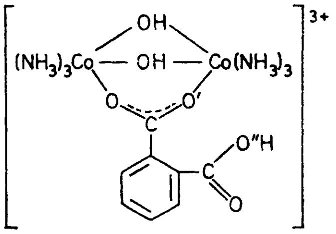
The Cr^{2+} and V^{2+} Reductions of μ-Carboxylato-dicobalt(III) Ammine Complexes. Part IV.‡ The Mechanism of Reduction of the Di-μ-hydroxo-μ-phthalato-bis[triamminecobalt(III)] and Penta-ammine-phthalatocobalt(III) Complexes†

By **Andrew T. Thornton, 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 di-μ-hydroxo-μ-phthalato-bis[triamminecobalt(III)] complex, $[(NH_3)_3Co\cdot\mu(OH,OH,O_2CC_6H_4CO_2H)\cdot Co(NH_3)_3]^{3+}$, have been studied at temperatures in the range 9.7—40 °C, $I = 1.0$M$(LiClO_4)$. Comparisons are made with the Cr^{2+} reduction of penta-amminephthalatocobalt(III), $[Co(NH_3)_5(O_2CC_6H_4CO_2H)]^{2+}$. Second-order rate constants for the latter exhibit an $[H^+]$-dependence, $a + b[H^+]^{-1}$, where it has now been demonstrated using ion-exchange techniques that a yields the unidentate product $[Cr(H_2O)_5(O_2CC_6H_4CO_2H)]^{2+}$, and b the chelated product $[Cr(H_2O)_4(O_2CC_6H_4CO_2)]^+$. With the binuclear μ-phthalato-complex reduction of the first cobalt(III) is rate determining, and that of the second relatively rapid. Second-order rate constants conform to the $[H^+]$-dependence, $k_a + k_b[H^+]^{-1}$, where in this instance k_a corresponds to an outer-sphere process, and k_b involves some form of remote attack. Evidence for the latter is that phthalate is incorporated into a binuclear chromium(III) product. Full product analyses have been carried out. With an excess of Cr^{2+} a second stage involving Cr^{2+}-catalysed dissociation of primary chromium(III) products becomes increasingly important at the lower $[H^+]$ values.

It has previously been shown that Cr^{2+} and V^{2+} reductions of μ-carboxylatodicobalt(III) complexes cannot occur by adjacent inner-sphere attack at the bound carboxylate.[1,2] Instead reduction by an outer-sphere mechanism, or, if a suitable organic group is available, by remote inner-sphere attack is observed.[3] Studies on the Cr^{2+} reductions of mononuclear penta-amminecobalt(III) complexes $[Co(NH_3)_5X]^{2+}$, where $X^- = O_2CC_6H_4CO_2H$ represents the three forms of phthalic acid, have been reported.[4,5] Reduction of the terephthalato-(*para*) derivative (0.2 l mol^{-1} s^{-1} at 25 °C) is at the normal rate for adjacent attack, which it has been suggested [5] rules out appreciable contributions from remote attack. Remote attack is unlikely in the case of the isophthalato-(*meta*) derivative, which does not have conjugate double bonding, and the rate constant (0.13 l mol^{-1} s^{-1} at 25.1 °C) is likewise consistent with adjacent carboxylate attack.



(I)

However, probably the most interesting observation is that second-order rate constants for the Cr^{2+} reduction of the phthalato-(*ortho*) complex exhibit a hydrogen-ion dependence, $a + b\,[H^+]^{-1}$.[4] Detailed implications of the latter have not previously been considered, and further kinetic studies and product analyses have therefore been carried out. The Cr^{2+} reduction of the di-μ-phthalato-bis[triamminecobalt(III)] binuclear complex, (I), has now been carried out and provides the main theme of this paper. Studies with V^{2+} as reductant are also included to help make mechanistic assignments.

RESULTS

The Cr^{2+} *Reduction of the Mononuclear Phthalato-complex.*—The products of the Cr^{2+} reduction of penta-amminephthalatocobalt(III) were separated by ion-exchange chromatography, and formulae assigned on the basis of the charge which was apparent from the elution characteristics. Thus fractions containing blue $[Cr(H_2O)_4(O_2CC_6H_4CO_2)]^+$, pink Co^{2+}, and blue $[Cr(H_2O)_5(O_2CC_6H_4CO_2H)]^{2+}$ were eluted in that order from the column. When the $[H^+]$ of reactant solutions was increased from 0.06 to 1.0M the amount of 1+ chelated complex $\lambda_{max.}$ 417 nm (ε 24.6 l mol^{-1} cm^{-1}) and 580 nm (ε 27.8 l mol^{-1} cm^{-1}) decreased, and that of the 2+ complex $\lambda_{max.}$ 413 nm (ε 26.4 l mol^{-1} cm^{-1}) and 573 nm (ε 28.6 l mol^{-1} cm^{-1}) increased (Table 1). Since spectra of solutions of the 1+ and 2+ complexes (Figure 1) at $[H^+] =$ *ca.* 0.6M remained unchanged during periods ⩾4 h, on addition of 5×10^{-2}M Cr^{2+}($[H^+] = 0.06$M), and spectrophotometric changes giving $[Cr(H_2O)_6]^{3+}$ as final product were slow, $t_{\frac{1}{2}} > 4$ h, it seems fairly certain that these complexes are primary products. Second-order rate constants $k_{obs.}$ (Table 2) fit a hydrogen-ion dependence $a + b\,[H^+]^{-1}$ (Figure 2). Hence values of a and b are 0.12 l mol^{-1} s^{-1} and 0.006 15 s^{-1} respectively, in satisfactory agreement with the data of Sebera and Taube.[4] From the correspondence with product analyses in Table 1 it is concluded that path (a) yields the 2+ unidentate complex, and (b) the 1+ chelated complex. Sebera and Taube [4] have determined an acid

