The Cr^{2+} and V^{2+} Reduction of μ-Carboxylato Dicobalt(III) Ammine Complexes. Part VI.‡ Mechanism of the Reduction of μ-*p*-Formylbenzoato- and μ-*o*-Formylbenzoato-complexes †

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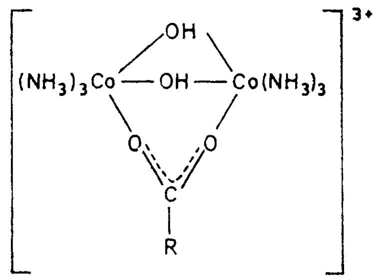
The kinetics of the Cr^{2+} and V^{2+} reductions of the μ-*p*-formylbenzoato- and μ-*o*-formylbenzoato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes, μ(pfb) and μ(ofb) respectively, have been studied, I = 1.0M ($LiClO_4$), by stopped-flow spectrophotometry. The reactions are first order in oxidant and reductant, and no $[H^+]$-dependence is observed, $[H^+]$ = 0.06—0.60M. Reduction of the first cobalt(III) centre is rate determining. At 25 °C with Cr^{2+} as reductant k_{Cr} = 122.5 l mol^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 1.4 ± 0.3 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = −44.2 ± 0.9 cal K^{-1} mol^{-1} for the μ(pfb) complex, and k_{Cr} = 31.6 l mol^{-1} s^{-1}, $\Delta H^{\ddagger}$ = −3.6 ± 0.7 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = −63.7 ± 0.9 cal K^{-1} mol^{-1} for the μ(ofb) complex. It is concluded that inner-sphere Cr^{2+} reduction *via* the remote aldehyde function is occurring in both cases, and that the primary chromium(III) product formed in the initial step aquates rapidly to give $[Cr(H_2O)_6]^{3+}$. Kinetic data (25 °C) with V^{2+} as reductant are k_V = 0.148 l mol^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 7.8 ± 1.9 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −36.4 ± 0.6 cal K^{-1} mol^{-1} for μ(pfb), and k_V = 0.235 l mol^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 6.1 ± 0.5 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = −41.0 ± 1.5 cal K^{-1} mol^{-1} for μ(ofb).

THE role played by organic bridging ligands X^{n-} in the inner-sphere Cr^{2+} reduction of mononuclear complexes $[Co(NH_3)_5X]^{(3-n)+}$ has been studied extensively.[1] Taube and his co-workers have provided evidence for different reduction mechanisms dictated by the nature of the organic ligands.[2] Additional information regarding the site of attack has been obtained from a consideration of the Cr^{2+} reduction of binuclear cobalt(III) complexes with carboxylato-ligands bridging the two cobalt(III) atoms.[3-8] With monocarboxylic acids (*e.g.* the μ-formato,[4] μ-acetato, and μ-benzoato [5] complexes) an outer-sphere mechanism is operative, the inference being that in the reactions of the related mononuclear cobalt(III) complexes {*e.g.* $[Co(NH_3)_5O_2CCH_3]^{2+}$} adjacent attack is at the carbonyl oxygen atom. Reduction of μ-oxalato-complexes [3] and μ-maleato-complexes [7] occurs at the remote end of the carboxylate ligand, whereas with corresponding mononuclear complexes adjacent attack with chelation has been proposed.[9-11]

For remote attack of mononuclear cobalt(III) complexes containing conjugated double-bonding a suitable remote polar group is necessary to ensure that there is no (or very little) attack at the adjacent carboxylate group. The divergent rate constants for the Cr^{2+} reduction of the terephthalatopenta-amminecobalt(III) (where terephthalate is the *para*-isomer) [12] and penta-ammine-*p*-formylbenzoatocobalt(III) complexes [13] suggests that a low-lying unoccupied orbital associated with the aldehyde function facilitates attack *via* a remote carbonyl group. Reduction of the second of these complexes is hydrogen-ion dependent, and it has been suggested that the site for protonation is the adjacent carboxylate group.

