The Uncatalysed and Mercury(II)- and Thallium(III)-catalysed Elimination of Chloride from the μ-Amido-μ-chloro-bis[tetra-amminecobalt(III)] Complex

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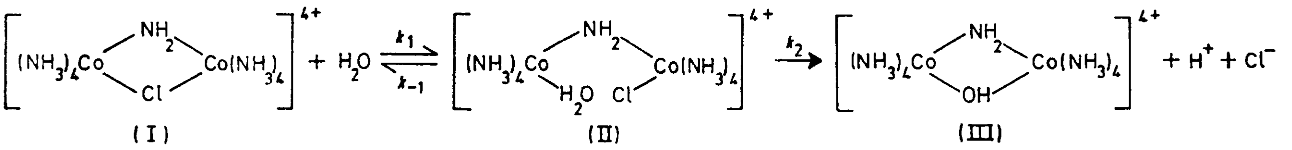
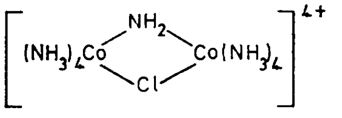
The kinetics of the mercury(II)- and thallium(III)-catalysed elimination of chloride from the title complex (I), equation (i), have been studied in aqueous $HClO_4$ solution, $I = 2.0$M ($NaClO_4$). Both reactions are independent



(i)

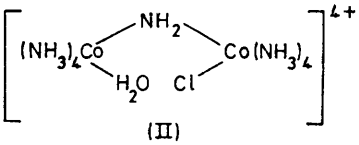
of [H^+] in the range 0·5—2·0M. With mercury(II) there is a less than first-order dependence on [Hg^{2+}] which cannot be satisfactorily accounted for in terms of a 1 : 1 adduct. Instead the dependence can be explained by considering Hg^{2+}-catalysed conversion of (II) into (III) and applying the steady-state approximation for (II). From the treatment (at 25 °C), $k_1 = 3.02 \times 10^{-3}$ s^{-1}, $\Delta H^‡_1 = 19.2 \pm 0.5$ kcal mol^{-1}, $\Delta S^‡_1 = -5.7 \pm 1.8$ cal K^{-1} mol^{-1}, and $k_2/k_{-1} = 0.028$. At 25 °C ratios $k_3/k_2 = 1.57 \times 10^3$ l mol^{-1} and $k_4/k_2 = 1.3 \times 10^3$ l mol^{-1} are measures of the effectiveness of Hg^{2+} and $HgCl^+$ as catalysts for (II) $\longrightarrow$ (III). Thallium(III) produces only a mild catalytic effect, a first-order dependence on [Tl^{3+}] is observed, and $k_5/k_2 = 15$ l mol^{-1} is a measure of the effectiveness of Tl^{3+} as a catalyst. It is concluded that Tl^{3+} is a relatively weaker catalyst compared to Hg^{2+} for (II) $\longrightarrow$ (III) than for the catalysed aquation of mononuclear chloro-complexes.

X-RAY diffraction[1] and i.r.-spectral[2] studies have indicated the structure of the μ-amido-μ-chloro-bis[tetra-amminecobalt(III)] complex (I).



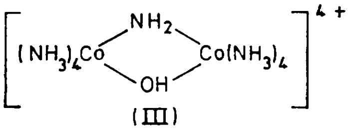
(I)

Earlier Werner[3] assigned the μ-amido-[aquotetra-amminecobalt(III)]-[chlorotetra-amminecobalt(III)] (hereafter aquo-chloro) structure (II) to this complex and this assignment has persisted in the literature.



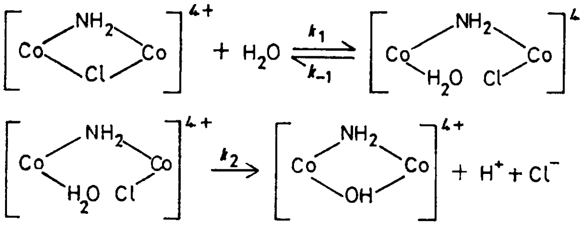
(II)

Recently[4] pH measurements and kinetic studies have indicated that there is retention of (I) rather than (II) as the dominant species in aqueous solution, prior to the conversion through to the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex (III).



(III)

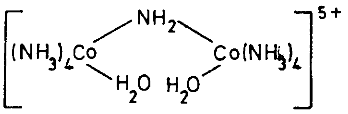
The aquo-chloro complex (II) is formed as an intermediate, but there is no appreciable build-up of (II), and the latter has not as yet been isolated. Rate constants previously[5] ascribed to the conversion of (II) into (III) therefore correspond to the conversion of (I) into (III) which occurs in a stepwise manner [equations (1) and (2), ammonia ligands omitted]. Information regarding k_1 and k_2/k_{-1} has now been obtained from studies on the mercury(II)-catalysed reaction, and details of the uncatalysed reaction are reconsidered in the light of the data presented.



(1)

(2)

Intermediate formation of the μ-amido-bis[aquotetra-amminecobalt(III)] complex, (IV), cannot be excluded in reaction (2), and was indeed one of the factors which prompted the present study, since in the presence of mercury(II) chloride is a good leaving group.



(IV)

Species (IV) has previously proved difficult to identify because of the unfavourable equilibrium constant for formation when (III) is dissolved in *e.g.* 2M-$HClO_4$.

Studies on the mercury(II)-catalysed aquation of chloride from mononuclear cobalt(III)[6] and chromium(III)[7] complexes have been numerous, and evidence for

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

[2] S.-W. Foong and A. G. Sykes, *J.C.S. Dalton*, 1974, 1453.

