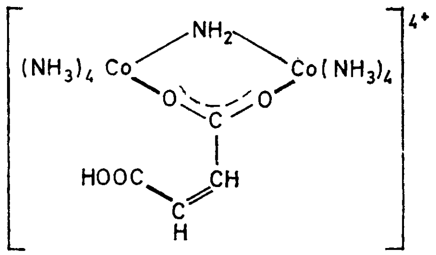
The Cr^{2+} and V^{2+} Reduction of μ-Carboxylato-dicobalt(III) Ammine Complexes. Part V.‡ The Mechanism of Reduction of μ-Maleato- and μ-Fumarato-complexes †

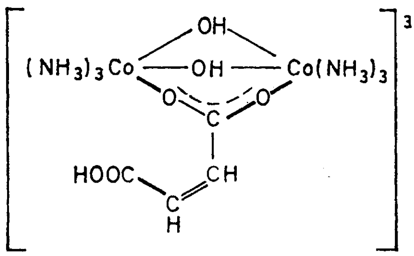
By **Michael R. Hyde, Keith L. Scott, Karl Wieghardt, and A. Geoffrey Sykes,*** Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

The Cr^{2+} and V^{2+} reductions of binuclear cobalt(III) complexes $[(NH_3)_4Co\cdot\mu(NH_2,maleato)\cdot Co(NH_3)_4]^{4+}$, $[(NH_3)_3Co\cdot\mu(OH,OH,maleato)\cdot Co(NH_3)_3]^{3+}$, and $[(NH_3)_3Co\cdot\mu(OH,OH,fumarato)\cdot Co(NH_3)_3]^{3+}$, referred to as μ(am), μ(hhm), and μ(hhf) respectively, proceed by a slow/fast reaction sequence. Kinetic data have been obtained for the first stages with Cr^{2+} as reductant and at 25 °C, I = 1.0M ($LiClO_4$), second-order rate constants (l mol^{-1} s^{-1}), enthalpies of activation (kcal mol^{-1}), and entropies of activation (cal K^{-1} mol^{-1}), are respectively for μ(am), 0.59, 5.5, and −41.3; μ(hhm), 1.87, 4.3, and −43.0; and μ(hhf), 2.64, 2.8, and −47.1. Rate constants are independent of $[H^+]$ in the range 0.02—1.00M. Product analyses are consistent with inner-sphere mechanisms involving remote attack. With V^{2+} as reductant kinetic data for the first stage are respectively for μ(am), 1.46, 9.8, and −24.9; μ(hhm), 0.164, 5.8, and −42.3; and μ(hhf), 0.099, 75. and −38.0. No dependence on $[H^+]$ was observed except in the V^{2+} reduction of μ(hhm), when significant contributions were obtained from an $[H^+]^{-1}$ term with kinetic parameters, 0.45 (s^{-1}), 10.6, and −29.3.

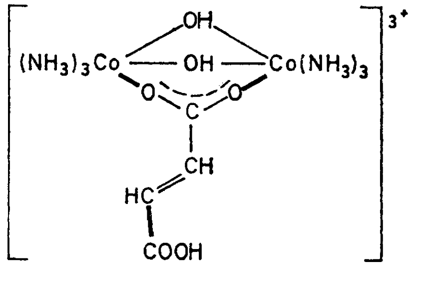
THE rate of the Cr^{2+} reduction of $[Co(NH_3)_5(maleato)]^{2+}$ has been shown [1] to be substantially faster than that of complexes containing monocarboxylate ligands, *e.g.* $[Co(NH_3)_5(acetato)]^{2+}$.[2] An inner-sphere mechanism is indicated with 80% of the chromium(III) product containing chelated maleate, and the remaining 20% monodentate maleate. At 25 °C the observed rate can be expressed $k_{Cr} = k_0 + k_1[H^+]$, where it has been suggested that k_1 (3.48 l^2 mol^{-2} s^{-1} at 25 °C) results from remote attack with protonation of the adjacent carboxylate group assisting conjugation. There remains some doubt as to the mechanism of the k_0 path (1.32 l mol^{-1} s^{-1} at 25 °C), and whether this also involves remote attack.



μ(am)



μ(hhm)



μ(hhf)

constant of 200 l mol^{-1} s^{-1} is independent of $[H^+]$ in the range 0.01—0.91M. The Cr^{2+} reduction [3] of the $[Co(NH_3)_5(fumarato)]^{2+}$ complex and related derivatives [4] also proceed by an inner-sphere attack, but at rates which are considerably slower than with maleate. Chelation cannot occur in this case in view of the *trans*-structure of the ligand. Second-order rate constants

To further evaluate the precise function of maleate and fumarate in electron-transfer processes we now consider the Cr^{2+} (and V^{2+}) reduction of μ-maleato- and μ-fumarato-complexes, where only the remote carboxylate group is available for inner-sphere attack.[5] The three oxidants investigated are displayed below with abbreviations μ(am) for the μ-amido-μ-maleato-, μ(hhm)

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† No reprints available.

