Cr^{2+} and V^{2+} Reductions of the μ-Amido-μ-formato-bis[tetra-amminecobalt(III)] and μ-Amido-μ-acetato-bis[tetra-amminecobalt(III)] Complexes

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The first and only observable stage in the Cr^{2+} reduction of μ-amido-μ-formato-bis[tetra-amminecobalt(III)] perchlorate (I), in aqueous perchlorate media, obeys the rate law (i), where the Cr^{2+} reactant is present in large excess.

$$-\frac{d\ln[(Co^{III})_2]}{dt} = k_{Cr}[Cr^{2+}] + \frac{k_1k_2[Cr^{2+}]}{k_{-1} + k_2[Cr^{2+}]} \qquad \text{(i)}$$

With $[Cr^{2+}] > ca.\ 0{\cdot}015\text{M}$, so that $k_2[Cr^{2+}] \gg k_{-1}$, the right-hand side of (i) reduces to $k_{Cr}[Cr^{2+}] + k_1$. At 25 °C and $\mu = 1{\cdot}0\text{M}$ ($LiClO_4$), $k_{Cr} = (1{\cdot}68 \pm 0{\cdot}02) \times 10^{-3}$ l mol^{-1} s^{-1} and $k_1 = (9{\cdot}2 \pm 0{\cdot}8) \times 10^{-6}$ s^{-1}. For the μ-amido-μ-acetato-bis[tetra-amminecobalt(III)] complex, only the first term in (i) could be detected with certainty and at 25° and $\mu = 1{\cdot}0\text{M}$ ($LiClO_4$), $k_{Cr} = (4{\cdot}7 \pm 0{\cdot}5) \times 10^{-4}$ l mol^{-1} s^{-1}. Activation parameters have been obtained corresponding to k_{Cr} for both complexes and k_1 for the μ-formato-complex (I). Reduction of the complexes with V^{2+} follows the rate law (ii). At 25° and $\mu = 1{\cdot}0\text{M}$ ($LiClO_4$), $k_V = (6{\cdot}0 \pm 0{\cdot}3) \times 10^{-2}$ l mol^{-1} s^{-1}, for the

$$-d\ln[(Co^{III})_2]/dt = k_V[V^{2+}] \qquad \text{(ii)}$$

μ-formato-complex (I) and $(2{\cdot}2 \pm 0{\cdot}1) \times 10^{-2}$ l mol^{-1} s^{-1} for the μ-acetato-complex. The ratios $k_{Cr}:k_V$ are 0·028 and 0·021 respectively, suggesting that an outer-sphere mechanism is operative in each case. The effect of chloride ions on the Cr^{2+} reduction of the μ-formato-complex (I) has also been studied.

THE study of the Cr^{2+} reduction of cobalt(III) ammine complexes containing carboxylate ligands has contributed in a major way to the understanding of inner-sphere electron-transfer processes.[1,2] Of particular interest in these studies is the position of attack of the Cr^{2+}, three types of reaction having been defined; adjacent attack, adjacent attack with chelation, and remote attack.[3] The precise point of attack has not been established for the simplest of these, the adjacent attack situation, which could occur at the carbonyl oxygen or at the oxygen bonded directly to the cobalt(III) centre (the cobalt-bonded oxygen). Moreover in the absence of labelling techniques to distinguish the oxygens of a monocarboxylic acid, there is no direct method of identifying the point of attack. However, there is evidence to suggest that the carbonyl group is the likely position. Thus in the Cr^{2+} reduction of the corresponding formatopenta-ammineruthenium(III) complex[4] the binuclear complex $[(NH_3)_5Ru^{II}{-}O{\cdots}CH{\cdots}O{-}Cr^{III}(H_2O)_5]^{4+}$ has been identified. Also, by reacting Cr^{2+} with the two formamidopenta-amminecobalt(III) complexes, $[(NH_3)_5Co(NH_2CHO)]^{3+}$ and $[(NH_3)_5Co(OCHNH_2)]^{3+}$, Balahura and Jordan[5] have been able to distinguish possible points of attack. Isolation of an *O*-bonded chromium(III) product from the former suggests that the carbonyl group is the likely site.

The present study is concerned with the Cr^{2+} reductions of μ-formato- and μ-acetato-binuclear cobalt(III) complexes in which there is only one type of oxygen atom and no carbonyl groups are present. By comparing the rates of reduction of these complexes with those of the mononuclear penta-ammine analogues, which contain both types of oxygen atom, we hoped to be able to say something about the precise point of attack of Cr^{2+} in an adjacent attack situation.