Reasons for the beneficial effects of protonation are not quite clear and further information is required. In conjunction with this, more information concerning the role which the aldehyde group plays when the carboxylate group is bridging two cobalt atoms is also desirable, since the presence of two dicobalt(III) centres may or may not improve conjugation. With these questions in mind it was decided to study the Cr^{2+} reduction of the μ-*p*-formylbenzoato (pfb) and μ-*o*-formylbenzoato (ofb) complexes (I).



R = *p*- and *o*-C_6H_4CHO (I)

Studies with V^{2+}, although playing a secondary role, were also carried out.

Stability of Complexes.—Solutions of complex (I) in 1.0M-$HClO_4$ were stable for 72 h at 25 °C and there was no evidence for the cleavage of either the hydroxo- or carboxylato-bridges. Slow hydroxo-bridge cleavage of the μ-benzoato-complex (I; R = Ph) is only apparent when Cr^{2+} is present to scavenge the aquation product.[5] It has previously been demonstrated that μ-hydroxo-ligands do not provide a site for inner-sphere electron transfer,[14] and outer-sphere Cr^{2+} and V^{2+} reduction at a μ-hydroxo-group is likewise slow and ineffective.[14]

Products and Stoicheiometry.—LaFollette has reported that in the Cr^{2+} reduction of $[Co(NH_3)_5(pfb)]^{2+}$ it is possible to recover the organic ligand by solvent extrac-

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† No reprints available.

‡ Reference 7 is Part V of this work.

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

[2] H. Taube, ' Electron Transfer Reactions of Complex Ions in Solution,' Academic Press, 1970.

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

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

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

[6] A. T. Thornton, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, submitted.

[7] M. R. Hyde, K. L. Scott, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, submitted.

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

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

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

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

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

tion.[15] Gould [16] has found that the Cr^{2+} reduction of *p*- and *o*-formylbenzoic acid (3 g l^{-1}) is slow, and at 25 °C with $[H^+] = 0.6\text{M}$, $[Cr^{2+}] = 0.01\text{M}$, only 6 and 4% reduction is observed during 15 min. Products from the Cr^{2+} reduction of both complexes (I) at 25 °C were separated by ion-exchange techniques for runs $[Cr^{2+}] = 8.8 \times 10^{-3}\text{M}$, $[Co^{III}_2] = 4 \times 10^{-3}\text{M}$, $[H^+] = 0.5\text{M}$, and determined by procedures as described in the Experimental section. The reaction of the μ(pfb) complex gave equivalent amounts of $[Co(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ (95% recovery). With μ(ofb) a single chromium(III) band 407 nm (ε 19.2 l mol^{-1} cm^{-1}), λ 571 (ε 16.6), was obtained which most likely consists of equivalent amounts of $[Cr(H_2O)_6]^{3+}$, λ 408 (ε 15.5), λ 571 (ε 13.2), and $[Cr(H_2O)_5(ofb)]^{2+}$, λ 407 (ε 24.1) and λ 572 (ε 21.5).[16] We were unable to separate the two species using Dowex or Sephadex G-25 columns. Ion-exchange experiments and spectrophotometric changes are consistent with 2 : 1 reactions as in equation (1).

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

Observations with V^{2+} as reductant are also consistent with 2 : 1 stoicheiometries.

TABLE 1

Rate constants for the first stage of the Cr^{2+} reduction of the μ-*p*-formylbenzoate (pfb) and μ-*o*-formylbenzoate (ofb) complexes, λ = 524 nm, $I = 1.0\text{M}$ ($LiClO_4$). Number of runs which have been averaged indicated in parentheses