‡ Part IV, preceding paper.

[1] M. V. Olson and H. Taube, *Inorg. Chem.*, 1970, **9**, 2072.

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

[3] D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 1785.

[4] J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 1178.

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

for the di-μ-hydroxo-μ-maleato-, and μ(hhf) for the μ-fumarato-di-μ-hydroxo-complexes.

The preparation of μ(am) is described for the first time in the Experimental section. Details of the preparations of μ(hhm) and μ(hhf) have been reported elsewhere.[6] All three complexes are stable to bridge cleavage, $[H^+] = 0.1$—1.0M, during periods of up to 3 days at 25 °C. Free maleic acid is slowly reduced by Cr^{2+} (reaction time *ca.* 15 min at 28 °C, concentrations *ca.* 0.02M).[7]

Kinetics of the Cr^{2+} *Reduction of* μ*-Maleato- and* μ*-Fumarato-complexes.*—Absorbance decreases corresponding to consumption of the binuclear cobalt(III) complexes were monitored at $\lambda = 517$ nm ($\varepsilon = 367$ l mol^{-1} cm^{-1}) for μ(am), and at $\lambda = 524$ nm ($\varepsilon = 110 \pm 2$ l mol^{-1} cm^{-1}) for μ(hhm) and μ(hhf), with Cr^{2+} in large excess. Under these pseudo-first-order reaction conditions plots of $\log(O.D._t - O.D._\infty)$ against time were linear to at least 93% completion. There was no dependence on $[H^+]$, which was varied most extensively for μ(am), $[H^+] = 0.02$—0.95M. Pseudo-first-order rate constants give a first-order dependence on $[Cr^{2+}]$, and the kinetic data for

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

all three reactions are consistent with the rate law (1). Second-order rate constants k_{Cr} at temperatures within the range 2.5—45 °C are listed in Table 1. Included in the data for μ(am) are two runs at $\lambda = 470$ nm which again show linearity to 95% completion, and are in good agreement with runs at 517 nm. All data were computed using a non-linear least-squares programme [8] with a weighting factor $1/k^2_{Cr}$. Resultant activation parameters and second-order rate constants at 25 °C are listed in Table 2. Detailed analysis of absorbance changes indicated that complete reduction occurs during the observed single-stage reduction process. Thus absorbance changes at 517 and 470 nm are $\Delta\varepsilon = 340 \pm 10$ and 178 ± 4 l mol^{-1} cm^{-1} respectively. These are in excellent agreement with calculated values for complete reduction $\Delta\varepsilon = 340$ and 186 l mol^{-1} cm^{-1}, and show the second stage of reduction to be faster than the first stage. All observations are consistent with a stoicheiometric equation, (2). Further information regarding the nature

$$2Cr^{2+} + (Co^{III})_2 \longrightarrow 2Cr^{III} + 2Co^{2+} \qquad (2)$$

of the chromium(III) products was obtained from ion-exchange experiments (see below).

Reaction Products of the Cr^{2+} *Reductions.*—Reactant solutions (25 °C) were mixed and kept in air-tight vessels for up to 30 min after mixing, $I = 1.0$M$(LiClO_4)$. The reaction mixture (*ca.* 10 ml) was then exchanged onto a column of Dowex 50W-X12 cation exchange resin and eluted with $HClO_4$–$LiClO_4$ as required. Cobalt(II) and various chromium(III) species were collected, and analysed as described in the Experimental section. Analyses (relative to Co^{2+}) for the Cr^{2+} reduction of μ(am) with $[Cr^{2+}]/[(Co^{III})_2]$ in ratios 1 : 1 and 2 : 1 are shown in Table 3. Products obtained included trace amounts of a chromium(III) complex of charge 1+ or 2+, a Co^{2+} band, and two more substantial chromium bands. From spectra as well as the strength of acid required to move these bands (3M-$HClO_4$), it could be concluded that $[Cr(H_2O)_6]^{3+}$ was not present, and that instead binuclear chromium(III) species with 3+ or 4+ charges were formed. No free maleate (<0.5%) was obtained (titration at 60° with $KMnO_4$) in the initial solution collected from the ion-exchange column. Similar 2 : 1 experiments were carried out with μ(hhm) and μ(hhf),