RESULTS

The Cr^{2+} *Reduction of the μ-Formato-complex.*—The reaction of μ-amido-μ-formato-bis[tetra-amminecobalt(III)], (I),[6] with Cr^{2+} was studied under pseudo-first-order conditions (20—200-fold excess of Cr^{2+}) by following the decrease in absorption of (I) at its 515 nm peak ($\varepsilon = 360$ l mol^{-1} cm^{-1}). The perchlorate salt of the complex was used (see effect of chloride below) and the ionic strength adjusted to 1·0M ($LiClO_4$). The runs reported were followed for at least one half-life and most were followed to 75% reaction. Plots of $\log(OD_t - OD_\infty)$ against time were linear over such periods. The final absorbance (OD_∞) was measured for each run, but involved waiting in some cases for 60 h. A number of runs were subsequently rejected because of the difficulty in maintaining a completely stable Cr^{2+} background absorbance. Figure 1 shows a first-order plot for one of the faster runs which was monitored to 97% completion. Linearity is seen to be retained over this period. Pseudo-first-order rate constants, k_{obs}, obtained from such plots are listed in Table 1. No dependence on hydrogen-ion concentration was observed over the range 0·04—0·98M. When $[Cr^{2+}] > ca.\ 0{\cdot}015\text{M}$, the $[Cr^{2+}]$ dependence of k_{obs} is of the form (1). With

$$k_{obs} = k_{Cr}[Cr^{2+}] + k_1 \qquad (1)$$

$[Cr^{2+}] < ca.\ 0{\cdot}015\text{M}$, the apparent intercept, k_1, begins to disappear, and on the time scale relevant to these runs, $k_{obs} = 0$ when $[Cr^{2+}] = 0$.* Deviations from linearity at

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* The stability of the μ-amido-μ-formato-complex ($1{\cdot}3 \times 10^{-3}\text{M}$) in 0·5 and 0·9M-$HClO_4$, $\mu = 1{\cdot}0\text{M}$ ($LiClO_4$), has been investigated spectrophotometrically (ref. 6). There are no observable absorbance changes at 515 (maximum) and 427 nm (minimum) over 16 h at 30 °C.

[1] H. Taube and E. S. Gould, *Accounts Chem. Res.*, 1969, **2**, 321.

[2] H. Taube, Mechanisms of Inorganic Reactions, *Adv. Chem. Ser.*, Amer. Chem. Soc. Publ. No. 49, 1965, 107.

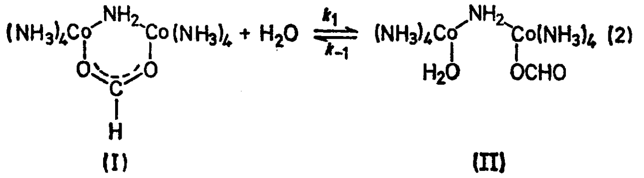
[3] See for example, A. G. Sykes, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 193 and N. Sutin, *Ann. Rev. Phys. Chem.*, 1966, **17**, 157.

[4] J. A. Stritar and H. Taube, *Inorg. Chem.*, 1969, **8**, 2281.

[5] R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, 1970, **92**, 1533.

[6] For details of the preparation and characterization of this complex see K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, in the press.

low Cr^{2+} concentrations, Figure 2, can be accounted for by assuming an equilibrium (2) between (I), and an aquo-formato-species (II). Both (I) and (II) react with Cr^{2+},



with rate constants k_{Cr} and k_2 respectively. By applying stationary-state kinetics to (II) equation (3) is obtained, and, when $k_2[Cr^{2+}] \gg k_{-1}$ (which presumably applies at $[Cr^{2+}] > ca.\ 0{\cdot}015$M), this reduces to the form (1). Accordingly, the rate constants k_{Cr} and k_1, at each temperature (Table 2), and their corresponding activation parameters (Table 6) were evaluated using values of k_{obs} for which $[Cr^{2+}] \geqslant 0{\cdot}015$M (Table 1). A non-linear least-squares

$$k_{obs} = k_{Cr}[Cr^{2+}] + \frac{k_1 k_2[Cr^{2+}]}{k_{-1} + k_2[Cr^{2+}]} \qquad (3)$$

Table 1

Pseudo-first-order rate constants, k_{obs}, for the reaction of Cr^{2+} with μ-amido-μ-formato-bis[tetra-amminecobalt(III)] perchlorate, $\mu = 1{\cdot}0$ M($LiClO_4$)

Temp. (°C)	$10^2[Cr^{2+}]$ (M)	$[H^+]$ (M)	$10^4[(Co^{III})_2]$ (M)	$10^5 k_{obs}$ (s^{-1})
40	0·65	0·98	2·8	4·34
	1·12	0·95	2·8	7·64
	1·15	0·20	2·8	7·83
	1·54	0·94	2·8	10·6
	2·56	0·90	2·8	16·3
	2·62	0·50	1·8	16·4
	4·40	0·84	2·8	25·9
	5·75	0·80	2·8	33·0
35	1·11	0·95	2·8	5·37
	1·12	0·95	2·8	5·57
	1·50	0·95	2·8	7·22
	3·85	0·54	18·0	16·1
	4·14	0·80	18·0	16·3
	4·40	0·84	2·8	19·4
	5·75	0·80	2·8	23·5
30	1·10	0·45	2·8	3·73
	1·50	0·94	2·8	5·20
	2·70	0·30	6·7	7·75
	2·70	0·53	6·7	7·91
	4·40	0·84	2·8	12·6
25	1·12	0·95	2·8	2·68
	1·73	0·94	1·8	3·81
	1·88	0·78	3·5	3·99
	2·52	0·04	8·8	5·14
	2·60	0·90	2·8	5·34
	2·60	0·90	2·8	5·37
	2·62	0·70	9·2	5·18
	2·62	0·70	9·2	5·33
	3·65	0·06	6·7	7·10
	3·80	0·88	3·5	7·28
	3·80	0·55	6·7	7·41
	3·85	0·55	6·7	7·56
	3·85	0·15	3·3	7·29
	5·00	0·42	4·8	9·21
	5·00	0·42	4·8	9·14
	5·75	0·80	2·8	10·4