TABLE 1

Reaction products [a] for the Cr^{2+} (0.028M) reduction of $[Co(NH_3)_5(O_2CC_6H_4CO_2H)]^{2+}$ (0.01M) at room temperature as determined following ion-exchange separation

$\frac{[H^+]}{M}$	Co^{2+} (%)	$[Cr(H_2O)_4$-$(O_2CC_6H_4CO_2)]^+$ (%)	$[Cr(H_2O)_5$-$(O_2CC_6H_4CO_2H)]^{2+}$ (%)
0.06	100	53	46
0.20	93	37	54
0.50	95	17	72
1.00	97	5	80

[a] Expressed as percentage of initial cobalt(III) concentration.

---

† No reprints available.

‡ Part III is reference 2.

[1] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 2364.

[2] K. Wieghardt and A. G. Sykes, *J.C.S. Dalton*, 1974, 651.

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

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

[5] E. S. Gould, *J. Amer. Chem. Soc.*, 1965, **87**, 4730.

dissociation constant, $K_a = 2.5 \times 10^{-3}$ mol l^{-1} at 25 °C, for protonated phthalate in $[Co(NH_3)_5(O_2CC_6H_4CO_2H)]^{2+}$. Assuming deprotonation precedes attack of the Cr^{2+} reductant, the rate constant for reduction of the deprotonated complex by Cr^{2+} is 2.46 l mol^{-1} s^{-1}.

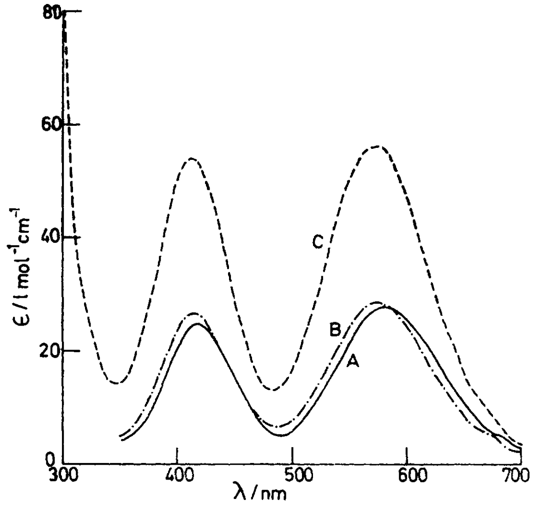


FIGURE 1 Spectra of chromium(III) products A(—) $[Cr(H_2O)_4(O_2CC_6H_4CO_2)]^+$, B(—.—) $[Cr(H_2O)_5(O_2CC_6H_4CO_2H)]^{2+}$, and C(– – – –) the dimeric species $[Cr^{III}_2(phth)]$, $[H^+] = 0.1$M

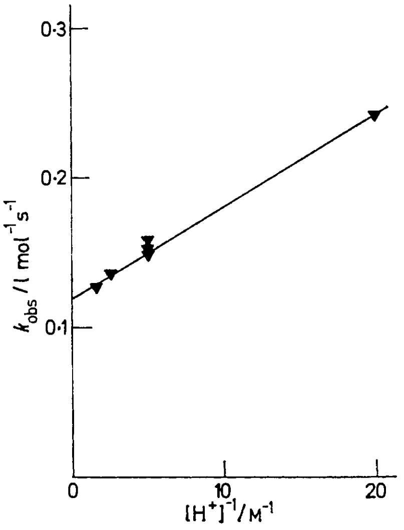


FIGURE 2 The $[H^+]$-dependence of second-order rate constants $k_{obs.}$ for the Cr^{2+} reduction of $[Co(NH_3)_5(O_2CC_6H_4CO_2H)]^{2+}$ at 25 °C, $I = 1.0$M$(LiClO_4)$

TABLE 2

Rate constants for the Cr^{2+} reduction of $[Co(NH_3)_5(O_2CC_6H_4CO_2H)]^{2+}$ at 25°, $I = 1.0$M$(LiClO_4)$

$\frac{[H^+]}{M}$	$\frac{10^2[Cr^{2+}]}{M}$	$\frac{10^3[Co^{III}]}{M}$	$\frac{k_{obs.}}{l\ mol^{-1}s^{-1}}$
0.05	6.72	1.0	0.241
0.20	2.92	2.0	0.149
0.20	8.54	2.0	0.151
0.20	12.3	2.0	0.158
0.40	5.53	2.0	0.137
0.60	5.66	0.5	0.126

Preliminary Studies on the μ-Phthalato-complex.—The di-μ-hydroxo-μ-phthalato-complex is stable for >72 h at 30 °C, $[H^+] = 0.1$—1.0M. By varying the pH 1.0 to 3.3 an acid dissociation constant $(4.47 \pm 0.30) \times 10^{-3}$ mol l^{-1} was determined by a spectrophotometric method (λ = 280 and 292 nm). This compares with a first acid dissociation constant of 2.34×10^{-3} mol l^{-1} for phthalic acid.[6] Ion-exchange experiments (see below) indicate a 2 : 1 stoicheiometry for the Cr^{2+} reduction, as in equation (1). Scan

