The Cr^{2+} and V^{2+} Reduction of μ-Carboxylato Dicobalt(III) Ammine Complexes. Part VIII.† The Mechanism of Reduction of the Di-μ-hydroxo-μ-oxalato-bis[triamminecobalt(III)] Complex‡

By **Ioan Baldea, Karl Wieghardt,** and **A. Geoffrey Sykes,*** Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

The kinetics of the Cr^{2+} and V^{2+} reductions of the dicobalt(III) complex $[(NH_3)_3Co{\cdot}\mu(OH,OH,C_2O_4){\cdot}Co(NH_3)_3]^{2+}$ have been studied, $I = 1.0$M ($LiClO_4$). Reduction of the first cobalt(III) is rate determining and the only observed step. With Cr^{2+} the products are equivalent amounts of $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_4C_2O_4]^+$. It is concluded that reduction of the first cobalt(III) occurs with Cr^{2+} attack at the remote end of the oxalate. The constant for protonation of the μ-oxalato-ligand has been determined by spectrophotometric method and at 25 °C is 19.9 l mol^{-1}. Rate constants (l mol^{-1} s^{-1}), enthalpies (kcal mol^{-1}) and entropies of activation (cal K^{-1} mol^{-1}) are for the protonated complex 4.7, 9.0, −25.1, and for the unprotonated complex 1.31×10^2, 6.3, −27.9 respectively at 25 °C. The second stage differs from that observed in the Cr^{2+} reduction of the $[(NH_3)_4Co{\cdot}\mu(NH_2,C_2O_4){\cdot}Co(NH_3)_4]^{3+}$ complex which yields a binuclear chromium(III) product in a slower second stage (consecutive treatment required). Rate constants (l mol^{-1} s^{-1}) at 25 °C for the V^{2+} reduction of $[(NH_3)_3Co{\cdot}\mu(OH,OH,C_2O_4){\cdot}Co(NH_3)_3]^{2+}$ are 1.55 for the protonated and 27.8 for the unprotonated complex.

To help in the further understanding of electron transfer occurring *via* organic ligands, and the behaviour of dicobalt(III) complexes we have studied the Cr^{2+} and V^{2+} reductions of the di-μ-hydroxo-μ-oxalato-bis[triamminecobalt(III)] complex, $[(NH_3)_3Co{\cdot}\mu(OH,OH,C_2O_4){\cdot}Co(NH_3)_3]^{2+}$. With Cr^{2+} the first stage has similar features to those observed for reduction of the μ-amido-μ-oxalato-bis[tetra-amminecobalt(III)] complex, $[(NH_3)_4Co{\cdot}\mu(NH_2,C_2O_4){\cdot}Co(NH_3)_4]^{3+}$. Different behaviour is apparent in the second stage however. The overall pattern of behaviour for Cr^{2+} and V^{2+} reductions of μ-carboxylato binuclear cobalt(III) complexes in the μ-amido- and di-μ-hydroxo-series is summarized.

The isolation and characterization of the di-μ-hydroxo-μ-oxalato-complex has been described previously.[1]

RESULTS

Stability of the Complex.—Solutions of the oxalato-complex, $[HClO_4] = 0.1$ and 1.0M, $I = 1.0$M ($LiClO_4$), $\lambda = 350$—600 nm, gave no change in spectra for at least 55 h at room temperature. There was no evidence for hydroxo-bridge cleavage processes.

Protonation Constant.—The constant for protonation of the oxalate bridge, K, was determined by spectrophotometry at 340 nm, $[H^+] = 0.01 - 1.0$M, as described previously for the μ-amido-μ-oxalato-complex.[2] At 25 °C, $I = 1.0$M ($LiClO_4$) a value of 19.9 ± 1.8 l mol^{-1} was obtained.