Table 2

The temperature dependence of rate constants k_{Cr} and k_1 for the Cr^{2+} reduction of the μ-amido-μ-formato-bis-[tetra-amminecobalt(III)] complex, $\mu = 1{\cdot}0$M ($LiClO_4$)

Temp. (°C)	$10^3 k_{Cr}$ (l mol^{-1} s^{-1})	$10^5 k_1$ (s^{-1})
25	1·68 ± 0·02	0·92 ± 0·08
30	2·5 ± 0·2	1·3 ± 0·5
35	3·7 ± 0·3	1·7 ± 1·2
40	5·43 ± 0·04	2·3 ± 0·1

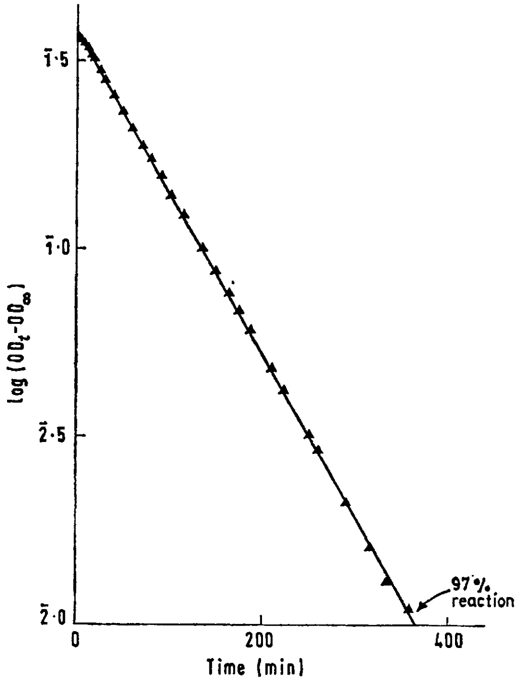


Figure 1 Pseudo-first-order plot for the reaction of Cr^{2+} with the μ-amido-μ-formato-bis[tetra-amminecobalt(III)] complex at 40 °C and $\mu = 1{\cdot}0$M ($LiClO_4$). $[Cr^{2+}] = 2{\cdot}56 \times 10^{-2}$M, $[(Co^{III})_2] = 2{\cdot}8 \times 10^{-4}$M, and $[H^+] = 0{\cdot}9$M

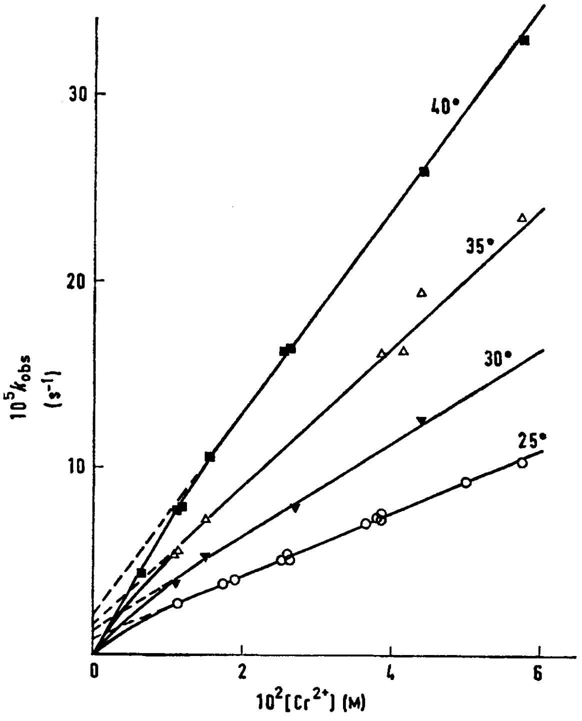


Figure 2 Plot of k_{obs} against $[Cr^{2+}]$ for the reduction of the μ-amido-μ-formato-bis[tetra-amminecobalt(III)] complex, $\mu = 1{\cdot}0$M ($LiClO_4$)

program [7] with a weighting factor of $1/k^2_{obs}$ was used, errors for the activation parameters being obtained as output. Errors on the rate constants had to be computed separately. Attempts to obtain a reasonable value of the ratio $k_2 : k_{-1}$ by a graphical method were not successful.

The reaction was also studied in the presence of chloride ion, and found to be strongly catalysed. A third term, $k_3[Cr^{2+}][Cl^-]$, was introduced into the rate law (3) and its modified form (1). Values of k_{cat} in the presence of chloride are shown in Table 3 from which it can be seen (first four entries) that concentrations of chloride introduced into the reaction by using the chloride salt of the complex are sufficient to give a *ca.* 10% increase in k_{obs}. A value for k_3 of 0·11 ± 0·01 l² mol⁻² s⁻¹ was obtained at 25° and μ = 1·0M ($LiClO_4$).

