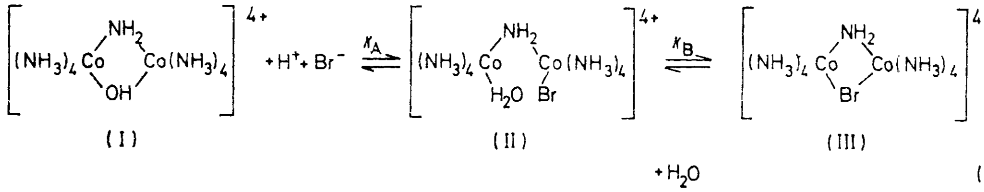
Reactions of μ-Hydroxo-dicobalt(III) Complexes. Part XI.† Kinetic Studies on the Reaction of Bromide with the μ-Amido-μ-hydroxo-bis-[tetra-amminecobalt(III)] Complex

By (Miss) **Siew-Wan Foong** and **A. Geoffrey Sykes**,* Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

The kinetics of hydroxo-bridge cleavage of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex (I) by bromide in aqueous perchloric acid have been investigated spectrophotometrically with $[Br^-] = 0{\cdot}5$—$2{\cdot}0$M, $[H^+] = 0{\cdot}5$—$2{\cdot}0$M, and $I = 2{\cdot}0$M ($NaClO_4$). The product in the rate-determining step is the aquo-bromo-complex, (II), which is in rapid equilibrium with the μ-amido-μ-bromo-complex (III), equation (i). The bromo-complex

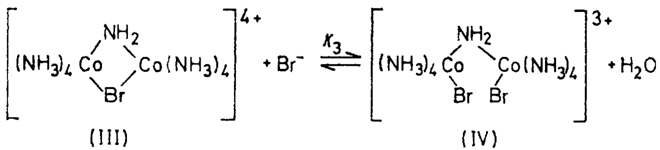


(i)

(III) and not (II) is predominant. Pseudo-first-order rate constants, k_{eq}, for the equilibration in (i) can be expressed as in equation (ii), where k_1 and k_2 are for hydroxo-bridge cleavage, and k_b for the back reaction (product

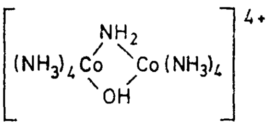
$$k_{eq} = k_1[H^+][Br^-] + k_2[Br^-] + k_b \qquad \text{(ii)}$$

of a rate constant and the equilibrium constant K_B) is as determined previously. At 25 °C $k_1 = (4{\cdot}33 \pm 0{\cdot}17) \times 10^{-4}$ l^2 mol^{-2} s^{-1}, $k_2 = (1{\cdot}4 \pm 0{\cdot}2) \times 10^{-4}$ l mol^{-1} s^{-1}, and $K_AK_B = ca.\ 1{\cdot}1$ l^2 mol^{-2}. From the temperature dependence $\Delta H_1^\ddagger = 17{\cdot}3 \pm 0{\cdot}8$ kcal mol^{-1}, $\Delta S_1^\ddagger = -16{\cdot}2 \pm 2{\cdot}6$ cal mol^{-1} K^{-1}, $\Delta H_2^\ddagger = 25{\cdot}7 \pm 1{\cdot}8$ kcal mol^{-1},



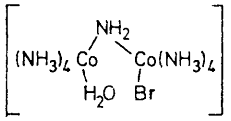
(iii)

and $\Delta S_2^\ddagger = 10{\cdot}8 \pm 5{\cdot}7$ cal mol^{-1} K^{-1}. Reaction (iii) is effective at $[Br^-] > 1{\cdot}7$M, where (II) may be involved as an intermediate. At 25 °C $K_3 = ca.\ 0{\cdot}03$ l mol^{-1}, and $k_{-3} > 2 \times 10^{-2}$ s^{-1} (at 1·5 °C), $I = 2{\cdot}0$M ($NaClO_4$).



(I)

DETAILS of hydroxo-bridge cleavage reactions of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex (I) in aqueous perchloric acid solutions with a variety of anions including chloride,[1] nitrate,[2] sulphate,[3] selenate,[4] phosphate,[5] and acetate,[6] have been described previously. The reactions have yielded new complexes, which have been characterized, while kinetic data are relevant in considering the mechanism of bridge cleavage and whether this is S_N1 or S_N2 in character.[7] The chloride study previously described [1] has similar features to the bromide study which is now considered. With chloride Werner originally assigned an aquo-chloro-structure to the crystalline product.[8] Similarly he assigned the aquo-bromo-structure (III) to the bromo-complex obtained on treating the sulphate salt of (I) with concentrated HBr.[9] A bromo-complex has been isolated in connection with the present study, and from analyses and i.r. spectrometry (first part of paper), it is concluded that this has a μ-amido-μ-bromo-structure (III). Aqueous solutions of (III) are believed to give small (<6%) amounts of (II) in a relatively rapid equilibrium,[10] and subsequently at low or zero bromide concentrations (I) is formed. The reaction of (I) with bromide in aqueous perchloric acid solutions ($I = 2{\cdot}0$M)



(II)

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† Part X is ref. 5.

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

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

[3] M. B. Stevenson, A. G. Sykes, and R. S. Taylor, *J. Chem. Soc.* (*A*), 1970, 3214.

[4] S. W. Foong and A. G. Sykes, *J.C.S. Dalton*, 1973, 504.

[5] J. D. Edwards, S. W. Foong, and A. G. Sykes, *J.C.S. Dalton*, 1973, 829.

[6] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 2364.

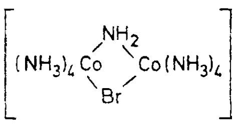
[7] R. S. Taylor and A. G. Sykes, *J.C.S. Dalton*, in the press.

[8] A. Werner, *Annalen*, 1910, 375, 45.

[9] Ref. 8, p. 50.