Products from the Cr^{2+} Reduction.—These were determined by ion-exchange separation of reactant solutions with $Cr^{2+} : (Co^{III})_2$ in the ratio 1 : 1 and 2 : 1. Fractions of $[Cr(H_2O)_4C_2O_4]^+$, Co^{2+}, and $[Cr(H_2O)_6]^{3+}$ were collected and analysed for chromium and cobalt content (Table 1).[3] The fraction $[Cr(H_2O)_4C_2O_4]^+$ gave peaks at 415 and 553 nm which are in accordance with published values for this complex.[4] All observations are consistent with a stoicheiometry $2Cr^{2+} + (Co^{III})_2$, and the same stoicheiometry is assumed for the V^{2+} reaction.

The products obtained from the Cr^{2+} reduction of the μ-amido-μ-oxalato-complex were not previously determined.[2] Consistent with the reaction sequence proposed in that study we confirm that a binuclear chromium(III) species is the dominant product (>90%) for 1 : 1 and 2 : 1 ratios of $Cr^{2+} : (Co^{III})_2$, $[H^+] = 0.2$M.

Kinetics.—Both the Cr^{2+} and V^{2+} reductions were investigated by stopped-flow spectrophotometry, $\lambda = 524$ nm (ε 110 l mol^{-1} cm^{-1}), with the reductant in large excess. Solutions were adjusted to ionic strength $I = 1.0$M ($LiClO_4$), and $[H^+]$ 0.02—0.80M. Only a single stage of reaction was observed, with Δε as for the complete reaction, and absorbance (O. D.) plots of log (O. D.$_t$ − O. D.$_\infty$) against time linear to >93% completion. Rate constants obtained from such plots gave a first-order dependence on reductant. Second-order rate constants are as listed in Tables 2 and 3. The hydrogen-ion dependence of k_{obs} can be accounted for by the sequence (1)—(3).

TABLE 1

Reaction products as determined following ion-exchange separation of reactant solutions $[(Co^{III})_2] = 4.8 \times 10^{-2}$M, $[H^+] = 0.38$M, $I = 1.00$M($LiClO_4$). Reactions carried out at *ca.* 20 °C

$[Cr^{2+}] : [(Co^{III})_2]$	$[Co(H_2O)_6]^{2+}$	$[Cr(H_2O)_4C_2O_4]^+$	$[Cr(H_2O)_6]^{3+}$
1 : 1 [a]	1.0 [b]	0.53	0.42
2 : 1 [a]	2.0 [c]	0.92	0.98
2 : 1	2.0 [d]	0.84	0.96

[a] $[Cr^{2+}]$ made up *ca.* 4% in excess of this ratio. [b] 92% recovery, $[H^+] = 0.38$. [c] 97% recovery, $[H^+] = 0.38$. [d] 96% recovery, $[H^+] = 0.10$.

$$\mu(OH,OH,C_2O_4) + H^+ \overset{K}{\rightleftharpoons} \mu(OH,OH,C_2O_4H) \quad (1)$$

$$Cr^{2+} + \mu(OH,OH,C_2O_4H) \xrightarrow{k_a} \quad (2)$$

$$Cr^{2+} + \mu(OH,OH,C_2O_4) \xrightarrow{k_b} \quad (3)$$

Assuming reaction (1) to be rapid the relationship (4) is obtained.

$$k_{obs}(1 + K[H^+]) = k_aK[H^+] + k_b \quad (4)$$

A good linear fit was obtained at all temperatures with $K = 20 \pm 2$ l mol^{-1} (Figure 1). The latter is consistent with the measured value of 19.9 l mol^{-1}. Rate constants

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† Part VII of this work is ref. 14.

‡ No reprints available.

[1] K. Wieghardt, *Z. anorg. Chem.*, 1972, **391**, 142.

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

[3] A. T. Thornton, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, 1976, 147.

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

k_a and k_b were obtained using an unweighted least-squares treatment with $K = 20$ l mol^{-1}; activation parameters were obtained from a non-linear least-squares programme (weighting factor unity).[5] The same treatment was used for the V^{2+} study. All the data are summarized in Table 5.

