# Chromium(II) and Vanadium(II) Reductions of μ-Amido-μ-chloro- and μ-Amido-μ-bromo-bis[tetra-amminecobalt(III)] Complexes

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Intermediate formation of $Co(NH_3)_5H_2O^{2+}$ is observed in the Cr^{2+} reductions of the title complexes in aqueous solutions, $I = 2 \cdot 0_M$ $(LiClO_4)$, $[H^+] = 0 \cdot 1$—$1 \cdot 97_M$, but is not detected (<6%) in the corresponding V^{2+} reductions. Intermediate formation of $Co(NH_3)_5X^{2+}$ ($X^- = Cl^-$, Br^-) is observed in the latter with a 1 : 1 ratio of reactants. From pH and n.m.r. measurements it is concluded that (I) and not (II), equation (i), is predominant under the conditions


(I)   (II)
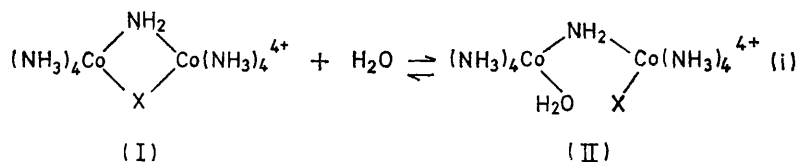
investigated. The Cr^{2+} reactions are inner sphere and involve (I). The V^{2+} reactions proceed with outer-sphere reduction of (I) to give $Co(NH_3)_5X^{2+}$ which reacts at about the same rate with a second V^{2+}. Under pseudo-first-order conditions, with V^{2+} in large excess, build-up of $Co(NH_3)_5X^{2+}$ as an intermediate is not therefore observed. Full kinetic data including activation parameters are reported.

WERNER[1] first prepared the monochloro- and mono-bromo-binuclear cobalt(III) complexes considered here, but assigned formulae μ-amido-[tetra-ammineaquocobalt(III)][tetra-amminechlorocobalt(III)], [(NH₃)₄(H₂O)Co·NH₂·Co(Cl)(NH₃)₄]Cl₄,4H₂O, and μ-amido-[tetra-ammineaquocobalt(III)][tetra-amminebromocobalt(III)], [(NH₃)₄(H₂O)Co·NH₂·Co(Br)(NH₃)₄]-Br₄,2H₂O, to these compounds. Barro *et al.*[2] have more recently carried out an X-ray crystallographic study of the chloro-complex and were the first to report a μ-amido-μ-chloro-structure. Infrared studies[3] are also consistent with this assignment (I) where $X^- = Cl^-$ or


(I)
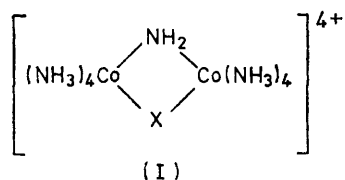
Br^-. Bridge cleavage, resulting in a structure (II), Werner's original formula, must occur in aqueous

The position of equilibrium between (I) and (II) is uncertain, (1). Visible-range scan spectra recorded

(II)

(III)
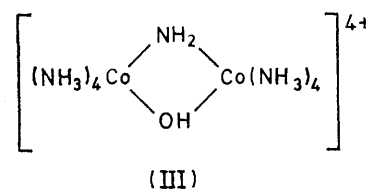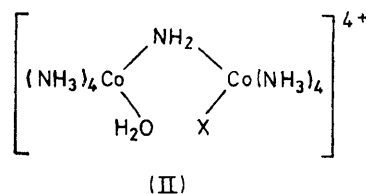
during the conversion through into (III) [equation (2)] suggests that either (I) or (II) predominates, and following Werner's lead it has previously been assumed that (II) is predominant.
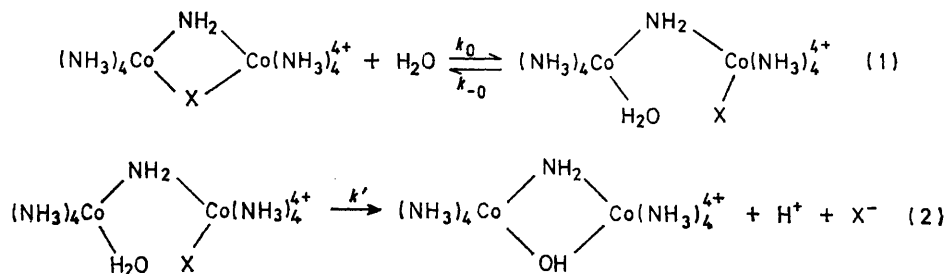
solutions, since formation of the μ-amido-μ-hydroxo-complex, (III), results upon dissolution of solid samples of (I) in aqueous solution.[4]

A kinetic study of the V^{2+} reduction of (I)/(II), where $X^- = Cl^-$, has been made previously and an outer-sphere mechanism for reduction,[5] which may involve

[1] A. Werner, *Annalen*, 1910, **375**, 1.
[2] R. Barro, R. E. Marsh, and W. P. Schaefer, *Inorg. Chem.*, 1970, **9**, 2131.
[3] S. W. Foong and A. G. Sykes, *J.C.S. Dalton*, 1974, 1453.

[4] M. B. Stevenson, R. D. Mast, and A. G. Sykes, *J. Chem. Soc. (A)*, 1969, 937.
[5] R. S. Taylor, R. N. F. Thorneley, and A. G. Sykes, *J. Chem. Soc. (A)*, 1970, 856.

(I) and/or (II), is indicated. The V^{2+} reduction of the bromo-complex was investigated in the hope of further substantiating this mode of attack. Studies on the chromium(II) reduction were also undertaken because a marked preference for attack of species (II) ($X^- = Cl^-$, Br^-) was expected, based upon the inner-sphere reactivity of Cr^{2+}.

The formation of (III) although slow compared with the proposed redox reactions, makes some contribution during the time required for thermostatting, and has to be allowed for when calculating stoicheiometries. The Cr^{2+} and V^{2+} reductions of complex (III) are known to be slow.[6] Complexes (I) and (II) in equilibrium are referred to collectively as Co_2Cl^{4+} ($X^- = Cl^-$) and Co_2Br^{4+} ($X^- = Br^-$).

Stoicheiometry.—The conversion of both the μ-amido-μ-chloro- and μ-amido-μ-bromo-complexes into the μ-amido-μ-hydroxo-complex in acidic perchlorate media is well established.[4] Although this reaction is slow in both cases, it was necessary to make due allowance for it in the kinetic analysis. There are no difficulties introduced from consideration of parallel paths for Cr^{2+} (or V^{2+}) reduction of, for example, the μ-amido-μ-chloro- and μ-amido-μ-hydroxo-complexes present at the time of reduction, since the latter is much less redox-active than the former.[5,6] However, problems did arise when stoicheiometric measurements were made from molar absorbance changes (Δε 1 mol^{-1} cm^{-1}) in each run. These measurements are significant in elucidating the course of reaction, and the precise concentration of binuclear cobalt(III) reactant at the start of each run was required (see Experimental section).

