Reactions of μ-Hydroxo-dicobalt(III) Complexes. Part XII.† Equilibrium and Kinetic Studies on Hydroxo-bridge Cleavage Reactions of Two Triply-bridged Dicobalt(III) Complexes in Aqueous Perchloric Acid Solutions

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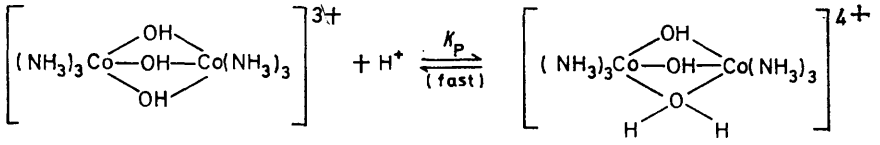
The equilibration kinetics of the first hydroxo-bridge cleavage of the triply-bridged complexes tri-μ-hydroxo-bis[triamminecobalt(III)], $[(NH_3)_3Co\cdot\mu(OH,OH,OH)\cdot Co(NH_3)_3]^{3+}$, (I), and μ-amido-di-μ-hydroxo-bis[triamminecobalt(III)], $[(NH_3)_3Co\cdot\mu(NH_2,OH,OH)\cdot Co(NH_3)_3]^{3+}$, (II), have been studied, I = 1·0M ($LiClO_4$). Within the range $[H^+]$ = 0·01—0·5M first-order rate constants, k_{obs}, for the equilibration of (I) fit the dependence (i)

$$k_{obs} = \frac{k_1 K_P [H^+]}{1 + K_P [H^+]} + k_{-1} \qquad \text{(i)}$$

where K_P, k_1, and k_{-1} are for the reaction sequence (ii) and (iii).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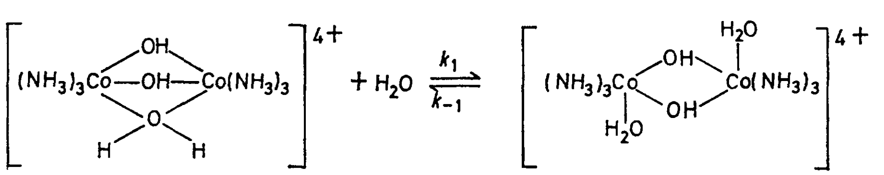
(iii)

At 25 °C K_P = 1·51 (±0·18) l mol⁻¹, k_1 = 1·86 (±0·15) × 10^{-1} s⁻¹, and k_{-1} = 6·62 (±0·36) × 10^{-3} s⁻¹. For (II) the dependence of k_{obs}' on $[H^+]$ is of the simpler form (iv),

$$k_{obs}' = k_2 K_P' [H^+] + k_{-2} \qquad \text{(iv)}$$

and at 25 °C $K_P' < 0·05$ l mol⁻¹, k_2K_P' = 1·01 (±0·02) l mol⁻¹ s⁻¹, and k_{-2} = 1·96 (±0·4) × 10^{-2} s⁻¹. Activation parameters for k_1, k_{-1}, k_2K_P', and k_{-2} have been determined. Equilibrium data have also been evaluated from spectrophotometric measurements.

THE mechanism of hydroxo-bridge cleavage of binuclear cobalt(III) complexes in aqueous perchloric acid solutions has been the subject of several investigations.[1-9] These have shown that $[H^+]$-dependent paths feature prominently in rate laws for bridge cleavage of the singly-, doubly-, and triply-bridged complexes. Previous studies on tri-μ-hydroxo-bis[triamminecobalt(III)],[10] (I), and μ-amido-di-μ-hydroxo-bis[triamminecobalt(III)] (II),[8] have shown that the equilibria (1) and (2) are quickly established. The bis-aquo-complexes (III) and (IV) are written here with *trans*-H_2O ligands (see below). Both bis-aquo-complexes have been isolated as nitrate, sulphate, and perchlorate salts, and u.v.–visible spectra of complexes (I)—(IV) have been reported.[7,10] Further hydroxo-bridge cleavage reactions of (III) and (IV) are sufficiently slow to be ignored in rate studies on (1) and (2). The co-ordinated water molecules in (III) and (IV) can be replaced by anions to give complex cations of the type (V) and (VI), where NH_3 and bridging NH_2^- and OH^- ligands have been omitted for clarity. Derivatives of (III) in which X = F^-, N_3^-, and NCS^-,[10] and of (III) and (IV) with X = NO_3^- [11,12] have been reported. Bridging ligands Y can be RCO_2^- (where R = H, alkyl, or aryl) [13] and NO_2^- [12] for derivatives of (III), and $CH_3CO_2^-$ for (IV). Previously it has been assumed that the water ligands in (III) and (IV), and the X groups in (V), occupy *cis*-positions. However recent *X*-ray studies [14,15] on the nitrate salt of (III) have shown

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† Part XI is S. W. Foong and A. G. Sykes, *J.C.S. Dalton*, 1974, 1453.