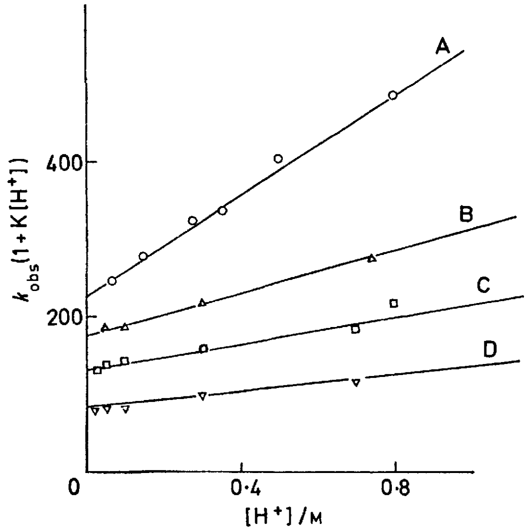

FIGURE 1 The dependence of k_{obs} on $[H^+]$, equation (4), for the Cr^{2+} reduction of the complex with $K = 20$ l mol^{-1}, $I = 1.0M$ ($LiClO_4$): A = 45, B = 35, C = 25, and D = 15 °C

TABLE 2

Second-order rate constants for the Cr^{2+} reduction of the complex $[(NH_3)_3Co\cdot\mu(OH,OH,C_2O_4)\cdot Co(NH_3)_3]^{2+}$ complex, first stage rate determining, $I = 1.0M$ ($LiClO_4$)

Temp. (t/°C)	$[H^+]$ M	$10^2[Cr^{2+}]$ M	$10^3[(Co^{III})_2]$ M	k_{obs} l mol^{-1} s^{-1}
15.0	0.02	2.96	1.02	56.4(4)
	0.05	2.63	1.02	40.3(3)
	0.10	2.67	1.02	27.6(3)
	0.30	2.65	1.02	14.2(3)
	0.70	2.90	1.02	7.8(3)
25.0	0.024	3.92	2.03	88.8(3)
	0.05	3.81	2.03	68.0(2)
	0.10	7.94	2.03	47.7(3)
	0.30	3.81	2.03	22.8(3)
	0.70	3.81	2.03	12.2(3)
	0.80	6.25	2.00	12.8(4)
35.0	0.045	3.70	1.02	97.5(5)
	0.10	3.02	1.02	62.5(4)
	0.30	2.74	1.02	31.2(4)
	0.74	3.06	1.02	18.0(3)
45.0	0.07	1.04	0.4	102(3)
	0.136	1.28	0.4	75.0(3)
	0.272	2.78	0.8	50.5(3)
	0.35	4.80	1.2	42.2(4)
	0.50	1.17	0.4	36.7(2)
	0.80	6.25	2.0	28.7(4)

DISCUSSION

The identification of $[Cr(H_2O)_4C_2O_4]^+$ as a reaction product indicates that one of the Cr^{2+} reductions involves inner-sphere attack at the oxalate. A binuclear chromium(III) product would be expected if the Cr^{2+} reduction of both cobalt(III) centres occurred at the oxalate, as is the case for the μ-amido-μ-oxalato-complex. It is unlikely that either stage in the Cr^{2+} reduction of the di-μ-hydroxo-μ-oxalato is outer-sphere in view of the rapidity of both steps. Rather do we favour a reaction sequence (5)—(6), where (6) is occurring by Cr^{2+} attack at the site of the aquo-ligands attached to the cobalt(III). Only one stage for reduction is observed, and this

$$Cr^{2+} + Co^{III}(oxal)Co^{III} \longrightarrow Cr^{III}(oxal)Co^{III} + Co^{2+} \quad (5)$$

$$Cr^{2+} + Cr^{III}(oxal)Co^{III} \longrightarrow Cr^{III} + Cr^{III}(oxal) + Co^{2+} \quad (6)$$

together with the similarity of product analyses for 1 : 1 and 2 : 1 reactant solutions (Table 1), clearly indicates that reaction (6) is rapid compared with reaction (5).