TABLE 1

Rate constants for the first stage [a] of the Cr^{2+} reduction of μ-maleato- and μ-fumarato-complexes, $I = 1.0$M-$(LiClO_4)$. Number of runs which have been averaged indicated in parentheses

t/°C	$[H^+]$ / M	$10^2[Cr^{2+}]$ / M	$10^3[(Co^{III})_2]$ / M	k_{Cr} / l mol^{-1} s^{-1}
(i) μ(am) [b]				
15.0	0.10	5.03	0.50	0.412(2)
	0.60	5.03	0.50	0.398(2)
25.0	0.02	1.33	0.35	0.60(1)
	0.10 [c]	4.87	0.50	0.65(3)
	0.52	1.37	0.54	0.57(1)
	0.59	2.51	0.35	0.61(1)
	0.60 [c]	4.87	0.50	0.608(4)
	0.73	3.45	0.54	0.59(1)
	0.95	1.31	0.35	0.61(1)
35.0	0.10	5.49	0.50	0.798(2)
	0.20	5.32	0.50	0.776(2)
	0.40	1.17	0.50	0.773(2)
	0.40	2.20	0.50	0.795(2)
	0.40	5.32	0.25	0.881(2)
	0.40	5.32	0.50	0.797(2)
	0.40	10.50	0.50	0.797(2)
	0.40	5.32	1.25	0.810(2)
	0.85	5.45	0.50	0.798(2)
45.0	0.10	4.98	0.50	1.20(2)
	0.60	4.98	0.50	1.17(2)
(ii) μ(hhm) [d]				
3.5	0.64	4.44	2.0	1.03(4)
25.0	0.06	1.10	0.5	1.77(3)
	0.14	2.31	1.0	1.74(4)
	0.14	2.31	2.0	1.69(2)
	0.14	4.77	2.0	1.88(3)
	0.14	9.53	2.0	1.90(4)
	0.64	2.31	1.0	1.71(2)
	0.64	2.31	2.0	1.67(4)
	0.64	4.77	2.0	1.90(4)
	0.64	9.53	2.0	2.00(4)
35.0	0.64	4.44	2.0	2.53(3)
45.0	0.64	4.44	2.0	3.22(4)
(iii) μ(hhf) [d]				
2.5	0.06	5.61	2.0	1.78(2)
	0.56	5.61	2.0	1.61(2)
25.0	0.05	5.97	2.0	2.81(2)
	0.12	2.91	2.0	2.61(2)
	0.12	5.81	2.0	2.86(2)
	0.62	1.80	0.5	2.45(2)
	0.62	2.91	2.0	2.57(2)
	0.62	5.85	2.0	2.59(2)
	0.62	11.65	0.5	2.63(2)
	0.62	11.65	3.0	2.55(2)
35.0	0.06	5.47	2.0	3.11(1)
	0.56	5.47	2.0	3.18(2)
45.0	0.06	5.47	2.0	3.95(2)
	0.56	5.47	2.0	4.02(2)

[a] Second stage not detected. [b] $\lambda = 517$ nm. [c] $\lambda = 517$ and 470 nm. [d] $\lambda = 524$ nm.

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[6] K. Wieghardt, *J.C.S. Dalton*, 1973, 2548.

[7] E. S. Gould, *J. Amer. Chem. Soc.*, 1966, **88**, 2983.

[8] Los Alamos Report LA 2367 (1959) and Addenda by R. H. Moore and R. K. Zeigler.

[H$^+$] = 0.1 and 0.9M (Table 4) and again indicated formation of substantial amounts of binuclear chromium(III) product. The total chromium(III) collected was in all cases in satisfactory agreement with the Co^{2+} produced (>92% recovery).

TABLE 2

Kinetic data for the Cr^{2+} reduction of cobalt(III) complexes containing maleate and fumarate, I = 1.0M(LiClO$_4$)

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.
μ(am)	0.59 ± 0.03	5.5 ± 0.2	−41.3 ± 0.7	This work
μ(hhm)	1.87 ± 0.05	4.3 ± 0.2	−43.0 ± 0.5	This work
μ(hhf)	2.64 ± 0.09	2.8 ± 0.2	−47.1 ± 0.7	This work
[Co(NH$_3$)$_5$(maleato)]$^{2+}$	200 [a]	2.9	−38	1
[Co(NH$_3$)$_5$(fumarato)]$^{2+}$	1.32 [b]	6.7	−36	3
	3.48 [c]	2.9	−45	3

[a] Data for paths yielding chelated and unidentate products have not been separated. [b] [H$^+$]-Independent path. [c] [H$^+$]-Dependent path; rate constant has units l^2 mol^{-2} s^{-1}.