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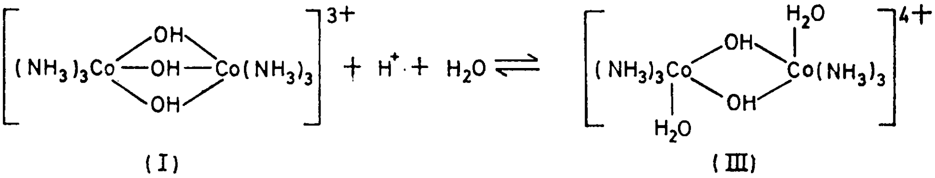
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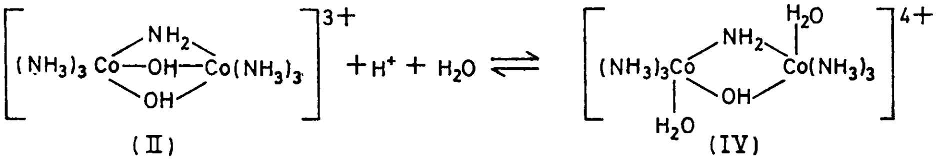
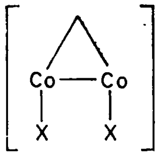

(II) (IV) (2)

conclusively that the co-ordinated water molecules take up *trans*-positions, a fact which could be of considerable importance in assigning mechanisms to bridge-cleavage reactions of binuclear cobalt(III) ammine complexes.



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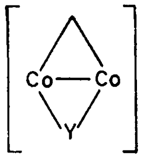

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TABLE 1

Rate constants (k_{obs}) for the equilibration in acid solution of the tri-μ-hydroxo-bis[triamminecobalt(III)] complex, I = 1·0M ($LiClO_4$), λ = 450 nm

Temp. °C	[H⁺] M	10³[Complex] M	10^2k_{obs} [a] s^{-1}
25·0	0·01	0·5	0·98 (1)
	0·03	1·0	1·41 (2)
	0·05	1·0	2·03 (2)
	0·05	1·0	1·93 (1) [b]
	0·15	1·0	4·13 (2)
	0·15	1·0	4·12 (2) [b]
	0·30	1·0	6·94 (1)
	0·30	1·0	6·40 (1) [b]
	0·40	1·0	7·87 (1)
	0·50	1·0	8·50 (2)
30·0	0·01	0·5	1·52 (2)
	0·03	1·0	2·26 (2)
	0·05	1·0	3·32 (2)
	0·15	1·0	7·20 (1)
	0·30	2·0	10·6 (1)
	0·40	2·0	12·2 (2)
	0·50	0·5	14·3 (4) [b]
	0·50	1·0	13·4 (1)
	0·50	1·0	12·8 (2) [b]
	0·50	2·0	14·1 (1)
35·0	0·01	0·5	2·61 (1)
	0·03	1·0	3·71 (2)
	0·05	1·0	4·82 (2)
	0·15	1·0	10·7 (2)
	0·30	1·0	17·5 (2)
	0·40	1·0	20·7 (1)
	0·50	1·0	23·7 (2)
40·0	0·01	0·5	5·17 (1)
	0·03	1·0	6·61 (2)
	0·05	1·0	8·82 (2)
	0·15	1·0	17·8 (2)
	0·30	1·0	25·7 (2)
	0·40	1·0	32·6 (1)
	0·50	1·0	36·5 (2)

[a] Figures in parentheses indicate number of runs averaged. [b] Runs followed at λ 450 and 544 nm.

The *trans*-structure is assumed to be the predominant form also with the bis-aquo-complex (IV). We must, however, stress the tentative nature of this assignment which is based on expected similarity of behaviour of (I) and (II). Since a rearrangement of ammonia ligands is required in (1) and (presumably) also in (2), we felt it highly relevant to carry out full kinetic studies on both (1) and (2).*

TABLE 2

Rate constants (k_{obs}') for the equilibration in acid solution of the μ-amido-di-μ-hydroxo-bis[triamminecobalt(III)] complex, I = 1·0M ($LiClO_4$), λ = 460 nm

Temp. °C	[H⁺] M	10³[Complex] M	k_{obs}' [a] s^{-1}
20·0	0·01	0·25	0·015 (2)
	0·03	0·25	0·030 (2)
	0·05	0·25	0·043 (2)
	0·15	0·25	0·120 (2)
	0·30	0·25	0·202 (1)
	0·40	0·25	0·282 (1)
	0·50	0·25	0·370 (1)
25·0	0·01	0·50	0·029 (2)
	0·03	0·50	0·047 (2)
	0·05	0·50	0·067 (3)
	0·15	0·50	0·173 (3) [b]
	0·30	0·50	0·331 (3) [b]
	0·50	0·50	0·518 (2)
30·0	0·01	1·0	0·060 (2)
	0·03	1·0	0·082 (2)
	0·05	1·0	0·123 (3) [b]
	0·15	1·0	0·261 (2)
	0·30	1·0	0·482 (3) [b]
	0·40	1·0	0·610 (1)
	0·50	1·0	0·770 (2)
35·0	0·01	1·5	0·106 (2)
	0·03	1·5	0·152 (2)
	0·05	1·5	0·206 (3) [b]
	0·15	1·5	0·408 (3) [b]
	0·30	1·5	0·710 (2)

[a] Figures in parentheses indicate the number of runs which have been averaged. [b] Runs followed at λ 460 and 510 nm.