Ion-exchange and kinetic analysis from the reduction Co_2X^{4+} ($X^- = Cl^-$, Br^-) by Cr^{2+} or V^{2+} indicate an overall stoicheiometry requiring two equivalents of reductant per oxidant species. The reaction may be represented by

$$Co_2X^{4+} + 2M^{2+} \longrightarrow 2Co^{2+} + 2M^{III} + X^-$$
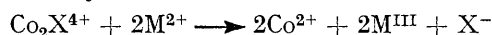
where M^{2+} is either Cr^{2+} or V^{2+}, and X^- may be complexed or uncomplexed depending upon the identity of the reductant.

RESULTS

Kinetics of the Cr^{2+} Reduction of Co_2Cl^{4+}.—The rate of disappearance of Co_2Cl^{4+} was monitored at the 554 nm peak position (ε = 165 1 mol^{-1} cm^{-1}) using the stopped-flow method. Pseudo-first-order reaction conditions were employed, with [Cr^{2+}] in 10-to 80-fold excess of [Co_2Cl^{4+}], and plots of log (O.D.$_t$ − O.D.$_∞$) *versus* time were linear to 85—90% completion. Final absorbance, O.D.$_∞$, readings were clearly defined at the end of the first stage. The reduction is first order in both reactants, and the rate is independent of hydrogen-ion concentration in the range [H^+] = 0·2 to 1·97M. The rate law is therefore as in (3).

$$-\frac{d}{dt} [Co_2Cl^{4+}] = k_1[Cr^{2+}][Co_2Cl^{4+}] \qquad (3)$$

Second-order rate constants, k_1, at temperatures in the range 3·5—35° are listed in Table 1. Data were computed

using a non-linear least-squares programme, with a weighting factor of $1/k_1{}^2$. Activation parameters and second-order rate constant k_1, at 25°, are listed in Table 9, and the errors quoted are taken directly from the computer-data output.

TABLE 1

Rate constants and Δε values for the first stage of Cr^{2+} reduction of Co_2Cl^{4+}, I = 2·0M (LiClO$_4$), λ = 554 nm. The numbers of runs which have been averaged for data in the last two columns are indicated in parentheses

Temp.	[H$^+$]	10^2[Cr^{2+}]	10^4[Co$_2$Cl^{4+}]	k_1	Δε ^{a,b}
°C	M	M	M	l mol^{-1} s^{-1}	l mol^{-1} cm^{-1}
35·0	0·20	3·90	9·1	15·6	119 (2)
	1·19	3·90	8·4	13·6	111 (2)
25·0	0·25	2·44	14·9	11·5	119 (2)
	0·55	2·44	14·6	11·8	123 (2)
	1·02	2·44	15·6	11·4	116 (2)
	1·03	2·55	24·4	10·6	117 (2)
	1·04	2·55	3·4	10·6	105 (2)
	1·86	0·63	8·8	11·9	— (2)
	1·97	4·53	9·5	11·7	127 (2)
15·0	0·20	4·06	9·7	9·1	121 (2)
	1·19	4·06	9·7	8·7	118 (2)
3·5	0·20	4·15	9·9	6·4	116 (2)
	1·19	4·15	9·8	6·1	112 (2)

^{a} The absorption change, Δε, for the first stage has been determined per mol of complex present at the start of each reaction. ^{b}Δε = 126·6 1 mol^{-1} cm^{-1} assuming equation (9) applies.

When measuring absorbance changes at λ = 490 nm, a peak position of $Co(NH_3)_5H_2O^{3+}$, a second stage was observed. This reaction was studied under the same
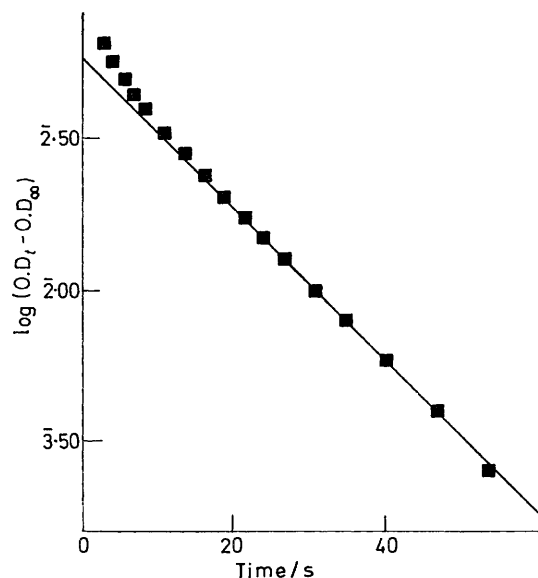

FIGURE 1 A pseudo-first-order rate plot for the second stage of Cr^{2+} reduction of Co_2Cl^{4+}. The initial curvature corresponds to the faster first stage of reduction. [Co_2Cl^{4+}] = 1 × 10^{-3}M, [Cr^{2+}] = 4·53 × 10^{-2}M, [H^+] = 1·86M, I = 2·0M (LiClO$_4$), k_{obs} = 7·65 × 10^{-2} s^{-1}, and Δε = 36·6 1 mol^{-1} cm^{-1}

conditions as the first stage and plots of log (O.D.$_t$ − O.D.$_∞$) against time were linear to at least 93% completion. A typical run is shown in Figure 1, where the initial part of the trace is due to the first stage of reduction. The second

^{6} R. S. Taylor and A. G. Sykes, *J. Chem. Soc. (A)*, 1970, 1991.

stage is first order in both reactants and exhibits an inverse hydrogen-ion dependence over the range $[H^+] = 0\cdot2$—$1\cdot97$M. From a comparison of our data with that of Toppen and Linck [7] the intermediate is clearly identified as

TABLE 2

Rate constants and $\Delta\varepsilon$ values for the second stage of Cr^{2+} reduction of Co_2Cl^{4+}, $I = 2\cdot0$M $(LiClO_4)$; $\lambda = 490$ nm. The data correspond to reduction of $Co(NH_3)_5H_2O^{3+}$. Numbers of runs which have been averaged for the data in the last two columns are indicated in parentheses

Temp. °C	[H+] M	$10^2[Cr^{2+}]$ M	$10^4[Co_2Cl^{4+}]$ M	k_2 l mol⁻¹ s⁻¹	$\Delta\varepsilon^{a,b}$ l mol⁻¹ cm⁻¹
35·0	0·20	3·90	7·9	12·5	c (2)
	1·19	3·90	7·6	3·9	41·0 (2)
25·0	0·25	2·44	15·6	7·7	42·5 (2)
	0·55	2·44	14·6	4·5	46·3 (2)
	1·02	2·55	24·4	2·4	39·5 (2)
	1·03	2·44	14·9	2·7	38·6 (2)
	1·04	2·55	3·4	2·5	39·2 (2)
	1·86	4·53	9·5	1·7	36·6 (2)
	1·97	0·63	8·8	1·1	(2)
15·0	0·20	4·06	9·5	5·3	c (2)
	1·19	4·06	9·6	1·2	36·0 (2)
3·5	0·20	4·15	9·8	2·0	37·0 (2)
	1·19	4·15	9·7	0·6	38·0 (2)

 [a] The absorption change $\Delta\varepsilon$, has been measured assuming reduction of one mol of cobalt(III) complex generated at the end of the first stage. [b] $\Delta\varepsilon = 39\cdot8$ l mol⁻¹ cm⁻¹ assuming reaction proceeds entirely via $Co(NH_3)_5H_2O^{3+}$. [c] Under these conditions the rate of the second stage is comparable to that of the first and $\Delta\varepsilon$ could not be estimated accurately.