Kinetics of the V^{2+} *Reduction of μ-Maleato- and μ-Fumarato-complexes.*—Absorbance changes were monitored at the peak position λ = 517 or 524 nm for the dicobalt(III) reactant. Reactions were studied with V^{2+} in large excess of (Co$^{\mathrm{III}}$)$_2$ and plots of log(O.D.$_t$ − O.D_∞) against time were linear to at least 93% completion. There was no indication under any of the conditions reported for a second stage slower than the first. All three reactions conform to the simple rate expression (3).

TABLE 3

Product analyses for the Cr^{2+} reduction (25 °C) of μ(am), [(Co$^{\mathrm{III}}$)$_2$] = 5.6 × 10^{-2}M, [H$^+$] = 0.2M, I = 1.0M-(LiClO$_4$). Products are quoted relative to Co^{2+}

Reactant ratio [Cr^{2+}]/[(Co$^{\mathrm{III}}$)$_2$]	Co^{2+}	Cr$^{\mathrm{III}}$ product [a] Species 1	Cr$^{\mathrm{III}}$ product [a] Species 2
1.05 [b]	1.0	0.69	0.24
2.11	2.0	1.18	0.78

[a] Species 1 and 2 are believed to be dimeric. Product ratios are calculated on basis of number of metal atoms present. [b] Approximately half the (Co$^{\mathrm{III}}$)$_2$ remains unreacted.

TABLE 4

Product analyses for the Cr^{2+} reduction (*ca.* 20 °C) of μ(hhm) and μ(hhf), [(Co$^{\mathrm{III}}$)$_2$] = *ca.* 0.006M, I = 1.0M-(LiClO$_4$). Concentrations of the binuclear cobalt(III) complex were in *ca.* 3% excess of the stoicheiometric amount of Cr^{2+}. Products are quoted relative to Co^{2+}

Complex	[H$^+$]/M	Co^{2+}	Low charge Cr$^{\mathrm{III}}$	[Cr(H$_2$O)$_6$]$^{3+}$	Cr$^{\mathrm{III}}$ dimer [a]
μ(hhm)	0.9	2.0	0.10	0.16	1.70
	0.1	2.0	0.16	0.24	1.74
μ(hhf)	0.9	2.0	0.06	0.12	1.80
	0.1	2.0	0.08	0.20	1.78

[a] Expressed as mononuclear chromium(III).

$$\frac{-\mathrm{d}[(\mathrm{Co^{III}})_2]}{\mathrm{d}t} = k_{\mathrm{V}}[\mathrm{V}^{2+}][(\mathrm{Co^{III}})_2] \qquad (3)$$

The reactions with μ(am) and μ(hhf) are independent of [H$^+$], whereas with μ(hhm), [H$^+$] = 0.1—0.7M, a dependence (4) is observed (Figure). Individual k_{V}

$$k_{\mathrm{V}} = k_0 + k_{-1}[\mathrm{H}^+]^{-1} \qquad (4)$$

values are listed in Table 5. Activation parameters and k_{V}(25 °C) values (computed as for Cr^{2+}) are listed in Table 6. Absorbance changes at λ = 517/524 nm indicated that total reduction of the binuclear cobalt(III) complexes occurred during the observed single-stage process. Calculated absorbance changes for complete reduction of μ(am), Δε = 351 l mol^{-1} cm^{-1}, were in satisfactory agreement with values obtained by extrapolating (to zero time) plots of log (O.D.$_t$ − O.D.$_\infty$) against time, Δε = 320 ± 30 l mol^{-1} cm^{-1}. Substitution on vanadium(III) is rapid and the maleate is probably uncomplexed on completion of the reaction. No evidence for V^{2+} reduction of uncomplexed maleic acid was obtained. A satisfactory correspondence between

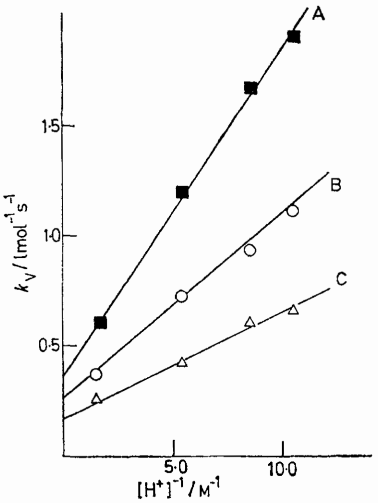
TABLE 5

Rate constants for the first stage [a] of the V^{2+} reduction of μ-maleato- and μ-fumarato-complexes, I = 1.0M-(LiClO$_4$). Number of runs which have been averaged are indicated in parentheses