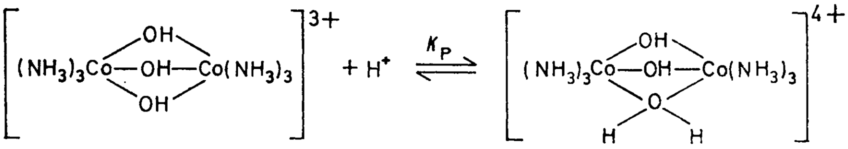
* *Added in proof:* Kinetic studies at 20 °C on the hydroxo-bridge cleavage reactions of three tri-μ-hydroxo-complexes with NH_3, diethylenediamine, and *cis,cis*-1,3,5-triaminocyclohexane as terminal ligands have recently been reported by H. C. Kahler, G. Geier, and G. Schwarzenbach, *Helv. Chim. Acta*, 1974, **57**, 802. Their data for (I), also at I = 1·0M (k_1 = 0·094 s^{-1}, K_P = 2·7 l mol^{-1}), are in good agreement, and to be regarded as complementary to those reported (25—40 °C) in this paper. Their studies did not yield an accurate estimate of k_{-1}, but they were able to measure forward and back rate constants corresponding to the protonation step (K_P).

RESULTS

Kinetic Studies.—The kinetics of the equilibration reactions (1) and (2) were investigated by the stopped-flow method with [H$^+$] = 0·01—0·5M, I = 1·0M (LiClO$_4$). Solutions of (I) or (II) in 1·0M LiClO$_4$ were mixed with solutions of HClO$_4$/LiClO$_4$ as required, I = 1·0M, and absorbance (O.D.) changes were recorded at λ 450 and 544 nm for (1), and 460 and 510 nm for reaction (2). Experiments in the absence of complex demonstrated that no medium effect occurred as a result of mixing HClO$_4$ and LiClO$_4$. Plots of log (O.D.$_t$ − O.D.$_\infty$) were linear for at least four half-lives. Pseudo-first-order rate constants, k_{obs} for reaction (1) and k_{obs}' for reaction (2), were obtained from the gradients (×2·303). The temperature dependence of k_{obs} (Table 1), and k_{obs}' (Table 2), was also investigated. Figure 1 is consistent with a dependence on [H$^+$] as in (3). Such

$$k_{obs} = \frac{a[H^+]}{1 + b[H^+]} + c \qquad (3)$$

a dependence can be accounted for by a mechanism as in reactions (4) and (5) where $a = k_1K_P$, $b = K_P$, and $c = k_{-1}$.



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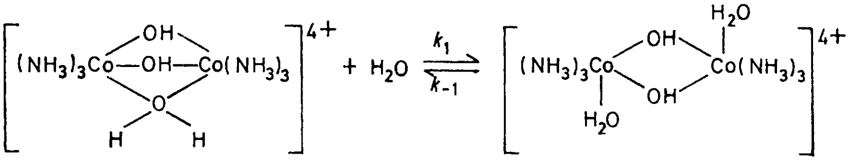
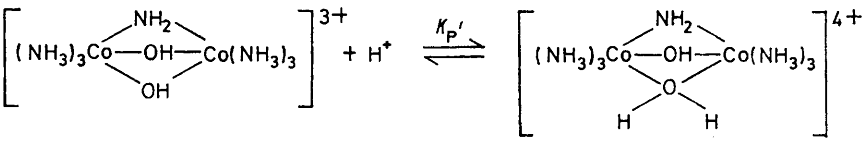


(5)

Values of k_1, k_{-1}, and K_P were determined using a non-linear least-squares programme,[16]* each point being given a weighting of $1/k_{obs}^2$. At 25 °C k_1 = 1·86 (±0·15) × 10^{-1} s^{-1}, k_{-1} = 6·62 (±0·36) × 10^{-3} s^{-1}, and K_P = 1·51 (±0·18) l mol^{-1}. Values of activation parameters (for k_1 and k_{-1}) and thermodynamic parameters (for K_P) are given in Table 3.

$$k_{obs}' = d[H^+] + e \qquad (6)$$



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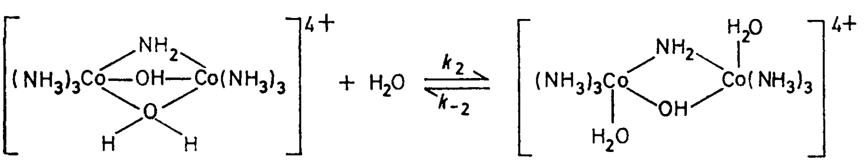

(8)

The equilibration (2) gives simpler kinetic behaviour. Thus Figure 2 is a plot of k_{obs}' against [H$^+$], consistent with a dependence as in (6). The mechanism is we believe as illustrated in equations (4) and (5), where (6) is a limiting case of (3) with $b[H^+] \leqslant 1$. Thus a protonation constant K_P' and rate constants k_2 and k_{-2} may be defined for (7) and (8). Values of k_2K_P' (= d) and k_{-2} (= e) were evaluated using a non-linear least-squares programme,[16] each point being weighted by a factor $1/k_{obs}'^2$. At 25 °C k_2K_P' = 1·01 (± 0·02) l mol^{-1} s^{-1} and k_{-2} = 1·96 (±0·4) × 10^{-2} s^{-1}. Activation parameters for k_2K_P' and k_{-2} are listed in Table 3.