$Co(NH_3)_5H_2O^{3+}$. Second-order rate constants $k_{obs}/[Cr^{2+}]$, as defined in equations (4) and (5), are listed in Table 2.

$$-\frac{d}{dt}[Co(NH_3)_5H_2O^{3+}] = k_{obs}[Co(NH_3)_5H_2O^{3+}] \quad (4)$$

where

$$k_{obs} = k_2[Cr^{2+}][H^+]^{-1} \quad (5)$$

The first-order rate constant k_2, was evaluated at each temperature using the non-linear least-squares programme already outlined, with a $1/y^2$ weighting $(y = k_{obs}/[Cr^{2+}])$. Activation parameters and k_2 (25°) are listed in Table 9.

Plots of $\log(O.D._t - O.D._{\infty})$ for the second stage were extrapolated to zero time to estimate how much $Co(NH_3)_5H_2O^{3+}$ was available for reduction. The $\Delta\varepsilon$ values obtained, Table 2, indicate $100 \pm 10\%$ formation of $Co(NH_3)_5H_2O^{3+}$ per mol of dicobalt complex undergoing reaction in the first stage. There was no observable trend in product formation with temperature, in the range $3\cdot5$—$35\cdot0°$. A similar extrapolation of plots for the first stage of reduction also gave absorbance changes which corresponded to the production of $Co(NH_3)_5H_2O^{3+}$ from Co_2Cl^{4+} (see Table 1).

Kinetics of the Cr^{2+} Reduction of Co_2Br^{4+}.—Reduction was again studied with $[Cr^{2+}]$ in 10-to 80-fold excess of $[Co_2Br^{4+}]$, and two stages were identified. The disappearance of Co_2Br^{4+} was monitored at $\lambda = 560$ nm $(\varepsilon = 155$ l mol⁻¹ cm⁻¹$)$ and pseudo-first-order plots were linear to 85%, sometimes 95% completion. The reaction was first order in both reactants and independent of hydrogen-ion concentration in the range $[H^+] = 0\cdot10$ to $1\cdot06$M. Data were computed using the non-linear least-squares programme, with a weighting factor $1/y^2$ $(y = k_{obs}/[Cr^{2+}])$, and gave a good fit to the rate expression (6). Second-order rate constants, k_3,

$$-\frac{d}{dt}[Co_2Br^{4+}] = k_3[Cr^{2+}][Co_2Br^{4+}] \quad (6)$$

at temperatures in the range 4—25° are listed in Table 3; computed activation parameters and k_3 (25°) are listed in Table 9.

TABLE 3

Rate constants and $\Delta\varepsilon$ values for the first stage of the Cr^{2+} reduction of Co_2Br^{4+}, $I = 2\cdot0$M $(LiClO_4)$; $\lambda = 560$ nm. Number of runs which have been averaged for data in last two columns are indicated in parentheses

Temp. °C	[H+] M	$10^2[Cr^{2+}]$ M	$10^4[Co_2Br^{4+}]$ M	k_3 l mol⁻¹ s⁻¹	$\Delta\varepsilon^{a,b}$ l mol⁻¹ cm⁻¹
3·7	0·10	3·77	7·5	122	115 (2)
	0·40	2·14	7·5	121	119 (2)
	0·40	0·79	7·5	117	124 (2)
	0·40	3·72	25·0	114	113 (2)
	0·40	3·72	4·5	124	135 (2)
	0·40	3·88	7·5	112	116 (2)
	1·06	3·77	7·5	127	134 (2)
10·0	0·17	3·89	7·5	138	119 (2)
	0·47	3·89	7·5	142	125 (2)
17·0	0·17	3·81	7·5	170	98 (2)
	0·47	3·81	7·5	173	98 (2)
25·0	0·17	3·88	7·5	220	97 (2)
	0·47	3·88	7·5	220	100 (2)

[a] The absorption change, $\Delta\varepsilon$, for the first stage has been determined per mol of complex present at the start of the reaction. [b] $\Delta\varepsilon = 119\cdot4$ l mol⁻¹ cm⁻¹ assuming equation (9) applies.

The intermediate was identified as $Co(NH_3)_5H_2O^{3+}$ from rate data (k_4) for the second stage at $\lambda = 490$ nm (Table 4). The conditions of reaction were identical to those for the first stage; pseudo-first-order plots were linear to at least 85% completion. The rate law is defined by (7) and rate constants k_4 are in good agreement with k_2 (obtained from

$$-\frac{d}{dt}[Co(NH_3)_5H_2O^{3+}] =$$
$$k_4[Cr^{2+}][Co(NH_3)_5H_2O^{3+}][H^+]^{-1} \quad (7)$$

the second stage of reduction of Co_2Cl^{4+}) (Figure 2). Absorbance changes calculated after extrapolation to zero

TABLE 4

Rate constants and $\Delta\varepsilon$ values for the second stage of the Cr^{2+} reduction of Co_2Br^{4+}, $I = 2\cdot0$M $(LiClO_4)$; $\lambda = 490$ nm. The data correspond to reduction of $Co(NH_3)_5H_2O^{3+}$ (see also k_2, Table 2). The number of runs, which have been averaged for data in the last two columns, are indicated in parentheses

Temp. °C	[H+] M	$10^2[Cr^{2+}]$ M	$10^4[Co_2Br^{4+}]$ M	k_4 l mol⁻¹ s⁻¹	$\Delta\varepsilon^{a,b}$ l mol⁻¹ cm⁻¹
3·7	0·10	3·77	7·5	5·41	31·3 (2)
	0·40	2·14	7·5	1·42	28·0 (2)
	0·40	0·79	7·5	1·37	33·0 (2)
	0·40	3·72	25·0	1·38	31·6 (2)
	0·40	3·72	4·5	1·37	27·1 (2)
	0·40	3·88	7·5	1·39	29·6 (2)
	1·06	3·77	7·5	0·77	31·5 (2)
10·0	0·17	3·89	7·5	5·22	31·0 (2)
	0·47	3·89	7·5	1·99	31·0 (2)
17·0	0·17	3·81	7·5	8·27	28·4 (2)
	0·47	3·81	7·5	3·28	28·0 (2)
25·0	0·17	3·88	7·5	15·1	32·7 (2)
	0·47	3·88	7·5	5·6	31·8 (2)

[a] The absorption change, $\Delta\varepsilon$, has been measured assuming one mol of cobalt(III) generated at the end of the first stage. [b] $\Delta\varepsilon = 39\cdot8$ l mol⁻¹ cm⁻¹ assuming reaction proceeds entirely via $Co(NH_3)_5H_2O^{3+}$.

time suggest that there is only $90 \pm 10\%$ production of $Co(NH_3)_5H_2O^{3+}$ (see Table 4). However, there is no

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

temperature dependence of the product distribution, and $\Delta\varepsilon$ values will be somewhat imprecise since reaction (2) is about four times faster with $X^- = Br^-$ than with $X^- = Cl^-$.

