Reduction of Tetranuclear μ-Oxalato-cobalt(III) Complexes by the Ions Chromium(II) and Vanadium(II)

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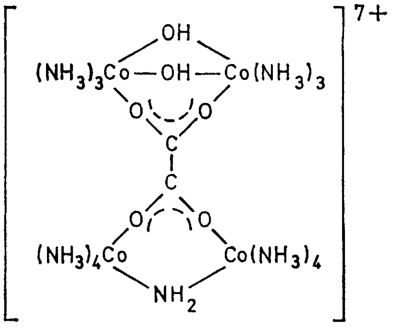
The kinetics of reduction of three highly charged tetranuclear μ-oxalato-cobalt(III) complexes by the ions Cr^{2+} and V^{2+} have been studied. All four cobalt(III) centres of each complex are reduced and the first stage of reaction is rate determining. Second-order rate constants k_{Cr} and k_V for the chromium(II) and vanadium(II) reactions have been obtained and the ratios $k_{Cr}:k_V$ at 25 °C are 0·022, 0·017, and 0·020. It is concluded that the mechanism of reduction is in each case outer sphere. Activation parameters have been determined for the Cr^{2+} reduction of two of the complexes, and the magnitude of these parameters is discussed.

THE preparation and characterization of μ-oxalato-complexes of cobalt(III) in which the oxalate ligand is bonded to two (binuclear), three (trinuclear), and four (tetranuclear) cobalt centres is reported elsewhere.[1] Supporting evidence for the structures of these complexes included a consideration of rate constants for the reductions by the ions Cr^{2+} and V^{2+} The corresponding reductions of the mononuclear penta-ammine-oxalatocobalt(III) [2] and tetra-ammineoxalatocobalt(III) [3] complexes, and the binuclear μ-amido-μ-oxalato-bis-[tetra-amminecobalt(III)] complex [4] have also been studied, and it seemed of interest to investigate more fully the reactions of the tetranuclear complexes, not only for the sake of completeness, but also because the reduction of complexes of such high charge is somewhat novel. This paper reports kinetic studies of reductions by the ions Cr^{2+} and V^{2+} of three tetranuclear complexes: μ_4-oxalato-[di-μ-hydroxo-bis{tri-amminecobalt-(III)}][μ-amido-bis{tetra-amminecobalt(III)}], charge 7+ (I); μ_4-oxalato-bis[di-μ-hydroxo-bis{tri-amminecobalt-(III)}], charge 6+ (II); and μ_4-oxalato-[μ-amido-μ-hydroxo-bis{tri-amminecobalt(III)}][μ-amido-bis{tetra-amminecobalt(III)}], charge 7+ (III). Structures (I)—(III) are displayed in the appropriate sections below. Spectrophotometric changes in the u.v.-visible range clearly indicate that all four cobalt(III) centres of each complex are reduced. Since oxalate ion remains bonded to a metal ion throughout the reactions, we do not expect it to be reduced.[5] However this point has little effect on the outcome of the present study.