[3] A. Werner, *Annalen*, 1910, **375**, 44.

[4] M. R. Hyde and A. G. Sykes, *J.C.S. Dalton*, 1974, 1583.

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

[6] C. Bifano and R. G. Linck, *Inorg. Chem.*, 1968, **7**, 908 and references therein.

[7] J. H. Espenson and J. P. Birk, *Inorg. Chem.*, 1965, **4**, 527.

S_N1 mechanisms has been adduced.[8,9] Comparisons of the relative effectiveness of mercury(II) and thallium(III) in catalysing the aquation of cobalt(III) complexes have been made.[10,11] The kinetics of the mercury(II)-catalysed aquations of *cis*-$[Co(en)_2Cl_2]^+$ [6,10] and *cis*-$[Cr(H_2O)_4Cl_2]^+$ [12] are considered relevant since a less than first-order dependence on mercury(II) is observed in both cases.

RESULTS

The Uncatalysed Reaction.—Spectra of (I) and (III) give cross-over points at 462 and 535 nm. For the uncatalysed reaction good isosbestic points are observed at 45 °C. At <25 °C there is some slight movement (*ca.* 5 nm) of the 535 nm isosbestic to lower wavelengths. Possible explanations are that either a side reaction is effective or that some (II) and/or (IV) is present. Since at 25 °C first-order plots at 554, 500, and 435 nm are linear to 85% completion, for the interconversion of (I) and (III) in both directions and rate constants determined at different wavelengths are in good agreement, we do not consider this effect to be of prime importance. Moreover V^{2+} has been used as a sensitive probe for (II), since the latter is expected to yield $[Co(NH_3)_5(H_2O)]^{3+}$ as the product of the first stage of reduction,[4] and reaction of $[Co(NH_3)_5(H_2O)]^{3+}$ with V^{2+} would then be observed as a second stage at 490 nm.

TABLE 1

Pseudo-first-order rate constants k_{obs} for the Hg^{2+}-catalysed elimination of chloride from $[(NH_3)_4Co{\cdot}\mu(NH_2,Cl){\cdot}Co(NH_3)_4]^{4+}$, (I) $\longrightarrow$ (III), $I = 2{\cdot}0\text{M}(NaClO_4)$

Temp. °C	[H+] M	10^3[Complex] M	$10^2[Hg^{2+}]$ M	10^4k_{obs} s^{-1}
25·0	0·50	0·66	1·33	11·0 [a]
	0·50	0·62	1·33	11·8
	1·00	0·65	1·33	11·3
	1·50	0·47	1·33	11·6 [a]
	1·50	0·62	1·33	11·0
	1·96	0·66	1·33	11·8
	1·50	0·67	2·0	14·8
	1·50	1·26	5·0	20·3
	1·50	0·64	5·0	21·4 [b]
	1·50	2·38	10·0	25·2
	1·50	1·88	10·0	23·6 [c]
30·0	1·50	0·63	1·33	17·9
	1·50	0·67	2·0	23·4
	1·50	0·64	4·0	30·3
	1·50	0·56	10·0	40·1
35·0	1·50	0·66	1·33	26·7
	1·50	0·64	2·0	33·5
	1·50	0·66	4·0	45·8
	1·50	0·63	10·0	66·0
40·0	1·50	0·65	1·33	37·2
	1·50	0·67	2·0	48·1
	1·50	0·66	4·0	81·2
	1·50	0·63	10·0	103·3

[a] $I = 2{\cdot}0\text{M}(LiClO_4)$. [b] Chloride salt of complex used; 5% of mercury(II) present as $HgCl^+$. [c] Chloride salt of complex used; 7·5% of mercury(II) present as $HgCl^+$.

Such experiments indicate no significant formation of $[Co(NH_3)_5(H_2O)]^{3+}$, and at no time during the conversion of (I) into (III) at 25 °C is there $>6\%$ of (II) present. Similar experiments on solutions of (I) in 0·4M-HCl and of (III) in 0·4M-HCl also failed to give evidence for build-up of (II) during 3 h at 25 °C.

The Mercury(II)*-catalysed Reaction.*—Kinetic runs were followed by monitoring absorbance (O.D.) changes at the 554 nm maximum for (I) ($\varepsilon = 165$ l mol^{-1} cm^{-1}) with $[Hg^{II}]$ in the range $(1{\cdot}3—10{\cdot}0) \times 10^{-2}\text{M}$. At this wavelength (III) has an absorption coefficient $\varepsilon = 128$ l mol^{-1} cm^{-1}. Final absorbances ($O.D._{\infty}$) were measured after 7—8 half-lives. No evidence for any build-up of (II) or (IV) was obtained and first-order plots of log ($O.D._t - O.D._{\infty}$) against time were linear to at least 85% completion. Rate constants k_{obs} (s^{-1}) evaluated from the gradients of such plots (Table 1) were independent of [H+] in the range 0·5—2·0M (the first acid dissociation constant of Hg^{2+} is $2{\cdot}8 \times 10^{-4}$ mol l^{-1} at 25 °C in 3M-$NaClO_4$,[13] and $[Hg^{II}]$ is therefore equivalent to $[Hg^{2+}]$), but gave a less than first-order dependence on $[Hg^{2+}]$ (Figure 1). Plots of $(k_{obs} - k_{uncat})^{-1}$ against $[Hg^{2+}]^{-1}$ at each temperature are linear (Figure 2) where k_{uncat} is the rate constant for uncatalysed conversion of (I) into (III).