$\frac{t}{°C}$	$\frac{[H^+]}{\text{M}}$	$\frac{10^2[Cr^{2+}]}{\text{M}}$	$\frac{10^4[Co^{III}_2]}{\text{M}}$	$\frac{k_{Cr}}{\mathrm{l\,mol^{-1}\,s^{-1}}}$
(i) Reduction of μ(pfb)				
2.8	0.12	2.82	10.0	94.3 (2)
	0.62	2.82	10.0	100 (2)
25.0	0.12	2.82	10.0	121 (2)
	0.62	2.82	10.0	117 (2)
35.0	0.059	5.60	5.0	143 (2)
	0.161	11.6	5.0	128 (1)
	0.161	11.6	10.0	131 (2)
	0.559	5.60	10.0	130 (2) [a]
	0.559	5.60	1.0	138 (2) [a]
	0.62	5.65	10.0	142 (1)
	0.62	2.82	10.0	142 (3)
	0.62	1.38	10.0	122 (2)
45.0	0.12	2.68	10.0	166 (2)
	0.62	2.68	10.0	174 (2)
(ii) Reduction of μ(ofb)				
2.7	0.078	5.46	1.5	45.2 (2)
	0.578	5.46	1.50	43.4 (2)
	0.578	5.46	3.00	45.8 (2)
15.0	0.078	5.46	1.50	43.6 (2)
	0.578	5.46	1.50	43.3 (2)
25.0	0.053	6.29	3.0	32.7 (2)
	0.078	5.78	3.0	32.2 (1)
	0.106	5.89	3.0	35.6 (2)
	1.106	3.12	3.0	35.5 (2)
	0.106	1.47	3.0	35.4 (2)
	0.156	10.6	5.0	32.6 (2)
	0.156	10.6	1.0	29.7 (2)
	0.156	5.47	3.0	32.3 (2)
	0.156	2.81	3.0	29.6 (2)
	0.156	1.54	3.0	28.6 (2)
	0.656	10.6	3.0	31.9 (1)
35.0	0.578	5.53	3.0	26.0 (4)
45.0	0.078	5.46	3.0	21.9 (2)
	0.578	5.46	3.0	21.8 (2)

[a] λ = 292 nm, no second stage observed.

Cr^{2+} and V^{2+} Reduction of μ(pfb) and μ(ofb) Complexes.—All reactions were monitored at the peak at 524 nm for the binuclear cobalt(III) complexes (ε = 110 ± 2 l mol^{-1} cm^{-1}) using the stopped-flow method. The reductant was in large excess and plots of $\log(OD_t - OD_\infty)$ against time gave good first-order behaviour with linearity to >85% completion. Absorbance changes corresponding to reduction of the second cobalt(III) were not detected and are presumably occurring concurrently with the first stage. First-order rate constants were independent of hydrogen-ion concentration, $[H^+] = 0.06$—0.6M, and gave a first-order dependence on reductant for an 8-fold variation in Cr^{2+}, and a 3- to 6-fold variation in V^{2+}. The rate law is therefore as in equation (2).

$$-d[Co_2^{III}]/dt = k_M[M^{2+}][Co^{III}_2] \qquad (2)$$

Second-order rate constants k_{Cr} with Cr^{2+} as reductant are given in Table 1, and k_V with V^{2+} as reductant in Table 2. Some of the runs for the Cr^{2+} reduction of the μ(pfb) complex were also followed at 292 nm, which Zanella and Taube [13] have reported to be the peak position of the intermediate observed in the reduction of $[Co(NH_3)_5(pfb)]^{2+}$. The data at the two wavelengths are in good agreement, although generally the runs at 292 nm were of slightly poorer quality (≤87% linearity) owing to the lower signal-to-noise ratio at the higher oscilloscope voltages required for studies at this wavelength. Decreases in absorbance were observed at both wavelengths and there was no evidence for the formation of an intermediate under the conditions used.

TABLE 2

Rate constants for the first stage [a] of the V^{2+} reduction of the μ-*p*-formylbenzoate (pfb) and μ-*o*-formylbenzoate (ofb) complexes, λ = 524 nm, $I = 1.0\text{M}$ ($LiClO_4$). Number of runs which have been averaged indicated in parentheses

$\frac{t}{°C}$	$\frac{[H^+]}{\text{M}}$	$\frac{10^2[V^{2+}]}{\text{M}}$	$\frac{10^3[Co^{III}_2]}{\text{M}}$	$\frac{k_V}{\mathrm{l\,mol^{-1}\,s^{-1}}}$
(i) Reduction of μ(pfb)				
25.0	0.7	6.67	1.0	0.147 (2)
35.0	0.7	6.67	1.0	0.237 (2)
44.0	0.2	3.33	0.5	0.349 (2)
	0.2	6.67	1.0	0.334 (3)
	0.7	2.28	1.0	0.346 (2)
	0.7	3.33	0.5	0.349 (2)
	0.7	6.67	1.0	0.342 (2)
(ii) Reduction of μ(ofb)				
25.0	0.195	6.34	5.0	0.224 (2)
	0.695	6.34	5.0	0.235 (2)
35.0	0.195	2.00	3.00	0.337 (2)
	0.695	2.00	3.00	0.354 (2)
	0.700	7.85	5.00	0.361 (2)
45.0	0.065	2.04	1.00	0.529 (2)
	0.195	6.34	1.00	0.487 (2)
	0.195	6.34	5.00	0.442 (2)
	0.695	1.13	5.00	0.431 (2)
	0.695	3.07	5.00	0.476 (2)
	0.695	6.34	5.00	0.505 (2)