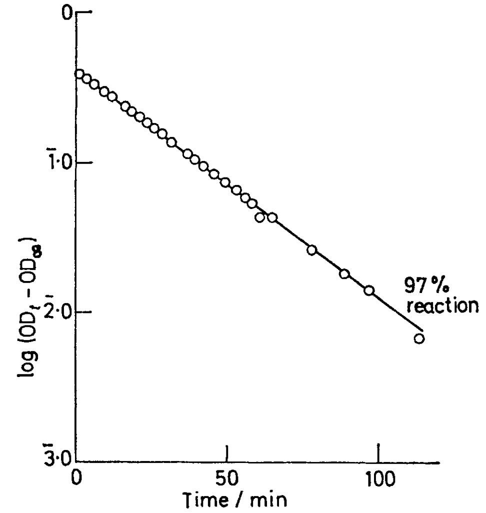
RESULTS

Reduction of the 7+ *Complex* (I).—The rate of reduction of μ_4-oxalato-[di-μ-hydroxo-bis{tri-amminecobalt(III)}]-[μ-amido-bis{tetra-amminecobalt(III)}], the 7+ complex (I), by Cr^{2+} ions was studied by conventional spectrophotometry at the 518 nm absorption maximum of the complex (ε 480 l mol^{-1} cm^{-1}). A large 40—400 fold excess of reductant was used. The average absorbance change for the reaction corresponded to $\Delta\varepsilon = 410 \pm 7$ l mol^{-1} cm^{-1}, which is consistent with a 4 : 1 reaction yielding cobalt(II) and chromium(III) ions as products. Initial absorbance measurements corresponded to predicted values, thus indicating that the reaction followed was in fact the first stage. It was possible to follow runs at 40 and 45 °C to completion and plots of log $(OD_t - OD_\infty)$ against time were linear to >93% reaction (Figure). Some of the slower runs had to be left overnight in order to obtain final absorbance (OD_∞) readings. Second-order rate constants, k_{Cr} (Table 1) were obtained from plots such as that in the Figure and were found to be independent of $[H^+]$ (0·1—0·9M) and $[Cr^{2+}]$ ($1·85 \times 10^{-2}$—$7·60 \times 10^{-2}$M). The rate law is therefore as in (1) and at 25 °C and I = 1·0M ($LiClO_4$),

$$-d[(Co^{III})_4]/dt = k_{Cr}[Cr^{2+}][(Co^{III})_4] \qquad (1)$$



(I)



Pseudo-first-order plot for the Cr^{2+} reduction of the 7+ complex (I) at 45 °C: $[H^+] = 0·08$M; $[Cr^{2+}] = 2·12 \times 10^{-2}$M; $[(Co^{III})_4] = 2·43 \times 10^{-4}$M; and I = 1·0M ($LiClO_4$)

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[1] K. L. Scott, K. Wieghardt, and A. G. Sykes, *Inorg. Chem.*, 1973, in the press.

[2] H. J. Price and H. Taube, *Inorg. Chem.*, 1968, **7**, 1.

[3] C. Hwang and A. Haim, *Inorg. Chem.*, 1970, **9**, 500.

[4] K. L. Scott, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 3651.

[5] R. M. Milburn and H. Taube, *J. Phys. Chem.*, 1960, **64**, 1776. However, see comments in ref. 27 of T. Spinner and G. M. Harris, *Inorg. Chem.*, 1972, **11**, 1068.

k_{Cr} = (8·1 ± 0·4) × 10^{-3} l mol^{-1} s^{-1}. Values of k_{Cr} at 25—45 °C and corresponding activation parameters are given in Table 2. The latter were obtained from a plot of log (k_{Cr}/T) against $1/T$ using a standard least-squares program with each data point given equal weighting.

TABLE 1

Rate constants, k_{Cr}, for the Cr^{2+} reduction of the 7+ complex (I), I = 1·0M ($LiClO_4$)

Temp. °C	[H^+] M	10^2[Cr^{2+}] M	10^4[$(Co^{III})_4$] M	$10^3 k_{Cr}$ l mol^{-1} s^{-1}
25	0·12	1·85	2·43	8·5
	0·13	6·20	2·43	8·2
	0·20	3·70	2·43	8·7
	0·74	7·60	2·43	7·8
	0·80	5·60	1·46	7·7
	0·80	5·60	1·46	8·5
	0·87	3·41	1·46	7·6
	0·87	3·41	2·43	7·8
30	0·07	1·82	2·43	11·1
	0·58	2·06	2·43	11·6
35	0·07	1·82	2·43	16·0
	0·47	1·82	2·43	15·3
40	0·08	2·12	2·43	20·3
	0·20	3·67	2·43	20·7
	0·25	3·56	9·70	20·6
	0·47	1·82	2·43	20·3
45	0·08	2·12	2·43	27·7
	0·58	2·06	2·43	27·2
	0·93	2·09	2·43	27·4

TABLE 2

A summary of rate constants, k_{Cr}, and activation parameters for the Cr^{2+} reduction of the 7+ complex (I), I = 1·0M ($LiClO_4$)

Temp. °C	$10^3 k_{Cr}$ l mol^{-1} s^{-1}
25	8·1 ± 0·4
30	11·4 ± 0·3
35	15·7 ± 0·4
40	20·5 ± 0·2
45	27·4 ± 0·2

$\Delta H^‡$ = 10·9 ± 0·2 kcal mol^{-1}. $\Delta S^‡$ = −31·6 ± 0·9 cal K^{-1} mol^{-1}.