Kinetics of the V^{2+} Reduction of Co_2Cl^{4+}.—A full kinetic study of the first stage of reduction has already been made.[5] The same rate process is observed at $\lambda = 554$ nm and 490 nm [the former an absorption maximum for Co_2Cl^{4+}, the latter a maximum for $Co(NH_3)_5H_2O^{3+}$]. At $\lambda = 490$ nm an absorbance change, $\Delta\varepsilon = 90$ l mol^{-1} cm^{-1}, was recorded. If $Co(NH_3)_5H_2O^{3+}$ is formed as an intermediate then $\Delta\varepsilon$ for the first stage would be 56 l mol^{-1} cm^{-1}, and if there is no intermediate a value of $\Delta\varepsilon = 97\cdot6$ l mol^{-1} cm^{-1} would be expected at $\lambda = 490$ nm. Careful monitoring of absorbance changes for up to 6 min indicated a maximum of 6% formation of $Co(NH_3)_5H_2O^{3+}$. Rate constants for the V^{2+} reduction of Co_2Cl^{4+} and $Co(NH_3)_5Cl^{2+}$ are almost identical, and with V^{2+} in large excess a build-up of $Co(NH_3)_5Cl^{2+}$ would not be expected and is not observed.

Kinetics of the V^{2+} Reduction of Co_2Br^{4+}.—The disappearance of Co_2Br^{4+} was monitored at $\lambda = 560$ nm ($\varepsilon = 155$ l mol^{-1} cm^{-1}) and $\lambda = 490$ nm [absorption maximum for $Co(NH_3)_5H_2O^{3+}$] with the stopped-flow apparatus. Only one stage was observed at both wavelengths, indicating no observable formation of $Co(NH_3)_5H_2O^{3+}$. Pseudo-first-order reaction conditions were employed with $[V^{2+}]$ in excess, and plots of log (O.D.$_t$ − O.D.$_\infty$) *versus* time were linear to at least 85% completion. A first-order dependence

Product Analyses.—Experiments to identify and quantify the primary products of the first stage of Cr^{2+} and V^{2+} reductions of both Co_2Cl^{4+} and Co_2Br^{4+} were based upon ion-exchange separation of reaction mixtures. Yields of products subsequent to the reduction of one mol of binuclear oxidant by one mol of reductant should substantiate the information obtained from kinetic analysis regarding mechanism.

Reaction solutions were made up with a 10—100% excess of binuclear complex, thereby allowing for the occurrence of reaction (2). Typical reactant concentrations were $[Co_2X^{4+}] = 3\cdot3 \times 10^{-3}$M, $[Cr^{2+}] = 2\cdot8 \times 10^{-3}$M, $[H^+]$ in the range 0·1—1·0M, and ionic strength $I = 2\cdot0$M. Reactions were investigated at 0 °C under air-free conditions in an air-tight vessel, and after sufficient time had elapsed for complete reaction (calculated from the relevant Tables) the reaction mixture was introduced onto the column of cation-exchange resin (Dowex 50W-X8, H$^+$-form).

With Cr^{2+} as reductant four fractions were eluted, where the strength of $HClO_4$ required for separation is as indicated; CrX^{2+} (0·1M [H$^+$]), Co^{2+} (0·2M [H$^+$]), Cr^{3+} (2·0M [H$^+$]), and finally $Co(NH_3)_5H_2O^{3+}$ (3·0M [H$^+$]). The chromium(III) fractions, $X^- = Cl^-$ or Br^-, were identified spectrophotometrically [8] and analysed by oxidation to chromium(VI) using H_2O_2 in NaOH (1·0M). Solutions of chromium(VI) were then determined spectrophotometrically for CrO_4^{2-} at $\lambda = 372$ nm ($\varepsilon = 4\cdot815 \times 10^3$ l mol^{-1} cm^{-1}).

TABLE 5

Rate constants and $\Delta\varepsilon$ values for the single-stage V^{2+} reduction of Co_2Br^{4+}, $I = 2\cdot0$M (LiClO$_4$); $\lambda = 560$ and 490 nm as indicated. The numbers of runs, which have been averaged for data in the last four columns, are indicated in parentheses

Temp.	[H$^+$]	$10^2[V^{2+}]$	$10^3[Co_2Br^{4+}]$	k_5 [a]	$\Delta\varepsilon$ [a,c,d]	k_5 [b]	$\Delta\varepsilon$ [b,c,e]
°C	M	M	M	l mol^{-1} s^{-1}	l mol^{-1} cm^{-1}	l mol^{-1} s^{-1}	l mol^{-1} cm^{-1}
3·0	0·4	3·96	0·6	12·2	150	12·7	93 (3)
	0·8	6·12	0·6	13·1	153	13·9	90 (2)
	0·8	0·79	0·6	13·9	139	14·4	91 (2)
	0·8	3·91	1·5	11·4	145	11·7	84 (2)
	0·8	3·90	0·3	11·3	143	11·8	82 (2)
	0·8	4·16	0·6	11·9	157	11·5	103 (2)
	1·4	3·96	0·6	12·0	151	13·1	91 (2)
10·0	0·4	4·11	0·6	17·1	143	18·1	90 (2)
	1·4	4·11	0·6	17·4	141	18·2	87 (2)
17·0	0·4	4·01	0·6	22·8	132	22·8	80 (1)
	1·4	4·01	0·6	23·3	137	23·0	89 (2)
25·0	0·4	4·00	0·6	32·7	140	32·7	76 (1)
	1·4	4·00	0·6	33·2	132	34·3	82 (2)

[a] $\lambda = 560$ nm. [b] $\lambda = 490$ nm. [c] The absorption change $\Delta\varepsilon$, has been measured per mol of complex present at the start of each reaction. [d] $\Delta\varepsilon = 138\cdot4$ l mol^{-1} cm^{-1} assuming Co^{2+} and V^{3+} are the products. [e] $\Delta\varepsilon = 92\cdot6$ l mol^{-1} cm^{-1} assuming Co^{2+} and V^{3+} are the products.

on both reactants was observed, and there was no hydrogen-ion dependence in the range $[H^+] = 0\cdot4$—1·4M (see Table 5). The rate dependence is therefore as given in equation (8).

$$-\frac{d}{dt}[Co_2Br^{4+}] = k_5[V^{2+}][Co_2Br^{4+}] \qquad (8)$$

Second-order rate constants, k_5, at temperatures in the range 3·7—25·0°, are listed in Table 5. Activation parameters and k_5 (25 °C) were obtained after computation of the data using the non-linear least-squares programme with weighting $= 1/k_5^2$, and are listed in Table 9. Data were taken from runs at both wavelengths.

Absorbance changes are listed in Table 5 and the correspondence between calculated and observed values is quite good, although some scatter is observed. The average value further supports the kinetic evidence that reduction of Co_2Br^{4+} produces no $Co(NH_3)_5H_2O^{3+}$ intermediate.

Cobalt(II) fractions were determined as $CoCl_4^{2-}/CoCl_3H_2O^-$ following addition of concentrated hydrochloric acid up to $[HCl] = 10$M. The final product $Co(NH_3)_5H_2O^{3+}$ was estimated by direct spectrophotometric measurement at $\lambda = 490$ nm ($\varepsilon = 47\cdot31$ l mol^{-1} cm^{-1}), using a Unicam SP 800 (recording) spectrophotometer with a scale expansion. The results of these experiments have been averaged and are shown in Table 6. Since the exact concentration of Co_2X^{4+} present initially is not known precisely the product fractions are given relative to Co^{2+}.