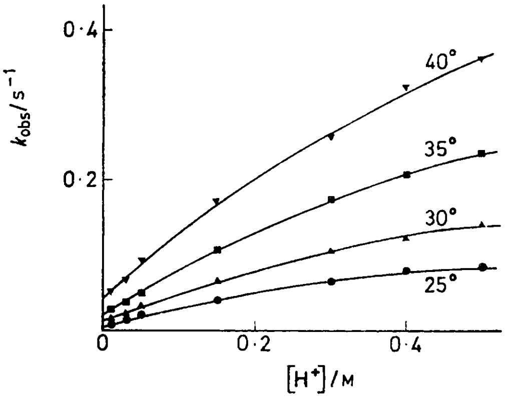

Figure 1 [H$^+$]-Dependence of equilibration rate constants k_{obs} for reaction (I) $\rightleftharpoons$ (III), 25—40 °C, I = 1·0M (LiClO$_4$)

The kinetics of reaction (1) were also investigated by dissolving the *trans*-bis-aquo-complex (III) (nitrate salt) in thermostatted solutions of HClO$_4$/LiClO$_4$ with [H$^+$] = 0·001—0·01M, I = 1·0M (LiClO$_4$), and monitoring absorbance changes by conventional spectrophotometry at

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* We are grateful to Dr. P. Gans and Dr. A. Thornton for helpful comments.

[16] Los Alamos Report LA2367 (1959) and Addenda by R. H. Moore and R. K. Ziegler.

λ 450 nm and 25 °C. Plots of log (O.D.$_\infty$ − O.D.$_t$) were linear to at least four half-lives, and pseudo-first-order rate constants k_{obs} (Table 4) were in good agreement (±4%) with values calculated from experiments with (I) as the starting material (Table 1). Rate constants k_{obs} obtained from runs with added $NaNO_3$ ($[NO_3^-] = 0{\cdot}011$M in run solutions) were indistinguishable from those containing nitrate from the solid complex only. Thus no effect of nitrate was apparent.

TABLE 3

Summary of rate constants and activation parameters for hydroxo-bridge cleavage and formation; the protonation constant (K_P) and corresponding thermodynamic parameters are also given, I = 1·0M ($LiClO_4$)

Constant	Value at 25 °C	ΔH / kcal mol^{-1}	ΔS / cal K^{-1} mol^{-1}
k_1	$1{\cdot}86 \times 10^{-1}$ (s^{-1})	23·4 (±2·7) [a]	16·6 (±8·9) [a]
k_{-1}	$6{\cdot}62 \times 10^{-3}$ (s^{-1})	22·8 (±1·4) [a]	7·6 (±4·4) [a]
K_P	1·51 (l mol^{-1})	−9·7 (±3·7) [b]	−31·2 (±12·2) [b]
$k_2K'_P$	1·01 (l mol^{-1} s^{-1})	12·4 (±0·5) [a]	−17·1 (±1·7) [a]
k_{-2}	$1{\cdot}96 \times 10^{-2}$ (s^{-1})	28·9 (±1·0) [a]	30·6 (±3·4) [a]

[a] Activation parameters. Thermodynamic parameters.

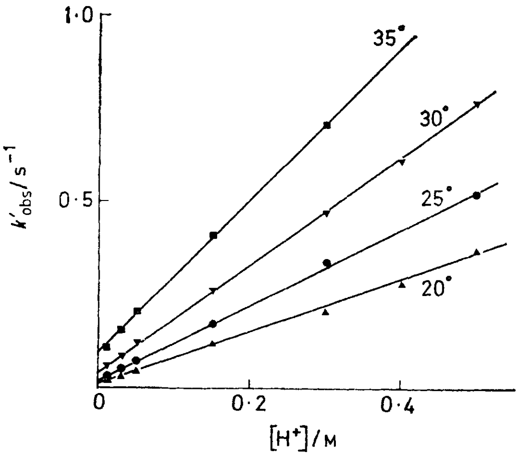


FIGURE 2 [H$^+$]-Dependence of equilibration rate constants k_{obs}' for reaction (II) $\rightleftharpoons$ (IV), 20—35 °C, I = 1·0M ($LiClO_4$)

TABLE 4

Rate constants, k_{obs}, for the equilibration in acid solutions of the di-μ-hydroxo-*trans*-bis[aquotriamminecobalt(III)] complex (nitrate salt), I = 1·0M ($LiClO_4$) at 25 °C

10^2 [H$^+$] / M	10^3 [Complex] / M	10^3 [NO_3^-] / M	10^3 k_{obs} / s^{-1}
0·1	1·0	4·0	7·22
0·1	1·0	11·0	6·71
0·1	1·0	11·0	7·29
0·5	1·0	4·0	7·57
0·5	1·0	11·0	8·20
0·5	1·0	11·0	7·88
1·0	1·0	4·0	9·80
1·0	1·0	4·0	8·26

Equilibrium Studies.—Equilibrium constants for (4)—(5) and (7)—(8) were determined by u.v.–visible spectrophotometry. Perchlorate salts of (I) and (II) were used and the ionic strength adjusted to I = 1·0M ($LiClO_4$). The complex, (0·44—2·02) × 10^{-3}M, was allowed to equilibrate with perchloric acid, [H$^+$] = 0·005—1·00M at 25 °C. Absorbance (O.D.$_{obs}$) values for equilibrated solutions were recorded at first λ 450 nm and then 545 nm for (I), and 460 and 505 nm for (II), and gave absorption coefficients, ε_{obs}.