t/°C	[H$^+$] / M	10^2[V^{2+}] / M	10^3[(Co$^{\mathrm{III}}$)$_2$] / M	k_{V} / l mol^{-1} s^{-1}
(i) μ(am) [b]				
25.0	0.40	6.40	1.0	1.46(2)
35.0	0.40	6.40	1.0	2.53(2)
45.0	0.065	2.60	1.0	4.61(2)
	0.40	1.15	0.25	3.91(2)
	0.40	2.00	1.0	4.76(2)
	0.40	3.14	1.0	4.30(2)
	0.40	6.48	1.0	4.43(1)
	0.70	2.00	0.5	4.90(2)
	0.70	3.14	1.0	4.08(2)
	0.70	6.48	1.0	4.37(1)
(ii) μ(hhm) [c]				
25.0	0.096	3.33	2.0	0.655(3)
	0.120	3.33	2.0	0.603(3)
	0.186	6.84	2.0	0.422(2)
	0.686	6.84	2.0	0.360(2)
35.0	0.096	3.33	2.0	1.12(3)
	0.120	3.33	2.0	0.937(3)
	0.186	6.84	2.0	0.722(4)
	0.686	6.84	2.0	0.360(1)
45.0	0.096	3.33	2.0	1.90(1)
	0.120	3.33	2.0	1.67(2)
	0.186	6.84	2.0	1.19(3)
	0.593	1.23	0.5	0.585(2)
	0.593	3.38	2.0	0.605(2)
	0.686	6.84	2.0	0.650(2)
(iii) μ(hhf) [c]				
25.0	0.71	6.86	1.0	0.102
35.0	0.71	6.36	1.0	0.150(2)
44.0	0.22	2.52	1.0	0.238(2)
	0.22	6.36	1.0	0.233(2)
	0.71	1.12	0.5	0.211(2)
	0.71	2.52	2.0	0.234(1)
	0.71	6.36	1.0	0.231(2)

[a] Second stage not observed. [b] λ = 517 nm. [c] λ = 524 nm.

observed and calculated absorbance changes based on total reaction is noted.



The dependence of rate constants k_V on $[H^+]^{-1}$ for the V^{2+} reduction of the first cobalt(III) of the di-μ-hydroxo-μ-maleato-bis[triamminecobalt(III)] complex, I = 1.0M($LiClO_4$). A = 45 °C, B = 35 °C, and C = 25 °C

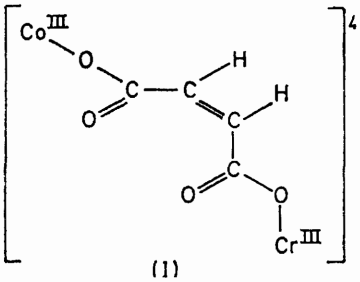
DISCUSSION

Reduction of acetato- and formato-bridged binuclear cobalt(III) complexes by Cr^{2+} has been shown to occur by an outer-sphere mechanism.[5] Consequently the oxygen atoms of the adjacent carboxylate group in binuclear complexes are fully utilised when bridging between cobalt(III) centres, and are not available for inner-sphere attack by Cr^{2+} (see also Discussion in ref. 9). Any evidence for an inner-sphere mechanism in the present studies therefore requires attack at the remote carboxylate function.

Outer-sphere reduction of carboxylato-bridged dicobalt(III) complexes by Cr^{2+} generally occurs with second-order rate constants of *ca.* 10^{-3} l mol^{-1} s^{-1}.[10] If outer-sphere reductions are effective then the rate constants, k_{Cr}(25 °C) $\geqslant 0.59$ l mol^{-1} s^{-1} (Table 2), are considerably higher than any reasonable estimate might suggest. Coupled with this k_{Cr}/k_V ratios of >0.41 are certainly not in line with values predicted for outer-sphere reduction of a common oxidant by Cr^{2+} and V^{2+} (ratio *ca.* 0.020).[10] Either k_{Cr} or k_V (or both) must, therefore, be inner sphere.

An excellent test of mechanism in the case of Cr^{2+} reduction is whether the proposed bridging ligand is complexed in the normally substitution-inert chromium(III) product. Analysis of primary products shows that little or no $[Cr(H_2O)_6]^{3+}$ is produced, and an outer-sphere reduction of the first cobalt(III) is not, therefore, feasible. If the second stage of reaction is also inner sphere then the maleate and fumarate will be incorporated into binuclear chromium(III) products. We consider a two-equivalent change with intermediate formation of chromium(IV) as extremely unlikely (see footnote comments, ref. 9).