A similar procedure was carried out with V^{2+} as reductant. The vanadium(III) product is labile and readily oxidised on contact with the air to VO^{2+}. Consequently V^{III} fractions could not be determined and VO^{2+} was slowly eluted from

[8] P. Moore and F. Basolo, *Inorg. Chem.*, 1965, **4**, 1670; T. W. Swaddle and E. L. King, *ibid.*, p. 532.

the ion-exchange column (it moves only slightly faster than the Co²⁺ species). Two other fractions, Co²⁺ and Co(NH₃)₅X²⁺ (X⁻ = Cl⁻ or Br⁻), were eluted from the column and yields are shown in Table 7. There was no

TABLE 6

Ion-exchange separation of products for the Cr²⁺ reductions of Co₂Cl⁴⁺ and Co₂Br⁴⁺ at 0 °C, $I = 2\cdot0$M (LiClO₄). The binuclear cobalt(III) complex is always in excess [a]

Product/Reactant	Co₂Cl⁴⁺ [a]	Co₂Br⁴⁺ [a]
Co²⁺	1·0	1·0
Co(NH₃)₅H₂O³⁺	0·86	0·87
CrX²⁺ [b]	0·89	0·90
Cr³⁺	0·06	0·06

[a] Average of three experiments with dicobalt(III) complex in 10—100% excess, [H⁺] in the range 0·5—1·0M, [Cr²⁺] ca. $2\cdot8 \times 10^{-3}$M. [b] X⁻ = Cl⁻ and Br⁻ respectively.

TABLE 7

Ion-exchange separation of products for the V²⁺ reductions of Co₂Cl⁴⁺ and Co₂Br⁴⁺ at 0 °C, $I = 2\cdot0$M (LiClO₄)

Product/Reactant	Co₂Cl⁴⁺ [a]	Co₂Br⁴⁺ [a]
Co²⁺	1·0	1·0
Co(NH₃)₅X²⁺ [b]	0·47	0·44
Co(NH₃)₅H₂O³⁺	—	—

[a] Average of four runs, with dicobalt(III) reactant in 10—15% excess of V²⁺, [H⁺] in the range 0·1—1·0M, [V²⁺] ca. $1\cdot5 \times 10^{-2}$M. [b] X⁻ = Cl⁻ and Br⁻ respectively.

evidence for the formation of Co(NH₃)₅H₂O³⁺ and a yield of <6% is appropriate. The Co²⁺ was determined as before and Co(NH₃)₅X²⁺ ions were identified and estimated from known spectra.

The ion-exchange results for Cr²⁺ reduction of both Co₂Cl⁴⁺ and Co₂Br⁴⁺ indicate that reaction gives about 90% recovery of the expected chromium(III)/cobalt(III) products. The missing 10% cannot be accounted for in terms of alternative products, and the results indicate that each reduction can be represented by a single equation.
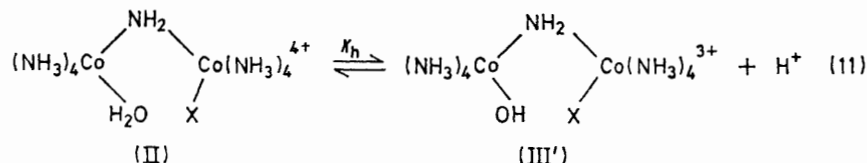
For the first stage of Cr²⁺ reduction of both Co₂X⁴⁺ complexes it is concluded that Co(NH₃)₅H₂O³⁺ is a primary

$$Cr^{2+} + Co_2X^{4+} \xrightarrow{H^+/H_2O} CrX^{2+} + Co(NH_3)_5H_2O^{3+} + Co^{2+} \quad (9)$$
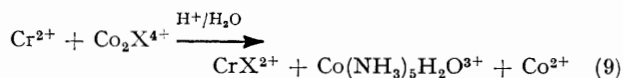
product, along with CrX²⁺, and the stoicheiometry may be represented by (9). For the corresponding first stage

$$V^{2+} + Co_2X^{4+} \xrightarrow{H^+/H_2O} V^{3+} + Co(NH_3)_5X^{2+} + Co^{2+} \quad (10)$$
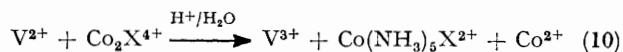
reduction of Co₂X⁴⁺ by V²⁺, predominantly Co(NH₃)₅X²⁺ is a primary product, and may be represented by (10).

some, but not all, pH measurements on aqueous solutions of Co₂Cl⁴⁺ and Co₂Br⁴⁺ have indicated significant acid dissociation prior to reaction (2).[4] Acid dissociation constants K_a were in most cases close to those for Co(NH₃)₅H₂O³⁺, and since at that time there was no evidence for complex (I) it was assumed that the data were consistent with complex (II) being the predominant form in aqueous solution. In view of certain inconsistencies in
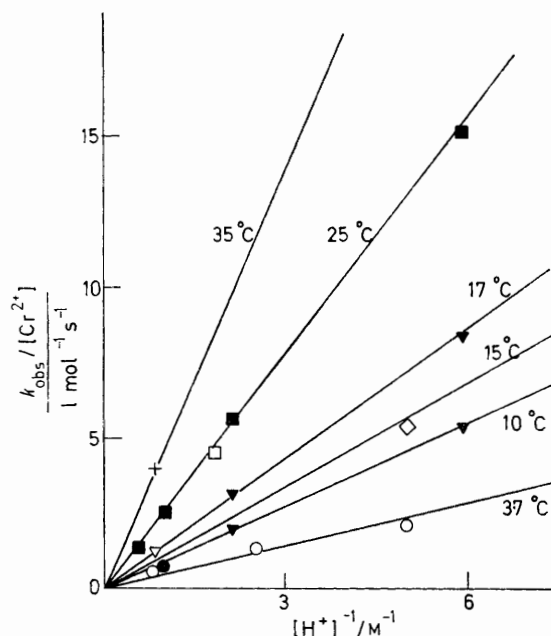

FIGURE 2 The variation of second-order reduction rate with [H⁺] for the Cr²⁺ reduction of Co(NH₃)₅H₂O³⁺. Data are taken from the second stage Cr²⁺ reduction of Co₂Cl⁴⁺ and Co₂Br⁴⁺ (open and solid symbols respectively), in the temperature range 3·7—35 °C, at λ = 490 nm

the previous work and the identification of (I) in the solid, this work has now been repeated.

Hydrogen ions are produced during the course of reaction (2) and this reaction can be monitored by measuring pH changes with time. The elementary step required to produce hydrogen ions is given by reaction (11), which, since it is more rapid, must occur prior to formation of the μ-amido-μ-hydroxo-complex. Species (II) is in equilibrium with (I) such that $K_0 = (II)/(I)$, equation (1), and the acid dissociation constant is given by $K_a = K_0K_h$. The total

These simplified reaction schemes will be considered in more detail in the Discussion section.

After corrections for Cr³⁺ initially present in Cr²⁺ stock solutions, the Cr³⁺ reaction product is estimated at no greater than 6% of total chromium(III), and is most probably not a significant product.