The expression (9) can be derived for equilibria (4)—(5),

$$(\varepsilon_T - \varepsilon_{obs})^{-1} = (\varepsilon_T - \varepsilon_{BA})^{-1}(1 + 1/K_1) + (\varepsilon_T - \varepsilon_{BA})^{-1}(K_1K_P[H^+])^{-1} \quad (9)$$

where ε_T and ε_{BA} are the absorption coefficients of (I) and (III) respectively at λ 450 nm, and $K_1 = k_1/k_{-1}$. The value ε_T was obtained from the absorbance of (I) in 1·0M ($LiClO_4$). Plots of $(\varepsilon_T - \varepsilon_{obs})^{-1}$ against $[H^+]^{-1}$ gave satisfactory linearity. At 545 nm the same expression applies, except that $\varepsilon_{BA} > \varepsilon_T$ at this wavelength. The quantity $K_1K_P(1 + 1/K_1)$ was evaluated from the ratio of intercept : slope for plots of (9); within experimental error these values were independent of wavelength. From an unweighted least-squares analysis of the experimental data $K_1K_P(1 + 1/K_1)$ = 45 (± 4) l mol^{-1} at 25 °C. The value of this quantity when derived from the kinetics, with $K_1 = k_1/k_{-1}$, is 44 (±4) l mol^{-1} in satisfactory agreement. No significant contribution (to c) from [H$^+$]-independent bridge-cleavage paths is apparent.

From (7) and (8), equation (10) can be obtained, which is

$$(\varepsilon_T - \varepsilon_{obs})^{-1} = (\varepsilon_T - \varepsilon_{BA})^{-1} + (\varepsilon_T - \varepsilon_{BA})^{-1}(K_2[H^+])^{-1} \quad (10)$$

analogous to (9) with $K_2 = k_2K_P'/k_{-2}$. Plots of $(\varepsilon_T - \varepsilon_{obs})^{-1}$ against $[H^+]^{-1}$ were linear, and K_2 values were evaluated from the ratio intercept : slope. These were independent of wavelength and from an unweighted least-squares analysis of experimental data K_2 = 62 (±3) l mol^{-1} at 25 °C. From the kinetics (at 25 °C) k_2K_P'/k_{-2} = 52 (±5) l mol^{-1}. Again there was no significant [H$^+$]-independent path for bridge cleavage.

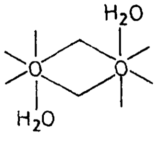
At higher temperatures other bridge-cleavage processes interfered with measurements of reactions (1) and (2); at 20 °C it was found that K_2 = 110 (±10) l mol^{-1}.

DISCUSSION

While superficially the behaviour exhibited by the two triply-bridged complexes (I) and (II) is very similar, a significant difference has been detected. Protonation of the tri-μ-hydroxo-complex, (I), is extensive and is required as a separate step (4) in the kinetic treatment [equation (3)]. It is assumed that there is also prior protonation of (II) and therefore that the rate constant for bridge cleavage is a composite term containing a first-order rate constant k_2 and a protonation constant K_P'. Thus k_2K_P' for (II) is directly comparable to k_1K_P for (I).

From the data obtained it is concluded that $K_P' <$ 0·05 l mol^{-1} at 25 °C which is considerably smaller than K_P = 1·51 (±0·18) l mol^{-1} at 25 °C. These values suggest that replacement of the amido-bridge by a hydroxo-bridge in binuclear cobalt(III) complexes affects the basicity of neighbouring hydroxo-bridges. The protonation constant for the μ-hydroxo-bis[penta-amminecobalt(III)] complex [9] is <0·02 l mol^{-1}. It is possible that there is weak hydrogen bonding between OH-bridging groups which tends to stabilise the protonated form, although this would not of itself explain why protonation of (II) is not more extensive.

The mechanism of hydroxo-bridge cleavage involves rapid protonation of (I) and (II) as a first step. A water molecule then bridges the cobalt atoms and protonation results in a weakening of the Co–O–Co bonds. Baur[17] has suggested using the 'extended electrostatic valence rule' that these bonds are probably *ca.* 0·2 Å longer than those in the μ-hydroxo-situation, that is they are *ca.* 2·1 Å. At this point, because bonding is energetically less favourable, the Co–O bond could well break, leaving one cobalt atom in a five-co-ordinate state, *i.e.* the mechanism is S_N1 (limiting) or *D*. Such an intermediate may also be postulated to account for the apparently ready rearrangement of NH_3 ligands, to give the *trans*-arrangement of aquo-ligands in the product. At least one of the Co–O bonds must be greatly extended in the transition state, sufficient for the Co atom to have no preferred site for co-ordination of an incoming water molecule. Basolo and Pearson[18] have discussed the geometry of transient five-co-ordinate cobalt(III) species, and it has been postulated that such intermediates should give a statistical distribution of all possible isomers in the product. These four isomers are indicated, (VII)—(X), of which (IX) and (X) are enantiomorphic.



