the μ-hydroxo-bis[penta-amminecobalt(III)] complex, $(NH_3)_5\cdot Co\cdot OH\cdot Co(NH_3)_5^{5+}$, which undergoes bridge cleavage much more rapidly.

In the presence of thiocyanate ions a thiocyanate-dependent term is obtained in the rate law and k_1 and k_2 (now *a* and *b* respectively) are *ca.* 15% smaller due to ion-pair formation. From the inset to Figure 3 it is concluded that ion-pairing is complete at *ca.* 0·05M-lithium thiocyanate. If further ion-pairing occurs over the range $[NCS^-] = 0·05—0·5$M it does not affect the kinetics in any way. From the trend shown in the inset of Figure 3 it is concluded that ion-pairing is half complete as $[NCS^-]$ *ca.* 0·025M, and that the ion-pair formation constant (with just one thiocyanate ion involved) is *ca.* 40 l mol^{-1}. A different value would be obtained if ion-pairing were occurring at both extremities of the complex. No thiocyanato-complex is formed from paths *a* and *b*, although the complex is believed to be ion-paired. Similarly, for the thiocyanate-induced dissociation of the complex (path *c*), more than one thiocyanate ion is present in the activated complex and yet quantitative formation of equal amounts of the complexes $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5NCS^{2+}$ is observed. There was no evidence from ion-exchange experiments for the formation of the complex $Co(NH_3)_5SCN^{2+}$ containing *S*-bonded thiocyanate ion.

An interesting feature of this study is the relatively large contribution from the $[H^+]$ independent path *b* and the absence of a thiocyanate-dependent path which is independent of $[H^+]$. For hydroxo-bridge cleavage of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex in the presence of chloride [24] and bromide ions (X^-),[25] both $[H^+][X^-]$ and $[X^-]$ dependent terms are observed. The corresponding reaction in the presence of thiocyanate gives a relatively rapid first stage (the details of which appear complex),[26] followed by formation of the μ-amido-bis[tetra-amminethiocyanatocobalt(III)] complex.

EXPERIMENTAL

μ-Hydroxo-bis[penta-amminecobalt(III)] nitrate, $[(NH_3)_5Co\cdot OH\cdot Co(NH_3)_5](NO_3)_5$, was prepared as described in ref. 9. A sample of the complex was converted to the bromide salt $[(NH_3)_5Co\cdot OH\cdot Co(NH_3)_5]Br_5,H_2O$.[9] The nitrate salt of penta-amminethiocyanatocobalt(III), $[Co(NH_3)_5NCS](NO_3)_2$, was prepared by treating the penta-ammineaquocobalt(III) complex with an excess of thiocyanate and recrystallizing from nitrate ion media. Lithium perchlorate was prepared by adding perchloric acid (Hopkin and Williams, AnalaR) to lithium carbonate (Hopkin and Williams, Laboratory Reagent); the product was recrystallised three times. AnalaR grade sodium perchlorate (B.D.H.) and sodium nitrate (Hopkin and Williams) were used without recrystallization. Lithium thiocyanate (B.D.H., Laboratory Reagent) was purified by recrystallizing three times from water. Fresh solutions of the solid were standardized by titration of the acid released after passing aliquot portions down a column of Amberlite IR-120(H) ion-exchange resin. The concentration of the solution was also checked by direct titration of the thiocyanate ions with freshly prepared silver(I) nitrate using dichlorofluoroscein as indicator. The two methods agreed to within 2%.

Because of the low solubility of the μ-hydroxy-complex in 2M perchlorate ion solutions, the following procedure was used for kinetic runs. A known weight of complex was dissolved in *ca.* 3 cm^3 of thermostatted perchloric acid (10^{-4}M). The complex dissolved rapidly under these conditions and could then be added, with rinsing, to a thermostatted solution of $HClO_4$–ionic medium. Kinetic runs were followed on a Unicam SP 500 spectrophotometer fitted with a thermostatted cell housing. For the faster runs the direct read-out from an SP 500 Series 2 spectrophotometer was used.

The products obtained in a run, with $3·9 \times 10^{-3}$M-binuclear complex, $[H^+] = 0·1$M and $[NCS^-] = 1·0$M at 25 °C and $I = 2·0$M ($LiClO_4$), were separated using an ion-exchange procedure. An aliquot portion (20 cm^3) of the run solution was diluted to 1 l, passed down a Dowex(H^+) 50X 2—400 ion-exchange column, and eluted with 1M-$NaClO_4$ (procedure as described in ref. 16). A second aliquot portion (20 cm^3) of run solution was diluted to 1 l and passed down a Dowex(H^+) 50X 12—400 resin column. An eluent of 0·5M-$NaClO_4$–0·1M-$HClO_4$ gave two bands, the first (orange) of which was then eluted with 1·0M-$NaClO_4$–0·5M-$HClO_4$. Two bands were obtained in both cases. On elution both fractions were analysed by visible spectrophotometry and found to correspond to the complexes $Co(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5H_2O^{3+}$. We were unable to detect any purple bands on the resin columns (9 cm long) which might correspond to the *S*-bonded

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[20] R. E. Connick and G. Thompson, *Abs. 148th Nat. Meeting Amer. Chem. Soc.*, Chicago, Illinois, September 1964, Paper Nos. 0-23 and 0-24.

[21] D. Wolcott and J. B. Hunt, *Abs. 150th Nat. Meeting Amer. Chem. Soc.*, Atlantic City, New Jersey, September 1965, Paper No. 0-88.

[22] D. Wolcott and J. B. Hunt, *Inorg. Chem.*, 1968, **7**, 755.

[23] W. K. Wilmarth, H. Graff, and S. T. Gustin, *J. Amer. Chem. Soc.*, 1956, **78**, 2683.

[24] S. W. Foong, R. D. Mast, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc. (A)*, 1971, 1266.

[25] S. W. Foong and A. G. Sykes, to be published.

[26] S. W. Foong, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc. (A)*, 1970, 1064.

thiocyanato-complex. Total recovery of the complex was 92%.

The following procedure was employed for spectrophotometric product analyses of run solutions in the presence of thiocyanate ions. A known weight of complex was added to the required volume of water containing *ca.* 10^{-3}M-$HClO_4$ in a thermostatted double-walled vessel. The solution was stirred using a magnetic stirrer, and dissolution of the complex was virtually instantaneous. The required volume of a thermostatted solution of $HClO_4$, $LiClO_4$, and LiNCS was then added. The few seconds needed for transfer of this solution meant that very little of the binuclear complex had decomposed prior to addition of the thiocyanate ion solution. After *ca.* 30 min the absorbance at 492 nm was recorded.

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