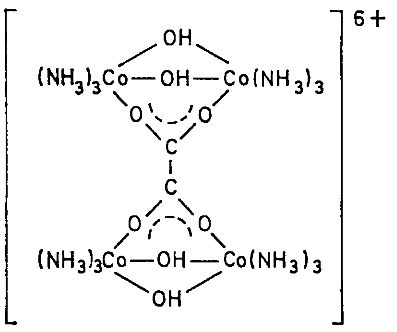
A similar experimental procedure was used for the V^{2+} reduction of complex (I). Plots of log ($OD_t - OD_\infty$) against time were linear to *ca.* 90% completion. The average value of the second-order rate constant, k_V (Table 3) is 0·363 ± 0·011 l mol^{-1} s^{-1} at 25 °C and I = 1·0M ($LiClO_4$) and the ratio $k_{Cr} : k_V$ = 0·022.

TABLE 3

Rate constants, k_V, for the V^{2+} reduction of the 7+ complex (I) at 25 °C and I = 1·0M ($LiClO_4$)

[H^+] M	10^2[V^{2+}] M	10^4[$(Co^{III})_4$] M	k_V l mol^{-1} s^{-1}
0·54	0·80	2·43	0·372
0·93	2·33	1·16	0·366
0·98	0·48	1·16	0·344
0·98	0·76	2·43	0·371

Reduction of the 6+ *Complex* (II).—Despite various attempts to follow the Cr^{2+} reduction of μ₄-oxalato-bis[di-μ-hydroxo-bis{tri-amminecobalt(III)}], the 6+ complex (II), at ionic strength I = 1·0M ($LiClO_4$), it was finally decided that the solubility of the complex under these conditions was not sufficiently high to permit accurate studies. Reluctantly the reaction was therefore studied at lower ionic strengths and most data were obtained at I = 0·20M ($LiClO_4$). Absorbance changes were monitored at the 525 nm peak of the complex (ε 227 l mol^{-1} cm^{-1}) with the Cr^{2+} ion in a 30—70 fold excess. The smaller ionic strength imposed severe limitations on concentration variations and also caused a drastic reduction in the rate of reaction. All runs were followed to >60% completion and the final absorbance measured on the following day. There was no further absorbance change over 24 h. The faster runs were followed to completion, in which case plots of log ($OD_t - OD_\infty$) were linear to >90% completion. The only observable stage of the reaction was that of the first. Second-order rate constants, k_{Cr} (Table 4), conform to the rate law (1). At 25 °C, k_{Cr} = (3·6 ± 0·1) × 10^{-3} l mol^{-1} s^{-1} with I = 0·20M ($LiClO_4$). Mean values of rate constants at other temperatures and corresponding activation parameters are given in Table 5. Errors were obtained by a



(II)

TABLE 4

Rate constants, k_{Cr}, for the Cr^{2+} reduction of the 6+ complex (II), I = 0·20M ($LiClO_4$)

Temp. °C	[H^+] M	10^2[Cr^{2+}] M	10^4[$(Co^{III})_4$] M	$10^3 k_{Cr}$ l mol^{-1} s^{-1}
25	0·111	2·51	4·5	3·3
	0·111	2·65	4·5	3·8
	0·111	3·02	4·5	3·5
	0·146	1·68	2·3	3·6
	0·164	1·10	3·0	3·6
30	0·054	1·30	4·5	4·6
35	0·111	2·51	4·5	5·6
	0·111	2·65	4·5	5·8
	0·150	1·14	4·5	5·3
40	0·054	1·30	4·5	7·6
	0·111	2·65	4·5	7·7
	0·146	1·65	2·3	7·8
	0·173	0·80	2·3	7·2
45	0·111	2·51	4·5	8·7
	0·111	2·51	4·5	8·8
	0·111	3·05	4·5	9·3
	0·150	1·14	4·5	8·8