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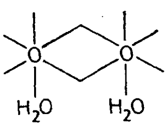

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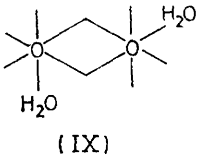

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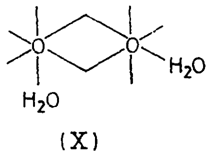

(X)

If the *trans*-isomer (VII) is the most insoluble nitrate salt then it could crystallise out following rapid isomerisation of (VII)—(X) through a common five-co-ordinate intermediate. Precipitation of crystals of (VII) can be initiated after *ca.* 10 min from aqueous nitric acid solutions of (I) by the addition of solid $NaNO_3$. Our observation that the same equilibration rate constants are obtained whether (I) or (VII) is the starting material necessarily means that the bridge-cleavage process is stereospecific, *i.e.* the *trans*-isomer is a primary product, and/or that isomerisation of (VIII)—(X) to (VII) is relatively rapid.

A stereospecific bridge-cleavage process giving only (VII) might be interpreted in terms of considerable associative character for the reaction. Schwarzenbach *et al.*[19] have found that (11) is rapidly established, where

$$[(\text{tach})\text{Co}\cdot\mu(\text{OH,OH,OH})\cdot\text{Co}(\text{tach})]^{3+} + H^+ + H_2O \rightleftharpoons [(\text{tach})(H_2O)\text{Co}\cdot\mu(\text{OH,OH})\cdot\text{Co}(H_2O)(\text{tach})]^{4+} \quad (11)$$

the magnitude of *K* at 25 °C (79 l mol^{-1}) suggests that bridge cleavage may be similar to that for reactions (1) and (2). However an important feature is that the *cis,cis*-1,3,5-triaminocyclohexane (= tach) ligand can only co-ordinate facially to the cobalt atoms. If the mechanism of bridge cleavage is associative the steric effects encountered by an incoming ligand would be expected to significantly affect the rate of bridge cleavage as compared to that of (I) and (II). A dissociative mechanism might on the other hand be common to all three reactions, where ligand rearrangement to give *cis*/*trans* (or any other) arrangement of H_2O ligands can occur subsequently and be independent of the rate-determining step.

A comparison of activation parameters for hydroxo-bridge cleavage by [H$^+$]-independent paths in binuclear cobalt(III) complexes reveals that the difference in rates is almost entirely due to changes in $\Delta S^\ddagger$, implying that the same general mechanism for bridge cleavage applies to all the reactions summarised in Table 5. Investigations of the X^{n-} induced hydroxo-bridged cleavage reactions of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex, $[(NH_3)_4Co\cdot\mu(NH_2,OH)\cdot Co(NH_3)_4]^{4+}$, in aqueous perchloric acid solutions, $I = 2{\cdot}0$M, where $X^{n-} = SO_4^{2-}, SeO_4^{2-}, NO_3^-, NCS^-, HSO_4^-, Cl^-, H_2PO_4^-, Br^-, H_2O, H_3PO_4$, and CH_3CO_2H have shown that the dominant pathway generally (but not always) involves protonation prior to bridge cleavage by a dissociative process in which bond formation plays little part.[1] The cleavage of the single hydroxo-bridge in the μ-hydroxo-bis[penta-amminecobalt(III)] complex in aqueous perchloric acid solutions[9] may also be dissociative in character. The [H$^+$]-independent path is more significant in this latter case, and it has been suggested

TABLE 5

Values of rate constants (kK_P) and corresponding activation parameters for [H$^+$] dependent hydroxo-bridge cleavage reactions of dicobalt(III) complexes, 25 °C

Complex	$10^2 kK_P$ / l mol^{-1} s^{-1}	$\Delta H^\ddagger$ / kcal mol^{-1}	$\Delta S^\ddagger$ / cal K^{-1} mol^{-1}
$[(NH_3)_3Co\cdot\mu(OH,OH,OH)\cdot Co(NH_3)_3]^{3+}$	28 [a]	13·7 (±3·2)	−14·6 (±10·7)
$[(NH_3)_3Co\cdot\mu(NH_2,OH,OH)\cdot Co(NH_3)_3]^{3+}$	101 [a]	12·4 (±0·5)	−17·1 (±1·7)
$[(NH_3)_4Co\cdot\mu(NH_2,OH)\cdot Co(NH_3)_4]^{4+}$	0·008 [b]	12·5 (±1·1)	−35·3 (±3·6)
$[(NH_3)_5Co\cdot\mu(OH)\cdot Co(NH_3)_5]^{5+}$	0·54 [c]	12·0 (±0·8)	−28·7 (±2·7)

[a] This work, $I = 1{\cdot}0$M. [b] Ref. 20, $I = 2{\cdot}0$M. [c] Ref. 9, $I = 2{\cdot}0$M.