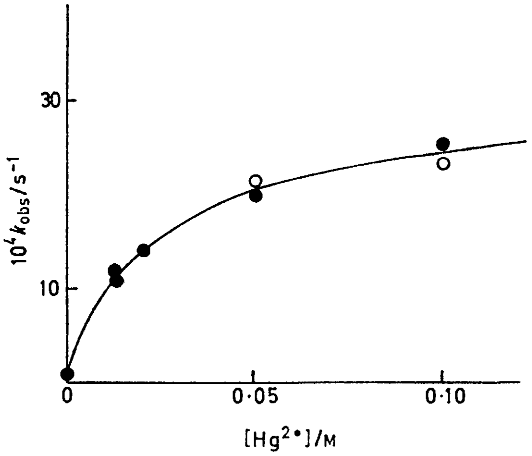

FIGURE 1 The variation of k_{obs} for the conversion of (I) into (III) with concentration of mercury(II) at 25 °C, $I = 2{\cdot}0\text{M}$ ($NaClO_4$)

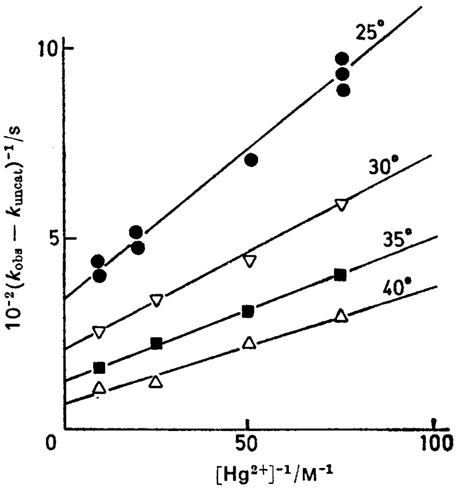

FIGURE 2 The dependence of $(k_{obs} - k_{uncat})$ for the conversion of (I) into (III) on the concentration of mercury(II) as a function of temperature, $I = 2{\cdot}0\text{M}(NaClO_4)$

The dependence on mercury(II) can therefore be sum-

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[8] F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, 1957, **79**, 225.

[9] J. P. Birk and C. M. Ingerman, *Inorg. Chem.*, 1972, **11**, 2019.

[10] S.-W. Foong, B. Kipling, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 118.

[11] S. C. Chan and S. F. Chan, *Austral. J. Chem.*, 1973, **26**, 1235.

[12] J. P. Birk, *Inorg. Chem.*, 1970, **9**, 735.

[13] I. Ahlberg, *Acta Chem. Scand.*, 1962, **16**, 887.

marised by equation (3), or by the alternative expression

$$\frac{1}{(k_{\mathrm{obs}} - k_{\mathrm{uncat}})} = \frac{1}{a[\mathrm{Hg}^{2+}]} + \frac{1}{b} \qquad (3)$$

(4). Values of a and b at temperatures 25—40 °C deter-

$$k_{\mathrm{obs}} = k_{\mathrm{uncat}} + \frac{ab[\mathrm{Hg}^{2+}]}{(a[\mathrm{Hg}^{2+}] + b)} \qquad (4)$$

mined from (3) using a linear least-squares programme with weighting factor $(k_{\mathrm{obs}} - k_{\mathrm{uncat}})^2$ are listed in Table 2.

TABLE 2

Summary of a and b values at different temperatures for the Hg^{2+}-catalysed elimination of chloride from $[(\mathrm{NH_3})_4\mathrm{Co}\cdot\mu(\mathrm{NH_2,Cl})\cdot\mathrm{Co}(\mathrm{NH_3})_4]^{4+}$, (I) ⟶ (III), I = 2·0M(NaClO$_4$)

Temp. °C	10^2a [a] l mol^{-1} s^{-1}	10^3b [a] s^{-1}
25·0	12·4 ± 0·2	2·94 ± 0·06
30·0	19·6 ± 0·5	4·79 ± 0·10
35·0	25·6 ± 0·6	8·26 ± 0·22
40·0	33·0 ± 1·1	15·4 ± 0·9

[a] As defined in (3).

Absorbance (O.D.$_0$) values at 554 nm obtained by extrapolating first-order plots to the start of the reaction were within experimental error as calculated for (I).

The effect of small amounts of chloride, $[\mathrm{Cl}^-] < [\mathrm{Hg^{II}}]$, was also investigated. Rate constants obtained are shown in Table 3. Concentrations of HgCl^+ were calculated assuming an equilibrium constant of 0·38 at 25 °C for (5).[6,7]

TABLE 3

The effect of chloride on the mercury(II)-catalysed elimination of chloride from $[(\mathrm{NH_3})_4\mathrm{Co}\cdot\mu(\mathrm{NH_2,Cl})\cdot\mathrm{Co}(\mathrm{NH_3})_4]^{4+}$ at 25 °C, I = 2·0M(NaClO$_4$)

$10^3[\mathrm{Cl}^-]$ [a] M	$[\mathrm{H}^+]$ M	$10^3[\mathrm{Hg}^{2+}]$ [b] M	$10^3[\mathrm{HgCl}^+]$ [c] M	10^4k_{obs} s^{-1}
0	1·50	13·3	0	11·3
2·5	1·00	10·8	2·36	10·7
2·6	1·96	10·8	2·39	11·0
4·6	1·50	9·2	3·69	10·6
6·7	1·50	7·1	5·61	10·6

[a] Total chloride present. [b] Mercury(II) not present as HgCl^+ or $\mathrm{HgCl_2}$. [c] Calculated for equilibration (5).

$$2\mathrm{HgCl}^+ \rightleftharpoons \mathrm{Hg}^{2+} + \mathrm{HgCl_2} \qquad (5)$$

Concentrations of $\mathrm{HgCl_2}$ were less than 5% of the total mercury(II), and since catalysis by $\mathrm{HgCl_2}$ is small in other similar studies,[7] contributions from a pathway involving this species were assumed to be negligible. From the data obtained it is concluded that HgCl^+ and Hg^{2+} are about equally effective in catalysing the conversion of (I) into (III) [equations (1) and (2)].