$$2Cr^{2+} + (Co^{III})_2 \longrightarrow 2Cr^{III} + 2Co^{2+} \qquad (1)$$

spectra indicate slow changes following reduction of the cobalt(III) (Figure 3). These are attributed to Cr^{2+}-catalysed aquation of the primary chromium(III) products. The final chromium(III) product after *ca.* 2 days is $[Cr(H_2O)_6]^{3+}$, $\lambda_{max.}$ 408 nm (ε 15.8 l mol^{-1} cm^{-1}) and 574 nm (ε 13.3 l mol^{-1} cm^{-1}). There is no detectable reduction of phthalic acid by Cr^{2+} during 48 h at 25 °C. The same stoicheiometry applies to the V^{2+} reduction, which yields V^{3+} as product. It has previously been demonstrated that Cr^{2+} and V^{2+} are unable to utilize μ-hydroxo-sites of dicobalt(III) complexes for inner-sphere reduction.[7] Hydrogen-ion dependent hydroxo-bridge cleavage is not favourable for di-μ-hydroxo-μ-carboxylato-complexes, and is only observed as a slow process, *e.g.* in the Cr^{2+} reduction of the μ-benzoato-di-μ-hydroxo-complex,[2] when Cr^{2+} is present to scavenge the bis-aquo-product.

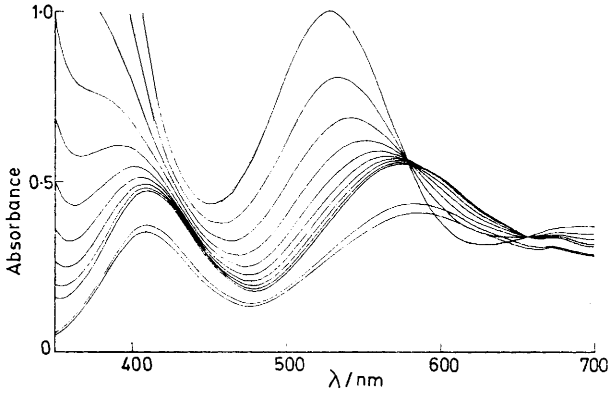


FIGURE 3 Scan spectra recorded at 15 min intervals (1-cm light path) for the reaction of Cr^{2+}(0.082M) with the di-μ-hydroxo-μ-phthalato-complex (1×10^{-3}M) at 25 °C, $[H^+] = 0.2$M, $I = 1.0$M$(LiClO_4)$. The lower two traces (left-hand side) were recorded after 20 h and (final spectrum) 44 h

The Cr^{2+} Reduction of the μ-Phthalato-complex.—The kinetics were studied with 25 to 100-fold excess of Cr^{2+} by following absorbance changes at the 524 nm peak of the oxidant (ε = 110 l mol^{-1} cm^{-1}). Absorbance (O.D.) changes corresponded to complete reduction of cobalt(III) (isosbestic 580 nm), and formation of chromium(III) species with maxima at *ca.* 410 and *ca.* 575 nm (Figure 3). Plots of log $(O.D._t - O.D._\infty)$ against time gave linearity to *ca.* 2—3 half-lives, at $[H^+] \gg 0.6$M. First-order rate constants, and from these second-order rate constants k_{Cr}, (2), were

$$\text{Rate} = k_{Cr}[Cr^{2+}][(Co^{III})_2] \qquad (2)$$

obtained (Table 3). It is concluded that there is one rate-determining step during which time both cobalt(III) centres are reduced. At lower $[H^+]$ values using $O.D._\infty$ determined after 24—72 h, the linearity of plots was reduced, and at

---

[6] K. S. Rajan, and A. E. Martell, *J. Inorg. Nuclear Chem.*, 1967, **29**, 523.

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

$[H^+] < 0.2$M was $< 50\%$. Under these conditions secondary processes involving primary chromium(III) products are incident before reduction of the cobalt(III) is complete. These changes are more extensive the lower the $[H^+]$ used. The data obtained for the secondary processes were not sufficiently precise or the processes involved sufficiently clearcut to justify a full investigation. For runs $[H^+] > 0.2$M there was generally no difficulty in determining O.D.$_\infty$ corresponding to completion of the first stage. At $[H^+] < 0.2$M there was significant overlap of the two stages making this procedure difficult. Values of O.D.$_\infty$ were therefore chosen so as to achieve maximum linearity of first-order plots. This procedure was shown to be satisfactory by carrying out a full consecutive treatment [3] for selected runs (Figure 4). The latter gave agreement with k_{Cr} for the first stage to within 5%. The second stage of the reaction in Figure 4 gives a rate constant 4.2×10^{-5} s^{-1}.

TABLE 3

Second-order rate constants, k_{Cr}, for the Cr^{2+} reduction of the di-μ-hydroxo-μ-phthalato-complex, $I = 1.0$M ($LiClO_4$)