TABLE 3

Rate constants at 25 °C for the chloride-catalysed Cr^{2+} reduction of the μ-amido-μ-formato-bis[tetra-amminecobalt(III)] complex, μ = 1·0M ($LiClO_4$)

$10^3[Cl^-]$ (M)	$10^4[(Co^{III})_2]$ (M)	$10^2[Cr^{2+}]$ (M)	$[H^+]$ (M)	10^5k_{cat} (s^{-1})	10^5k_{obs} [a] (s^{-1})	k_3 (l^2 mol^{-2} s^{-1})
3·1	7·8	3·85	0·06	8·55	7·4	*b*
3·1	7·8	7·7	0·25	15·8	13·8	*b*
3·1	7·8	7·7	0·75	15·4	13·8	*b*
3·1	7·8	7·9	0·12	15·4	14·2	*b*
50	6·0	3·85	0·47	27·7	7·4	0·106
125	2·8	1·15	0·70	19·2	2·8	0·114
125	2·8	2·35	0·90	36·7	4·8	0·109
125	2·8	3·04	0·90	50·9	6·0	0·118
125	1·4	3·08	0·90	49·9	6·1	0·114
125	1·4	3·08	0·90	53·7	6·1	0·123
250	3·3	3·85	0·40	99·4	7·4	0·096

[a] Rate constant for the uncatalysed reaction, equation (3).
[b] Catalytic effect not sufficiently large to give accurate value of k_3.

The Cr^{2+} *Reduction of the μ-Acetato-complex.*—The reaction was followed at the 517 nm peak (ε = 368 l mol⁻¹ cm⁻¹) under pseudo-first-order conditions (excess Cr^{2+}), μ = 1·0M ($LiClO_4$). Final absorbance (OD_∞) readings were measured and k_{obs} evaluated as before. Values of k_{obs} are listed in Table 4 and the variation of k_{obs} with Cr^{2+} is shown in Figure 3. Since rate constants are nearly four times slower than those for (I) it was more difficult to determine accurate values of OD_∞. The precision of runs (especially those at 25 and 30°) suffered, therefore, and it was not possible to detect with certainty an intercept k_1. Assuming that the μ-formato- and μ-acetato-complexes behave in an analogous manner, values of k_{obs} were computed to obtain k_{Cr} and k_1 as in (1) with the weighting factor $1/k^2_{obs}$. An intercept, k_1, was obtained (1·2 × 10⁻⁶ s⁻¹ at 25°) but the resultant slope, k_{Cr}, at 45° passed above all the data points. When all points were weighted equally, k_1 was found to decrease with increasing temperature! Because of the uncertainty and inconsistency of fitting the data to a two-term rate law, the results were eventually treated on the basis of the rate law (4). Values of k_{Cr} at each temperature

$$k_{obs} = k_{Cr}[Cr^{2+}] \qquad (4)$$

are given in Table 5. The activation parameters (Table 6) were obtained from a standard least-squares treatment of log (k_{Cr}/T) against $1/T$ for each run in Table 4.

TABLE 4

Pseudo-first-order rate constants, k_{obs}, for the reaction of Cr^{2+} with μ-amido-μ-acetato-bis[tetra-amminecobalt-(III)] perchlorate, μ = 1·0M ($LiClO_4$)

Temp. (°C)	$10^2[Cr^{2+}]$ (M)	$[H^+]$ (M)	$10^4[(Co^{III})_2]$ (M)	10^5k_{obs} (s^{-1})	10^4k_{Cr} (l mol^{-1} s^{-1})
45	3·39	0·37	2·3	5·74	16·9
	3·39	0·87	2·3	5·76	17·0
	6·60	0·30	1·4	10·9	16·5
40	2·25	0·60	2·3	3·10	13·8
	3·00	0·30	2·3	3·92	13·1
	3·00	0·70	2·3	4·05	13·5
	3·75	0·87	5·1	4·99	13·3
	3·80	0·87	2·3	5·10	13·4
	5·80	0·80	2·3	7·68	13·2
35	2·26	0·92	2·3	2·23	9·9
	3·75	0·87	5·1	3·53	9·4
	3·82	0·84	2·3	3·79	9·9
30	2·26	0·92	2·3	1·55	6·9
	3·39	0·87	2·3	2·55	7·5
	5·60	0·80	2·3	3·88	6·9
25	2·25	0·60	2·3	1·23	5·5
	3·39	0·37	2·3	1·43	4·2
	5·60	0·80	2·3	2·48	4·4
	5·80	0·80	2·3	2·84	4·9

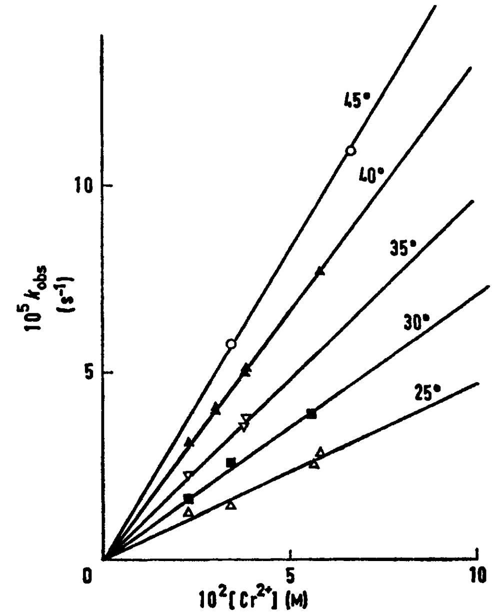


FIGURE 3 Plot of k_{obs} against $[Cr^{2+}]$ for the reduction of the μ-amido-μ-acetato-bis[tetra-amminecobalt(III)] complex, μ = 1·0M ($LiClO_4$)