More detailed inspection of ion-exchange results with μ(am) (Table 3) shows that two predominant chromium(III) species, (1) and (2), are produced, whether a 1 : 1 or 2 : 1 ratio of $[Cr^{2+}]/[(Co^{III})_2]$ is taken. Together with absorbance changes from kinetic runs this evidence requires a second stage of reduction which is faster than the first. Although the precise structures of (1) and (2) are uncertain, evidence for binuclear chromium(III) species incorporating the organic ligand and with either 3+ or 4+ charges has been obtained. The product of the first stage is believed to be a cobalt(III)–chromium(III) intermediate as illustrated (ammonia and water ligands are omitted for clarity). The Cr^{2+} reduction of $[Co(NH_3)_5(maleato)]^{2+}$ occurs with and without chelation of Cr^{2+} to the maleato-ligand in the activated complex, and further Cr^{2+} reduction of the intermediate (I) can no doubt proceed by any or all of the three mechanisms adjacent attack, adjacent attack with chelation, or remote attack.[11] It is not, therefore, surprising that the second stage is more rapid and that different chromium(III) products are obtained. Whatever the precise structure of the final products, and details of the second stage of reduction, it is clear that the first stage must be inner sphere to produce any binuclear maleatochromium(III) species.



(I)

With both di-μ-hydroxo-complexes further variations are possible because following reduction and loss by aquation of the first cobalt, the second cobalt(III) has two water molecules in its inner-co-ordination sphere, which along with the carboxylate ligand can be utilized in the subsequent reduction *via* a single- or double-bridged activated complex. Mononuclear chromium(III) products (Table 4) probably result from utilization of H_2O sites alone for inner-sphere reduction. Whether only a single chromium(III) dimer species is obtained in these experiments was not clearly established. If mixed cobalt(III)–chromium(III) products were present we would expect the red cobalt(III) chromophore to be dominant, and clearly evident in the ionic-exchange experiments, since it generally absorbs more strongly. No such colour was observed which suggests that mixed products are not present in significant amounts following 1 : 1 consumption of the Cr^{2+} reductant.

The widely differing rate constants observed for the

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[9] A. T. Thornton, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, preceding paper.

[10] See *e.g.* K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, **1973**, 736.

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

Cr^{2+} reduction of μ(am) and [Co(NH$_3$)$_5$(maleato)]$^{2+}$, both of which involve the remote carboxylate group, requires further comment. Rate constants in the case [Co(NH$_3$)$_5$(maleato)]$^{2+}$ benefit from chelation of the Cr^{2+} to the maleate, where 80% of the reaction is known to proceed in this manner. The other 20% of reaction yielding the unidentate chromium(III) product also proceeds at an enhanced rate, and some sort of association between adjacent and remote carboxylate groups (possibly involving the H$^+$ of the pendant carboxylate) seems likely. A similar association is not, we feel, possible in the case of the dimer.

Rate constants and activation parameters for the Cr^{2+} reduction of [Co(NH$_3$)$_5$(fumarato)]$^{2+}$, [H$^+$]-dependent path, and μ(hhf) (Table 2) are in very good agreement. This strongly suggests that attack *via* the remote carboxylate function is operative in both cases. The absence of any [H$^+$]-dependence in the case of the binuclear complex supports the explanation involving protonation at the adjacent carboxylate group for the mononuclear complex.[3,4] Thus a cobalt(III) in the binuclear complex, and a proton in the mononuclear case would seem to effect the same function.

The ability of both fumarate and maleate to conduct electrons is very similar, except when maleate exercises a geometric advantage stemming from the proximity of the carboxylate groups, as in the reduction of [Co(NH$_3$)$_5$(maleato)]$^{2+}$. All the examples in Table 2 have low activation enthalpies (2.8—6.7 kcal mol^{-1}), which is in accordance with the low energy requirements for electron transfer through a carbonyl function.