[a] Second stage not detected.

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[15] Experiments of D. LaFollette reported by H. Taube, 'Mechanisms of Inorganic Reactions,' Adv. in Chem. Series, No. 49, Amer. Chem. Soc., 1965, p. 119.

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

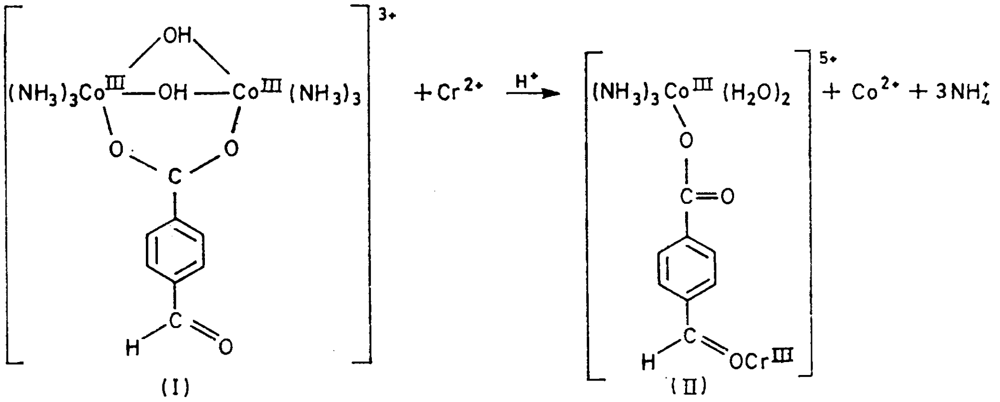
Final absorbance readings monitored on the stopped-flow apparatus at both wavelengths were stable, and no Cr^{2+} or V^{2+} reduction of the free organic acids was observed over the time scale of these experiments. Activation parameters were obtained using a non-linear least-squares programme,[17] weighting factor $1/k^2$, and are shown alongside available data for the Cr^{2+} and V^{2+} reductions of mononuclear complexes in Table 3.

Detection of Chromium(III) *Intermediates*.—A full study of the Cr^{2+} reduction of $[Co(NH_3)_5(pfb)]^{2+}$ by Zanella and Taube [13] has provided substantial evidence for an intermediate in which chromium(III) is bonded to the carbonyl of the aldehyde group. Under the most favourable conditions employed by Zanella and Taube, $[Cr^{2+}] = 0.12$M, $[H^+] = 1.14$M, and $[Co(NH_3)_5(pfb)^{2+}] = 3 \times 10^{-4}$M,[13] we have obtained evidence for an intermediate which at 25 °C using the stopped-flow spectrophotometer, $\lambda = 302$ nm, decayed with a rate constant *ca.* 30 s^{-1}. For less favourable conditons $[Co(NH_3)_5(pfb)^{2+}] = 10^{-3}$M, $[Cr^{2+}] = 1.3 \times 10^{-2}$M, $[H^+] = 0.5$M at 25 °C, $I = 1.0$M$(LiClO_4)$ as required for the reduction of the μ(pfb) complex, absorbance changes monitored at $\lambda = 503$ nm (peak position of complex), $\lambda = 302$ nm (wavelength used in ref. 13), and $\lambda = 292$ nm (peak position of intermediate in ref. 13) gave no evidence for the build-up and decay of chromium(III)–pfb species. Higher concentrations of Cr^{2+} and μ(pfb), which might be more appropriate for the detection of chromium(III) intermediates, could not be monitored at 302 nm owing to the much stronger absorbances.