TABLE 3

Rate constants for the V^{2+} reduction of $[(NH_3)_3Co\cdot\mu(OH,OH,C_2O_4)\cdot Co(NH_3)_3]^{2+}$ first stage rate determining at 25 °C, $I = 1.0M$ ($LiClO_4$)

$[H^+]$ M	$10^2[V^{2+}]$ M	$10^3[(Co^{III})_2]$ M	k_{obs} l mol^{-1} s^{-1}
0.104	0.88	0.4	10.6(4)
0.30	1.18	0.4	5.34(3)
0.50	2.36	0.8	3.77(3)
0.80	4.72	0.4	3.05(2)
0.80	4.72	1.2	3.21(3)

TABLE 4

Summary of rate constants for the Cr^{2+} reduction of protonated (k_a) and unprotonated (k_b) μ-oxalato-complex, $I = 1.0M$ ($LiClO_4$)

Temp. (t/°C)	k_a l mol^{-1} s^{-1}	k_b l mol^{-1} s^{-1}
15	2.85 ± 0.22	78.5 ± 1.5
25	4.68 ± 0.6	131 ± 5
35	6.57 ± 0.3	177 ± 2
45	16.4 ± 0.7	200 ± 8

TABLE 5

Summary of data for Cr^{2+} and V^{2+} reductions of the μ-amido-μ-oxalato-complex (ref. 1), and the di-μ-hydroxo-μ-oxalato-complex (this work)

Reactant		k (25 °C) l mol^{-1} s^{-1}	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$ cal K^{-1} mol^{-1}
$k_a(Cr^{2+})$	$\mu(NH_2,C_2O_4H)$	1.45	8.7	−28.6
	$\mu(OH,OH,C_2O_4H)$	4.7	9.0	−25.1
$k_b(Cr^{2+})$	$\mu(NH_2,C_2O_4)$	35.2	9.8	−18.6
	$\mu(OH,OH,C_2O_4)$	131	6.3	−27.9
$k_a(V^{2+})$	$\mu(NH_2,C_2O_4H)$	3.51	11.2	−18.6
	$\mu(OH,OH,C_2O_4H)$	1.55		
$k_b(V^{2+})$	$\mu(NH_2,C_2O_4)$	22.7	12.0	−11.2
	$\mu(OH,OH,C_2O_4)$	27.8		

This behaviour therefore contrasts with that observed for the reduction of the μ-amido-μ-oxalato-complex, reaction (5) followed by reaction (7), where the second

$$Cr^{2+} + Cr^{III}(oxal)Co^{III} \longrightarrow Cr^{III}(oxal)Cr^{III} + Co^{2+} \quad (7)$$

stage is slower than the first and formation of a chromium(III)–cobalt(III) intermediate is apparent. Kinetic data for the first stages are similar for both complexes (Table 5), where in both cases Cr^{2+} attack is believed to occur at the remote carboxylate group. Previous work has indicated that the bonded carboxylate of binuclear

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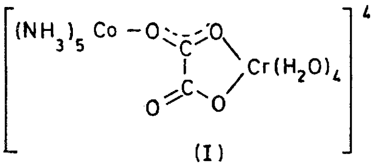
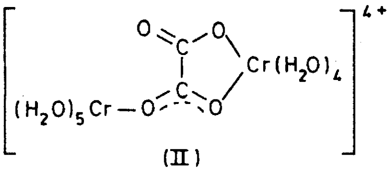
[5] Los Alamos Report LA 2367 (1959) and Addenda by R. H. Moore and R. K. Zeigler.