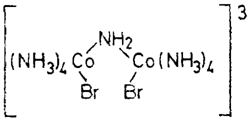
[10] M. R. Hyde and A. G. Sykes, *J.C.S. Dalton*, in the press.

provides the subject of this paper where (II) is again to be regarded as a transient species. Thus at low bromide-ion concentrations ($<1{\cdot}7$M) (II) is formed in the rate-determining step and reacts rapidly to give (III). At



(III)

higher bromide concentrations the bis-bromo-complex (IV) is formed but this species is not predominant until concentrations of HBr approaching 8M.



(IV)

Characterization of the Bromo-product.—It was not possible in this work to isolate the dihydrate of (II) reported by Werner.[9] Solutions containing predominantly (IV) give samples of (III) as the least-soluble form. Bromide and perchlorate salts were isolated following the reaction of (I) with HBr (details in Experimental section). Analyses indicated no water molecules, and are consistent with structure (III). This structural assignment has been confirmed by i.r. spectrometry as follows. First of all a comparison of metal–chloride stretching frequencies for $[Co(NH_3)_5Cl]Cl_2$ and $[(NH_3)_4Co{\cdot}\mu(NH_2,Cl){\cdot}Co(NH_3)_4]Cl_4$ was made (see Figure 1). The second of these complexes is known to have a μ-amido-μ-chloro-structure.[11] Perchlorate salts give identical spectra to those of the chlorides. Metal–bromide stretching frequencies for bromide and perchlorate salts of $[Co(NH_3)_5Br]^{2+}$ and $[(NH_3)_4Co{\cdot}\mu(NH_2,Br){\cdot}Co(NH_3)_4]^{4+}$ were then recorded. The bromide salt of the latter does not give satisfactory resolution in the region 220—170 cm^{-1}, possibly due to lattice vibrations. However the frequencies observed for the perchlorate salts (see Figure 2) confirm the μ-amido-μ-bromo-bridged structure. The assignments made (see Table 1) give ν(M–Br)/(M–Cl) ratios for mononuclear and binuclear complexes in the range 0·71—0·75, as observed for halide complexes of other metals.[12] The frequencies for the mononuclear complex are in good agreement with values previously reported;[13-16] aquopenta-amminecobalt(III) has no similar absorption bands in the 300—180 cm^{-1} region (see Figures 1 and 2). Ratios of frequencies observed for binuclear to mononuclear complexes are in the range 0·90—0·94. Similar ratios have been observed for bridging and terminal halide ions in complexes $M_2Cl_9^{3-}$ (M = V, Cr),[17] in which the metal is also in oxidation state (III) and the geometry octahedral. The lowering of metal–chloride and metal–bromide frequencies for the binuclear compared to mononuclear complexes is consistent with bridging halide ions. In the case of the bromo-complex no other information is available regarding the structure.

TABLE 1

Metal–halide stretching vibrations. Numbers in parentheses indicate number of spectra recorded

Complex	Frequency/cm^{-1}
$[Co(NH_3)_5Cl]Cl_2$	285 (3) [a,b]
$[Co(NH_3)_5Cl](ClO_4)_2$	295 (2) [b]
$[(NH_3)_4Co{\cdot}\mu(NH_2,Cl){\cdot}Co(NH_3)_4]Cl_4,4{\cdot}5H_2O$	269 (5)
$[(NH_3)_4Co{\cdot}\mu(NH_2,Cl){\cdot}Co(NH_3)_4](ClO_4)_4$	268 (4)
$[Co(NH_3)_5Br](ClO_4)_2$	214 (2) [c]
$[(NH_3)_4Co{\cdot}\mu(NH_2,Br){\cdot}Co(NH_3)_4](ClO_4)_4$	192 (3)

[a] With the chloride (but not the perchlorate) salt splitting is apparent as reported in references 15 and 16 (see footnote *b*). [b] Previous values 283 cm^{-1} for $[Co(NH_3)_5Cl]Br_2$ and $[Co(NH_3)_5Cl](NO_3)_2$ and 290 cm^{-1} for $[Co(NH_3)_5Cl]Cl_2$ (ref. 13); 284 cm^{-1} for $[Co(NH_3)_5Cl]Cl_2$ (ref. 14); 278, 284 cm^{-1} for $[Co(NH_3)_5Cl]Cl_2$ (ref. 15); 279, 285 cm^{-1} for $[Co(NH_3)_5Cl]Br_2$ (ref. 16). The value given in ref. 12, p. 157, appears to be in error. [c] Previous values for $[Co(NH_3)_5Br]Br_2$ are 205 cm^{-1} (ref. 14) and 203 cm^{-1} (ref. 15); and for $[Co(NH_3)_5Br]Cl_2$, 201 cm^{-1} (ref. 16). Ref. 12, p. 157, gives value 215 cm^{-1}, anions unspecified.

Equilibration Processes.—Solutions of (I) ($\lambda_{max.}$ 520 nm, ε = 149 l mol^{-1} cm^{-1} in 2M-HClO$_4$) on equilibration with HBr, concentrations in the range 0·3—1·7M, give (III) ($\lambda_{max.}$ 560 nm, ε = 154 l mol^{-1} cm^{-1}). The complex (III) rather than (II) is favoured as the dominant species in solution. Cross-over points are observed at 475 and

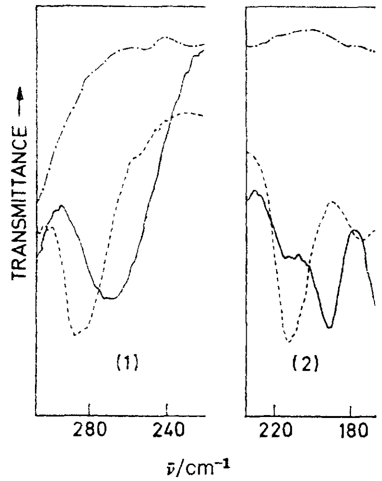


FIGURE 1 Infrared spectra of bridging and terminal chloride in cobalt(III) complexes $[(NH_3)_4Co{\cdot}\mu(NH_2,Cl){\cdot}Co(NH_3)_4]Cl_4$, 4·5 H_2O (——); $[Co(NH_3)_5Cl]Cl_2$ (— — —). The spectrum of the complex $[Co(NH_3)_5H_2O]Cl_3$ (— · — · —), which has no bonded chloride, is also shown.

