The Cr^{2+} and V^{2+} Reduction of μ-Carboxylato Dicobalt(III) Ammine Complexes. Part VII.† The Preparation and Mechanism of Reduction of μ-Malonato-, μ-Dimethylmalonato-, and μ-Glycolato-complexes

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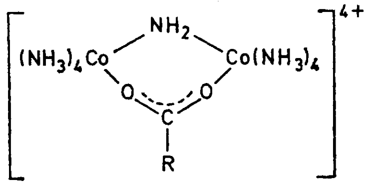
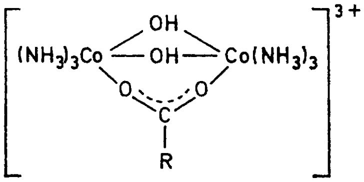
Perchlorate salts of the μ-malonato-, μ-dimethylmalonato-, and μ-glycolato-complexes $[(NH_3)_4Co{\cdot}\mu(NH_2,O_2CR){\cdot}Co(NH_3)_4]^{4+}$ [R = CH_2CO_2H (I) and R = $C(CH_3)_2CO_2H$ (II)] and $[(NH_3)_3Co{\cdot}\mu(OH,OH,O_2CR){\cdot}Co(NH_3)_3]^{3+}$ [R = CH_2CO_2H (III), R = $C(CH_3)_2CO_2H$ (IV), and R = CH_2OH (V)] have been prepared. Kinetic studies on the Cr^{2+} reductions of complexes (I)—(V), and the V^{2+} reductions of (I), (III), and (V) at 25 °C, I = 1.00M ($LiClO_4$) are reported. Reduction of the first cobalt(III) is in all cases slow and rate determining. On varying the hydrogen-ion concentration from 0.10 to 0.90M, rate constants for complexes (I)—(IV) give a dependence $k_{obs} = k_1 + k_2[H^+]^{-1}$, where k_2 makes relatively large contributions for the μ-amido-complexes (I) and (II). No $[H^+]$-dependence is observed for (V). The k_1 pathway is common to and about the same, (1—3.6) × 10^{-3} l mol^{-1} s^{-1}, for all Cr^{2+} reductions. Outer-sphere mechanisms are assigned to k_1 on the basis of k_{Cr}/k_V ratios. Separation and determination of the Cr^{III} products, $[Cr(H_2O)_6]^{3+}$ (50%), $[Cr(H_2O)_5(O_2CCH_2CO_2H)]^{2+}$ (31%), and $[Cr(H_2O)_4(O_2CCH_2CO_2)]^+$ (19%), for the Cr^{2+} reduction of complex (I), $[H^+]$ = 0.05M, suggest that the Cr^{2+} attaches itself to the unprotonated (pendant) carboxylate for pathway k_2. Since the C-atoms of the malonate are saturated it is proposed that electron transfer from the attached reductant occurs as in an outer-sphere process and not *via* the malonate.

CHROMIUM(II) reductions of mononuclear penta-ammine-carboxylato-cobalt(III) complexes have been extensively studied.[1] Reactions of related binuclear μ-carboxylato-dicobalt(III) complexes often exhibit different behaviour because the carboxylate, now bonded to two cobalt(III) centres, is no longer available as a site for inner-sphere Cr^{2+} attack. Because of this additional information regarding the mechanism of electron transfer in systems involving organic ligands is obtained. Thus Cr^{2+} reductions of μ-acetato-,[2] μ-formato-,[2] and μ-benzoato-[3] complexes, have been shown to proceed by slow outer-sphere reduction. Remote inner-sphere attack has been shown to be effective for the μ-oxalato-,[4] μ-maleato-,[5] μ-fumarato-,[5] and μ-(*o* and *p*)formylbenzoato-complexes.[6]



R
(I) CH_2CO_2H
(II) $CMe_2{\cdot}CO_2H$



R
(III) CH_2CO_2H
(IV) $CMe_2{\cdot}CO_2H$
(V) CH_2OH

The Cr^{2+} reduction of μ-carboxylato-complexes having a second pendant carboxylate but no conjugate system of double-bonds is examined in this paper with complexes (I)—(IV). Also included in these studies is the Cr^{2+} reduction of the μ-glycolato-complex (V). Parallel studies with V^{2+} as reductant were carried out for complexes (I), (III), and (V) since ratios of rate constants k_{Cr}/k_V of *ca.* 0.020 for the reduction of a common oxidant provide supporting evidence for outer-sphere mechanistic assignments.[2,7,8]

RESULTS

Reaction products obtained for the Cr^{2+} reduction of complex (I) at $[H^+]$ = 0.05M, I = 1.00M ($LiClO_4$), were separated and determined as described in the Experimental section (see Table 1 for details). Amounts of Co^{2+} and the total mononuclear chromium(III) product were consistent with a 2 : 1 stoicheiometry as indicated in equation (1). The chromium(III) species were identified spectrophotometrically from known spectra of $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_5(O_2CCH_2CO_2H)]^{2+}$, and $[Cr(H_2O)_4(O_2CCH_2CO_2)]^+$,[9-11] and determined quantitatively as chromate(VI)

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

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† Part VI is ref. 6.