Protonated and unprotonated forms of dicobalt(III) complexes containing dibasic ligands often exist within the range of acidities covered by studies of this kind, and [H$^+$]$^{-1}$ terms can, therefore, contribute to rate laws. Such terms are observed in the Cr^{2+} and V^{2+} reductions of the μ(NH$_2$,oxalato) complex,[12] when the unprotonated form reacts significantly faster than the protonated form. With maleate and fumarate in mononuclear and binuclear situations [H$^+$]$^{-1}$ dependences are not generally observed, and it follows that protonated and unprotonated forms must react at the same rate, or acid dissociation constants must be $\ll$ [H$^+$]. The one exception is the V^{2+} reduction of μ(hhm). It is of course remarkable that an [H$^+$]$^{-1}$ dependence should manifest itself in the V^{2+} but not the Cr^{2+} reduction of μ(hhm), and that no similar [H$^+$]$^{-1}$ dependence should be operative for the V^{2+} reduction of μ(am). An examination of molecular models suggests that the pendant carboxylate of the μ(hhm) complex approaches the cobalt(III) centres more closely than in the case of the μ(am) complex.* We suggest, therefore, that binding of the reductant to the pendant carboxylate and reduction of the first cobalt(III) as in an outer-sphere reaction, and not *via* the organic ligand, is occurring with μ(hhm) but not μ(am). The formation of such a precursor complex would be expected to be sensitive to [H$^+$], see for example ref. 14. It is known[15] that V^{2+} does not generally avail itself of electron transfer by remote inner-sphere attack as does Cr^{2+}. Precursor complex formation followed by ' outer-sphere ' electron transfer has already been proposed as a possible mechanism for the Cr^{2+} and V^{2+} reduction of the μ(OH,OH,phthalato) complex *via* the [H$^+$]$^{-1}$ path.[9] A similar pathway in the Cr^{2+} reduction of μ(hhm) does not make an effective contribution because the route involving remote attack (and electron transfer by way of the conjugate-double bonds) is much more favourable. The mechanism which we suggest for the [H$^+$]$^{-1}$ path in the V^{2+} reduction of μ(hhm) is also apparent in the Cr^{2+} and V^{2+} reductions of the μ(NH$_2$,malonato) complex, and will be considered further in the context of that study.[16]

TABLE 6

Summary of kinetic data for the first stage of the V^{2+} reduction of μ-maleato- and μ-fumarato-complexes, $I = 1.0$M(LiClO$_4$)

Complex	k_V(25 °C) l mol^{-1} s^{-1}	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$ cal K^{-1} mol^{-1}
μ(am)	1.46 ± 0.06	9.8 ± 0.5	−24.9 ± 2.0
μ(hhm)	0.164 ± 0.05 [a]	5.8 ± 0.7	−42.3 ± 2.0
	0.045 ± 0.002 [b]	10.6 ± 0.5	−29.3 ± 2.0
μ(hhf)	0.099 ± 0.005	7.5 ± 0.4	−38.0 ± 1.0

[a] [H$^+$]-Independent path. [b] [H$^+$]$^{-1}$-Dependent path; if acid dissociation constant is assumed to be same as first acid dissociation constant of maleic acid, $K = 2.24 \times 10^{-2}$ l mol^{-1}, K. S. Rajan and A. E. Martell, *J. Inorg. Nuclear Chem.*, 1967, **29**, 523, then corrected rate constant is 2.01 l mol^{-1} s^{-1}.

Finally it is concluded that the V^{2+} reduction of μ(hhm), [H$^+$]$^{-1}$-independent pathway, and μ(hhf) are outer sphere. Activation parameters lie well away from the range associated with inner-sphere substitution controlled reactions,[17] and rate constants are in the range expected for outer-sphere reactions (k_{Cr}/k_V = *ca.* 0.020 is obtained assuming an outer-sphere k_{Cr} contribution of *ca.* 10^{-3} l mol^{-1} s^{-1}). The rate constant for the V^{2+} reduction of the μ(am) complex is borderline, although in view of the assignment for μ(hhm) an outer-sphere process would seem likely. The kinetic parameters for the [H$^+$]$^{-1}$ pathway in the reaction of μ(hhm) (which have to be corrected for the acid dissociation process) do not rule out a V^{2+} substitution-controlled process.

EXPERIMENTAL

Aqueous perchloric acid solutions of chromium(II) perchlorate and vanadium(II) perchlorate were prepared by electrolytic reduction of chromium(III) and vanadium(IV) perchlorate solutions respectively at a mercury-pool cathode. The chromium(III) (from CrO$_3$) and vanadium(IV)

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* Non-planarity of the atoms in the ring formed by the bridging ligands and the two metals is assumed as in the case for the μ-amido-μ-sulphato-complex.[13]

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

[13] U. Thewalt, *Acta Cryst.*, 1971, **B27**, 1744.

[14] C. Norris and F. R. Nordmeyer, *Inorg. Chem.*, 1971, **10**, 1235.

[15] See for example J. C. Chen and E. S. Gould, *J. Amer. Chem. Soc.*, 1973, **95**, 5544; A. Zanella and H. Taube, *ibid.*, 1972, **94**, 6403. An example of V^{2+} remote attack has been reported in ref. 14.

[16] B. Kipling, K. Wieghardt, and A. G. Sykes, unpublished work.