Determination of Acid-dissociation Constants.—Previously

concentration of dicobalt complexes is a and [H⁺] is the hydrogen-ion concentration at zero time, giving:

$$a = [I] + [II] + [III']$$
$$= \frac{[III'][H^+]}{K_0K_h} + \frac{[III'][H^+]}{K_h} + [III']$$

$$[H^+] = [OH^-] + [III']$$

[OH⁻] is very small and can be ignored.

$$a = \frac{[H^+]^2}{K_0 K_h} + \frac{[H^+]^2}{K_h} + [H^+]$$

$$\frac{a - [H^+]}{[H^+]^2} = \frac{1 + K_0}{K_a}$$

and providing $K_0 \ll 1$ this simplifies to give equation (12).

$$K_a = [H^+]^2/(a - [H^+]) \qquad (12)$$

Crystalline samples of (I) are generally obtained from either 6—8M-HX (for the halide salt) or 8M-HClO₄ (perchlorate salt). Occlusion of the free acid is now believed to be responsible for the lower pH readings reported in the earlier work. Higher pH (and corresponding pK_a) values
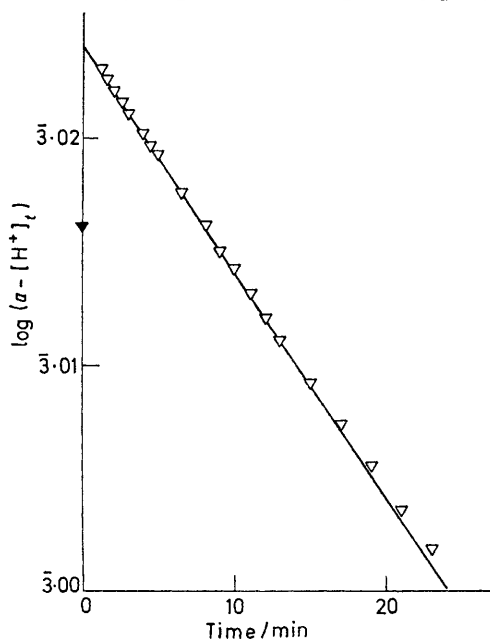

FIGURE 3 The graphical evaluation of acid dissociation constants for Co₂X⁴⁺ complexes (X⁻ = Cl⁻, Br⁻). Plots of log $(a - [H^+]_t)$ versus time are extrapolated to zero time in order that $[H^+]_0$ may be evaluated. Reaction conditions are $I = 0.1M$ (LiClO₄), temp. = 0 °C, [Co₂Cl⁴⁺] = 1.06 × 10⁻³M. Under these conditions an intercept at ▼ represents a value of pK_a = 6.4. The experimental intercept gives pK_a = 8.42

are obtained when samples are stored for ca. 1 week in vacuo over P₂O₅, suggesting the removal of any free acid which may have been present initially. A sample of the perchlorate was also prepared from saturated NaClO₄ solution.

The reaction was followed by adding a precise weight of Co₂X⁴⁺ (finely powdered) to the background solution and aiding its rapid dissolution with a gas jet. The electrodes were allowed to stabilise for up to 1 min and pH readings were subsequently measured at regular time intervals. Reactions were followed for a change in pH of at least one unit. Initial hydrogen-ion concentrations were calculated by extrapolation of plots of log $(a - [H^+]_t)$ versus time $(a = $ total dicobalt concentration, $[H^+]_t = [H^+]$ at time $t)$ to zero time. An example of one of these plots is displayed in Figure 3. The results of pH measurements are listed in Table 8.

Nuclear Magnetic Resonance Experiments.—Studies on the proton n.m.r. spectroscopy shown by Co₂Cl⁴⁺ in 0.1M-

⁹ J. N. Bronsted and K. Volqvartz, Z. Phys. Chem., 1928, **134**, 97.

HClO₄ indicate that there are 4 proton resonances with τ values 5.3, 5.7, 6.2, and 6.8. These resonances are located close to the broad and intense water resonance found in aqueous solutions, and are poorly resolved even when

TABLE 8

Determination of acid dissociation constant K_a for perchlorate salts of Co₂Cl⁴⁺ and Co₂Br⁴⁺ (last entry) in aqueous solution, at 0°

10^4[Co₂Cl⁴⁺]	10^6[H⁺]₀ ᵃ	$10^9 K_a$	
M	M	M	pK_a
10.34	1.0	0.98	9.01 ᵇ
10.59	2.0	3.78	8.42 ᵇ
17.87	2.0	2.24	8.65 ᵇ
5.17	1.4	3.79	8.42 ᵇ
8.61	1.0	1.16	8.93 ᶜ
9.72	1.0	1.03	8.99 ᵈ
8.22 ᵍ	1.3	2.06	8.69 ᵈ
9.00 ᵉ	1.3	1.93	8.71 ᵈ,ᶠ
4.12 ᵉ	1.0	2.40	8.61 ᵇ

ᵃ [H⁺]₀ readings as measured from extrapolation of plots of log $(a - [H^+]_t)$ versus time to zero time. ᵇ $I = 1.0M$ (LiClO₄), KCl calomel electrode. ᶜ $I = 0.1M$ (LiClO₄), NaCl calomel electrode. ᵈ $I = 2.0M$ (LiClO₄), KCl electrode. ᵉ Sample of Co₂Cl⁴⁺ recrystallised from saturated NaClO₄. ᶠ Temp. 25° C. ᵍ [Co₂Br⁴⁺].

using the Bruker HFX3 n.m.r. spectrometer, with Fourier transform facilities. However, these 4 resonances are associated with ammonia and amide groups which, in turn, suggests that there are 4 different ammonia groups. Structure (I), with a bridging X⁻ group, should produce 4 different (N–H) systems, whereas structure (II) is expected to produce 8 such different environments. Although by no means conclusive this evidence does support the assignment of structure (I) as the predominant species in solution.

Preliminary studies on ⁵⁹Co n.m.r. spectra of ca. 0.06M-solutions of Co₂Cl⁴⁺ in 0.1M-HClO₄ (at a frequency of 13.81 MHz) have shown that there is build-up of a single broad line (5.1 kHz wide) at a position 9388 ± 25 p.p.m. downfield from the line due to Co(CN)₆³⁻ as conversion into the μ-amido-μ-hydroxo-complex takes place. No other lines ±25 kHz were observed, and we were not therefore able to evaluate rate constants k_0 and k_{-0}, equation (1), using the line broadening technique.

DISCUSSION

The evidence from pH and n.m.r. experiments suggests that (I) rather than (II) is predominant in aqueous solution. An assumption that the acid dissociation constant for (II), K_h in reaction (11), should be of the same order of magnitude as that for the related complex Co(NH₃)₅H₂O³⁺ has been adopted. Consequently a value of pK_h in the range 6.6—5.7 may be expected.[9,10] Allowance for K_h can therefore be made such that estimates of K_0, equation (1), fall in the range 10⁻² to 10⁻³. Equilibrium concentrations of (II) are correspondingly ⩽1%.

Equations (9) and (10) summarise the essential findings of the ion-exchange experiments and details of the kinetic studies are also consistent with these. It is now opportune to consider these equations in more detail, and whether the mechanism of reduction is inner or outer sphere. Relevant kinetic data are listed in Table 9.