DISCUSSION

There are at present no known examples in which Cr^{2+} reduction of μ-carboxylatodicobalt(III) complexes occurs *via* the adjacent bonded carboxylate function. If there is no alternative site for attack an outer-sphere reduction mechanism is operative and rates are slow.[4,8] However the complexes (I) reported here are reduced quite rapidly by Cr^{2+}. At 25 °C rate constants for the Cr^{2+} reduction of the μ(pfb) and μ(ofb) complexes are 122 l $mol^{-1}s^{-1}$ and 31.6 l $mol^{-1}s^{-1}$ respectively. Rate constants of this magnitude are between 4 and 5 orders of magnitude larger than those normally associated with outer-sphere Cr^{2+} reductions (*ca.* 10^{-3} l $mol^{-1}s^{-1}$).[4,18] The similarity of rate constants for binuclear and mononuclear pfb [13] and ofb [16,19] complexes respectively (Table 3) is noted, where the Cr^{2+} reductions of the mononuclear complexes are known to be inner-sphere. Also rate constants (25 °C) for the V^{2+} reduction of μ(pfb) (0.148 l $mol^{-1}s^{-1}$) and μ(ofb) (0.235 l $mol^{-1}s^{-1}$) give ratios k_{Cr}/k_V for reduction by Cr^{2+} and V^{2+} of *ca.* 10^3 with μ(pfb), and *ca.* 10^2 with μ(ofb), which are vastly different from the value *ca.* 0.020 expected if both reductions are outer-sphere.* We conclude that the first stage of the Cr^{2+} reduction of both binuclear complexes is occurring by an inner-sphere mechanism. Since the adjacent carboxylate group is unavailable, attack must occur *via* the remote carbonyl function of the aldehyde group.

The primary product in the first stage of reduction of the μ(pfb) complex (I), is most probably (II) [equation (3)].



$+ Co^{2+} + 3NH_4^+$ (3)

We are unable to obtain direct spectrophotometric evidence for the build-up of such an intermediate, and decomposition, possibly by a process involving carbon–oxygen bond cleavage, giving hexa-aquochromium(III) is rapid. The product $[Co(NH_3)_3(H_2O)_2(pfb)]^{2+}$ is reduced by the second Cr^{2+} at a rate comparable with or faster than the first stage. This second stage can occur by Cr^{2+} attack at a water–ligand site (in its conjugate-base form) or by attack of the adjacent carboxylate group (now unidentate), or once again *via* the remote aldehyde function. Of these alternatives the latter is expected to be the most rapid. Both reduction steps therefore yield $[Cr(H_2O)_6]^{3+}$ and Co^{2+} consistent with the products identified. The failure to detect an intermediate for the second stage is in no way contrary to the observations of Zanella and Taube.[13] Conditions in the

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* Rate constants for 17 outer-sphere Cr^{2+} and V^{2+} reductions of cobalt(III) complexes (including binuclear and tetranuclear species) give a linear correlation $\log k_V = 1.02 \log k_{Cr} + 1.73$ (ref. 20). Since the gradient for $\log k_V$ against $\log k_{Cr}$ is close to unity the ratio k_{Cr}/k_V is constant. Chen and Gould [19] from data for six outer-sphere Cr^{2+} and V^{2+} reductions of penta-amminecobalt(III) complexes have previously reported a correlation $\log k_V = 1.10 \log k_{Cr} + 1.85$.

[17] Los Alamos Report LA 2367, 1959 and addenda by R. H. Moore and R. K. Ziegler.

[18] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1973, 736.

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

[20] M. R. Hyde, Ph.D. Thesis, University of Leeds, 1973.

experiments described here were never sufficiently favourable to observe an intermediate decaying at the rate *ca.* 30 s^{-1}.

The first stage of the Cr^{2+} reduction of the μ(ofb) complex yields $[Cr(H_2O)_6]^{3+}$. The second stage involving reduction of $[Co(NH_3)_3(H_2O)_2(ofb)]^{2+}$ is expected to proceed by a mechanism of remote attack with chelation, followed by rapid aquation of the aldehyde function from the chromium(III) to yield $[Cr(H_2O)_5(ofb)]^{2+}$. Product analyses are consistent with this although we were unable to achieve a separation of the two mononuclear chromium(III) species.