cobalt(III) complexes is not available for inner-sphere attack.[6]

We now consider the mechanisms of (6) and (7) in more detail. No unidentate oxalate complex $[Cr(H_2O)_5C_2O_4]^+$ has yet been isolated, and oxalate in such a situation is presumed to chelate rapidly to give $[Cr(H_2O)_4C_2O_4]^+$.[7] We propose that a similar chelation step occurs in the case of the chromium(III)–cobalt(III) complex formed in reaction (5) after departure of the labile cobalt(II). Thus in the reduction of the μ-amido-μ-oxalato-complex the primary product chelates rapidly at the chromium(III) to yield complex (I). Chelation has the effect of making attack of the second Cr^{2+} at the remaining oxalate site relatively slow. This second stage yields a binuclear chromium(III) complex (II), or if chelation occurs, (III). Similarly in the Cr^{2+} reduction of the di-μ-hydroxo-μ-oxalato-complex, it is proposed that the primary product rapidly chelates to give complex (IV).



(I)



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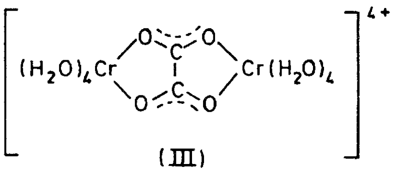
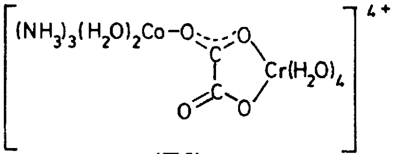


(III)



(IV)

If chelation did not occur then the second Cr^{2+} would presumably use the oxalate (with chelation) as well as the H_2O sites for reduction of the remaining cobalt(III). Such a process would yield a $(Cr^{III})_2$ product, whereas none was detected.

Acid dissociation at the H_2O ligand site is presumed to occur prior to reduction of complex (IV). The overall rate is, however, significantly faster than for the Cr^{2+} reduction of $[Co(NH_3)_5H_2O]^{3+}$.[8] This is attributed to an increase in acid dissociation, and/or a faster rate of reduction of the conjugate-base form, both effects stemming from the presence of three oxygens in the cobalt(III) co-ordination sphere.[9]

The data obtained for the V^{2+} reduction of the di-μ-hydroxo-μ-oxalato-complex indicate a slow/fast reaction sequence, as is observed for the V^{2+} reduction of the μ-amido-μ-oxalato-complex.[2] Rate constants are of similar magnitude for the reduction of protonated (k_a) and unprotonated (k_b) forms in the two studies (Table 5). For k_b at least the rate constant and previous data for V^{2+} reductions of oxalato Co^{III} complexes suggest a V^{2+} substitution-controlled mechanism.[10]

With the results of this study we conclude that all reductions of di-μ-hydroxo-μ-carboxylato-complexes so far studied proceed by a slow/fast reaction sequence. The reactions with phthalate,[3] maleate, and fumarate [11] carboxylate ligands yield binuclear chromium(III) products. Complexes in the μ-amido-series give fast/slow sequences not only with the μ-oxalato-complex,[2] but with the μ-sulphato-, μ-selenato-,[12] and μ-phosphato-complexes.[13] A slow (outer-sphere) first stage and slow/fast reaction sequence is however observed with the μ-acetato-, μ-formato-,[6] and μ-malonato-complexes.[14] The latter reaction contains an additional path as has already been discussed.[14]

The rate constants obtained for the first stages of Cr^{2+} and V^{2+} reductions are summarized in the form of a log–log plot (Figure 2). Points for two μ-superoxo-complexes,[15,16] a di-μ-hydroxo-complex,[17] three μ-oxalato-complexes,[18] and the μ-amido-complex,[19] all of which are outer-sphere, are also included. A linear correlation (8) is obtained for the Cr^{2+} and V^{2+} reductions

$$\log k_V = 1.02 \log k_{Cr} + 1.73 \qquad (8)$$

which are outer sphere. The line is coincident with a similar correlation for mononuclear cobalt(III) oxidants.[20] All other oxidants are reduced by Cr^{2+} *via* an inner-sphere mechanism. We wish to comment further on the mechanisms of V^{2+} reductions of this latter group.