TABLE 5

A summary of rate constants, k_{Cr}, and activation parameters for the Cr^{2+} reduction of the 6+ complex (II), I = 0·20M ($LiClO_4$)

Temp. °C	$10^3 k_{Cr}$ l mol^{-1} s^{-1}
25	3·6 ± 0·1
30	4·6
35	5·6 ± 0·2
40	7·6 ± 0·2
45	8·9 ± 0·2

$\Delta H^‡$ = 8·2 ± 0·3 kcal mol^{-1}. $\Delta S^‡$ = −42·1 ± 0·9 cal K^{-1} mol^{-1}.

least-squares treatment with each data point given equal weighting. The effect of varying the ionic strength from 0·20 to 0·60M, at 25 and 40 °C, was investigated briefly (Table 6).

TABLE 6

Variation of k_{Cr} with ionic strength ($LiClO_4$) for the Cr^{2+} reduction of the 6+ complex (II): $[(Co^{III})_4] = 4\cdot5 \times 10^{-4}$M

Temp. / °C	I / M	[H+] / M	$10^2[Cr^{2+}]$ / M	10^3k_{Cr} / l mol^{-1} s^{-1}
25	0·5	0·23	3·69	6·6
45	0·25	0·205	2·9	10·2
	0·3	0·205	2·9	11·3
	0·5	0·26	7·65	16·7
	0·5	0·45	1·44	17·3
	0·6	0·36	7·65	17·6

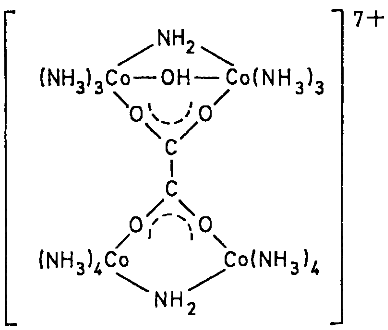
A similar procedure was adopted for the study of the V^{2+} reduction of complex (II). Plots were linear to >94% and second-order rate constants (Table 7) gave $k_V = (0\cdot21 \pm 0\cdot01)$ l mol^{-1} s^{-1} at 25 °C and $I = 0\cdot20$M ($LiClO_4$). The ratio $k_{Cr} : k_V = 0\cdot017$.

TABLE 7

Rate constants, k_V, for the V^{2+} reduction of the 6+ complex (II) at 25 °C and $I = 0\cdot20$M ($LiClO_4$)

[H+] / M	$10^2[V^{2+}]$ / M	$10^4[(Co^{III})_4]$ / M	k_V / l mol^{-1} s^{-1}
0·055	1·26	9·1	0·228
0·055	1·32	4·5	0·224
0·112	2·78	4·5	0·217
0·155	1·22	4·5	0·204
0·155	1·22	4·5	0·206
0·155	1·22	9·1	0·208

Reduction of the 7+ *Complex* (III).—The reduction of μ_4-oxalato-[μ-amido-μ-hydroxo-bis{tri-amminecobalt(III)}]-[μ-amido-bis{tetra-amminecobalt(III)}], the 7+ complex (III), was studied at 25 °C and $I = 1\cdot0$M ($LiClO_4$). Absorption changes were monitored at 514 nm (ε 505 l mol^{-1} cm^{-1}). The Cr^{2+} reactant was in a 200—500 fold excess, the V^{2+} in a 70—140 fold excess. Plots of log ($OD_t - OD_\infty$) against time were linear to *ca.* 80% completion and from these second-order rate constants k_{Cr} (Table 8) and k_V (Table 9) were evaluated. The values obtained are consistent with a rate law of the same form as that of (1). However, the low solubility of the complex did not allow extensive variations in the concentration of the complex. The results obtained gave $k_{Cr} = (4\cdot4 \pm 0\cdot1) \times 10^{-3}$ l mol^{-1} s^{-1} and $k_V = 0\cdot217 \pm 0\cdot008$ l mol^{-1} s^{-1} at 25 °C and $I = 1\cdot0$M ($LiClO_4$). The ratio $k_{Cr} : k_V$ is 0·020.