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that this is because stretching of a Co–O bond without prior protonation is more likely to result in bridge cleavage since there are no supporting bridging groups. No contributions from [H$^+$]-independent paths were detected in the present studies and (indirectly) would seem to support this suggestion. Some assistance from an incoming H_2O is a more likely requirement for bridge cleavage occurring by an [H$^+$]-independent path. We note also that the rate of water exchange for $[Co(NH_3)_5H_2O]^{3+}$ is many times faster than the corresponding process for $[Co(NH_3)_5OH]^{2+}$.[21]

TABLE 6

A comparison of rate constants and activation parameters for hydroxo-bridge formation reactions of (III) and (IV), with those for water exchange of mononuclear aquo-penta-ammine complexes, 25 °C

Complex	$10^5 k$ / s^{-1}	$\Delta H^\ddagger$ / kcal mol^{-1}	$\Delta S^\ddagger$ / cal K^{-1} mol^{-1}	$\Delta V^\ddagger$ / cm^3 mol^{-1}
(III)	662 [a]	22·8 (±1·4)	7·6 (±4·4)	
(IV)	1960 [a]	28·9 (±1·0)	30·6 (±3·4)	
$[Co(NH_3)_5H_2O]^{3+}$	0·66 [b]	26·6 (±0·3)	6·7 (±1·0)	1·2 (±0·2)
$[Cr(NH_3)_5H_2O]^{3+}$	6·3 [c]	23·2 (±0·5)	0·0 (±1·6)	−5·8 (±0·02)
$[Rh(NH_3)_5H_2O]^{3+}$	0·56 [c]	24·6 (±0·3)	0·8 (±1·1)	−4·1 (±0·4)

[a] This work, $I = 1·0$M ($LiClO_4$). [b] Ref. 22. [c] Ref. 23.

The water exchange for $[Co(NH_3)_5H_2O]^{3+}$ has been demonstrated to occur by a dissociative mechanism,[22] with $\Delta S^\ddagger$ (Table 6) and $\Delta V^\ddagger$ both positive. The large positive $\Delta S^\ddagger$ values (Table 6) for the reactions of the bis-aquo-complexes to (I) and (II), reverse of equations (1) and (2), may also be cited in support of a dissociative mechanism. The small (around zero) $\Delta S^\ddagger$ values observed for water exchange with $[Cr(NH_3)_5(H_2O)]^{3+}$ and $[Rh(NH_3)_5(H_2O)]^{3+}$, as well as negative $\Delta V^\ddagger$ values, on the other hand favour more associative character for these reactions.[23] If $\Delta H^\ddagger$ for water exchange with $[Co(NH_3)_5H_2O]^{3+}$ is taken as a typical value for Co–O bond rupture in the rate-determining step, then the corresponding values for complexes (III) and (IV) seem perfectly reasonable and not inconsistent with a dissociative process. There would thus seem to be a substantial case for a dissociative mechanism for both reactions (1) and (2). Whether this is *D* rather than I_d requires substantiation.

We have so far considered the mechanism of bridge cleavage, but as yet offered no explanation as to the rapidity of reactions (1) and (2), the study of which required the stopped-flow technique. Buckingham *et al.*[24] have discussed the labilisation of Cl^- during base hydrolysis of pentakisalkylamine complexes of the form $[CoA_5Cl]^{2+}$ (where A = methylamine, n-propylamine, or isobutylamine) in terms of the relief of steric hindrance, with the formation of a 'less-crowded' five-co-ordinate intermediate. The relief of the ring strain present in the triply-bridged complexes,[25] by the formation of a dissociative transition state may be an explanation of the relatively rapid rate of bridge cleavage in these complexes. It can only be a partial explanation however since the reformation of the bridge from a doubly-bridged complex in which there is little ring strain,[15,26] is also fast. It is also apparent that reformation of the μ-amido-μ-hydroxo-complex from the corresponding μ-amido-bis-aquo-complex and elimination of a water ligand from other μ-amido-complexes is unusually rapid.[27-29]

The labilisation of the aquo-ligands is, we believe, particularly significant since there is considerable evidence that hydroxo-bridge cleavage and therefore, from microscopic reversibility, bridge reformation proceeds by a dissociative mechanism. Interpenetration of the aquo-ligands in (III) and (IV) with accompanying associative character is not a possible explanation of these fast rates.*

The most likely explanation is that the NH_2^- and OH^- bridges have a labilising effect which is similar to, but less extensive, than that of terminal NH_2^- and OH^- groups in the base hydrolysis of mononuclear cobalt(III) complexes.[31] The S_N1 CB mechanism has been discussed in terms of the formation of a five-co-ordinate intermediate,[31] which is stabilised by NH_2^- or OH^- unidentate ligands. The mechanism of the labilisation of the leaving group and concomitant stabilisation of the intermediate has been proposed to occur by electron repulsion in the ground state (σ-bonding effect), and by d_π–p_π orbital overlap between filled orbitals on the anionic ligand with empty *d*-orbitals on the metal (π-bonding effect). Thus *cis*- and *trans*-labilisation may both be effective depending on the particular environment, the order of labilisation, *i.e.* $NH_2^- > OH^-$ for mononuclear cobalt(III) complexes, being determined by the relative importance of σ- and π-bonding effects. Such effects would be expected to be considerably reduced for bridging NH_2^- or OH^- groups, which are less co-ordinatively unsaturated.