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

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

[5] M. R. Hyde, K. L. Scott, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, 1976, 153.

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[9] D. G. Huchital and H. Taube, *Inorg. Chem.*, 1965, **4**, 1660.

[10] M. V. Olson and C. E. Behnke, *Inorg. Chem.*, 1974, **13**, 1329.

[11] Y. Sulfab, J. D. Edwards, and A. G. Sykes, *Inorg. Chem.*, 1975, **14**, 1474.

TABLE 1

Product analyses for the Cr^{2+} reduction of complex (I). Reactant concentrations and chromium(III) products, $[H^+] = 0.05$M, $I = 1.00$M($LiClO_4$), *ca.* 22 °C

$10^3[Cr^{2+}]$ / M	$10^3[(Co^{III})_2]$ / M	$[Cr(H_2O)_6]^{3+}$ (%)	$[Cr(H_2O)_5(O_2CCH_2CO_2H)]^{2+}$ (%)	$[Cr(H_2O)_4(O_2CCH_2CO_2)]^+$ (%)
15.0	5.9	49.6	30.1	19.5
13.8	5.9	49.8	28.7	18.6
12.7	3.2	49.0	35.2	16.3
4.3	4.3	49.7	28.8	21.5

(see Table 1). All the malonate is recovered in the form of 1+ and 2+ chromium(III) complexes. Product analyses are less meaningful for runs at higher $[H^+]$ because the reductions are much slower, and secondary reactions of the unidentate and chelated malonatochromium(III) complexes occur within the reaction time. The stoicheiometry indicated in equation (1) is assumed to apply for other reactions and conditions investigated.

TABLE 2

Rate constants (25 °C) for the Cr^{2+} reduction of μ-malonato-, μ-dimethylmalonato-, and μ-glycolato-complexes (I)—(V), $I = 1.0$M($LiClO_4$)

Complexes	$[H^+]$ / M	$10^2[Cr^{II}]$ / M	$10^4[(Co^{III})_2]$ / M	10^3k_{obs} / l mol^{-1} s^{-1}
(I)	0.10	3.43	5.0	17.8
	0.11	5.31	5.0	19.4
	0.12	3.74	5.0	16.9
	0.20	1.06	5.0	11.9
	0.20	2.20	5.0	10.2
	0.20	5.35	5.0	10.8
	0.20	10.3	5.0	10.9
	0.29	6.10	6.2	8.55
	0.35	3.59	5.0	6.12
	0.65	3.75	2.3	4.00
	0.70	10.3	5.0	4.47
	0.91	3.70	5.0	3.13
	0.94	2.15	5.0	3.18
(II)	0.12	3.74	2.5	14.7
	0.23	1.86	1.2	7.83
	0.24	5.40	2.5	7.88
	0.24	9.10	5.0	7.93
	0.24	11.3	5.0	8.01
	0.36	3.65	2.5	5.08
	0.92	3.65	2.5	3.06
(III)	0.086	3.36	5.0	2.92
	0.12	4.07	5.0	2.88
	0.20	1.76	5.0	2.71
	0.21	4.48	5.0	2.82
	0.21	5.48	3.3	2.89
	0.22	9.48	5.0	2.84
	0.30	7.84	2.6	2.74
	0.91	3.29	5.0	2.60
(IV)	0.10	4.0	5.0	2.70
	0.20	1.76	5.0	2.12
	0.20	5.38	5.0	2.07
	0.20	8.64	5.0	2.08
	0.21	3.55	5.0	1.97
	0.21	3.84	5.2	1.93
	0.35	3.62	5.0	1.69
	0.35	3.74	5.2	1.70
	0.66	7.07	10.0	1.70
	0.66	7.56	5.0	1.67
	0.66	7.28	2.5	1.93
	0.91	3.86	5.0	1.72
(V)	0.10	3.62	5.0	3.57
	0.20	1.56	5.0	3.56
	0.20	5.42	5.0	3.58
	0.20	9.22	5.0	3.49
	0.35	3.67	5.0	3.60
	0.91	3.42	5.0	3.58