The shaded area in Figure 2 corresponds to the upper

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

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

limit for V^{2+} substitution-controlled reactions,[10] and the $\mu(NH_2,C_2O_4)$,[2] $\mu(OH,OH,C_2O_4)$, $\mu(NH_2,SeO_4)$,[20] and $\mu(NH_2,SO_4)$ [21] complexes (points 16—19), almost certainly react with V^2 by this mechanism. It is equally clear that the rate constants for V^{2+} reductions of the μ(OH,OH, maleate),[11] μ(OH,OH,fumarate),[11] μ(OH,OH,-OFB), and μ(OH,OH,PFB) complexes [22] (points 24—27) are in the outer-sphere range. At present the only reactions in which V^{2+} is known to take advantage of the remote inner-sphere attack is with the N-co-ordinated nicotinic and isonicotinic penta-amminecobalt(III) complexes.[23] Of the remaining oxidants we are inclined to assign the V^{2+} reduction of $\mu(NH_2$,maleate) (point 23) to the outer-sphere category for consistency with μ(OH,OH, maleate), and the others tentatively to the substitution-controlled category. It is interesting to note that the latter includes the three complexes $\mu(NH_2,C_2O_4H)$, $\mu(NH_2,PO_4H)$, and $\mu(OH,OH,C_2O_4H)$ (points 20—22) which are protonated. We have no evidence for inner-sphere electron-transfer controlled V^{2+} reductions.[20] The latter assignment requires a relatively rapid substitution-controlled equilibration to be established, followed by electron transfer. Although a perfectly reasonable assignment to consider, it is not yet firmly established whether any V^{2+} reductions of mononuclear or binuclear cobalt(III) complexes yet studied fall within this category.