(III)

TABLE 8

Rate constants, k_{Cr}, for the Cr^{2+} reduction of the 7+ complex (III) at 25 °C and $I = 1\cdot0$M ($LiClO_4$)

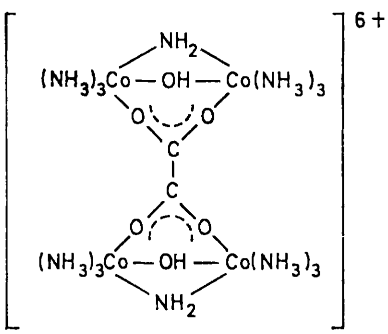
[H+] / M	$10^2[Cr^{2+}]$ / M	$10^4[(Co^{III})_4]$ / M	10^3k_{Cr} / l mol^{-1} s^{-1}
0·41	2·74	1·3	4·4
0·41	2·74	1·3	4·6
0·55	6·1	1·6	4·4
0·72	8·5	1·6	4·2
0·80	5·6	1·3	4·4
0·80	5·6	1·3	4·5

TABLE 9

Rate constants, k_V, for the V^{2+} reduction of the 7+ complex (III) at 25 °C and $I = 1\cdot0$M ($LiClO_4$)

[H+] / M	$10^2[V^{2+}]$ / M	$10^4[(Co^{III})_4]$ / M	k_V / l mol^{-1} s^{-1}
0·20	2·23	2·23	0·215
0·22	0·93	1·3	0·214
0·22	0·94	1·3	0·233
0·45	1·83	1·3	0·210
0·60	2·25	1·6	0·215

Other Studies.—The reduction of μ_4-oxalato-bis[μ-amido-μ-hydroxo-bis{tri-amminecobalt(III)}], the 6+ complex (IV), was also briefly studied at 25 °C, and $I = 0\cdot2$M ($LiClO_4$). Both the Cr^{2+} and V^{2+} reactions are very much slower than with the complexes (I)—(III). A run followed at 500 nm with $[Cr^{2+}] = 2\cdot7 \times 10^{-2}$M, $[(Co^{III})_4] = 3 \times 10^{-4}$M, and $[H^+] = 0\cdot1$M was not complete in 60 h; hence $k_{Cr} < 10^{-3}$ l mol^{-1} s^{-1}. A similar run with V^{2+} ions gave a plot of log ($OD_t - OD_\infty$) against time which was linear to *ca.* 80% completion; k_V *ca.* 8×10^{-3} l mol^{-1} s^{-1}.



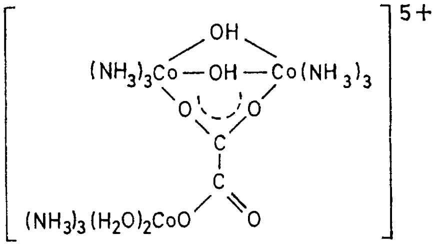
(IV)

DISCUSSION

At the outset of these studies, it was possible that rate-determining hydroxo-bridge cleavage would contribute to the kinetics as had been observed previously for the Cr^{2+} and V^{2+} reductions of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex $[(NH_3)_4Co{\cdot}\mu(NH_2,OH){\cdot}Co(NH_3)_4]^{4+}$.[6] No dependence on hydrogen-ion concentration was observed, however, and there was a first-order dependence on the reductant. The rate constants therefore correspond to reduction of the tetranuclear complexes (I)—(III). Furthermore, although four stages are required to reduce each cobalt(III) complex entirely, it is the first stage of reduction which is rate determining. Why this should be so can