Thallium(III)-*catalysed Reaction*.—The catalysis by thallium(III), concentrations in the range (0·9—10·7) × 10^{-2}M, was also followed at 554 nm, I = 2·0M (NaClO$_4$). Plots of log (O.D.$_t$ − O.D.$_\infty$) against time were linear to at least 75% reaction, where O.D.$_\infty$ was the absorbance after 7—8 half-lives of reaction. Pseudo-first-order rate constants, k'_{obs}, are listed in Table 4. There was no appreciable dependence on the concentration of hydrogen ions, and since the acid dissociation constant of Tl^{3+} is 7 × 10^{-2} mol l^{-1} at 25 °C in 3M-NaClO$_4$[14] it is concluded that Tl^{3+} and TlOH^{2+} have about the same catalytic effect. A similar result was obtained in the studies with *cis*-$[\mathrm{Co(en)_2Cl_2}]^+$.[10] At temperatures in the range 25—40 °C a linear dependence on $[\mathrm{Tl^{III}}]$ was observed (Figure 3) and from the gradients second-order rate constants, k_{Tl}, for the $[\mathrm{Tl^{III}}]$-dependent path were obtained (Table 5). Activation parameters, $\Delta H^{\ddagger}_{\mathrm{Tl}}$ = 14·8 ± 1·2 kcal mol^{-1}, $\Delta S^{\ddagger}_{\mathrm{Tl}}$ = −22·4 ± 4 cal K^{-1} mol^{-1}, were determined using a standard least-squares treatment with weighting according to the number of data points at each temperature.

TABLE 4

Pseudo-first-order rate constants, k'_{obs}, for the thallium(III)-catalysed elimination of chloride from $[(\mathrm{NH_3})_4\mathrm{Co}\cdot\mu(\mathrm{NH_2,Cl})\cdot\mathrm{Co}(\mathrm{NH_3})]^{4+}$, (I) ⟶ (III), I = 2·0M-(NaClO$_4$)

Temp. °C	$[\mathrm{H}^+]$ M	10^4[Complex] M	$10^2[\mathrm{Tl^{III}}]$ M	$10^4k'_{\mathrm{obs}}$ s^{-1}
25·0	0·3	6·06	0·9	0·93
	1·0	6·06	0·9	0·86
	1·9	5·58	0·9	0·80
	1·0	6·19	5·3	1·34
	1·5	6·19	5·3	1·45
	1·4	6·40	10·7	2·10
30·0	1·4	6·22	5·0	2·34
	1·4	6·41	10·0	3·25
35·0	0·5	6·22	3·3	2·89
	1·4	6·41	3·3	2·79
	1·4	24·8	3·3	3·04
	0·7	6·15	5·0	3·61
	1·4	25·8	5·0	3·50
	1·4	6·36	5·0	3·24
	1·4	6·36	10·0	4·62
	1·4	24·8	10·0	4·89
40·0	1·4	19·5	3·3	4·67
	1·4	6·02	5·0	5·33
	1·4	6·02	10·0	7·70

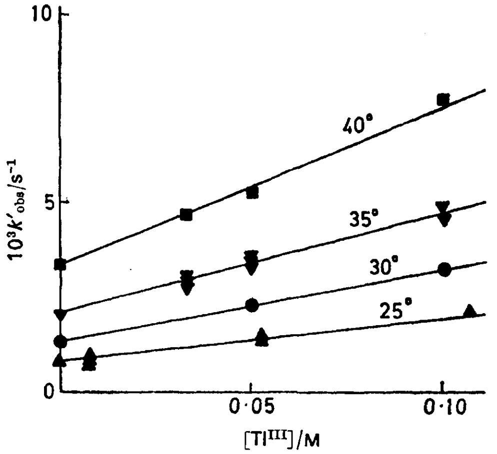

FIGURE 3 The dependence of k'_{obs} for the conversion of (I) into (III) on the concentration of thallium(III) as a function of temperature, I = 2·0M(NaClO$_4$)

Other Studies.—Although a linear dependence on $[\mathrm{Hg}^{2+}]$ has been demonstrated for the mercury(II)-catalysed aquation of $[\mathrm{Co(NH_3)_5Cl}]^{2+}$,[6] the activation parameters have not previously been determined. The following runs were therefore carried out with $[\mathrm{Hg}^{2+}]$ = 1·33 × 10^{-3}M, $[\mathrm{H}^+]$ = 1·5M, I = 2·0M (NaClO$_4$). Rate constants obtained were k'_{Hg} = 20·2 (25·0 °C), 32·8 (30·1 °C), and 55·0 (35·0 °C) l mol^{-1} s^{-1}. Activation parameters determined by

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[14] G. Biedermann, *Arkiv. Kemi*, 1953, **5**, 441; *Rec. Trav. chim.*, 1956, **75**, 716; T. E. Rogers and G. M. Waind, *Trans. Faraday Soc.*, 1961, **57**, 1360.