FIGURE 2 Evidence for bridging bromide from infrared spectra. Spectra shown correspond to $[(NH_3)_4Co{\cdot}\mu(NH_2,Br){\cdot}Co(NH_3)_4](ClO_4)_4$ (——); $[Co(NH_3)_5Br]Br_2$ (— — —); and $[Co(NH_3)_5H_2O]Cl_3$ (— · — · —)

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[11] R. Barro, R. E. Marsh, and W. P. Schaefer, *Inorg. Chem.*, 1970, **9**, 2131.

[12] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1970, pp. 214—218.

[13] G. W. Watts and D. S. Klett, *Inorg. Chem.*, 1964, **3**, 782.

[14] L. Sacconi, A. Sabatini, and P. Gans, *Inorg. Chem.*, 1964, **3**, 1772.

[15] K. W. Bowker, E. R. Gardner, and J. Burgess, *Inorg. Chim. Acta*, 1970, **4**, 626.

[16] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1966, **22**, 759.

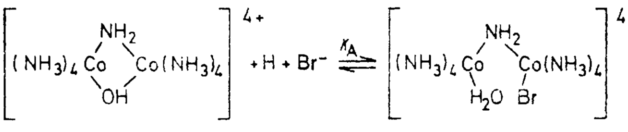
[17] R. J. H. Clark, *Spectrochim. Acta*, 1965, **21**, 955.

TABLE 2

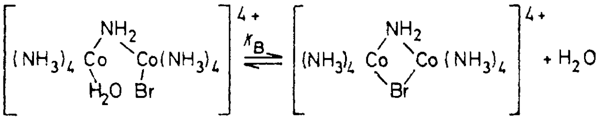
Pseudo-first order rate constants for the equilibration of (I) and (III); $I = 2{\cdot}0$M (NaClO$_4$). Complex (I) present initially

Temp. / °C	[Br$^-$] / M	[H$^+$] / M	10^3[Complex] / M	$10^3 k_{eq}$ / s^{-1}
25·0	2·00	0·50	0·92	1·12
	2·00	0·75	0·75	1·29
	2·00	0·75	1·01	1·29
	2·00	1·00	0·92	1·46
	2·00	1·50	0·51	1·90
	2·00	1·75	0·75	2·15
	2·00	1·75	1·01	2·12
	2·00	2·00	0·51	2·32
	1·50	0·50	0·90	0·89
	1·50	1·00	0·75	1·21
	1·50	1·50	1·00	1·53
	1·50	2·00	0·90	1·73
	1·00	0·50	0·92	0·67
	1·00	1·00	0·89	0·96
	1·00	1·50	0·69	1·10
	1·00	2·00	1·00	1·41
	1·00	2·00	0·89	1·39
	0·50	1·00	0·87	0·66
	0·50	1·50	0·87	0·79
	0·50	1·50	1·05	0·73
30·0	1·50	0·50	0·90	1·79
	1·50	0·80	0·90	2·08
	1·50	1·00	0·92	2·31
	1·50	1·30	0·92	2·56
	1·50	1·50	0·86	2·85
	1·50	2·00	0·86	3·44
35·0	1·50	0·50	0·86	2·92
	1·50	0·80	0·92	3·50
	1·50	1·00	0·86	3·62
	1·50	1·30	0·92	4·10
	1·50	1·50	0·89	4·50
	1·50	2·00	0·89	5·40
40·15	1·50	0·50	0·91	5·28
	1·50	0·80	0·91	5·93
	1·50	1·00	0·92	6·53
	1·50	1·30	0·92	7·27
	1·50	1·50	0·90	8·13
	1·50	2·00	0·90	9·10

541 nm, and during the conversion of (I) into (III) (and the reverse) a well defined isosbestic is observed at 473 nm, and a less well defined isosbestic (± 4 nm) is observed at 540 nm. Redox studies with V^{2+} indicate that there is never >6% of (II) and the amount present may be considerably less than this value.[10] Direct conversion of (I) into (III) is hardly possible and for this reason alone intermediate formation of (II) is necessary. The movement in the isosbestic at 540 nm is probably due to a small build up of (II). Kinetic plots of absorbance changes for the conversion (I) ⟶ (III) and (III) ⟶ (I), wavelengths in the range 435—560 nm, indicate only a single rate-determining step, and support a reaction sequence (1) followed by the relatively rapid equilibration (2). Figure 3 indicates the variation of absorption coefficients ε_{obs}, $\lambda = 560$ nm, for equilibrated solutions of (I) with varying amounts of HBr. The value of ε_{obs} (partially) levels off *ca.* 1·7M-HBr, when ε_{obs} has the same value as for (III). With (HBr) > 1·7M, ε_{obs} increases further, and (IV) with an absorption maximum at (or close to) 560 nm is formed $200 < \varepsilon < 400$ l mol^{-1} cm^{-1}. The increase in absorption with [HBr] is similar in appearance to that reported for the addition of HCl to (I) (Figure 4).[1] It will be recalled that in the case of chloride absorbance changes could be followed on adjusting [HCl] in the range 2—8M, and rate constants for the observed re-equilibration gave an approximately first-order dependence on [Cl$^-$].[1] This is consistent with the formation of the bis-chloro-analogue of (IV). From the similarity in the two curves for HCl and HBr in Figure 4 we conclude that the bis-bromo-complex (IV) is formed on increasing [HBr] > 1·7M. We choose to express this further equilibration as in (3), since (III) rather than (II) is the dominant mono-bromo-species. The reaction may of course proceed by way of (II).