TABLE 5

The temperature dependence of k_{Cr} for the Cr^{2+} reduction of the μ-amido-μ-acetato-bis[tetra-amminecobalt(III)] complex, μ = 1·0M ($LiClO_4$)

Temp. (°C)	10^3k_{Cr} (l mol^{-1} s^{-1})	Temp. (°C)	10^3k_{Cr} (l mol^{-1} s^{-1})
25	0·47 ± 0·05	40	1·34 ± 0·02
30	0·71 ± 0·03	45	1·68 ± 0·02
35	0·97 ± 0·03		

The Reactions with V^{2+}.—Rate constants k_V, defined in equation (5), were obtained experimentally as previously

$$-\mathrm{d}\ln[(Co^{III})_2]/\mathrm{d}t = k_V[V^{2+}] \qquad (5)$$

described for Cr^{2+}. There was no dependence of k_V on

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

TABLE 6

Rate constants k_{Cr} and k_1 at 25 °C and activation parameters for the Cr^{2+} reductions of the μ-amido-μ-formato-bis[tetra-amminecobalt(III)] and μ-amido-μ-acetato-bis[tetra-amminecobalt(III)] complexes, μ = 1·0M ($LiClO_4$)

Complex	Rate constant	$\Delta H^‡$ (kcal mol^{-1})	$\Delta S^‡$ (e.u.)
μ-Formato	$k_{Cr} = 1·68 \times 10^{-3}$ l mol^{-1} s^{-1}	13·9 ± 0·4	−24·5 ± 1·4
	$k_1 = 9·2 \times 10^{-6}$ s^{-1}	10·6 ± 2·5	−46 ± 8
μ-Acetato	$k_{Cr} = 4·7 \times 10^{-4}$ l mol^{-1} s^{-1}	11·5 ± 0·4 [a]	−35 ± 2 [a]

[a] Activation parameters obtained for k_{Cr} assuming equation (1) to apply (ref. 7, weighting $1/k^2_{obs}$) are $\Delta H^‡ = 11·2 \pm 0·9$ kcal mol^{-1} and $\Delta S^‡ = -36 \pm 3$ e.u.

hydrogen-ion concentration (Table 7). Since the aim was to determine the ratio $k_{Cr} : k_V$ at 25°,[8] the temperature was not in this case varied. At 25° and μ = 1·0M ($LiClO_4$), $k_V = (6·0 \pm 0·3) \times 10^{-2}$ l mol^{-1} s^{-1} and $k_{Cr} : k_V = 0·028$ for the μ-formato-complex, and $k_V = (2·2 \pm 0·1) \times 10^{-2}$ l mol^{-1} s^{-1} and $k_{Cr} : k_V = 0·021$ for the μ-acetato-complex.

TABLE 7

Rate constants, k_V, for the V^{2+} reduction of the μ-amido-μ-formato-bis[tetra-amminecobalt(III)] and μ-amido-μ-acetato-bis[tetra-amminecobalt(III)] complexes at 25 °C, μ = 1·0M ($LiClO_4$)

Complex	$10^2[V^{2+}]$ (M)	$10^4[(Co^{III})_2]$ (M)	$[H^+]$ (M)	$10^2 k_V$ (l mol^{-1} s^{-1})
μ-Formato	1·0	2·8	0·54	6·0
	1·0	2·8	0·54	6·0
	1·86	1·5	0·93	5·7
	1·86	1·5	0·93	5·8
	2·15	2·8	0·93	6·4
	2·22	2·8	0·43	6·2
	2·22	2·8	0·43	6·0
μ-Acetato	0·83	2·3	0·3	2·1
	1·90	2·3	0·7	2·2

The Reaction Products from the Cr^{2+} *Reductions.*—Intercepts corresponding to log ($OD_0 - OD_\infty$) on first-order plots (t = 0, Figure 1) yield $\Delta\varepsilon$, the difference in absorption coefficients between the original binuclear complex and the total products. Such values were obtained for the μ-formato- and μ-acetato-complexes by averaging data from all the runs in Tables 1 and 4 respectively. It can be concluded that the products from the Cr^{2+} reduction of the μ-formato-complex have a combined ε value of (360 ± 7) − (325 ± 15) = (35 ± 22) l mol^{-1} cm^{-1} at 515 nm, and for the μ-acetato-complex, (368 ± 5) − (335 ± 15) = (33 ± 20) l mol^{-1} cm^{-1} at 517 nm. No cobalt(III) species remains as product and due allowance can therefore be made for the cobalt(II) produced. Although the spectrum of acetatopenta-aquochromium(III) ($CrO_2CCH_3^{2+}$) is known,[9] the absorption coefficient of the chromium(III) products from the reaction of the μ-acetato-complex, 24 ± 20 l mol^{-1} cm^{-1} (calculated per mole of dicobalt complex), is too inaccurate to allow a distinction to be made between production of two moles of Cr^{3+} per dicobalt complex, which would give ε *ca.* 12 l mol^{-1} cm^{-1}, and equivalent amounts of Cr^{3+} and $CrO_2CCH_3^{2+}$, which would give ε *ca.* 18 l mol^{-1} cm^{-1}. However, these values do show that any aquation of the carboxylatochromium(III) product, in this case catalysed by chromium(II),[9,10] would not manifest itself in our kinetics, since it would represent <2% of the total absorbance change.