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

be readily understood by consideration of, for example, the Cr^{2+} reduction of the 6+ tetranuclear complex (II). The products of the first and second stages are believed to be the trinuclear and binuclear complexes (V) and (VI). After the first stage one of the four equivalent cobalt(III) centres has been reduced to cobalt(II) with subsequent rapid loss of labile ligands. The cobalt(III) trinuclear complex (V) which remains possesses two aquo-ligands through which rapid inner-sphere electron transfer can occur by an $[H^+]^{-1}$ path.[7] The product from this stage, (VI), is the binuclear complex di-μ-hydroxo-μ-oxalato-bis[tri-amminecobalt(III)] which will be protonated at pH <1. A study of the Cr^{2+} reduction of the analogous binuclear complex μ-amido-μ-oxalato-bis-[tetra-amminecobalt(III)] has shown that the two stages leading to complete reduction are both fast.[4] Therefore once the initial slow outer-sphere reduction has taken place, sites for rapid inner-sphere attack become available, first at aquo-ligands and then at a free carboxylate group. Despite the complex nature of the tetranuclear complex, the observed single rate-determining step is not unusual but is rather as might be expected. Hoffman and Taube,[8] in their study of the Cr^{2+} reduction of a different type of tetranuclear cobalt(III) complex $[\{(NH_3)_4Co(OH)_2\}_3Co]^{6+}$, have also deduced that the first stage of reduction is rate determining. The availability of aquo-ligands once the first of the cobalt(III) centres has been reduced undoubtedly provides a satisfactory explanation.



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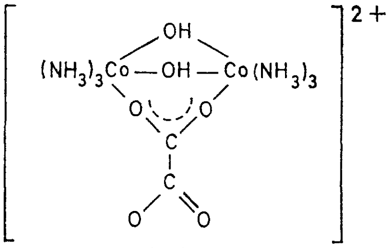

(VI)

The mechanism of the first stage of reduction of complexes (I)—(III) by the ions Cr^{2+} and V^{2+} is outer sphere. The ratio of the rate constants for Cr^{2+} and V^{2+} reductions of a common oxidant [generally a cobalt(III) species] has been observed to be *ca.* 0·02 when both reactions are outer sphere.[7] Ratios ($k_{Cr} : k_V$) for the 6+ tetranuclear (0·017) and for the two 7+ tetranuclear complexes (0·022 and 0·020) are in satisfactory agreement with this value. This point is further discussed in ref. 1.

Studies of the Cr^{2+} reductions of the μ-amido-μ-formato-bis[tetra-amminecobalt(III)] and μ-amido-μ-acetato-bis[tetra-amminecobalt(III)] complexes,[9] have shown the importance of a free carbonyl group in promoting inner-sphere electron transfer in the mononuclear penta-ammineformatocobalt(III) and acetatopenta-amminecobalt(III) complexes;[10] the absence of such a group in the binuclear complexes results in a drastic reduction in the rate of reaction. Similarly studies on the Cr^{2+} reduction of the μ-amido-μ-oxalato-bis[tetra-amminecobalt(III)] complex have reinforced the view [2] that it is the presence of two α-carbonyl groups in mononuclear penta-ammineoxalatocobalt(III) and the various acid derivatives which is responsible for the very fast rates of electron transfer observed. The present studies on the reductions of tetranuclear μ-oxalato-complexes complete the picture in that we can see the effect of having complexed both free carbonyl groups of the oxalate ligand. Respective rates of Cr^{2+} reduction of the mononuclear (two free carbonyl groups), binuclear (one free carbonyl group), and tetranuclear (no free carbonyl group) complexes are $4{\cdot}6 \times 10^4$, 35, and *ca.* 10^{-3} l mol^{-1} s^{-1}. The slow rate for the tetranuclear complexes confirms that the previously reported Cr^{2+} reduction of the binuclear μ-amido-μ-oxalato-complex proceeds by remote attack.[4]