(1)



(2)

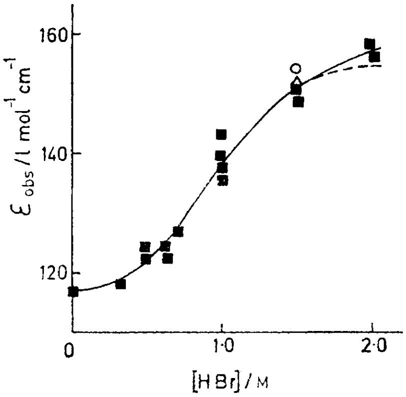


FIGURE 3 The variation of ε_{obs} with [HBr] at 25 °C, $\lambda = 560$ nm, $I = 2{\cdot}0$M (NaClO$_4$). The levelling off which is apparent at [HBr] = *ca.* 1·7M corresponds to complete formation of (II)–(III). Data detained at 35 (△) and 40 °C (○) are also indicated

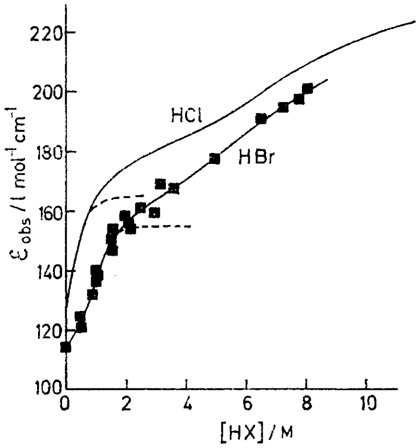
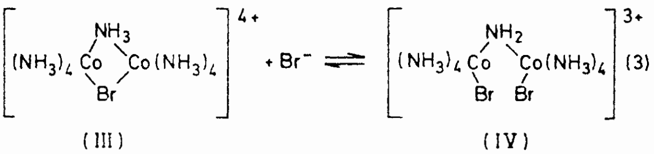


FIGURE 4 A comparison of the variation of ε_{obs} with [HX] (X$^-$ = Cl$^-$ and Br$^-$). The changes occurring at [HBr] 1·7M are attributed to the formation of (IV). Ionic strength not adjusted to constant value



(3)

(III) (IV)

Kinetics of Hydroxo-bridge Cleavage.—The decrease in concentration of (I) was monitored at 560 nm with $[Br^-] = 0{\cdot}5$—$2{\cdot}0$M and $[H^+] = 0{\cdot}5$—$2{\cdot}0$M. At ionic strength 2·0M the equilibrium (3) makes negligible contribution even when $[Br^-] = 2{\cdot}0$M, and is relatively rapid (see later section). The ionic strength was adjusted to 2·0M with $NaClO_4$, which has previously been shown to be satisfactory for reactions of (I).[1] Plots of log $(O.D._\infty - O.D._t)$ against time were linear to at least 80% completion; values of the final absorbance $O.D._\infty$ were as determined experimentally after 6—8 half-lives. Pseudo-first-order rate constants, k_{eq}, were obtained from these plots, and give a good fit to (4), where k_1

$$k_{eq} = k_1[H^+][Br^-] + k_2[Br^-] + k_b \qquad (4)$$

and k_2 relate to the forward reaction in (1) and the rate constant k_b is for the back reaction and is as determined previously.[18,*] It has been shown that k_b exhibits little dependence on $[H^+]$ over the range 0·5—2·0M, and since k_b makes only relatively small contributions in the experiments reported here the $[H^+]^{-1}$-dependent term is neglected. Plots of $(k_{eq} - k_b)/[Br^-]$ against $[H^+]$ give good linearity (Figure 5) from which k_1 (gradient) and

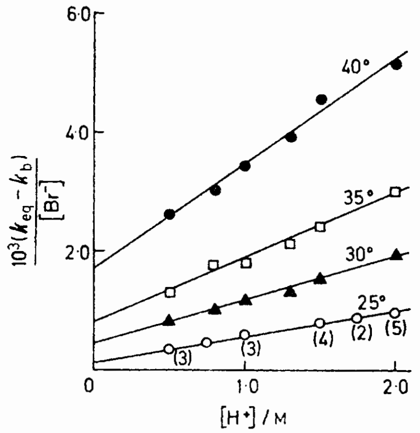


FIGURE 5 The hydrogen-ion dependence of k_{eq} after allowing for the back reaction k_b, $I = 2{\cdot}0$M ($NaClO_4$); the experimental data give a good fit to equation (4). Number of runs which have been averaged are indicated in parentheses

k_2 (intercept) were evaluated (Table 3) by a least-squares treatment with no weighting factor. Activation parameters for k_1 and k_2 were obtained using a non-linear least-squares programme,[19] with each data point given unit weighting, and are $\Delta H_1^\ddagger = 17{\cdot}3 \pm 0{\cdot}8$ kcal mol^{-1}, $\Delta S_1^\ddagger = -16{\cdot}2 \pm 2{\cdot}6$ cal mol^{-1} K^{-1}, $\Delta H_2^\ddagger = 25{\cdot}7 \pm 1{\cdot}8$ kcal mol^{-1}, and $\Delta S_2^\ddagger = 10{\cdot}8 \pm 5{\cdot}7$ cal mol^{-1} K^{-1}. Runs at 40 °C were acceptable (contrast the chloride study) because higher halide-ion concentrations could be used without interference from (2), and under these conditions (1) was sufficiently rapid to exclude decomposition of one or other of the binuclear complexes involved.[1]

TABLE 3

Summary of k_1 and k_2 values (forward reaction), and k_b values (back reaction), $I = 2{\cdot}0$M ($NaClO_4$)

Temp. / °C	10^4k_1 / l^2 mol^{-2} s^{-1}	10^4k_2 / l mol^{-1} s^{-1}	10^4k_b [a] / s^{-1}
25·0	4·33 ± 0·17	1·4 ± 0·2	3·4
30·0	7·30 ± 0·26	4·5 ± 0·3	5·4
35·0	10·80 ± 0·53	8·2 ± 0·7	8·6
40·2	17·62 ± 0·85	17·2 ± 1·1	13·4

[a] From best line in graph of temperature dependence of k_{-1}, ref. 18; for k_1 in that study read k_{-1}/K_B in this paper.