¹⁰ J. Bjerrum, ' Metal Ammine Formation in Aqueous Solution,' Haase, Copenhagen, 1957, p. 280.

No firm evidence for the intermediate formation of $Co(NH_3)_5H_2O^{3+}$ from the V^{2+} reduction of Co_2X^{4+} ($X^- = Cl^-$, Br^-) was obtained, and it is concluded that less than 6% of the reaction proceeds with formation of this complex. The proposed intermediate $Co(NH_3)_5X^{2+}$ is only observed when there is less than a 2-fold excess

and estimates for outer-sphere contributions (based upon observed V^{2+} reduction rates) are $<2\%$ ($X^- = Cl^-$) and $<0.2\%$ ($X^- = Br^-$).

With the information now obtained that (I) and not (II) is predominant in aqueous solutions it has been possible to evaluate rate constants k_0 for the conversion

TABLE 9

Summary of kinetic data for the Cr^{2+} and V^{2+} reductions of binuclear Co_2X^{4+}, and related mononuclear complexes, $I = 2.0M$ (LiClO$_4$) except where stated

Oxidant	Reductant	Mechanism [a]	k (25 °C) l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal K^{-1} mol^{-1}	Reference
Co_2Cl^{4+}	Cr^{2+}	I.S.	11.3 [b]	3.9 ± 0.2	-40.6 ± 0.8	This work
Co_2Br^{4+}	Cr^{2+}	I.S.	216 [b]	4.1 ± 0.2	-34.2 ± 0.7	This work
$Co(NH_3)_5Cl^{2+}$	Cr^{2+}	I.S.	4.5×10^5			11 [c]
$Co(NH_3)_5Br^{2+}$	Cr^{2+}	I.S.	6.5×10^5			11 [c]
Co_2Cl^{4+}	V^{2+}	O.S.	9.4 [b]	7.8 ± 0.1	-27.8 ± 0.3	5
Co_2Br^{4+}	V^{2+}	O.S.	33.0 [b]	6.7 ± 0.2	-29.0 ± 0.8	This work
$Co(NH_3)_5Cl^{2+}$	V^{2+}	O.S.	10.2	7.5 ± 0.2	-28.8 ± 0.5	5
$Co(NH_3)_5Br^{2+}$	V^{2+}	O.S.	30.0	7.2 ± 0.3	-27.6 ± 0.7	12
$Co(NH_3)_5H_2O^{3+}$	Cr^{2+}	I.S.	2.52 [d, e]	11.2 ± 0.5	-19.3 ± 1.6	This work
$Co(NH_3)_5H_2O^{3+}$	Cr^{2+}	I.S.	3.13 [e]			7 [c]
$Co(NH_3)_5H_2O^{3+}$	V^{2+}	O.S.	0.53	8.2	-32	13 [c]

[a] O.S. = Outer sphere: I.S. = Inner sphere. [b] Reactant is (I), $X^- = Cl^-$ or Br^-. [c] Reference 11, $I = 0.1M$ (NaClO$_4$); 7, $I = 1.0M$ (LiClO$_4$); 13, $I = 1.0M$ (NaClO$_4$). [d] Combined data for second stages of Cr^{2+} reduction of Co_2Cl^{4+} and Co_2Br^{4+} (Figure 2). [e] The rate law gives $[H^+]^{-1}$ dependence and k therefore corresponds to the product of a second-order rate constant and acid dissociation constant and has units s^{-1}. Reduction of the aquo-complex if it occurs will probably be outer sphere.

of V^{2+}, due to the concurrent reduction of this primary product. The V^{2+} reductions of $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ are outer sphere.[12] Activation parameters and rate constants are very similar for the V^{2+} reduction of Co_2X^{4+} ($X^- = Cl^-$, Br^-) which strongly suggests that these reactions are also of the outer-sphere type (Table 9). The similarity of kinetic data for the V^{2+} reductions of Co_2Cl^{4+} and $Co(NH_3)_5Cl^{2+}$, and Co_2Br^{4+} and $Co(NH_3)_5Br^{2+}$ indicate that active sites, Cl^- and Br^- respectively, are important in determining the kinetic pattern. If V^{2+} exerts an affinity for such an active site, when undergoing outer-sphere reduction, then there should be no preference for the structure of Co_2X^{4+}, both (I) and (II) reacting at a similar rate by an outer-sphere mechanism.

Reduction of (II) by V^{2+} must result in formation of $Co(NH_3)_5H_2O^{3+}$ since the chlorine-bonded cobalt(III) centre is much more redox active than the aquo-bonded cobalt(III).[13] Less than 6% of $Co(NH_3)_5H_2O^{3+}$ is observed and it can therefore be concluded that $<6\%$ of (II) is in the equilibrium mixture, equation (1).

Intermediate formation of $Co(NH_3)_5H_2O^{3+}$ is observed in the Cr^{2+} reductions of Co_2Cl^{4+} and Co_2Br^{4+}. Outer-sphere reduction of (I) can therefore be excluded since $Co(NH_3)_5X^{2+}$ would be produced. The latter are known to be reduced rapidly by Cr^{2+} (see Table 9) and if this pathway were effective an intermediate would not be detected. Furthermore, the ratio of rate constants k_{Cr}/k_V of ca. 0.020 for outer-sphere Cr^{2+} and V^{2+} reductions of common oxidants is well established.[14] The present studies give ratios far removed from this value

(I) $\longrightarrow$ (II) ($X^- = Cl^-$), from studies on the mercury(II)-catalysed reaction (I) $\longrightarrow$ (III).[15] At 25 °C k_0 is independent of $[H^+]$ and is 3.02×10^{-3} s^{-1}. Activation parameters are $\Delta H^{\ddagger} = 19.2 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5.7 \pm 1.8$ cal K^{-1} mol^{-1}. The ratio k'/k_{-0}, as defined in equations (1) and (2), has also been evaluated and at 25° is 0.028. Since k_0 is known it is possible to comment on whether the inner-sphere Cr^{2+} reduction of Co_2Cl^{4+} proceeds via (I) or (II). At 25 °C the rate constant k_0 is some 10^3—10^4 times too slow for (I) (present initially) to react to give (II) prior to Cr^{2+} reduction. It can therefore be concluded that Cr^{2+} reduces (I) directly when $X^- = Cl^-$. Although no information is at present available as to the magnitude of k_0 for $X^- = Br^-$, there seems little doubt that a similar mechanism applies here also.

A binuclear intermediate $Co^{III}\cdot X \cdot Cr^{III}$ will result from an inner-sphere Cr^{2+} reduction of (I). No evidence was obtained for such an intermediate which implies that the latter aquates rapidly to mononuclear species, or that aquation proceeds with very little change in absorbance at the wavelengths investigated. In view of the behaviour observed for the second stage (Figure 1) aquation of the intermediate must be complete within ca. 20 s (conditions as applying to Figure 1).