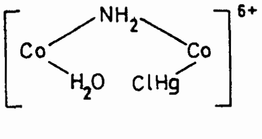
the same procedure as for k_{Hg} above are $\Delta H^{\ddagger} = 18{\cdot}4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -0{\cdot}3$ cal K^{-1} mol^{-1}.

DISCUSSION

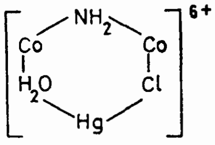
The less than first-order dependence on $[Hg^{II}]$ in the mercury(II)-catalysed conversion of (I) into (III) is similar to that observed in the Hg^{2+}-catalysed aquations of the first chloride from *cis*-$[Co(en)_2Cl_2]^+$ [6,10] and *cis*-$[Cr(H_2O)_4Cl_2]^+$.[12] The explanation for such a dependence in the latter cases was the formation of significant amounts of mercury(II)–cobalt(III) and –chromium(III) adducts. It is possible therefore that a similar adduct is formed in the present study. The dependence on $[Tl^{III}]$ in the thallium(III)-catalysed reaction was strictly first order for the range of concentrations investigated.

The conversion of (I) into (III) occurs in two stages [equations (1) and (2)]. Both stages, since they involve cleavage of a metal–chloride bond, may be influenced by the presence of Hg^{2+}. We consider possible adducts which might be formed during the conversion of (I) into (III), and which could therefore give rise to the observed dependence on $[Hg^{2+}]$.

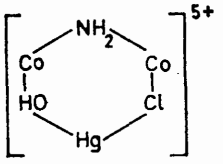
If Hg^{2+} functions as a catalyst for (2) alone, (V) and/or (VI) might be formed. By analogy with the Hg^{2+}-catalysed aquation of $[Co(NH_3)_5Cl]^{2+}$ and other mononuclear cobalt(III) complexes containing a single chloride,[6] no build-up of (V) would be anticipated, and a strictly first-order dependence on $[Hg^{2+}]$ would be expected. The adduct (VI) would not be particularly stable either, since water is known to be reluctant to function as a bridging ligand.[15] Rapid conversion of (VI) into the more stable species (VII) would give rise to an inverse hydrogen-ion dependence. No $[H^+]$ dependence was observed over the concentration range 0·5—2·0M, and it is therefore unlikely that either (VI) or (VII) can be formed at concentrations sufficiently high enough to give rise to a less than first-order dependence on catalyst. If the formation of a stable adduct is important, this must be occurring with species (I) and will have the structure (VIII). Formation of (VIII) would be very rapid, and would constitute a pre-equilibrium step. However the existence of (VIII) is perhaps even less likely than that of (VI) and (VII). There seems no logical reason why (VIII) containing a chloride bonded to three metal centres should be stable, when stable adducts are not formed between, for example, $[Co(NH_3)_5Cl]^{2+}$ and Hg^{2+}.[6]



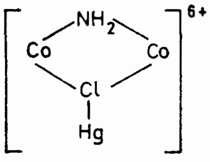
(V)



(VI)



(VII)



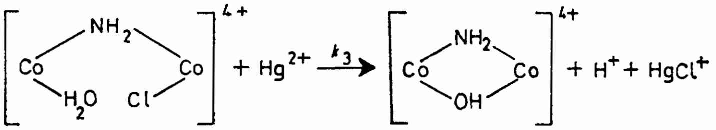
(VIII)

It is felt that the above reasoning does not favour formation of a Hg^{2+} adduct. As an alternative explanation of the $[Hg^{2+}]$-dependence we apply steady-state kinetics for (II) in the reaction sequence (1) and (2). Such an approximation is perfectly feasible since Hg^{2+} has a very strong catalytic effect on the aquation of chloride from $[Co(NH_3)_5Cl]^{2+}$,[6] and the catalysed elimination of chloride from (II) is therefore expected to be rapid. The various equations derived on this basis would seem to provide a satisfactory explanation of the experimental data.

If the steady-state approximation applies for (II) in the absence of added Hg^{2+}, the uncatalysed rate constant, k_{uncat}, is given by equation (6). In the presence of

$$k_{uncat} = \frac{k_1 k_2}{(k_{-1} + k_2)} \tag{6}$$

Hg^{2+} an additional reaction, (7), is included.



(7)

The overall observed rate constant, k_{obs}, is now given by (8),

$$k_{obs} = \frac{k_1(k_2 + k_3[Hg^{2+}])}{(k_{-1} + k_2 + k_3[Hg^{2+}])} \tag{8}$$

and, from (6), (8) can be written in the form (9). Values

$$\frac{1}{(k_{obs} - k_{uncat})} = \left(\frac{k_{-1} + k_2}{k_1 k_{-1}}\right)\left(\frac{k_{-1} + k_2}{k_3[Hg^{2+}]} + 1\right) \tag{9}$$

of *a* and *b* (Table 2) can accordingly be expressed as in

TABLE 5

Values of k_{Tl}, equation (8), for the thallium(III)-catalysed elimination of chloride from $[(NH_3)_4Co{\cdot}\mu(NH_2,Cl){\cdot}Co(NH_3)_4]^{4+}$, (I) → (III), $I = 2{\cdot}0$M(NaClO$_4$)

Temp. °C	$10^3 k_{Tl}$ l mol^{-1} s^{-1}
25	1·16 ± 0·05
30	1·99 ± 0·06
35	2·70 ± 0·08
40	4·18 ± 0·14

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[15] D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2635.