Determination of the Equilibrium Constant K.—The overall equilibrium constant K $(= K_AK_B)$ for equations (1) and (2) can be determined spectrophotometrically. The ratio of rate constants k_1/k_b is also a measure of this quantity. Solutions of (I) were allowed to equilibrate with $[H^+]$ and $[Br^-]$ in the range 0·3—2·0M and absorption coefficients ε_{obs} were determined at 560 nm. Equation (5) relating changes in ε_{obs} with $[H^+]$ and

$$\frac{1}{\varepsilon_{obs} - \varepsilon_{I}} = \frac{1}{K(\varepsilon_{III} - \varepsilon_{I})}\,\frac{1}{[H^+][Br^-]} + \frac{1}{\varepsilon_{III} - \varepsilon_{I}} \qquad (5)$$

$[Br^-]$ to K can be derived, where ε_I and ε_{III} are for (I) and (III) respectively. Values of K were determined first for each ε_{obs} and an average taken, and secondly from a plot of $(\varepsilon_{obs} - \varepsilon_I)^{-1}$ against $[H^+]^{-1}[Br^-]^{-1}$ (see Figure 6). The first treatment gives $K = 1{\cdot}12 \pm 0{\cdot}29$ l^2 mol^{-2} at 25 °C. The second, using a least-squares treatment with weighting such that the line is required to pass through the point $[H^+]^{-1}[Br^-]^{-1} = 0$ and $\varepsilon_{obs} = \varepsilon_{III} = 155 \pm 3$ l mol^{-1} cm^{-1} (no other weighting), gives $K = 0{\cdot}97 \pm 0{\cdot}10$ l^2 mol^{-2} at 25°. A comparison of K from spectrophotometric and kinetic studies is made in Table 4. The variation in temperature 25—40 °C is seen to have little or no effect on K.

TABLE 4

Determination of the overall equilibrium constant K $(= K_AK_B)$ for equations (1) and (2) by spectrophotometric and kinetic method, $I = 2{\cdot}0$M ($NaClO_4$)

Temp. / °C	K(Spec) [a] / l^2 mol^{-2}	K(Spec) [b] / l^2 mol^{-2}	k_1/k_b [c] / l^2 mol^{-2}
25·0	1·12 ± 0·29	0·97 ± 0·10	1·26
30·0	1·00 ± 0·34	0·84 ± 0·06	1·35
35·0	1·21 ± 0·27	1·08 ± 0·09	1·26
40·2	1·19 ± 0·43	0·94 ± 0·07	1·32

[a] Average of individual K values. [b] Computed from graph, Figure 6, with intercept given by $\varepsilon_{III} = 155 \pm 3$ l mol^{-1} cm^{-1}. [c] The ratio k_1/k_b from kinetic studies gives K.

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[*] The rate constant k_b is k_1 in ref. 18. It is also equal to k_{-1}/k_B elsewhere in this paper.

[18] M. B. Stevenson, R. D. Mast, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 937.

[19] Los Alamos Report LA 2367 (1959) and Addenda by R. H. Moore and R. K. Zeigler.

Estimation of Equilibrium Constant K_3.—The extent of formation of (IV) in equation (2) is small with [HBr] $< 2{\cdot}0$M, and it was not possible to determine K_3 from measurements on solutions $I = 2{\cdot}0$M as in the HCl study. We have assumed that changes in absorption spectra with [HBr] $> 2{\cdot}0$M are entirely due to the formation of (IV). Since the ionic strength was not adjusted, and concentrations of HBr up to 8M were used, it is necessary to take account of variation in the activities of the various species. An approximate value of K_3 was obtained assuming that activity coefficients for (III) and (IV) at 10^{-3}M concentrations effectively cancel out, and that for bromide as with chloride (see ref. 1), the activity of bromide is to a first approximation the same as $[\mathrm{Br}^-]$. Hence equation (6) can be derived,

$$\frac{1}{\varepsilon_{\mathrm{obs}} - \varepsilon_{\mathrm{III}}} = \frac{1}{K_3(\varepsilon_{\mathrm{IV}} - \varepsilon_{\mathrm{III}})} \frac{a_{\mathrm{W}}}{[\mathrm{Br}^-]} + \frac{1}{\varepsilon_{\mathrm{IV}} - \varepsilon_{\mathrm{III}}} \tag{6}$$

where $\varepsilon_{\mathrm{IV}}$ is for (IV) and a_{W} is the activity of water. Unfortunately values of a_{W} are available only for the more dilute HBr solutions. Values of a_{W} for concentrations of HBr up to 2·8M can be calculated from osmotic coefficients.[20] Above this concentration it is possible to base calculations of the activity of water upon the activity of HBr as a function of concentration.[21] By extrapolating data given by Spreer and King[22] values of a_{W} at 25 °C have been obtained (see Table 5). A linear plot of $(\varepsilon_{\mathrm{obs}} - \varepsilon_{\mathrm{III}})^{-1}$ against $a_{\mathrm{W}}/[\mathrm{Br}^-]$ is obtained (Figure 7) from which $K_3 = ca.\ 0{\cdot}03$ l mol^{-1} at 25 °C. From the intercept $\varepsilon_{\mathrm{IV}} = ca.\ 290$ l mol^{-1} cm^{-1}. At 1·5 °C we estimate $K_3 = ca.\ 0{\cdot}02$ l mol^{-1}.

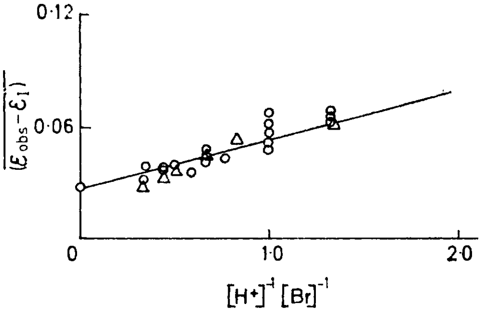

FIGURE 6 The spectrophotometric determination of K using equation (5). The points marked are for 25 (○) and 40·2 °C (△), $I = 2{\cdot}0$M (NaClO$_4$)

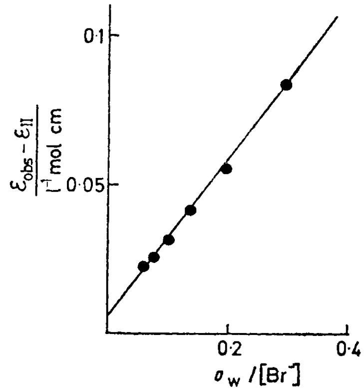

FIGURE 7 The estimation of K_3 at 25 °C for reaction (3) from spectrophotometric measurements using equation (6)

TABLE 5

The formation of (IV) at high HBr concentrations (25 °C), equation (3)

[HBr] [a] M	$\varepsilon_{\mathrm{obs}}$ [b] l mol^{-1} cm^{-1}	a_{W} [c]
3·0	167	0·89
4·0	173	0·78
5·0	179	0·69
6·0	186·5	0·60
7·0	194	0·54
8·0	200	0·48

[a] Ionic strength not adjusted; I = [HBr]. [b] From best line in Figure 4. [c] Obtained by extrapolation of data in ref. 22.