Two additional experiments were carried out in an attempt to identify a possible chromium(III) product other than $Cr(H_2O)_6^{3+}$. In the first the Cr^{2+} reduction of the μ-acetato-complex was followed to completion not only at 517 nm but also at 570 nm. At the latter wavelength, $\Delta\varepsilon$ for the cobalt(III) reduction is smaller and $\Delta\varepsilon$ for the change in concentration of chromium species is larger. The run was performed at 45°, μ = 1·0M ($LiClO_4$), with initial concentrations; [complex] = 4 × 10^{-3}M, [Cr^{2+}] = 0·13M, and [H^+] = 0·56M. Plots of log ($OD_t - OD_\infty$) against time were in both cases linear to 98% completion. At 517 nm, $k_{obs} = (2·03 \pm 0·06) \times 10^{-4}$ s^{-1} and at 570 nm, $k_{obs} = (1·86 \pm 0·04) \times 10^{-4}$ s^{-1}.

In the second experiment we attempted to ion-exchange the products from the Cr^{2+} reduction of the μ-formato-complex using a column of Dowex 50W-X12 cation-exchange resin. The reaction mixture (4 ml), containing initially 0·068M-complex, [Cr^{2+}] = 0·21M, and [H^+] = 0·5M, was maintained at 25° for *ca.* two half-lives (160 min). Excess Cr^{2+} was then allowed to react with oxygen before the reaction solution was exchanged on to the column. Separation of Co^{2+} and Cr^{3+} bands from those due to binuclear species was observed on eluting with solutions of up to 0·5M-$NaClO_4$–0·1M-$HClO_4$. A small amount of complex absorbing at *ca.* 400 and 550 nm was eluted prior to the Co^{2+} band which could be due to the presence of small amounts of formatopenta-aquochromium(III).

DISCUSSION

Although there is no spectroscopic evidence for the aquo-formato-species (II), the proposed k_1 pathway in the Cr^{2+} reduction of the μ-formato-complex (I) is certainly plausible. Aquo-complexes analogous to (II) are generally obtained as transients, except in those cases in which the double-bridged complex is itself unstable. Examples of the latter are the aquo-chloro- and aquo-bromo-analogues of (II).[11,12] Since the formation of (I) from the μ-amido-μ-hydroxo-complex, and the decomposition of (I) to the μ-amido-μ-hydroxo-complex involve ring opening and ring closing processes,[6] (II) must be an intermediate.[13] It is apparent from observations on the stability of (I) [6] that the equilibrium (2) lies well over to the left and that $k_1 \ll k_{-1}$. Consequently concentrations of (II) are very small and we are justified in assuming stationary-state kinetics.

The amount of reaction proceeding through the (k_1) pathway is small and as such, it is impossible to determine kinetically whether the Cr^{2+} attacks the water or formate ligand. The latter would seem more likely except at low [H^+]. At Cr^{2+} concentrations >0·015M, the Cr^{2+} is, in effect, scavenging (II) as quickly as it is

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

[9] E. Deutsch and H. Taube, *Inorg. Chem.*, 1968, **7**, 1532.

[10] See, for example, D. E. Pennington and A. Haim, *J. Amer. Chem. Soc.*, 1966, **88**, 3450 and A. Adin, J. Doyle, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1967, 2504.

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

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

[13] See also discussion pertaining to the existence of the aquo-sulphato-analogue of (II) in M. B. Stevenson, A. G. Sykes, and R. S. Taylor, *J. Chem. Soc.* (*A*), 1970, 3214.

formed, a type of mechanism previously invoked in studies on the μ-amido-μ-hydroxo-complex.[14] The rate constant for bridge cleavage (k_1) is smaller for the μ-acetato-complex than for the μ-formato-complex, possibly due to steric hindrance of the methyl group and the greater basicity of acetate. The aquo-formato-species does not contribute to the V^{2+} and chloride-catalysed Cr^{2+} reductions of the μ-formato-complex which are appreciably faster.