We consider now the mechanism of labilisation of terminal ligands by bridging NH_2^- and OH^- groups. It has been indicated previously that attachment of

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* It seems unlikely also for the formation and cleavage of a second bridge,[30] in view of the evidence now cited for a dissociative process (see ref. 1).

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

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two cobalt atoms to phosphate[29] and oxalate[32] has approximately the same effect on the basicity of these groups as monoprotonation. If this effect may be generalised to include amido- and hydroxo-bridging ligands then we may postulate that each cobalt(III) is bonded to an $NH_{2\cdot5}$ or $OH_{1\cdot5}$ group since the second cobalt atom is equivalent to half a proton. Such bridging ligands would in other words be expected to have donor properties somewhere between NH_2^- and NH_3, and OH^- and H_2O.

On present evidence the hydroxo-bridge appears to be more effective in labilising terminal ligands than is an amido-bridge. The basis of this conclusion is that no loss of ammonia has been observed during the slow bridge-cleavage decomposition of the μ-amido-bis[pentaamminecobalt(III)] complex[33] ($k = 1\cdot3 \times 10^{-4}$ s^{-1} at 65 °C; $\Delta H^\ddagger = 31\cdot5$ kcal mol^{-1}), while the μ-amido-μ-hydroxo-complex[20] loses ammonia ligands at a significant rate ($k = 4\cdot5 \times 10^{-5}$ s^{-1} at 35 °C, $\Delta H^\ddagger = 25\cdot8$ kcal mol^{-1}), which is able to compete with hydroxo-bridge cleavage. Loss of ammonia from other complexes, *e.g.* $[(NH_3)_5Co{\cdot}OH{\cdot}Co(NH_3)_5]^{5+}$,[9] has not so far been detected however, so that any conclusion that the hydroxo-bridge is more effective than the amido-bridge is tentative. The hydroxo-bridge may be effective because it has a lone pair of electrons which can be donated to the cobalt(III) centres (π-bonding), thus producing a labilisation of other ligands. The amido-bridge has no lone pair of electrons for donation, so that any labilisation produced by the amido-bridge must be entirely a σ-bonding effect.[31] It has been suggested[31] that for mononuclear cobalt(III) complexes the order of labilisation follows the basicity of the groups implying σ-bonding character, which is the same as the order of efficiency as a π-donor. Thus a general order of effectiveness is $NR_2^- > OH^- > Cl^-$ (where R = H or alkyl). In the present instance the hydroxo-bridge is more basic and the order of π-donor ability would be expected to be $OH^- > NH_2^-$ by virtue of the OH^- possessing a lone pair of electrons. However for the multibridged complexes (I) and (II) we cannot readily differentiate between NH_2^- and OH^- bridges, and the labilisation effects appear to be about the same in both cases.

To summarise, a comparison of kinetic data (Table 5) for hydroxo-bridge cleavage in singly-, doubly-, and now triply-bridged complexes suggests that a common mechanism is effective. There is considerable evidence supporting a dissociative mechanism but there is as yet no evidence that this is of the limiting *D* kind. Such a mechanism is however a possibility because of the inability of H_2O to function as a stable bridging entity. Labilisation by NH_2^- and OH^- bridging ligands is also important particularly in explaining the rapidity of reverse reactions involving bridge closure of bis-aquo-complexes.

EXPERIMENTAL

The complexes (I)—(IV) used in this study were prepared as described elsewhere.[8,10] The perchlorate salt of (III) has not been prepared previously and great care was required to obtain the complex free of nitrate ions. The nitrate salt (8 g) obtained from the preparation described by Werner (and Furstenberg),[12] but *not* recrystallised from concentrated nitric acid, was dissolved in water (130 ml) at 40 °C and $NaClO_4,H_2O$ (50 g) was added. The solution was cooled at 0 °C for several hours and the red-brown hexagonal crystal plates were filtered off. These were recrystallised several times by the same procedure until the sample was no longer contaminated by brown needle-shaped crystals. These latter gave rise to bands in the infrared spectrum (ν_1 1500 cm^{-1} and ν_2 1226 cm^{-1}) which are tentatively assigned to a nitrato-complex previously reported by Werner.[12] The pure sample of (III) as a perchlorate salt gave no such bands, but when treated with concentrated nitric acid the brown needles crystallised out as Werner has previously stated [Found: H, 4·2; Cl, 18·6; N, 16·3; water of crystallisation 3·22% (by dehydration over P_2O_5 *in vacuo*). Calc. for $[(NH_3)_2Co{\cdot}\mu(NH_2,OH,OH){\cdot}Co(NH_3)_3](ClO_4)_3,H_2O$: H, 4·3; Cl, 18·3; N, 16·8; water of crystallisation 3·09%].

All chemicals used were of AnalaR grade purity. Lithium perchlorate was prepared by methods used previously in these laboratories. U.v.–visible spectra were recorded on Unicam SP500 and SP800 (recording) spectrophotometers and kinetics were followed on these and the Durrum–Gibson stopped-flow apparatus.

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