Rate of Equilibration K_3.—Procedures similar to those for chloride were used. Solutions containing (IV) in 8·0M-HBr at 1·5 °C were diluted to 2·0M-HBr in the hope that it would be possible to follow the kinetics of the equilibration of (III) and (IV) at 560 nm. Volume changes on dilution were negligible, but temperature changes were significant and had to be allowed for. Blank experiments with precooled solutions (using an ice–salt mixture) were carried out in order to reproduce the desired final temperature (1·5 °C). The equilibration was complete within 3 min, so that the half-life is <30 s. Assuming the equilibration exhibits the dependence $k_3[\mathrm{Br}^-] + k_{-3}$ (where $K_3 = k_3/k_{-3}$), and $K_3 = ca.\ 0{\cdot}02$ l mol^{-1} at 1·5 °C, a value $> 2 \times 10^{-2}$ s^{-1} may be assigned to k_{-3} at 1·5 °C, $I = 2{\cdot}0$M (NaClO$_4$).

DISCUSSION

Although three bromo-complexes (II)—(IV) are relevant to this study, only one of these has been isolated, and analyses and i.r. spectra indicate that this is the μ-amido-μ-bromo-complex (III). The i.r. investigation has been put on a sound basis by comparisons with the corresponding chloro-complex which, from an X-ray crystallographic study,[11] has been shown to have a μ-amido-μ-chloro-structure as in (III). It has also been concluded that μ-bromo- and μ-chloro-structures (III) rather than aquo-complexes as in (II) are retained in aqueous solution from pH measurements on solutions of acid-free samples, from p.m.r. studies, and from the kinetics of reductions by V^{2+} and Cr^{2+}.[10] Furthermore kinetic plots for the conversion of (III) into (I),[1] and now for (I) into (III) give good linearity, and it is concluded that (II) is a transient species.

Attempts to isolate (II) and the chloro-analogue have so far proved unsuccessful. A particularly promising method of isolating the chloro-analogue of (II) following a procedure used by Werner,[23] was thought to be the

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[20] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, 1949, **45**, 612.

[21] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1959, p. 481; 'International Critical Tables,' ed. E. W. Washburn, McGraw-Hill, New York, 1928, vol. 3, p. 55.

[22] L. O. Spreer and E. L. King, *Inorg. Chem.*, 1971, **10**, 918.

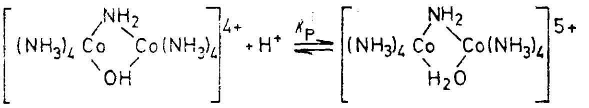
[23] Ref. 8, p. 47.

addition of dilute sulphuric acid to a freshly prepared solution of the chloride salt of (III). Rapid and quantitative precipitation occurred, and analyses (H, 5·75%; Cl, 6·7%) were as expected for the sulphate salt of a chloro-complex containing two water molecules. The metal–halide stretching frequency of the sample remained at 269 cm^{-1} however, which corresponds to a μ-chloro-structure as in (III) rather than (II).

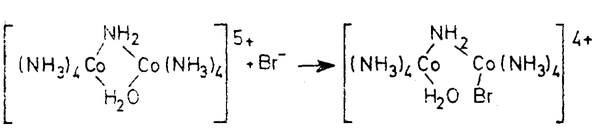
Some slight variation (±4 nm) in the isosbestic at 540 nm (but not that at 473 nm) could be explained by the build-up of small amounts of the aquo-bromo-complex (II). Sufficient checks have been carried out however which lead us to the conclusion that the build-up of (II) is unlikely to exceed 6%. Similar conclusions have been possible also for the chloro-analogue. Other side-reactions could alternatively account for the isosbestic shift and we do not presume that our observations are necessarily an indication of the extent of build-up of (II).

At the time of earlier kinetic studies it was assumed, following Werner's lead, that the starting bromo-complex was in fact (II).[9] The kinetics reported can be reassigned to the conversion (III) into (I) where the first stage involves a rapid equilibration (III) $\rightleftharpoons$ (II) [the formation constant for (II) is $1/K_B$], with (II) $\longrightarrow$ (I) rate-determining (rate constants k_{-1} and k_{-2}). Thus at 25 °C the measured rate constant for the dominant $[H^+]$-independent path is now the composite term $k_{-1}/K_B = 3{\cdot}43 \times 10^{-4}\ s^{-1}$, and activation parameters are $\Delta H^‡ = 16{\cdot}1 \pm 1{\cdot}0$ kcal mol^{-1} and $\Delta S^‡ = -20{\cdot}7 \pm 3{\cdot}0$ cal K^{-1} mol^{-1}. For the $[H^+]^{-1}$-dependent path the measured quantity is $k_{-2}K_a/K_B$, where K_a is the acid dissociation constant for the H_2O ligand of (II).