The major pathway (k_{Cr}) is the straightforward reaction between Cr^{2+} and the complex. Of particular interest are the rate constants compared to those for the reductions of the analogous mononuclear penta-amminecobalt(III) complexes. Thus the formatopenta-amminecobalt(III) complex, which possesses a free carbonyl group, is reduced by Cr^{2+} with a rate constant of 7·2 l mol^{-1} s^{-1} at 25°, $\mu = 1{\cdot}0$M ($LiClO_4$),[15] but when the carbonyl group is bonded to a second cobalt, as in the reduction of (I), the rate constant under the same conditions decreases dramatically to $1{\cdot}68 \times 10^{-3}$ l mol^{-1} s^{-1}. In the acetate case, the respective rate constants are 0·35 l mol^{-1} s^{-1} [15] for the mononuclear and $4{\cdot}7 \times 10^{-4}$ l mol^{-1} s^{-1} for the binuclear complex (this work). If all these rate constants were for inner-sphere reactions it would prove conclusively that the preferred mode of reduction of these carboxylatocobalt(III) complexes by Cr^{2+} is that through the free carbonyl group. However we feel that reduction of the two binuclear complexes proceeds via an outer-sphere mechanism. Our main evidence for this is that the ratio $k_{Cr} : k_V$ has values of 0·028 and 0·021 for the Cr^{2+} and V^{2+} reductions of the μ-formato- and μ-acetato-complexes respectively which are in good agreement with those for known outer-sphere reactions.[8] A comparison of such values for the reduction of binuclear cobalt(III) complexes is made in Table 8, the similarity being particularly striking. The mechanism of the reactions of the μ-amido-bis[penta-amminecobalt(III)] complex is *a priori* outer-sphere.[16]

TABLE 8

Second-order rate constants k_{Cr} and k_V (l mol^{-1} s^{-1}) at 25° for the reduction of binuclear cobalt(III) complexes

Complex	k_{Cr}	k_V	$k_{Cr} : k_V$	Reference
$(NH_3)_5Co{\cdot}NH_2{\cdot}Co(NH_3)_5^{5+}$	$3{\cdot}1 \times 10^{-3}$	$1{\cdot}5 \times 10^{-1}$	0·021	16
$(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5^{5+}$	$2{\cdot}3 \times 10^{3}$	$9{\cdot}6 \times 10^{4}$	0·023	*c*
$(trenen)Co{\cdot}O_2{\cdot}Co(trenen)^{5+}$ [a]	$8{\cdot}4 \times 10^{3}$	$4{\cdot}3 \times 10^{5}$	0·020	*d*
$(NH_3)_4Co{\cdot}\mu(OH,OH){\cdot}Co(NH_3)_4^{4+}$	$1{\cdot}73 \times 10^{-3}$	$1{\cdot}02 \times 10^{-1}$ [b]	0·017 [b]	*e*
$(NH_3)_4Co{\cdot}\mu(NH_2,O_2CH){\cdot}Co(NH_3)_4^{4+}$	$1{\cdot}68 \times 10^{-3}$	$6{\cdot}0 \times 10^{-2}$	0·028	This work
$(NH_3)_4Co{\cdot}\mu(NH_2,O_2CCH_3){\cdot}Co(NH_3)_4^{4+}$	$4{\cdot}7 \times 10^{-4}$	$2{\cdot}2 \times 10^{-2}$	0·021	This work

[a] Ligand trenen is 4-aminoethyl-1,4,7,10-tetra-azadecane. [b] Plot of log k_V/T against $1/T$ not linear. [c] A. B. Hoffman and H. Taube, *Inorg. Chem.*, 1968, **7**, 1971. [d] P. K. Zia, R. B. Fisher, and W. K. Wilmarth, *Abs. Amer. Chem. Soc.*, 161st Meeting, Los Angeles, 1971, Inorg. 027. [e] A. B. Hoffmann and H. Taube, *Inorg. Chem.*, 1968, **7**, 903.

An outer-sphere mechanism for the μ-formato- and μ-acetato-complexes is also apparent on other grounds. Thus, in all known cases where Cr^{2+} reduces a binuclear cobalt(III) complex *via* an inner-sphere mechanism,[17] forming a cobalt(III)–chromium(III) intermediate, the first stage is always followed by a second slower stage. No second stage was observed in this study. Moreover initial absorbance values were as predicted, ruling out a stage prior to that observed. We also note that the *O*-bonded formamidopenta-amminecobalt(III) complex is reduced by Cr^{2+} by an outer-sphere mechanism.[5] We conclude therefore that the major reaction pathway (k_{Cr}) for the μ-formato-complex is represented by the scheme (6)—(7), the μ-acetato-complex exhibiting similar

$$(NH_3)_4Co{\cdot}\mu(NH_2,O_2CH){\cdot}Co(NH_3)_4^{4+} + Cr^{2+} \xrightarrow{+H^+} Co^{2+} + Cr^{3+} + (NH_3)_5CoO_2CH^{2+} + 4NH_4^{+} \quad (6)$$

$$(NH_3)_5CoO_2CH^{2+} + Cr^{2+} \xrightarrow[+H^+]{\text{fast}} Co^{2+} + CrO_2CH^{2+} + 5NH_4^{+} \quad (7)$$

behaviour. The secondary pathway k_1, involving bridge cleavage and the aquo-formato-species (II), should yield identical final products but by an inner-sphere attack. We were unable to satisfactorily detect formatopenta-aquochromium(III) or acetatopenta-aquochromium(III) in the two experiments described, and can only conclude that this is due to the Cr^{2+}-catalysed aquation of these complexes[10] throughout the course of the reaction. This side of the study is not of first importance however since at the outset the aim was to obtain rate constants for the Cr^{2+} reduction of a carboxylatocobalt(III) complex which had no free carbonyl group.