$\frac{t}{°C}$	$\frac{[H^+]}{M}$	$\frac{10^2[Cr^{2+}]}{M}$	$\frac{10^3[(Co^{III})_2]}{M}$	$\frac{10^3 k_{Cr}}{l\ mol^{-1}\ s^{-1}}$
25.0	0.070	2.48	1.5	8.04 [a]
	0.070	4.77	1.0	7.93 [a]
	0.125	2.64	0.5	5.71 [a]
	0.125	5.10	1.0	5.72
	0.125	7.86	1.0	5.65
	0.200	2.48	0.5	4.61
	0.200	4.77	1.0	4.63
	0.200	7.00	1.0	4.59
	0.200	9.60	0.8	4.52 [a]
	0.210	8.95	2.0	4.40 [a]
	0.250	2.64	1.2	4.17
	0.250	5.10	0.9	4.10
	0.250	7.86	1.1	4.00
	0.300	2.48	1.0	3.74
	0.300	7.00	2.0	3.74
	0.300	7.00	1.0	3.88
	0.625	2.64	0.9	3.22
	0.625	5.10	1.0	2.91
	0.625	7.86	1.0	3.05
30.0	0.069	2.25	1.0	10.6
	0.088	3.00	1.0	9.0
	0.090	2.10	0.9	9.1
	0.090	4.05	1.1	9.1
	0.090	6.25	1.2	8.9
	0.117	4.12	1.0	8.1
	0.400	2.12	1.0	4.48
	0.400	5.93	1.1	4.47
	0.400	10.0	1.0	4.50
	0.725	2.12	1.0	3.92
	0.725	5.83	1.0	3.77
	0.725	10.0	1.0	3.85
35.0	0.069	2.25	1.0	14.4
	0.088	3.00	1.0	12.0
	0.117	4.12	1.0	9.9
	0.125	2.76	1.0	10.3
	0.125	5.31	0.9	9.6
	0.125	8.06	1.3	9.8
	0.250	2.82	1.0	6.71
	0.250	8.06	1.2	6.48
	0.625	2.83	1.0	4.93
	0.625	8.06	1.0	5.06
40.0	0.059	1.88	1.0	22.8
	0.088	3.00	1.0	16.0
	0.108	3.75	1.0	14.5
	0.117	4.12	1.0	14.1
	0.125	2.83	1.2	12.3
	0.250	2.83	1.1	9.5
	0.250	5.06	0.9	9.6
	0.625	5.06	1.2	6.57
	0.625	2.83	1.0	6.21

[a] Determined using consecutive treatment.

The hydrogen-ion dependence of k_{Cr}, (3), is illustrated in Figure 5. Values of k_a and k_b were evaluated at each temperature using an unweighted least-squares treatment (Table 4). Activation parameters, listed below in Table 7, were computed using a non-linear least-squares programme [8] with a weighting factor $1/k^2_{Cr}$.

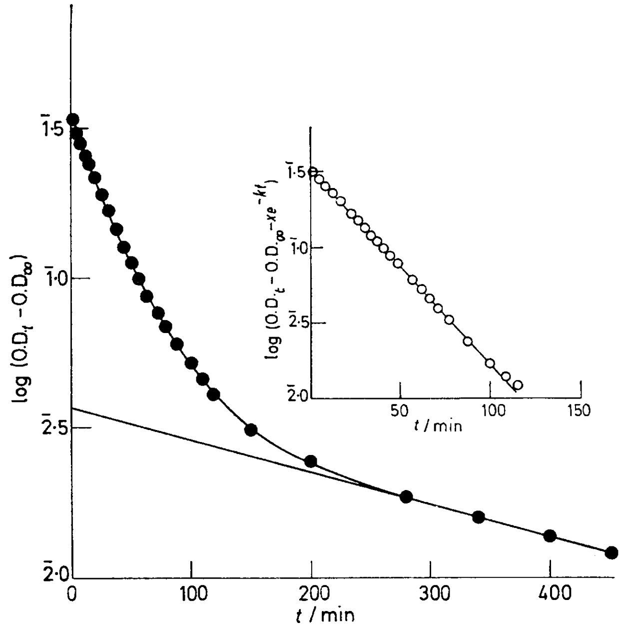


FIGURE 4 First-order plot for the Cr^{2+} reduction of the di-μ-hydroxo-μ-phthalato-dicobalt(III) complex at 25 °C, $[H^+] = 0.20$M, $[Cr^{2+}] = 0.096$M, $[(Co^{III})_2] = 0.8 \times 10^{-3}$M, $I = 1.0$M-($LiClO_4$). The inset illustrates the procedure used to evaluate the rate constant for the first stage (x is the intercept of the ordinate axis) using standard consecutive reaction treatment. The second stage corresponds to further reactions of primary chromium(III) products

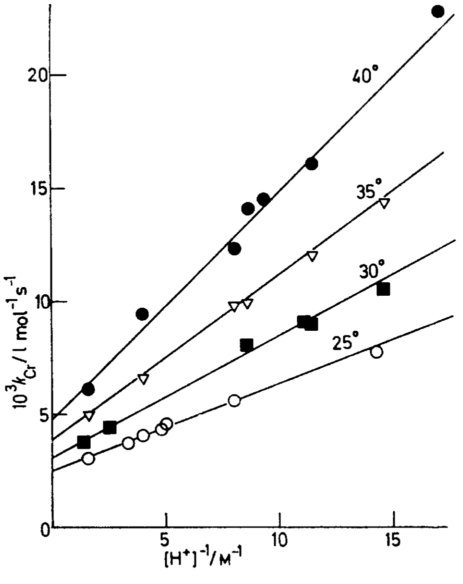


FIGURE 5 The dependence of rate constants k_{Cr} on $[H^+]$ for the rate determining Cr^{2+} reduction of the first cobalt(III) in the μ-phthalato-complex, $I = 1.0$M($LiClO_4$)

---

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

$$k_{Cr} = k_a + k_b[H^+]^{-1} \qquad (3)$$

To determine the products a solution containing a 10% excess of the di-μ-hydroxo-μ-phthalato-reactant, $[Cr^{2+}] = 0.022$M, $[(Co^{III})_2] = 0.0133$M, $[H^+] = 0.249$M, $I = 1.00$M was allowed to react at 30 °C for 24 h, after which time no further u.v.–visible spectrophotometric changes were observed. The products were then separated by both Sephadex and Dowex ion-exchange chromatography, and gave the following products expressed as percentages of the Cr^{2+} reactant. Free phthalate (32%), $[Cr(H_2O)_4(O_2CC_6H_4CO_2)]^+$ (1%), $[Cr(H_2O)_5(O_2CC_6H_4CO_2H)]^{2+}$ (18.5%), $[Cr(H_2O)_6]^{3+}$ (41%), $[Cr^{III}_2(phth)]$ (36%), and Co^{2+} (94%). The phthalate of the binuclear $[Cr^{III}_2(phth)]$ product was released by base hydrolysis and determined spectrophotometrically. This together with the chromium analysis gave a Cr : phthalate ratio of 2 : 1. The spectrum is included in Figure 1. Satisfactory recovery of the cobalt as Co^{2+} (94%), chromium(III) in four fractions (97%), and phthalate in four fractions (106%) was obtained.