Our interpretation of the k_1 and k_2 terms is the same as in the HCl study.[1] Thus for k_1 there is rapid protonation of the hydroxo-bridge (7) prior to cleavage (8).



$$[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4]^{4+} + H^+ \overset{K_P}{\rightleftharpoons} [(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}H_2O)Co(NH_3)_4]^{5+} \quad (7)$$



$$[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}H_2O)Co(NH_3)_4]^{5+} + Br^- \longrightarrow [(NH_3)_4(H_2O)Co(\mu\text{-}NH_2)Co(Br)(NH_3)_4]^{4+} \quad (8)$$

The rate constant k_1 is, therefore, the product of the protonation constant K_p and the rate constant for (8). Since there is a good linear dependence in Figure 5 (and in the corresponding figure for the chloride study) we conclude that $K_p < 0{\cdot}03$ l mol^{-1}. For the k_2 path bridge cleavage occurs without prior protonation of the bridge. The difference in $\Delta H^‡$ and $\Delta S^‡$ values for k_1 and k_2 (8·4 kcal mol^{-1} and 27·0 cal mol^{-1} K^{-1}) are similar in magnitude to those observed for HCl (8·8 kcal mol^{-1} and 25·5 cal mol^{-1} K^{-1}).[1] In view of this agreement there would seem to be little doubt that k_2, although it makes a relatively small contribution, is a genuine kinetic term and is not attributable to medium effects.

The formation of (IV) [equation (3)] is not effective until [HBr] > 1·7M at which stage formation of (III) is nearing completion. Formation of (III) ($K = K_AK_B =$ *ca.* 1·1 l^2 mol^{-2}) is less favourable than formation of the chloro-analogue of (III) (*ca.* 11 l^2 mol^{-2}) at 25 °C. The agreement of spectrophotometric and kinetic values of K is regarded as satisfactory, particularly as rate constants for (III) into (I) were determined in the absence of free halide ions. Estimates of K_3 for the formation of the bis-halogeno-complexes, *e.g.* (IV), indicate a less favourable value for bromide (*ca.* 0·03 l mol^{-1}) as compared to chloride (0·09 ± 0·04 l mol^{-1}) at 25 °C. Formation of the bisthiocyanato-complex $[(NH_3)_4(NCS)Co{\cdot}NH_2{\cdot}Co(NCS)(NH_3)_4]^{3+}$ is much more favourable,[24] and in this instance isolation and characterization of the product was possible.

The acid dissociation constant for the aquo-ligand of (II) is not known (values *ca.* 10^{-6} mol l^{-1} reported in ref. 18 are incorrect, see ref. 10), and the true rate constant k_{-2} for the $[H^+]^{-1}$-dependent pathway for (III) into (I) (the reverse of k_2) cannot, therefore, be evaluated. It is not possible at this juncture therefore to comment on the ratio k_2/k_{-2} and hence determine the overall equilibrium constant K for this kinetic path. It is, of course, still possible that the hydroxo-group of the conjugate-base form of (II) reacts slower than expected due to hydrogen bonding as suggested previously.[1]

TABLE 6

Summary of data for the interconversion of the μ-amido-μ-hydroxo- (I), μ-amido-μ-bromo- (III), and bis-bromo- (IV) complexes at 25 °C and $I = 2{\cdot}0$M ($NaClO_4$) except where stated

k_1	$= 4{\cdot}33\ (\pm 0{\cdot}17) \times 10^{-4}$ $l^2\ mol^{-2}\ s^{-1}$	$\Delta H_1^‡$ $\Delta S_1^‡$	$= 17{\cdot}3 \pm 0{\cdot}8$ kcal mol^{-1} $= -16{\cdot}2 \pm 2{\cdot}6$ cal mol^{-1} K^{-1}
k_2	$= 1{\cdot}4\ (\pm 0{\cdot}2) \times 10^{-4}$ $l\ mol^{-1}\ s^{-1}$	$\Delta H_2^‡$ $\Delta S_2^‡$	$= 25{\cdot}7 \pm 1{\cdot}8$ kcal mol^{-1} $= 10{\cdot}8 \pm 5{\cdot}7$ cal mol^{-1} K^{-1}
k_{-1}/K_B	$= 3{\cdot}43 \times 10^{-4}\ s^{-1}$ [a]	$\Delta H_{-1}^‡$ $\Delta S_{-1}^‡$	$= 16{\cdot}2 \pm 0{\cdot}5$ kcal mol^{-1} $= -23{\cdot}3 \pm 2{\cdot}0$ cal mol^{-1} K^{-1}
$k_{-2}K_a/K_B$	$= 0{\cdot}0114 \times 10^{-4}$ $l^{-1}\ mol\ s^{-1}$ [a]		
$K\ (= K_AK_B)$	$= 1{\cdot}1\ l^2\ mol^{-2}$ [b]	ΔH ΔS	~0 kcal mol^{-1} ~0·1 cal mol^{-1} K^{-1}
k_{-3}	$>2 \times 10^{-2}\ s^{-1}$ [c]		
K_3	~0·03 l mol^{-1} [d,e]	ΔH	positive

[a] From ref. 18, for k_1 and k_2 in that study read k_{-1}/K_B and $k_{-2}K_a/K_B$ respectively in present paper. [b] Average of values in Table 4. [c] At 1·5 °C. [d] Ionic strength not adjusted to constant value. A correction has been made for water activity (see text). [e] K_3 ~0·02 l mol^{-1} at 1·5 °C.

As in other previous studies there is no kinetic evidence for ion-pair saturation giving a rate law with a less than first-order dependence in bromide.[1–6] A good linear dependence on $[Br^-]$ is observed over the range

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

0·3—2·0M in this study. However a dissociative mechanism is believed to be effective in this and other hydroxo-bridge cleavage reactions of dicobalt(III) complexes, and ion-pairing of the incoming ligand is believed to occur. These effects are discussed in more detail elsewhere.[7]

EXPERIMENTAL

Samples of the bromide salt of the μ-amido-μ-complex were prepared from the chloride salt $[(NH_3)_4Co\cdot\mu(NH_2,OH)\cdot Co(NH_3)_4]Cl_4,4H_2O$,[1] by first dissolving the latter (0·86 g) in a minimum of 0·01M-$HClO_4$ (25 ml). The solution was filtered and saturated sodium bromide solution was added dropwise until crystals formed. The product was filtered off and washed with alcohol and ether; it was recrystallized by repetition of this procedure (Found: H, 5·2; Br, 47·8; N, 18·7. Calc. for $[(NH_3)_4Co\cdot\mu(NH_2,OH)\cdot Co(NH_3)_4]Br_4,4H_2O$: H, 5·15; Br, 47·2; N, 18·56%). In order to convert the μ-amido-μ-hydroxo-complex into the bromo-complex the former (0·3 g) was dissolved in a minimum of 0·01M-$HClO_4$. This solution was then filtered into an equal volume of concentrated HBr. Reddish brown crystals formed when the mixture was cooled to 0 °C; these were filtered off and washed with alcohol and ether (yield 69%). A sample of the perchlorate salt was prepared by the same procedure except that this time double the volume of concentrated $HClO_4$ was used instead of HBr[25] (yield 79%). A second sample of the bromide salt of the complex was prepared as described by Werner[9] from the sulphate salt of the μ-amido-μ-hydroxo-complex. This method entailed treating the complex with 47% HBr, and then recrystallizing the product by dissolving it in a minimum of ice–water and adding to the solution a third of its own volume of 47% HBr. The samples had analyses consistent with their being the μ-amido-μ-bromo- and not the aquo-bromo-complex (see Table 7).