(10) and (11). From (6) and (11) k_1 and k_2/k_{-1} can be

$$a = \frac{k_1k_3k_{-1}}{(k_{-1} + k_2)^2} \qquad (10)$$

$$b = \frac{k_1k_{-1}}{(k_{-1} + k_2)} \qquad (11)$$

evaluated, (12) and (13). Furthermore a term k_{Hg}

$$k_1 = b + k_{\mathrm{uncat}} \qquad (12)$$

$$k_2/k_{-1} = k_{\mathrm{uncat}}/b \qquad (13)$$

may be defined as $k_1k_3/(k_{-1} + k_2)$ which is similar in form to the expression for k_{uncat}, (6), and k_{Tl} (see below). This ratio can be obtained from (14). These various

$$k_{\mathrm{Hg}} = a\left(1 + \frac{k_{\mathrm{uncat}}}{b}\right) \qquad (14)$$

functions are listed in Table 6. Activation parameters for k_1 and K_{Hg}, computed by a least-squares treatment of data, weighted according to the number of runs at each temperature, are given in Table 7.

TABLE 6

Summary of data for the uncatalysed and Hg^{2+}-catalysed eliminations of chloride from $[(NH_3)_4Co{\cdot}\mu(NH_2,Cl){\cdot}Co(NH_3)_4]^{4+}$, (I) ⟶ (III), $I = 2{\cdot}0$M$(NaClO_4)$

Temp. °C	10^2k_{Hg} [a] l mol^{-1} s^{-1}	10^4k_{uncat} [b] s^{-1}	10^3k_1 [c] s^{-1}	k_2/k_{-1} [d]
25·0	12·7 ± 0·5	0·81	3·02 ± 0·06	0·028
30·0	20·1 ± 0·9	1·29	4·92 ± 0·12	0·027
35·0	26·1 ± 1·3	2·06	8·47 ± 0·20	0·025
40·0	33·5 ± 3·0	3·40	15·6 ± 0·5	0·022

[a] $k_{\mathrm{Hg}} = k_1k_3/(k_{-1} + k_2)$. [b] $k_{\mathrm{uncat}} = k_1k_2/(k_{-1} + k_2)$ from reference 5. [c] Calculated using equation (12). [d] Calculated using equation (13).

TABLE 7

A comparison of rate constants and activation parameters for the uncatalysed (k_{uncat}), Hg^{2+}(k_{Hg}), $HgCl^+$(k_{HgCl}), and Tl^{III}(k_{Tl}) catalysed eliminations of chloride [(I) ⟶ (III)] and for the conversion (I) ⟶ (II) (k_1) at $I = 2{\cdot}0$M$(NaClO_4)$

Rate constant (25 °C)	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$ cal mol^{-1} K^{-1}
$k_{\mathrm{uncat}} = 0{\cdot}81 \times 10^{-4}$ s^{-1} [a]	16·2 ± 0·5 [a]	−23·3 ± 2·0 [a]
$k_{\mathrm{Hg}} = 12{\cdot}7 \times 10^{-2}$ l mol^{-1} s^{-1}	11·5 ± 0·8	−24·1 ± 2·6
$k_{\mathrm{HgCl}} = 10{\cdot}6 \times 10^{-2}$ l mol^{-1} s^{-1}		
$k_{\mathrm{Tl}} = 1{\cdot}16 \times 10^{-3}$ l mol^{-1} s^{-1}	14·8 ± 1·2	−22·0 ± 4·0
$k_1 = 3{\cdot}02 \times 10^{-3}$ s^{-1}	19·2 ± 0·5	−5·7 ± 1·8

[a] Data from reference 5.

A similar treatment to that used above, for the Hg^{2+} catalysis in the presence of free chloride reveals a value of the function we define as $k_{\mathrm{HgCl}} = k_1k_4/(k_{-1} + k_2)$ where k_4 is the rate constant for $HgCl^+$-catalysed elimination of chloride from (II). At 25 °C, the value obtained for $k_{\mathrm{HgCl}} = 0{\cdot}106$ l mol^{-1} s^{-1} is very similar to $k_{\mathrm{Hg}} = 0{\cdot}127$ l mol^{-1} s^{-1}. Similar relative values of k_{Hg} and k_{HgCl} have been noted previously in the Hg^{2+}-catalysed aquation of mononuclear complexes.[6,10]

For the thallium(III)-catalysed reaction, the rate constant k_5, which is analogous to k_3, may be defined and substituted for k_3 in equation (8). Since k'_{obs} gives a first-order dependence on $[Tl^{III}]$ it is concluded that $(k_{-1} + k_2) \gg k_5[Tl^{III}]$. The experimentally determined quantity k_{Tl} is then given by equation (15) and is again of similar form to k_{uncat}, equation (6).

$$k_{\mathrm{Tl}} = \frac{k_1k_5}{(k_{-1} + k_2)} \qquad (15)$$

Although it has not been possible to determine the individual values of k_3, k_4, and k_5, various ratios, $k_{\mathrm{Hg}}/k_{\mathrm{uncat}}$, $k_{\mathrm{HgCl}}/k_{\mathrm{uncat}}$, and $k_{\mathrm{Tl}}/k_{\mathrm{uncat}}$, provide information regarding k_3/k_2, k_4/k_2, and k_5/k_2. These values along with related (activation) enthalpic and entropic differences between the catalysed and uncatalysed paths are compared with related data for $[Co(NH_3)_5Cl]^{2+}$ in Table 8.