TABLE 4

Summary of the kinetic data for the Cr^{2+} reduction of the di-μ-hydroxo-μ-phthalato-complex, $I = 1.0$M ($LiClO_4$)

t/°C	$\frac{10^3k_a}{l\ mol^{-1}\ s^{-1}}$	$\frac{10^3k_b}{s^{-1}}$
25.0	2.54 ± 0.05	0.39 ± 0.01
30.0	3.18 ± 0.09	0.52 ± 0.01
35.0	3.82 ± 0.16	0.73 ± 0.01
40.0	4.91 ± 0.31	1.03 ± 0.04

TABLE 5

Second-order rate constants k_V for the V^{2+} reduction of the di-μ-hydroxo-μ-phthalato-complex, $I = 1.0$M ($LiClO_4$)

t/°C	$\frac{[H^+]}{M}$	$\frac{10^2[V^{2+}]}{M}$	$\frac{10^3[(Co^{III})_2]}{M}$	$\frac{10k_V}{l\ mol^{-1}\ s^{-1}}$
9.7	0.20	2.30	1.2	1.03
	0.30	2.30	1.3	0.83
	0.70	2.30	1.1	0.65
20.3	0.20	1.00	0.4	1.88
	0.20	2.28	1.0	1.85
	0.30	1.00	0.5	1.55
	0.30	2.26	1.0	1.50
	0.30	4.05	2.1	1.51
	0.70	1.00	0.5	1.16
	0.70	4.05	1.8	1.09
25.0	0.20	1.18	0.5	2.44
	0.20	2.25	1.1	2.46
	0.20	4.90	0.9	2.47
	0.30	1.18	0.7	2.05
	0.30	4.90	1.4	2.01
	0.70	1.18	0.6	1.48
	0.70	2.25	1.0	1.52
	0.70	4.90	1.0	1.53

The V^{2+} *Reduction of the μ-Phthalato-complex.*—This reaction was also monitored at 524 nm. Plots of $\log(O.D._t - O.D._\infty)$ against time were linear to $\geqslant 92\%$ completion over the range $[H^+] = 0.2$—0.7M investigated, and there was no evidence for a second stage. The data are consistent with a rate law as in equation (2), and reduction of the second cobalt(III) is again rapid. Rate constants k_V are listed in Table 5. The dependence on $[H^+]$ is as given in equation (3) and values of k_a and k_b are given in Table 6. From these activation parameters were evaluated (Table 7).

TABLE 6

Summary of the kinetic data for the V^{2+} reduction of the di-μ-hydroxo-μ-phthalato-complex, $I = 1.0$M ($LiClO_4$)

t/°C	$\frac{10^2k_a}{l\ mol^{-1}\ s^{-1}}$	$\frac{10^2k_b}{s^{-1}}$
9.7	4.91 ± 0.26	1.06 ± 0.07
20.3	8.29 ± 0.29	2.07 ± 0.08
25.0	11.4 ± 0.2	2.65 ± 0.05

TABLE 7

Summary of kinetic data for $[H^+]$-independent (k_a) and $[H^+]^{-1}$-dependent (K_b) paths in the Cr^{2+} and V^{2+} reduction of the di-μ-hydroxo-μ-phthalato-complex, $I = 1.0$M ($LiClO_4$)

Rate constant	k(25 °C)	$\frac{\Delta H^\ddagger}{kcal\ mol^{-1}}$	$\frac{\Delta S^\ddagger}{cal\ K^{-1}\ mol^{-1}}$
$k_a(Cr^{2+})$	2.34×10^{-3} [a,b]	7.44 ± 0.46	−45.5 ± 1.5
$k_b(Cr^{2+})$	3.64×10^{-4} [b,c]	11.2 ± 0.49	−36.5 ± 1.6
$k_a(V^{2+})$	0.11 [a,b]	8.3 ± 0.6	−35.1 ± 2.0
$k_b(V^{2+})$	2.72×10^{-2} [b,c]	9.9 ± 0.9	−32.6 ± 3.0

[a] Units of $l\ mol^{-1}\ s^{-1}$. [b] Rate constant obtained from activation parameters. [c] Units of s^{-1}.