In order to compare rates of reduction for the tetranuclear complexes with other outer-sphere rate constants it is necessary to allow for the fact that the 6+ tetranuclear complex (II) was studied at $I = 0{\cdot}20$M ($LiClO_4$). From the data in Table 6 (which shows a similar trend to that observed in, for example ref. 11), a value k_{Cr} *ca.* 11×10^{-3} l mol^{-1} s^{-1} is inferred for $I = 1{\cdot}0$M ($LiClO_4$) at 25 °C. This is quite fast for an outer-sphere reduction of this type. Two factors would seem to merit consideration: the number of oxygen atoms bonded to each cobalt(III) centre, and the high charge on the oxidant. Each cobalt(III) centre in the 6+ tetranuclear complex (II), for example, is bonded to three nitrogen atoms and three oxygen atoms, and it can be argued that the effect of replacing nitrogen by oxygen atoms should make the centre more reducible because of a more favourable free-energy change [*cf.* the standard reduction potentials of 1·84 and *ca.* 0·1 V for the $Co(H_2O)_6{}^{3+}$–$Co(H_2O)_6{}^{2+}$ and $Co(NH_3)_6{}^{3+}$–$Co(NH_3)_6{}^{2+}$ couples].[12] Thus Cr^{2+} reductions of the tetranuclear complexes are 10—10^2 times faster than that of the mononuclear complex $Co(NH_3)_6{}^{3+}$.

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

[8] A. B. Hoffman and H. Taube, *Inorg. Chem.*, 1968, **7**, 903.

[9] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 1832.

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

[11] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 1964, **68**, 228.

[12] W. M. Latimer, ' Oxidation Potentials,' 2nd edn., Prentice-Hall Inc., New York, 1952.

Also, within the tetranuclear series of complexes, rate constants for the 6+ complex (II) (four hydroxo-bridges) are greater than those for complex (IV) (two hydroxo-bridges), and rate constants for the 7+ complex (I) (two hydroxo-bridges) are greater than those for complex (III) (one hydroxo-bridge). However the range of values is quite small, and the activation parameters for complexes (I) and (II) are such that at other temperatures a different reactivity pattern may be effective. The overall similarity in rate constants for the tetranuclear complexes is perhaps the most significant comment to make in this context.

As far as the charge on the oxidant is concerned, it is noted that $\Delta H^{\ddagger}$ values are in most cases smaller and $\Delta S^{\ddagger}$ slightly more negative, for the tetranuclear complexes than for the mononuclear and binuclear complexes (Table 10). This can be accounted for if the rate constants k_{Cr} are regarded as composite and equal to kK_0, where K_0 is the constant for ion-pair or outer-sphere complex formation of Cr^{2+} with the oxidant and k is the rate constant for electron transfer. Using the Fuoss equation,[13] * we can estimate ΔH_0 *ca.* —7 kcal mol^{-1} and ΔS_0 *ca.* —42 cal K^{-1} mol^{-1} for a 5 Å separation of the 2+ and 6+ reactants and activation parameters corresponding to k are therefore $\Delta H^{\ddagger}$ *ca.* 15 kcal mol^{-1} and $\Delta S^{\ddagger} = 0$ cal K^{-1} mol^{-1}. For a 10 Å separation ΔH_0 *ca.* 4 kcal mol^{-1} and ΔS_0 *ca.* -15 cal K^{-1} mol^{-1}, so that $\Delta H^{\ddagger}$ *ca.* 12 kcal mol^{-1} and $\Delta S^{\ddagger}$ *ca.* —27 cal K^{-1} mol^{-1}. Although these calculations are very approximate for such large complexes, they do seem to help explain the trend in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values observed.

TABLE 10

A summary of data for outer-sphere Cr^{2+} reductions of cobalt(III) complexes

Complex	k_{Cr} (25 °C) / l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$ / cal K^{-1} mol^{-1}	Ref.
$[Co(NH_3)_6]^{3+}$	$8{\cdot}8 \times 10^{-5}$	14·7	−30	*a*
$[(NH_3)_4Co{\cdot}\mu(NH_2,O_2CH){\cdot}Co(NH_3)_4]^{4+}$	$1{\cdot}68 \times 10^{-3}$	13·9	−24·5	9
$[(NH_3)_4Co{\cdot}\mu(NH_2,O_2CMe){\cdot}Co(NH_3)_4]^{4+}$	$0{\cdot}47 \times 10^{-3}$	11·5	−35	9
(I) ($I = 1{\cdot}0$M)	$8{\cdot}1 \times 10^{-3}$	10·9	−31·6	*b*
(II) ($I = 0{\cdot}2$M)	$3{\cdot}6 \times 10^{-3}$	8·2	−42·1	*b*
($I = 1{\cdot}0$M)	*ca.* 11×10^{-3}			*b*
(III) ($I = 1{\cdot}0$M)	$4{\cdot}4 \times 10^{-3}$			*b*
(IV) ($I = 0{\cdot}2$M)	$<10^{-3}$			*b*
$[\{(NH_3)_4Co(OH)_2\}_3Co]^{6+}$	$3{\cdot}2 \times 10^{-3}$	9·1	−39	8