Despite the fact that the reduction of the binuclear complexes has been forced to proceed by an outer-sphere mechanism, are we still entitled to attribute the decreases in rate to the absence of a free carbonyl group? The only other serious differences between the mononuclear and binuclear complexes are the charge and the steric factor. Charge effects are believed to be relatively unimportant and certainly could not explain rate differences of the observed order of magnitude. Steric factors on the other hand are known to be important in the mononuclear carboxylatopenta-amminecobalt(III) series, as shown by the second-order rate constants for Cr^{2+} reduction of the formato- (7·2), acetato- (0·35), and pivalato- (0·007) complexes.[15] The acetatopenta-amminecobalt(III) complex will adopt the conformation

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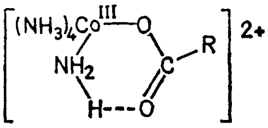
[14] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1991.

[15] M. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 1971, **10**, 1983.

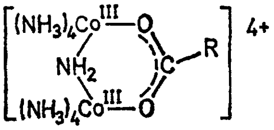
[16] J. Doyle and A. G. Sykes, *J. Chem. Soc.* (*A*), 1968, 2836.

[17] R. S. Taylor, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 277; M. Green, R. S. Taylor, and A. G. Sykes, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2157; K. L. Scott, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 3651.

(III) in which the carbonyl group is hydrogen-bonded to an ammine ligand and the methyl group (R) is pointing away from the ammine ligands.[18] Hydrogen bonding is also apparent in the crystal structure of carbonatopenta-amminecobalt(III) [19] and the larger pivalato group

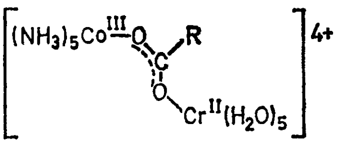


(III)

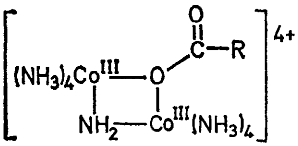


(IV)

(R = Bu^t) will demand this conformation more strongly than when R = H. The ease of approach of Cr^{2+} with its attendant co-ordination sphere towards the carbonyl group, and hence the rate of formation of the precursor complex and the rate of electron transfer, will be greatly reduced as the size of R is increased, as is evident from the rate constant for the pivalato complex. When the carbonyl group is not hydrogen-bonded but is bonded to another cobalt(III) centre as in (IV), the C–O bond is modified and the approach of Cr^{2+} is more severely restricted so that attack proceeds preferentially by an outer-sphere mechanism. Since the environment of the cobalt-bonded oxygen in (III) has not in essence changed in going to (IV) we feel that Cr^{2+} reduction of the mononuclear species by an inner-sphere mechanism must proceed at the free carbonyl group and not at the cobalt-bonded oxygen. The activated complex for electron transfer is therefore as in (V), the bonding of



(V)



(VI)

which closely resembles that in the binuclear cobalt(III) complex (IV). To summarize, complexes of the type (VI) have not as yet been prepared, the individual oxygen atoms of a carboxylate ligand showing no tendency to bond to more than one metal either in a stable or an activated complex.

EXPERIMENTAL

The preparation and properties of the μ-amido-μ-formato-bis[tetra-amminecobalt(III)] $[(NH_3)_4Co{\cdot}\mu(NH_2,O_2CH){\cdot}Co(NH_3)_4](ClO_4)_4,H_2O$ and the μ-amido-μ-acetato-bis[tetra-amminecobalt(III)] $[(NH_3)_4Co{\cdot}\mu(NH_2,O_2CH_3){\cdot}Co(NH_3)_4](ClO_4)_4,H_2O$ complexes will be described elsewhere.[6] Solutions of chromium(II) perchlorate were prepared electrolytically from hexa-aquochromium(III) perchlorate in perchloric acid and were determined spectrophotometrically at 715 nm (ε = 4·82 l mol^{-1} cm^{-1}), where an allowance was made for any remaining Cr^{3+}. The standardization was checked in two cases by reacting the Cr^{2+} with an excess of standard ferric ammonium sulphate, and then determining the excess ferric ion iodometrically. Air-free techniques for handling Cr^{2+} in these laboratories have been described previously. Lithium perchlorate was prepared from lithium carbonate and perchloric acid, and was recrystallized until free from trace anion impurities. Kinetic runs were followed on a Unicam SP 500 spectrophotometer with a thermostatted cell block.

The Dowex 50W-X12 cation-exchange resin used in one experiment was pre-treated as follows: 30% $HClO_4$, distilled water, 50% acetone, ethanol, and distilled water. After reduction of the binuclear cobalt(III) complex, the reaction mixture (4 ml) was oxygenated by passing oxygen through the solution for 15 min (to remove excess Cr^{2+}) and then diluted to 200 ml before addition to the column. The elution was carried out at 5 °C. Scan spectra of eluant fractions were performed in a 10 cm cell on a Unicam SP 800 recording spectrophotometer.

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[2/239 *Received, 4th February,* 1972]

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[18] E. B. Fleischer and R. Frost, *J. Amer. Chem. Soc.*, 1965, **87**, 3998.

[19] H. C. Freeman and G. Robinson, *J. Chem. Soc.*, 1965, 3194.