DISCUSSION

A single rate-determining step is observed for the Cr^{2+} and V^{2+} reductions of the di-μ-hydroxo-μ-phthalato-complex, and it can be concluded that in each case reduction of the second cobalt(III) is relatively rapid.* The second stage which is observed in the Cr^{2+} reduction, corresponds to the further reactions of primary chromium(III) products (Figure 3). The terms k_a and k_b [equation (3)] can be assigned to reaction paths in which the remote carboxylate of the μ-phthalato-ligand is protonated and deprotonated respectively. Thus rate constants $k_a = k_1$ and $k_b = k_2K_a$ for Cr^{2+}, and $k_a = k_3$ and $k_b = k_4K_a$ for V^{2+} reduction, can be defined, where K_a is the acid dissociation constant of the complex. An outer-sphere mechanism is assigned to k_1 and k_3 on the basis of the ratio $k_1/k_3 = 0.023$, which is in good agreement with values *ca.* 0.020 for known outer-sphere reactions.[1,9]

The detailed implications of the product analyses are now considered. At 30 °C, $[H^+] = 0.294$M, k_b makes a 40% contribution to the overall rate constant (Table 4). If k_a and k_b are exclusively outer- and inner-sphere respectively, equations (4)—(5), and the $Co^{III}(phth)Cr^{III}$

$$Cr^{2+} + [Co^{III}_2(phth)] \xrightarrow{k_a} [Co^{III}(phth)(H_2O)_2] + Cr^{3+} + Co^{2+} \qquad (4)$$

$$Cr^{2+} + [Co^{III}_2(phth)] \xrightarrow{k_b} [Co^{III}(phth)Cr^{III}] + Co^{2+} \qquad (5)$$

intermediate reacts by an inner-sphere mechanism,

$$Cr^{2+} + [Co^{III}(phth)Cr^{III}] \longrightarrow [Cr^{III}_2(phth)] + Co^{2+} \qquad (6)$$

---

* No evidence has been obtained for single two-electron steps in these and other reactions of dicobalt(III) ammine complexes, and we note that at $[H^+] = 0.5$M and with a large excess of tin(II) (0.026M), a good two-electron reductant, reduction of the μ-amido-μ-oxalato-bis[tetra-amminecobalt(III)], is slow $t_{\frac{1}{2}} > 12$ h at 45 °C.

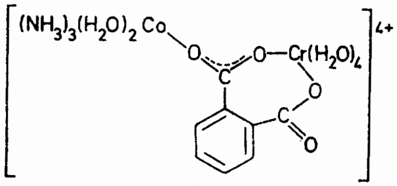
[9] J. C. Chen and E. S. Gould, *J. Amer. Chem. Soc.*, 1973, **95**, 5539.

equation (6), the yield of $[\mathrm{Cr^{III}}_2(\mathrm{phth})]$ should be 40%. The value observed is 36%, and we feel this explanation is therefore acceptable. The mononuclear product in (4) can react in three possible ways, equations (7)—(9),

$$\mathrm{Cr^{2+} + [Co^{III}(phth)(H_2O)_2]} \longrightarrow \begin{cases} \mathrm{Cr^{3+} + Co^{2+} + phth} & (7) \\ \mathrm{[Cr^{III}(phth)]^{+} + Co^{2+}} & (8) \\ \mathrm{[Cr^{III}(phth)]^{2+} + Co^{2+}} & (9) \end{cases}$$

where reaction (7) most likely corresponds to inner-sphere reduction at the H_2O sites of the cobalt(III).[10] The amount of $[\mathrm{Cr(H_2O)_4(O_2CC_6H_4CO_2)}]^+$ produced is small (1%), and it is concluded that reaction (8) makes negligible contribution. From the ratio of free phthalate to $[\mathrm{Cr(H_2O)_5(O_2CC_6H_4CO_2H)}]^{2+}$ of 0.8 it can be predicted that the overall yield of $[\mathrm{Cr(H_2O)_6}]^{3+}$ should be 43%, which is in good agreement with the observed value of 41%. Also the overall yield of $[\mathrm{Cr(H_2O)_5(O_2CC_6H_4CO_2H)}]^{2+}$ should be 16.5% in good agreement with the 18.5% observed. It is concluded that the yield of $[\mathrm{Cr^{III}}_2(\mathrm{phth})]$ is as predicted by the relative contributions of k_a and k_b in equation (3), and that all the $\mathrm{Cr^{2+}}$ reacting by the $[\mathrm{H^+}]^{-1}$ path leads subsequently to the $[\mathrm{Cr^{III}}_2(\mathrm{phth})]$ product. The other products are in accordance with equation (4) yielding $[\mathrm{Co^{III}(phth)(H_2O)_2}]$, which then reacts by reactions (7) and (8) to give $[\mathrm{Cr(H_2O)_6}]^{3+}$ (45%) and $[\mathrm{Cr(H_2O)_5(O_2CC_6H_4CO_2)}]^{2+}$ (55%). Thus from product identification and comparison of the $\mathrm{V^{2+}}$ and $\mathrm{Cr^{2+}}$ rate constants it is reasonable to assume that k_a is outer sphere. The formation of a binuclear $[\mathrm{Cr^{III}}_2(\mathrm{phth})]$ complex requires that for k_b $\mathrm{Cr^{2+}}$ must attack the phthalate group, and some form of remote attack seems likely. The precise nature of this path is open to conjecture however and now requires further discussion.

Phthalate and terephthalate have a conjugate system of double bonds and remote attack with electron transfer *via* the conjugate double bonds is certainly a possibility. With the mononuclear complexes contributions from such a path may be relatively small, since adjacent carboxylate attack is more favourable.[4,5] An *X*-ray crystal study of potassium hydrogenphthalate has indicated that the carboxylate groups are not in the same plane as the benzene ring, the out-of-plane angle being 31.7 °C for the protonated and 75.4 °C for the unprotonated carboxylate.[11] Non-planarity resulting from the close proximity of the carboxylate groups may make conjugation and hence remote attack more difficult particularly in the case of the di-μ-hydroxo-μ-phthalato-complex. Furthermore for $\mathrm{Cr^{2+}}$ and $\mathrm{V^{2+}}$ reduction of the di-μ-hydroxo-μ-terephthalato-complex rate constants are independent of $[\mathrm{H^+}]$ and all the reaction proceeds by an outer-sphere mechanism.[12] This together with the detection of an $[\mathrm{H^+}]^{-1}$ pathway for $\mathrm{Cr^{2+}}$ and $\mathrm{V^{2+}}$ reduction of the μ-amido-μ-malonato-complex,[13] which does not have conjugate double bonding, suggests that k_b may not be a case of remote attack with electron transfer through the conjugate system of the phthalate. Attack of oxygen atoms O′ and O″ of (I) is ruled out, since it is difficult to see how $[\mathrm{Cr^{III}}_2(\mathrm{phth})]$ could be formed (relatively) rapidly from $\mathrm{Cr^{2+}}$ attack on the primary product (II).