[a] A. M. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 793. [b] This work.

Finally it is recalled that the Cr^{2+}, V^{2+}, and Eu^{2+} reductions of the complex $[(NH_3)_5Co{\cdot}NH_2{\cdot}Co(NH_3)_5]^{5+}$ ($3{\cdot}1 \times 10^{-3}$ l mol^{-1} s^{-1} for Cr^{2+} at 25 °C) are *ca.* 35 times faster than those of $[Co(NH_3)_6]^{3+}$ ($8{\cdot}8 \times 10^{-5}$ l mol^{-1} s^{-1} for Cr^{2+} at 25 °C).[14] The difference in rate constants for these reactions would seem to be largely attributed to the $\Delta S^{\ddagger}$ values, and it is possible that the increase in size of the binuclear complex is responsible for its faster reaction. However, on this basis, even faster rate constants might have been expected for the tetranuclear complexes (Table 10).

EXPERIMENTAL

Perchlorate salts of the complexes μ_4-oxalato-[di-μ-hydroxo-bis{tri-amminecobalt(III)}][μ-amido-bis{tetra-amminecobalt(III)}] trihydrate (I), μ_4-oxalato-bis[di-μ-hydroxo-bis{tri-amminecobalt(III)}]tetrahydrate (II), and μ_4-oxalato-[μ-amido-μ-hydroxo-bis{tri-amminecobalt(III)}]-[μ-amido-bis{tetra-amminecobalt(III)}] tetrahydrate (III), were prepared as described elsewhere.[1] Solutions of hexa-aquochromium(II) perchlorate, hexa-aquovanadium(II) perchlorate (both in perchloric acid solutions), and lithium perchlorate were prepared as described in previous work from these laboratories.

For kinetic studies with the 7+ complexes, the procedure was as follows. The complex was dissolved in water, the required volume of $LiClO_4$–$HClO_4$–H_2O added to adjust [H^+] as required and the ionic strength to $I = 1{\cdot}0$M ($LiClO_4$), and the solution degassed by a procedure involving successive evacuations. Degassed solutions were mixed with solutions of Cr^{2+} or V^{2+} ions at $I = 1{\cdot}0$M ($LiClO_4$) and the decrease in concentration of the complex monitored spectrophotometrically. A different procedure was adopted in the case of the 6+ complexes because of their low solubility. Solutions of the complex were made up in water and were then degassed by alternately freezing, evacuating, and warming at low pressure. The Cr^{2+} or V^{2+} solution was made up at $I = 0{\cdot}4$M and equal volumes of the two reactant solutions were mixed at the commencement of each experiment.

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* The expression for K_0 is dependent on temperature and from the Fuoss equation the values $\Delta H_0 = -0{\cdot}58z_1z_2$ kcal mol^{-1} and $\Delta S_0 = -(2{\cdot}3 + 3{\cdot}3z_1z_2)$ cal K^{-1} mol^{-1} can be derived for a 5 Å separation of the two reactants, charges z_1 and z_2, at 25 °C and $I = 0{\cdot}5$M-$LiClO_4$. For a 10 Å separation, $\Delta H_0 = -0{\cdot}29z_1z_2$ kcal mol^{-1} and $\Delta S_0 = (1{\cdot}8 - 1{\cdot}4z_1z_2)$ cal K^{-1} mol^{-1}. Calculations for ionic strengths greater than 0·5M are not acceptable without an allowance for other ionic interactions (M. R. Hyde and A. G. Sykes, unpublished work.)

[13] R. M. Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059.

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