TABLE 8

A summary of the effectiveness of Hg^{2+}, $HgCl^+$, and Tl^{3+} as catalysts for the elimination of chloride from $[Co(NH_3)_5Cl]^{2+}$ and $[(NH_3)_4Co{\cdot}\mu(NH_2,Cl){\cdot}Co(NH_3)_4]^{4+}$ at 25 °C and $I = 2{\cdot}0$M$(NaClO_4)$

Catalyst	Ratio rate constants l mol^{-1}	$\Delta(\Delta H^‡)$ [a] kcal mol^{-1}	$\Delta(\Delta S^‡)$ [a] cal K^{-1} mol^{-1}
Reaction of $[(NH_3)_4Co{\cdot}\mu(NH_2Cl){\cdot}Co(NH_3)_4]^{4+}$ [b]			
Hg^{2+}	$k_3/k_2 = 1{\cdot}57 \times 10^3$	−4·7 ± 1·3	−0·8 ± 5
$HgCl^+$	$k_4/k_2 = 1{\cdot}30 \times 10^3$		
Tl^{3+}	$k_5/k_2 = 0{\cdot}15 \times 10^2$	−1·4 ± 1·7	+0·9 ± 6
Reaction of $[Co(NH_3)_5Cl]^{2+}$ [c]			
Hg^{2+}	$k_{\mathrm{Hg}}/k_{\mathrm{uncat}} = 8{\cdot}7 \times 10^4$	−4·0	+8·7
$HgCl^+$	$k_{\mathrm{HgCl}}/k_{\mathrm{uncat}} = 9{\cdot}3 \times 10^4$		
Tl^{3+}	$k_{\mathrm{Tl}}/k_{\mathrm{uncat}} = 5{\cdot}2 \times 10^3$	−3·5	+5·3

[a] Correspond to differences in activation parameters for catalysed and uncatalysed reactions. [b] This work. [c] Uncatalysed reaction; rate constant extrapolated from data for Tl^{3+}-catalysed reaction, reference 10. Activation parameters from A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261.

In addition to yielding information on the relative catalytic efficiencies of Hg^{2+}, $HgCl^+$, and Tl^{III}, this study has shed new light on the mechanism of the uncatalysed reaction. Now that (I) rather than (II) is known to be predominant in solution and k_1 and k_2/k_{-1} have been determined, some reappraisal of the uncatalysed reaction is called for. Rate constants previously reported for the conversion of (II) into (III) in fact correspond to the overall reaction (I) into (III), and to a first approximation are given by k_1k_2/k_{-1} (since $k_{-1} \gg k_2$). At 25 °C, $I = 2{\cdot}0$M, $k_1k_2/k_{-1} = 0{\cdot}84 \times 10^{-4}$ s^{-1} (Table 6) as compared to the experimentally observed rate constant of $0{\cdot}81 \times 10^{-4}$ s^{-1}.[5] Activation parameters for the latter case are $\Delta H^‡ = 16{\cdot}2 \pm 0{\cdot}5$ kcal mol^{-1}, $\Delta S^‡ = -23{\cdot}3 \pm 2{\cdot}0$ cal K^{-1} mol^{-1}. It is estimated that $k_1/k_{-1} < 0{\cdot}1$,[4] which means that for the intramolecular conversion (II) into (III) at 25 °C and $I = 2{\cdot}0$M $(NaClO_4)$, $k_2 > 8{\cdot}4 \times 10^{-4}$ s^{-1}. This is at least 300 times faster than the intermolecular aquation of chloride from $[Co(NH_3)_5Cl]^{2+}$, $k = 2{\cdot}3 \times 10^{-6}$ s^{-1}, $I = 2{\cdot}0$M $(LiClO_4)$.[10] Ligand substitution of mononuclear [16] and bridge cleavage and formation processes in binuclear [17] complexes of cobalt(III) are believed to be S_N1. It is concluded therefore that there is some

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[16] A. Haim, *Inorg. Chem.*, 1970, **9**, 426.

[17] R. S. Taylor and A. G. Sykes, *Inorg. Chem.*, 1974, **13**, 2524.

labilisation of the chloride and aquo-ligands in (II) which can be attributed to the presence of the amido-bridge. Previously, from an examination of protonation constants for bridging ligands, *e.g.* oxalate and phosphate,[18,19] it has been concluded that two cobalt(III) atoms bonded to the same ligand have approximately the same effect as a single proton. The amido-bridge might therefore be regarded as exhibiting behaviour intermediate between those of NH_2^- and NH_3. At the same time it must be noted that the NH_2-bridge has no free lone-pairs of electrons. The labilisation of ammonia ligands by the hydroxo-bridge in (III) has been detected in earlier work.[20] The observation that there is no build-up of the bisaquo-complex (IV) when (III) is made up in 2M-$HClO_4$ [21] may therefore be attributable to the labilisation of the aquo-ligands by the amido-bridge. Further discussion of these effects is to be found in ref. 22. No evidence was obtained for build-up of (IV) in the present study, nor is formation of (IV) evident in the uncatalysed reaction. Its formation from (II) would require intermolecular substitution of Cl^- by solvent H_2O. Intramolecular processes are generally preferred in this type of reaction, even though in the conversion of (II) into (III) a transitory μ-aquo-species must be formed.