Complex (I; $X^- = Cl^-$ and Br^-) would not be expected to undergo Cr^{2+} inner-sphere reduction as rapidly as the mononuclear complexes $Co(NH_3)_5X^{2+}$, because the halide ion is already bonded to two metals in a bridging situation. Large differences are indeed observed (see Table 9). Even though there are two electron lone-pairs on each halide ion the latter are not

[11] M. C. Moore and R. N. Keller, *Inorg. Chem.*, 1971, **10**, 747.
[12] M. R. Hyde, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1973, 2730.
[13] P. H. Dodel and H. Taube, *Z. phys. Chem. (Frankfurt)*, 1965, **44**, 92.
[14] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 1832; 1973, 736.
[15] S. W. Foong, J. D. Edwards, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, in the press.

expected to bond readily to a third metal to give the required precursor complex. We note however that with oxygen as a bridge, protonation can occur to give stable μ-hydroxo-dicobalt(III) complexes.[6] It has already been demonstrated that μ-amido-μ-carboxylato-dicobalt(III) complexes, $\mu(NH_2,O_2CR)$ with R = H or Me, are not able to utilise the oxygen atoms of the carboxylate group, one bonded to each cobalt(III), for inner-sphere attack.[14] Steric effects and the fact that some delocalisation of the electron lone-pairs is occurring may be responsible for this behaviour. Moreover no evidence has been obtained for inner-sphere Cr^{2+} reduction of the μ-amido-μ-hydroxo-complex (III),[6] indicating that k_{Cr} for this reaction is less than 10^{-4} l mol^{-1} s^{-1} at 25 °C. The corresponding mononuclear complex $Co(NH_3)_5OH^{2+}$ is reduced at a rate of ca. 10^6 l mol^{-1} s^{-1},[7] showing a rate enhancement of ten orders of magnitude when a second lone-pair of electrons is made available. Clearly a very delicate balance exists between availability of electron lone-pairs and rate constants for Cr^{2+} inner-sphere reduction at a particular site.

The aquation of the intermediate $Co^{III}\cdot X\cdot Cr^{III}$ to mononuclear species is unusually rapid. A binuclear intermediate $[Cl_5Ir^{III}\cdot Cl\cdot Cr^{III}(H_2O)_5]$ was identified in the Cr^{2+} reduction of $IrCl_6^{2-}$. Aquation to mononuclear complexes is more rapid $(4\cdot2 \times 10^{-2}$ s^{-1} at 25 °C)[16] than the aquation of chloride in the parent complexes $IrCl_6^{2-}$ $(9\cdot4 \times 10^{-6}$ s^{-1} at 25 °C)[17] and $Cr(H_2O)_5Cl^{2+}$ $(2\cdot8 \times 10^{-7}$ s^{-1} at 25 °C),[17] and $CrCl^{2+}$ and $IrCl_5H_2O^{2-}$ are the only detectable products. The chromium(III) may be said to have catalysed aquation at the iridium(III) centre, and formation of $CrCl^{2+}$ (not Cr^{3+}) is as might be predicted from a consideration of rate constants for the aquation of mononuclear species. An enhancement also exists for k_0 $(X^- = Cl^-)$ which is 10^3—10^4 times faster than the aquation of $Co(NH_3)_5Cl^{2+}$. Furthermore we note that mercury(II) produces a strong catalytic effect on the aquation of $Co(NH_3)_5Cl^{2+}$ $(1\cdot95 \times 10^{-6}$ s^{-1} for the uncatalysed, and $1\cdot16 \times 10^{-1}$ l mol^{-1} s^{-1} for the catalysed aquation at 25 °C).[18]

Aquation of $Co^{III}\cdot X\cdot Cr^{III}$ should give predominantly CrX^{2+} and $Co(NH_3)_5H_2O^{3+}$ since $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ aquate more rapidly than $CrCl^{2+}$ and $CrBr^{2+}$. Unfortunately the rate constants for aquation of these mononuclear complexes have not been determined at the ionic strengths employed in the present studies. The available data[17] suggest that $Co(NH_3)_5H_2O^{3+}$ should be the predominant but not the exclusive product. Values of $\Delta\varepsilon$ for the second stage of reduction, Table 2 $(X^- = Cl^-)$, suggest that $Co(NH_3)_5H_2O^{3+}$ is indeed the predominant product. Similar data in Table 4 $(X^- = Br^-)$ would seem to admit the possibility that $Co^{III}\cdot X\cdot Cr^{III}$ aquates to give some $Co^{III}X$ product which is rapidly reduced by Cr^{2+}.

EXPERIMENTAL

Preparation of the perchlorate salts of the μ-amido-μ-chloro-[19] and μ-amido-μ-bromo-complexes[3] $[(NH_3)_4Co\cdot\mu(NH_2,Cl)\cdot Co(NH_3)_4](ClO_4)_4,H_2O$ and $[(NH_3)_4Co\cdot\mu(NH_2,Br)\cdot Co(NH_3)_4](ClO_4)_4,H_2O$ have been reported previously. A sample of the perchlorate salt of the μ-amido-μ-chloro-complex was recrystallised from saturated sodium perchlorate at 0 °C. Spectrophotometric and elemental analyses were in good agreement with previous values. Stock solutions of chromium(II) and vanadium(II) perchlorates were prepared and standardised as described elsewhere. All solutions were handled with the necessary precautions required for air-sensitive materials.

Run solutions of all reactants were adjusted to ionic strength $I = 2\cdot0M$, using the required amounts of $HClO_4/LiClO_4$, and the reactions were monitored on a Durrum-Gibson stopped-flow spectrophotometer at the various peak positions for the complexes, as indicated in the text. The concentration of binuclear cobalt(III) reactant was determined at the start of each run using the following procedure. Reductant solutions (either Cr^{2+} or V^{2+}) were thermostatted in a drive-syringe of the stopped-flow apparatus, and the ionic-background solutions for the dicobalt complexes thermostatted in a separate flask, at the same temperature. The solid complex was then added to this previously outgassed, thermostatted, background solution, which was further deoxygenated for 4—5 min, transferred to the stopped-flow apparatus, and thermostatted for ca. 2 min. As each stopped-flow run was started the exact time after dissolution of the complex was noted, and using the data from ref. 4 the concentration of Co_2Cl^{4+} or Co_2Br^{4+} reactant was estimated. All redox reactions were followed within 7—15 min after making up run solutions, and in most cases this meant considerably less than 10% conversion into the μ-amido-μ-hydroxo-complex.

All pH measurements were made using a Radiometer pH-meter, type PHM 4d, calibrated at 0 °C with phosphate (pH solution = $6\cdot60 \pm 0\cdot02$) and phthalate (pH solution = $4\cdot00$) buffers. The pH values determined after calibration in this manner will be subject to small errors due to variations in activity with ionic strength. It is estimated from the corrections required to convert activities into concentrations of hydrogen ion that errors are less than 3% in final pK_a values. A solution of $LiClO_4$ $(0\cdot1M$ or $2\cdot0M$, 50 ml) was pipetted into the reaction vessel. This solution was thermostatted for at least 30 min at 0 °C, during which time any carbon dioxide present was removed by bubbling nitrogen gas through the solution. The temperature of 0 °C was chosen in order that reaction (2) would be sufficiently slow to enable accurate pH readings to be taken. Both electrodes, the glass (type G202C) and calomel (type K401, with either KCl or NaCl support electrolyte), were immersed in the thermostatting solution, and allowed to equilibrate over the 30 min time period. Solutions of $LiClO_4$ prior to runs generally gave pH readings in the range 6·9 to 7·0 indicating the removal of CO_2.

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