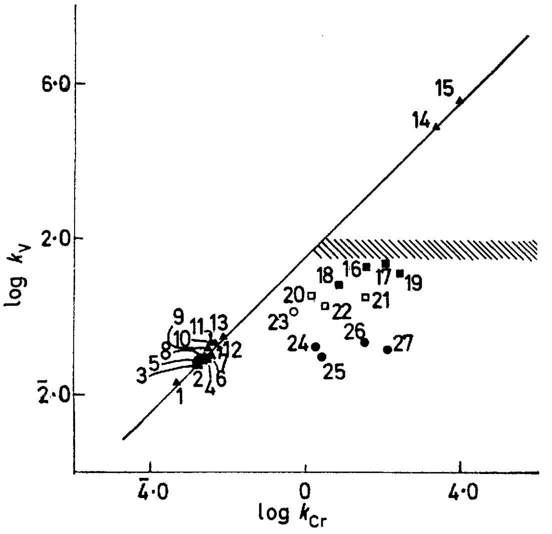

FIGURE 2 Plot of log k_V against log k_{Cr} for reduction of binuclear (and tetranuclear) cobalt(III) complexes. Binuclear complexes are (with the exception of 8 and 10) of type $[(NH_3)_3Co\cdot\mu(OH,OH,O_2CR)\cdot Co(NH_3)_3]^{n+}$ or $[(NH_3)_4Co\cdot\mu(NH_2,O_2CR)\cdot Co(NH_3)_4]^{n+}$. Pendant carboxylate groups are protonated except as stated. References as in text: 1 = $\mu(NH_2$,acetato), 2 = $\mu(NH_2$,formato), 3 = μ(OH,OH,benzoato), 4 = μ(OH,OH,2-Cl-benzoato), 5 = $\mu(NH_2$,malonato), 6 = μ(OH,OH,malonato), 7 = μ(OH,OH,glycolato), 8 = $[(NH_3)_4Co\cdot\mu(OH,OH)\cdot Co(NH_3)_4]^{4+}$, 9 = μ(OH,OH,phthalato), 10 = $[(NH_3)_5Co\cdot NH_2\cdot Co(NH_3)_5]^{5+}$, 11—13 = μ_4-oxalato, 14—15 = μ(superoxo) complexes, 16 = $\mu(NH_2$,oxalato) unprotonated, 17 = μ(OH,OH,-oxalato) unprotonated, 18 = $\mu(NH_2$,sulphato), 19 = $\mu(NH_2$,-selenato), 20 = $\mu(NH_2$,oxalato), 21 = $\mu(NH_2$,phosphato) monoprotonated, 22 = μ(OH,OH,oxalato), 23 = μ(OH,OH,-OFB), 27 = μ(OH,OH,PFB)

Finally achievements of this series of papers on the Cr^{2+} (and V^{2+}) reductions of dicobalt(III) complexes can be summarized as follows. (a) A carboxylate bonded to two cobalt atoms cannot function as a site for inner-sphere reduction, *e.g.* μ-acetato- and μ-formato-complexes.[6] (b) A carboxylate bonded to two cobalt atoms cannot function in a mechanism of adjacent attack with chelation, and with μ-oxalato- and μ-maleato-complexes Cr^{2+} reduction by remote attack only is observed.[2,11] Rates are some 10^2—10^3 times slower than for reduction of mononuclear cobalt complexes in which remote attack with chelation is observed. (c) Reduction of fumarato-complexes by Cr^{2+} is shown to be unambiguously by remote attack. Rate constants for Cr^{2+} reduction of μ-fumarato- and μ-maleato- (as well as mononuclear fumarato-) complexes are very similar.[11] (d) When the carboxylate of benzoate or *o*-chlorobenzoate is bonded to two cobalt atoms (thus blocking adjacent carboxylate attack) neither the aromatic ring nor the chloro-group serves as a lead-in for inner-sphere electron-transfer.[24] With an aldehyde function in the *ortho*- or *para*-positions fast, remote attack *via* this group is observed.[12] (e) An $[H^+]^{-1}$ dependence which is observed in the reductions of μ-malonato- (and dimethylmalonato-) complexes suggests a mechanism of attachment of the reductant with electron transfer possibly as in an outer-sphere reaction.[14] (f) Cr^{2+} and V^{2+} outer-sphere reductions gives an excellent log–log correlation of slope 1.02 (Figure 2).

EXPERIMENTAL

The perchlorate salt of the protonated form of the di-μ-hydroxo-μ-oxalato-complex $[(NH_3)_3Co\cdot\mu(OH,OH,C_2O_4H)\cdot Co(NH_3)_3][ClO_4]_3\cdot 1/2\ H_2O$ was prepared as described previously.[1] Solutions of Cr^{2+} and V^{2+} perchlorate in $HClO_4$ were prepared by electrolytic reduction as described in earlier studies. A Durrum-Gibson stopped-flow and Unicam SP 500 and SP 800 spectrophotometers were used. The separation of reaction products for the Cr^{2+} reduction was carried out using a Dowex 50W-X8 cation ion-exchange resin. The fraction containing $[Cr(H_2O)_4C_2O_4]^+$ was eluted with 0.2M-$HClO_4$, the Co^{2+} fraction with a solution 0.2M-$HClO_4$/0.5M-$LiClO_4$, and the $[Cr(H_2O)_6]^{3+}$ fraction with a solution 0.5M-$HClO_4$/1.0M-$LiClO_4$. Metal-ion concentrations were determined by standard procedures.[3,11,22]

I. B. is grateful for leave of absence from University of Cluj and the British Council for financial support, and K. W. to the University of Heidelberg for leave of absence.

[6/990 *Received, 24th May,* 1976]

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