At 25 °C rate constants (l $mol^{-1}s^{-1}$) for the reduction of the mononuclear complexes $[Co(NH_3)_5(pfb)]^{2+}$ and $[Co(NH_3)_5(ofb)]^{2+}$ are $53 + 380\,[H^+]$, $I = 1.1$M ($LiClO_4$),[13] and 90 l $mol^{-1}s^{-1}$, $I = 1.5$M ($LiClO_4$) [19] respectively. The Cr^{2+} reduction of the μ(pfb) complex exhibits no dependence upon hydrogen-ion concentration, and the rate constant (25 °C) is intermediate between values observed for $[Co(NH_3)_5(pfb)]^{2+}$ at high and low $[H^+]$. This, together with similar observations in the case of the μ-fumarato-complex,[7] supports the belief [13] that the site of protonation is an adjacent monodentate carboxylate group with the reductant attacking the remote position. No activation parameters are available for the Cr^{2+} reduction of the $[Co(NH_3)_5(ofb)]^{2+}$ complex. The rate constant at 25 °C is of similar magnitude to that for μ(ofb), the mononuclear complex possibly benefiting (factor of 3) from chelation of the Cr^{2+} in the activated complex. From the data in Table 3 it is clear that the aldehyde group remains a good lead-in group for electron transfer from Cr^{2+} in a variety of mononuclear and binuclear situations.

TABLE 3

Comparison of kinetic data for the Cr^{2+} and V^{2+} reductions of the μ-*p*-formylbenzoate and μ-*o*-formylbenzoate complexes, and the mononuclear penta-ammine analogues (pfb and ofb), $I = 1.0$M ($LiClO_4$)

Reductant	Oxidant	k (25 °C) [a] l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal K^{-1} mol^{-1}
Cr^{2+}	$[Co_2(NH_3)_6(OH)_2(pfb)]^{3+}$	122.5 ± 4	1.4 ± 0.3	−44.2 ± 0.9
	$[Co(NH_3)_5(pfb)]^{2+}$ (k_0) [b]	53	1.7 ± 0.6	−42 ± 2
	(k_1) [b]	380 [c]	0.3 ± 0.3	−46 ± 1
	$[Co_2(NH_3)_6(OH)_2(ofb)]^{3+}$	31.6 ± 2.0	−3.6 ± 0.7	−63.7 ± 0.9
	$[Co(NH_3)_5(ofb)]^{2+}$ [d]	90		
V^{2+}	$[Co_2(NH_3)_6(OH)_2(pfb)]^{3+}$	0.148 ± 0.004	7.8 ± 1.9	−36.4 ± 0.6
	$[Co(NH_3)_5(pfb)]^{2+}$ (k_0) [b]	0.88 [e]		
	(k_1) [b,c]	0.24 [e]		
	$[Co_2(NH_3)_6(OH)_2(ofb)]^{3+}$	0.235 ± 0.007	6.1 ± 0.5	−41.0 ± 1.5
	$[Co(NH_3)_5(ofb)]^{2+}$ [d]	1.24		

[a] Rate constants are k_{Cr} (from Table 1) and k_V (from Table 2) respectively. [b] From ref. 13. [c] Units l^2 mol^{-2} s^{-1}. [d] From ref. 19. [e] Ref. 19 gives $k_0 = 2.21$ l mol^{-1} s^{-1} and $k_1 = 0.66$ l^2 mol^{-2} s^{-1} at $I = 4.0$M ($LiClO_4$).

Activation parameters for the Cr^{2+} reductions are listed in Table 3. The enthalpy terms range from −3.6 to +2.7 kcal mol^{-1} and entropies from −42 to −64 cal K^{-1} mol^{-1}. Ion-pair association between two positively charged reactants can give negative contributions towards both activation parameters.[21] Observed parameters, Table 3, will also include a contribution for inner-sphere complex formation. Recent discussion of negative enthalpies of activation is also relevant.[22]