TABLE 7

Summary of analyses (%) and absorption coefficients (in $l\ mol^{-1}\ cm^{-1}$) for bromodicobalt complex

	H	N	Br	Co	H_2O	Cl	ε [a]
Bromide salt							
Sample 1 [b]	4·5	19·1	59·2		0 [c]		155
Sample 2 [b,d]	4·1	18·7					153
Werner 1 [e]		17·9	56·5	17·1			
Werner 2 [e]			56·8	17·0			
Calc. (anhydrous)	3·9	18·8	59·8	17·6			
Calc. $2H_2O$	4·3	17·8	56·7	16·7			
Perchlorate salt							
Sample 1 [b]	3·65		11·1		0 [c]	18·9	154
Calc. (anhydrous)	3·48		10·7			19·0	

[a] Absorption maximum at λ = 560 nm. [b] This work. [c] No loss in weight after leaving sample over P_2O_5 for 6 days. [d] Prepared by Werner method, ref. 9. [e] Values taken from ref. 9, presence of two water molecules indicated.

A sample of the chloride salt of the μ-amido-μ-chloro-complex was obtained by the procedure used elsewhere.[1,26] Crystallization from 6M-HCl at 0 °C was slow (several hours). The product was converted into the μ-amido-μ-hydroxo-complex $[(NH_3)_4Co\cdot\mu(NH_2,OH)\cdot Co(NH_3)_4]Cl_4,4H_2O$ as described previously. To prepare the perchlorate salt of the μ-amido-μ-chloro-complex the chloride salt of the μ-amido-μ-hydroxo-complex was dissolved in a minimum of 0·01M-$HClO_4$ at 40 °C, and added to twice its own volume of concentrated $HClO_4$.[26] Crystals were obtained on cooling the solution to room temperature and then to 0 °C. Analyses figures and details of the spectra consistent with formulae $[(NH_3)_4Co\cdot\mu(NH_2,Cl)\cdot Co(NH_3)_4]Cl_4,4\cdot5H_2O$ and $[(NH_3)_4Co\cdot\mu(NH_2,Cl)Co(NH_3)_4](ClO_4)_4,H_2O$ are given in ref. 1. There is some uncertainty as to whether the chloride salt contains 4 or 5 water molecules.[1]

Samples of the mononuclear complexes $[Co(NH_3)_5X]X_2$ and $[Co(NH_3)_5X](ClO_4)_2$ (X^- = Cl and Br^-), were prepared from penta-amminecarbonatocobalt(III) nitrate by standard procedures.[27] The purity of solutions in 0·1M-$HClO_4$ was checked against known visible absorption maxima, ε = 49·0 $l\ mol^{-1}\ cm^{-1}$ at λ = 533 nm for $Co(NH_3)_5Cl^{2+}$ and ε = 53 $l\ mol^{-1}\ cm^{-1}$ at λ = 551 nm for $Co(NH_3)_5Br^{2+}$. The complex $[Co(NH_3)_5H_2O](ClO_4)_3$ was also prepared from penta-amminecarbonatocobalt(III) nitrate (further details as in ref. 28).

All reaction solutions were made up with triply distilled water. Spectrophotometer cells were rinsed with triply distilled water and dried over silica gel in a desiccator. Hydrobromic acid (Hopkin and Williams 46—48% AnalaR solution) was purified by distillation after addition of hypophosphorus acid to react with free bromine.[21] Solutions were stored in darkness at 0 °C. Kinetic experiments were followed at the 560 nm maximum of the aquo-bromo-complex. When the concentration of bromide is increased from 0 to 2·0M by the addition of sodium bromide, the absorption coefficient of the μ-amido-μ-hydroxo-complex increases (linearly) from ε = 117 to 124 $l\ mol^{-1}\ cm^{-1}$; by increasing the concentration of hydrogen ions from $[H^+]$ = 0 to 2·0M ε increases from 117 to 118 $l\ mol^{-1}\ cm^{-1}$. Such variations were taken into account in all calculations.

Solutions of perchloric acid and sodium perchlorate (B.D.H. AnalaR), and sodium bromide (B.D.H. Laboratory Reagent) were made up in triply distilled water. The latter was obtained by redistilling singly distilled water first from alkaline potassium permanganate and then acidified potassium dichromate.

High-resolution i.r. spectra 400—40 cm^{-1} were recorded on a single-beam Beckman–R.I.I.C. model FS 720 interferometer with a coupled wave analyser. Wax discs were prepared, and spectra recorded using a black Polythene filter.

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[2/2766 *Received, 8th December*, 1972]

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

[26] See comments in R. S. Taylor and A. G. Sykes, *Chem. Comm.*, 1969, 1137 and *J. Chem. Soc. (A)*, 1969, 1425, regarding the isolation of the μ-amido-μ-chloro-complex as the perchlorate salt.

[27] See *e.g.* S. W. Foong, B. Kipling, and A. G. Sykes, *J. Chem. Soc. (A)*, 1971, 122.

[28] J. Doyle and A. G. Sykes, *J. Chem. Soc. (A)*, 1968, 2839.

[29] G. Bauer, ' Handbook of Preparative Inorganic Chemistry,' Academic Press, London, 1963, vol. 1, p. 288.