[17] N. Sutin, *Accounts Chem. Res.*, 1968, **1**, 225; M. R. Hyde, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1973, 2730.

(from $VOSO_4$) solutions were prepared by procedures previously described. Lithium perchlorate was obtained by neutralization of AnalaR perchloric acid with lithium carbonate (Hopkin and Williams Reagent Grade) and recrystallization until free from anion impurities. A Durrum–Gibson stopped-flow spectrophotometer and for some $\mu(NH_2,maleato)$ runs a Unicam SP 500 spectrophotometer were used for all kinetic runs. Rigorous air-free techniques (Atlas nylon syringes, serum caps) were required at all times for Cr^{2+} and V^{2+} solutions.

Details of the preparation and characterization of complexes di-μ-hydroxo-μ-maleato-bis[triamminecobalt(III)], $[(NH_3)_3Co\cdot\mu(OH,OH,C_2H_2C_2O_4H)\cdot Co(NH_3)_3](ClO_4)_3\cdot NaClO_4\cdot H_2O$, and μ-fumarato-di-μ-hydroxo-bis[triamminecobalt(III)], $[(NH_3)_3Co\cdot\mu(OH,OH,C_2H_2C_2O_4H)\cdot Co(NH_3)_3](ClO_4)_3\cdot 1.5H_2O$, are given elsewhere.[6] The preparation of the μ-amido-μ-maleato-complex, μ(am), was as follows.

Preparation of μ-Amido-μ-maleato-bis[tetra-amminecobalt(III)].—The μ-amido-μ-chloro-bis[tetra-amminecobalt(III)] chloride complex (1 g) [18] was dissolved in a solution of maleic acid (12 g, May and Baker, Laboratory Chemicals) in water (35 ml) at 50 °C and maintained at this temperature for 1 h. The solution was reduced to *ca.* 5 ml by evaporation under reduced pressure at 40—50 °C. The cooled solution was then filtered and the solid washed generously with ethanol to remove excess of maleic acid. Addition of an equal volume of concentrated $HClO_4$ to the initial filtrate was used to supplement the yield.

The crude μ(am) (1.1 g) was dissolved in the minimum (*ca.* 1 ml) of 0.1M-$HClO_4$ at 45 °C, filtered, and the solution allowed to cool slowly to room temperature. Large dark red crystals were obtained when the solution was set aside overnight, and these were filtered off, washed with ethanol and then ether, and dried by suction. The pink powder was dissolved in 0.1M-$HClO_4$ at room temperature (*ca.* 4 ml) and an equal volume of concentrated $HClO_4$ was added. The precipitate was collected and washed as before, yield 0.71 g. This sample was largely protonated μ-maleato-complex.

A solution of 1.0M-NaOH (0.8 ml) was added to μ(am) (0.6 g) dissolved in a minimum amount of water (*ca.* 5 ml) at room temperature. Sodium perchlorate crystals (4 g) were added and the solution was set aside at 0 °C for 3 h. The crystals were filtered off and washed with ethanol and ether; yield 0.3 g. Dehydration over P_2O_5 revealed negligible loss in weight over 4 weeks {Found: C, 7.3; H, 4.4; N, 17.9%. Calc. for $[(NH_3)_4Co\cdot\mu(NH_2,C_2H_2C_2O_4)\cdot Co(NH_3)_4][ClO_4]_3$: C, 7.0; H, 4.1; N, 18.4%}.

Solutions of cobalt(II) obtained following ion-exchange separation of reaction products were determined spectrophotometrically as a $[CoCl_4]^{2-}/[CoCl_3(H_2O)]^-$ mixture by making up the solution in *ca.* 10M-HCl and measuring the absorption at various peak positions in the range 600—700 nm. Since the equilibrium between $[CoCl_4]^{2-}$ and $[CoCl_3(H_2O)]^-$ is dependent upon [HCl] the spectrum will also be [HCl] dependent. Consequently solutions containing known amounts of cobalt(II) were used to standardize the procedure. Absorption coefficients measured after dilution of concentrated HCl (11.3M) by 20% (4 parts HCl, 1 part water) at $\lambda = 628$ nm (sh) were 256 ± 5 l mol^{-1} cm^{-1}. Chromium(III) fractions following ion-exchange separation were determined by oxidation to chromium(VI) using H_2O_2 in 1.0M-NaOH. Solutions of chromium(VI) were then determined spectrophotometrically $\lambda = 372$ nm, $\varepsilon = 4.82 \times 10^3$ l mol^{-1} cm^{-1} for $[CrO_4]^{2-}$.

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[18] M. B. Stevenson and A. G. Sykes, *J. Chem. Soc. (A)*, 1969, 2979.