(II)

We suggest instead that there is precursor complex formation by attachment of the $\mathrm{Cr^{2+}}$ (or $\mathrm{V^{2+}}$) to the unprotonated O″ group of (I). It is then possible for the co-ordination spheres of the $\mathrm{Cr^{2+}}$ and one cobalt(III) to move into close proximity by rotation about the bond joining the carboxylate group to the benzene ring, and for an electron to be transferred in an outer-sphere fashion. This mechanism is a direct consequence of the specific geometry of the phthalate ligand. For terephthalate such a process is not possible, no $[\mathrm{H^+}]^{-1}$ term is observed, and only an outer-sphere contribution is apparent.[12] We note that k_b values for the $\mathrm{Cr^{2+}}$ and $\mathrm{V^{2+}}$ reductions give a ratio 0.013 which is similar to that observed for other outer-sphere reactions (*ca.* 0.020). The large value of $\Delta H^{\ddagger}$ for k_b of 11.2 kcal mol^{-1} with $\mathrm{Cr^{2+}}$ as reductant is also consistent with a reaction having outer-sphere characteristics. Furthermore, it is known that $\mathrm{V^{2+}}$ does not normally make use of remote attack *via* a system of conjugate double bonds,[9,14] and only one example has so far been established.[15] However, in the present case it is not clear whether a prior equilibration involving association of the $\mathrm{V^{2+}}$ with the phthalate is effective, or whether k_b is substitution controlled.[16] Assuming that acid dissociation of the proton from the μ-phthalato-ligand occurs before $\mathrm{V^{2+}}$ attachment then $k_4 = 5.7$ l mol^{-1} s^{-1}, which would be acceptable for a substitution-controlled process. Alternatively $\mathrm{V^{2+}}$ may bind to the carboxylate, by a proton-displacement mechanism,[15] in which case it is not appropriate to use the measured pK_a.

Whatever the precise details of electron transfer *via* k_b, the $[\mathrm{Co^{III}(phth)Cr^{III}}]$ intermediate is likely to have

---

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

[11] Y. Okaya, *Acta Cryst.*, 1965, **19**, 879.

[12] M. Hery and K. Wieghardt, unpublished work.

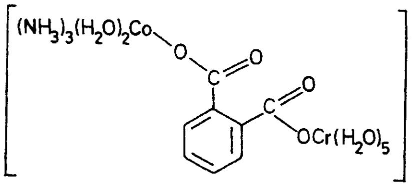
[13] B. Kipling, K. Wieghardt and A. G. Sykes, unpublished work.

[14] A. Zanella and H. Taube, *J. Amer. Chem. Soc.*, 1972, **94**, 6403.

[15] C. Norris and F. R. Nordmeyer, *Inorg. Chem.*, 1971, **12**, 1235.

[16] See for example M. L. Hyde, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1973, 2730.

structure (III). Reduction by the second Cr^{2+} could be at one or both of the unbonded phthalate oxygen atoms of complex (III). Only a single binuclear chromium(III) product (spectrum Figure 1) was identified in the product analyses.



(III)

To summarize, the Cr^{2+} reductions of mononuclear and binuclear cobalt(III) complexes containing phthalate provided evidence for adjacent carboxylate attack and adjacent attack with chelation (both with the mononuclear complex), together with outer-sphere and some form of remote attack (both with the binuclear complex).

EXPERIMENTAL.

Reactants.—The preparation and characterisation of the μ-phthalato-complex $[(NH_3)_3Co\cdot\mu(OH,OH,O_2CC_6H_4CO_2H)\cdot Co(NH_3)_3](ClO_4)_3\cdot 2H_2O$ has been described.[17] The perchlorate salt of $[Co(NH_3)_5(O_2CC_6H_4CO_2H)]^{2+}$ was prepared by treating $[Co(NH_3)_5CO_3](NO_3)$ with a three-fold excess of phthalic acid, at 80 °C for 15 min (pH = *ca.* 2.0). Crude $[Co(NH_3)_5(O_2CC_6H_4CO_2H)]^{2+}$ was precipitated with an alcohol–ether mixture, and the complex was recrystallized from water by addition of $NaClO_4$. The complex gave a peak at 502 nm ($\varepsilon = 80$ l mol^{-1} cm^{-1}) in accordance with previous values.[4,18]

Solutions of Cr^{2+} and V^{2+} were prepared as described previously in work from these laboratories; details of the preparation of $LiClO_4$ have also been given. Rigorous air-free techniques were required in all experiments with Cr^{2+} and V^{2+}.