The results obtained for the V^{2+} reductions although they do not feature prominently in our discussion are of significance. First of all the various kinetic data are not consistent with values normally associated with inner-sphere V^{2+} substitution-controlled processes, *i.e.* rate constants in the range 1—50 l $mol^{-1}s^{-1}$, enthalpies of activation 11—13 kcal mol^{-1}, and entropies of activation −13 to −19 cal K^{-1} mol^{-1}.[23,24] Other possible mechanisms which may be considered are either outer-sphere or inner-sphere electron-transfer controlled. We note that rate constants (25 °C, l $mol^{-1}s^{-1}$) for the V^{2+} reductions of some μ-carboxylato-di-μ-hydroxo-complexes are remarkably insensitive to the identity of the carboxylate bridge: μ-phthalato (0.11),[6] μ-maleato (0.164),[7] μ-fumarato (0.099) [7] μ-malonato (0.10),[25] μ-glycolato (0.10),[25] and now μ(pfb) (0.148) and μ(ofb) (0.235). This suggests a common mechanism. Since V^{2+} reduction of the μ-amido-μ-hydroxo-complex is slow (3.1×10^{-3} l $mol^{-1}s^{-1}$ at 35 °C) [14] we have no reason to suppose that inner-sphere reduction at the hydroxo-group is relevant. The most likely implication is that these V^{2+} reactions are all outer-sphere. We note also that whereas with some of these complexes Cr^{2+} can readily make use of conjugate bonding for remote inner-sphere attack, V^{2+} is reluctant to do so. An important difference is that whereas Cr^{2+} transfers electrons from σ-orbitals, V^{2+} transfers π-electrons.

EXPERIMENTAL

The preparation and characterization of the μ-*p*-formylbenzoato-di-μ-hydroxo-bis[triamminecobalt(III)] and μ-*o*-formylbenzoato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes, $[(NH_3)_3Co.\mu(OH,OH,O_2CC_6H_4CHO).Co(NH_3)_3][ClO_4]_3\cdot 2H_2O$ have been described previously.[26] A sample of *p*-formylbenzoic acid (m.p. found 246–248 °C, lit.,[26] 248—250 °C) was obtained from R. N. Emanuel, and *o*-formylbenzoic acid (m.p. found 97 °C, lit.,[26] 96 °C) from Cambrian Chemicals. Both were used without further purification.

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[21] See for example, M. R. Hyde and A. G. Sykes, *J.C.S. Chem. Comm.*, 1972, 1340.

[22] R. A. Marcus and N. Sutin, *Inorg. Chem.*, 1975, **14**, 216.

[23] N. Sutin, *Accounts Chem. Res.*, 1968, **1**, 225.

[24] M. R. Hyde, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1973, 2730.

[25] B. Kipling, K. Wieghardt, and A. G. Sykes, to be published.

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

The mononuclear *p*-formylbenzoatopenta-amminecobalt(III) was prepared by the procedure described by Zanella and Taube[13] (Found: C, 19.2; H, 4.3; Cl, 14.5%. Calc. for $[Co(NH_3)_5(O_2CC_6H_4CHO)](ClO_4)_2$ (no hydration): C, 19.55; H, 4.07; Cl, 14.3%). The u.v.–visible spectrum $\lambda_{max.}$ 503 nm (ε 84.2 l mol^{-1}cm^{-1}) 340sh (ε 101), and 257, (ε 22.8) was in good agreement with that of Zanella and Taube.

Dowex 50W-X8 ion-exchange resin was used for the separation of reaction products. Elution with 0.5M-perchloric acid (*ca.* 100 ml) gave the Co^{2+} fraction and with 1.0–2.0M-perchloric acid (*ca.* 500 ml) mononuclear chromium(III) fractions. Analyses for cobalt and chromium were as described previously.[6]

Solutions of Cr^{2+} and V^{2+} perchlorates in perchloric acid were prepared by electrolytic reduction of chromium(III) and vanadium(IV) solutions at a mercury-pool cathode as described in earlier papers in the series. Lithium perchlorate was obtained from lithium carbonate (Reagent Grade), and AnalaR perchloric acid, and purified by recrystallization. A Durrum–Gibson stopped-flow spectrophotometer was used for all kinetic studies.

K. W. is grateful for the Deutsche Forschungsgemeinschaft for a European Exchange Fellowship and to the University of Heidelberg for leave for absence, and M. R. H. for an S.R.C. post-graduate studentship.

[5/488 *Received, 12th March,* 1975]