The relative catalytic effects of Hg^{2+}, $HgCl^+$, and Tl^{3+} are much smaller in the conversion of (I) into (III) than in the aquation of $[Co(NH_3)_5Cl]^{2+}$ (Table 8). However the order of effectiveness is the same $Hg^{2+} \sim HgCl^+ > Tl^{3+}$.

Chan and Chan[11] have recently observed that second-order rate constants for Hg^{2+} and Tl^{3+}-catalysed aquations of mononuclear complexes containing a single chloride give enthalpies of activation, $\Delta H^{\ddagger}$, which for a particular complex are the same within experimental error, and conclude that differences in rate are resident in the entropy term. Activation parameters have now been determined for the Hg^{2+}-catalysed aquation of $[Co(NH_3)_5Cl]^{2+}$ and the same point may be made (Table 8). Interesting though this observation is further comment is called for because second-order rate constants are in fact composite terms, and catalysis presumably occurs by a stepwise mechanism [equations (16) and (17)]. According to this mechanism observed

$$Co^{III}\text{–}Cl + \text{catalyst} \xrightleftharpoons{K(\text{rapid})} Co^{III}\text{–}Cl\text{–catalyst} \qquad (16)$$

$$Co^{III}\text{–}Cl\text{–catalyst} \xrightarrow{k} Co^{III} + Cl\text{–catalyst} \qquad (17)$$

second-order rate constants correspond to Kk, and activation enthalpies contain contributions from both the pre-equilibrium (16) and the rate-determining step (17). It is not possible to comment on the values of ΔH for (16) directly. However enthalpy changes for the formation of $HgCl^+$ ($-5{\cdot}8$ kcal mol^{-1}) [23] and $TlCl^{2+}$ ($-5{\cdot}45$ kcal mol^{-1}) [24] at 3·0M ionic strength are about the same. For the overall enthalpies to be identical, $\Delta H^{\ddagger}$ values for reaction (17) with Hg^{2+} and Tl^{3+} as catalysts must also be the same. This is perhaps reasonable since (17) corresponds to the cleavage of a cobalt(III)–chloride bond and may therefore be independent of the identity of the catalyst. However for the binuclear complexes enthalpies of activation are different for Hg^{2+} and Tl^{3+}. The unfavourable enthalpy of activation for Tl^{3+} is reflected in a much reduced catalytic effect compared to Hg^{2+}. Previously [10] we expressed the belief that two factors explained the effectiveness of catalysts, $HgCl^+ \sim Hg^{2+} > Tl^{3+} > TlCl^{2+}$. The first was the affinity of the catalyst for chloride and the second was the charge on the catalyst. The results of this study would seem to reinforce this belief in that while Hg^{2+} and Tl^{3+} have similar affinities for chloride (*viz.* similar equilibrium constants for formation of $HgCl^+$ and $TlCl^{2+}$), Hg^{2+} is a more effective catalyst. For a comparison of effects in mononuclear and binuclear complexes (Table 8) it is perhaps more reasonable to consider the charge product in the activated complex rather than the charge on the catalyst. With this consideration in mind, the decrease in efficiency of Hg^{2+}, and the much more marked decrease with Tl^{3+} for binuclear as opposed to mononuclear complexes can be rationalised.

EXPERIMENTAL

Samples of the perchlorate salts of the complexes μ-amido-μ-chloro-bis[tetra-amminecobalt(III)], $[(NH_3)_4Co{\cdot}\mu(NH_2,Cl){\cdot}Co(NH_3)_4](ClO_4)_4,H_2O$, and μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)], $[(NH_3)_4Co{\cdot}\mu(NH_2,OH){\cdot}Co(NH_3)_4](ClO_4)_4,H_2O$, were prepared as described previously.[25] Solutions of mercury(II) perchlorate were obtained in the following manner. Mercury(II) perchlorate (50 g, G. F. Smith) was dissolved in 0·3M-perchloric acid solution (100 ml). The solution was exchanged onto an Amberlite IR-120(H) resin column (35 cm, 2-cm diam.). The column was washed with water until the pH was *ca.* 5·5, washed with 0·05M-perchloric acid to remove any 1+ ions, and finally the Hg^{2+} was eluted with 2M-perchloric acid. The concentration of mercury(II) was determined by titration with a freshly prepared standard 0·1M-ammonium thiocyanate solution using ferric alum as indicator. The hydrogen ion concentration was determined after removal of the Hg^{2+} using the same cation-exchange resin. Thallium(III) perchlorate hexahydrate (G. F. Smith) is hygroscopic and was dried and stored in a desiccator over P_2O_5. A weighed amount of the solid was dissolved in 5M-perchloric acid (10 ml), and diluted to 25 ml with distilled water. It was necessary initially to use 5M-perchloric acid to ensure that all the solid was dissolved. Subsequent dilutions were carried out carefully with mechanical stirring to avoid formation of insoluble Tl_2O_3 in regions of low acidity. The concentrated solutions were

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

standardised by addition of an excess of potassium iodide and titration with sodium thiosulphate. To prevent aerial oxidation of the potassium iodide in acidic solutions, solid sodium carbonate was added to the thallium(III) solution to displace air by carbon dioxide.

AnalaR grade perchloric acid (72%), sodium perchlorate (B.D.H.), and sodium chloride were used as required without further purification. The ionic strength in the present study was adjusted with $NaClO_4$, which has previously been shown to give satisfactory agreement with runs in which $LiClO_4$ was used.[25] The sodium perchlorate was shown to contain 0·02% of chloride, by titration with silver nitrate. Such an amount is negligible as far as this study is concerned.

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