Reaction Products.—For the Cr^{2+} reduction of the mononuclear complex, $[Co(NH_3)_5(O_2CC_6H_4CO_2H)]^{2+}$, concentrations as in Table 1, the maximum reaction time required was 20 min ($[H^+] = 1.00$M). Oxygen was bubbled through the solution (10 ml) to oxidize the remaining Cr^{2+} (dimeric and trimeric species are obtained),[19] and the solution was diluted (× 20), divided into two 100-ml portions (duplicate experiments), which were then loaded onto separate ion-exchange columns of Dowex 50 W X2 (200—400 mesh) resin in the H^+ form. Bands eluted were as follows: $[Cr(H_2O)_4(O_2CC_6H_4CO_2)]^+$(0.25M-$HClO_4$), Co^{2+} (0.5M-$HClO_4$), and $[Cr(H_2O)_5(O_2CC_6H_4CO_2H)]^{2+}$(1.0M-$HClO_4$). Here and elsewhere the chromium(III) fractions were identified by u.v.–visible spectrophotometry, and determined as chromium(VI) ($\lambda = 372$ nm; $\varepsilon = 4.815 \times 10^3$ l mol^{-1} cm^{-1}) following oxidation with H_2O_2 in 1M-NaOH. Cobalt(II) fractions were determined spectrophotometrically as $[CoCl_4]^{2-}/[CoCl_3H_2O]^-$ by addition of concentrated hydrochloric acid to give [HCl] = 10M, $\lambda_{max.}$ 628 nm ($\varepsilon = 283$ l mol^{-1} cm^{-1}).

The reaction products were determined for the Cr^{2+} reduction of the di-μ-hydroxo-μ-phthalato-complex by making up an approximately 2 : 1 reactant solution Cr^{2+} : $(Co^{III})_2$ (latter in 10% excess), details as in text. Oxygen was bubbled through the solution to ensure oxidation of all the Cr^{2+} (negligible at this stage since no products from this reaction were identified). The solution (50 ml) was diluted to 250 ml, and 25-ml samples (duplicate experiments) were loaded onto Sephadex SP C-25 columns (1.2 cm diameter, 4.5 cm high). The following bands were eluted: free phthalate (0.1M-$HClO_4$), $[Cr(H_2O)_4(O_2CC_6H_4CO_2)]^+$, and $[Cr(H_2O)_5(O_2CC_6H_4CO_2H)]^{2+}$ (0.1M-$HClO_4$, 0.1M-$NaClO_4$), $[Cr(H_2O)_6]^{3+}$, $[Co^{III}_2(phth)]^{3+}$, $[Co^{III}_2(phth)]$ and $[Cr^{III}_2(phth)]$ (all with 0.1M-$HClO_4$, 0.4M-$NaClO_4$). The diluted reactant solution (50-ml aliquots) was also separated by an ion-exchange method using Dowex 50 W × 8 (1.0 cm diameter, 10 cm high), when the following bands were eluted: free phthalate (0.1M-$HClO_4$), $[Cr(H_2O)_4(O_2CC_6H_4CO_2)]^+$ (0.1M-$HClO_4$/0.1—0.2-M-$NaClO_4$), Co^{2+} (0.1M-$HClO_4$/0.5—1.0M-$NaClO_4$), $[Cr(H_2O)_5(O_2CC_6H_4Co_2H)]^{2+}$ (0.1M-$HClO_4$/1.0M-$NaClO_4$), $[Cr(H_2O)_6]^{3+}$ (0.1M-$HClO_4$, 1.0—1.9M-$NaClO_4$). The Cr and Co content of different fractions was determined as above, and phthalate (as phthalic acid) spectrophotometrically at 280 nm ($\varepsilon = 1.25 \times 10^3$ l mol^{-1} cm^{-1}). The dimeric chromium(III) species is most readily obtained from the Sephadex column. This complex was base hydrolysed and the solution reacidified in order to liberate the co-ordinated phthalate. The free phthalate was then obtained by running the solution through a Dowex 50-X12 column to remove all chromium(III) species; the phthalic acid was collected as eluate. The ratio of Cr/phthalate in the dimer was $1.97 \pm 0.05 : 1$. A solution of the dimer in 0.1M-$HClO_4$ gave a negligible amount of free phthalate during 4 days as detected spectrophotometrically following ion exchange.

Acid Dissociation Constant.—To determine the pK_a of di-μ-hydroxo-μ-phthalato-complex the spectra of the complex in 0.1M-$HClO_4$ and in water were compared. The biggest differences were observed at 292 nm with an isosbestic at 280 nm. It is noted that the differences are in the region where the spectrum of phthalic acid itself shows changes on deprotonation, consistent with deprotonation at a phthalate site on the complex. The pK_a was determined by measuring the ratio R of $O.D._{292}/O.D._{280}$ as a function of $[H^+]$ in the range pH 1 to 3.3. Over this range *ca.* 10% change in R was observed. From a graph of $\log\{(R_H - R)/(R - R_B\}$ against $\log [H^+]$,[20] where R_H is the ratio at high acid, R_B the ratio at low acid (pH 4), and R the ratio at intermediate $[H^+]$, a straight line of slope 1.038 ± 0.046 was obtained in good agreement with the predicted value of 1.00.[20] The intercept was obtained by fixing the slope at 1.00 and obtaining the best fit to give $pK_a = 2.35 \pm 0.02$ at 25 °C, $I = 1.00$M($LiClO_4$).

We are grateful to the Deutsche Forschungsgemeinschaft for a European Exchange Fellowship and the University of Heidelberg for leave of absence (to K. W.), the University of Leeds and I.C.I. Ltd. for a post-doctoral award, and the British Council for a travel grant (to A. T. T.).

[4/2673 *Received, 23rd December, 1974*]

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

[18] E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, 1964, **86**, 1318.

[19] S. G. Thompson, *Diss. Abs.*, 1966, **26**, 5748.

[20] A. Albert and E. P. Serjeant, ' The Determination of Ionization Constants,' Chapman and Hall, 1971.