Kinetic studies were at 25 °C, $I = 1.00$M ($LiClO_4$), with the reductant in large excess. Reactions were monitored at peak positions 517 ± 2 nm (ε = 367 ± 3 l mol^{-1} cm^{-1}) for complexes (I) and (II), and 524 ± 2 nm (ε = 100 ± 3 l mol^{-1} cm^{-1}) for complexes (III)—(V). Plots of log $(A_t - A_\infty)$, where A_∞ is the absorbance after ten half-lives, were linear to 80—90% completion with Cr^{2+} as reductant, and >90% with V^{2+}. First-order rate constants were evaluated from the gradients (× 2.303) of such plots. A strictly first-order dependence on reductant was observed in all cases for a *ca.* eight-fold variation in concentration. Second-order rate constants k_{obs} are listed in Table 2 (Cr^{2+}) and Table 3 (V^{2+}). Hydrogen-ion concentrations were varied over the range 0.10—0.90M when rate constants for complexes (I)—(IV) gave a dependence of the form (2).

TABLE 3

Rate constants (25 °C) for the V^{2+} reduction of μ-malonato- and μ-glycolato-complexes (I), (III), and (V), $I = 1.0$M($LiClO_4$)

Complexes	$[H^+]$ / M	$10^2[V^{2+}]$ / M	$10^4[(Co^{III})_2]$ / M	10^3k_{obs} / l mol^{-1} s^{-1}
(I)	0.11	2.01	2.57	8.58
	0.11	1.04	2.50	8.34
	0.14	0.98	2.50	6.91
	0.25	5.30	5.00	4.30
	0.25	2.50	5.00	4.36
	0.25	0.92	5.00	4.24
	0.25	0.48	5.00	4.42
	0.37	1.91	2.57	2.88
	0.53	0.94	5.00	2.59
	0.65	2.04	2.57	2.06
	0.85	2.70	1.29	1.64
	0.86	0.84	2.57	1.85
	0.87	4.78	0.51	1.94
	0.95	2.42	2.57	1.80
	0.97	0.97	5.00	1.85
(III)	0.11	2.47	5.00	1.61
	0.37	2.65	5.00	1.18
	0.85	3.00	10.3	1.06
	0.86	1.12	2.58	1.19
	0.87	5.02	5.15	1.08
	0.95	1.52	5.00	1.09
(V)	0.11	2.01	5.00	1.00
	0.37	1.71	5.00	1.00
	0.43	0.76	2.53	1.06
	0.45	3.33	5.05	1.05
	0.46	5.84	10.1	1.02
	0.95	1.86	4.17	0.93

$$k_{obs} = k_1 + k_2[H^+]^{-1} \qquad (2)$$

Contributions from the $[H^+]^{-1}$-dependent term k_2 are much less significant for complexes (III) and (IV) (Figures 1 and 2). No $[H^+]$-dependence was observed for the reduction of (V). Values of k_1 for complexes (I)—(V), and k_2 for (I)—(IV), have been obtained by an unweighted least-squares treatment, and are listed in Table 4.

DISCUSSION

The evidence obtained supports a redox sequence in which the first step is rate determining, and the second relatively fast. At the outset a slow outer-sphere first step yielding, in the case of complex (I) $[Cr(H_2O)_6]^{3+}$ and $[Co(NH_3)_5(O_2CCH_2CO_2H)]^{2+}$, followed by a second stage, involving relatively rapid Cr^{2+} reduction of $[Co(NH_3)_5(O_2CCH_2CO_2)]^{2+}$,[12-14] seemed likely. However, from separate studies,[9] the Cr^{2+} reduction of $[Co(NH_3)_5(O_2CCH_2CO_2H)]^{2+}$ yields >85% of the chelated product $[Cr(H_2O)_4(O_2CCH_2CO_2)]^{+}$, and this product pattern is independent of $[H^+]$ in the range 0.2—2.4M.* The expected products are accordingly $[Cr(H_2O)_6]^{3+}$ (50%), $[Cr(H_2O)_5(O_2CCH_2CO_2H)]^{2+}$ (<8%), and $[Cr(H_2O)_4(O_2CCH_2CO_2)]^{+}$ (>42%), whereas observed products (Table 1) are 50, 31, and 19% respectively. Reactions involving aquation and chelation of $[Cr(H_2O)_5(O_2CCH_2CO_2H)]^{2+}$,[10] and the Cr^{2+}-catalysed chelation of the same complex,[11] have been studied and are slow on the time scale involved. The $[H^+]$-dependence (2) for the first stage, in particular the detection of a k_2 term, is further indication that the simple interpretation (as given above) does not explain all features of these reactions. It is necessary to consider the paths k_1 and k_2 separately.

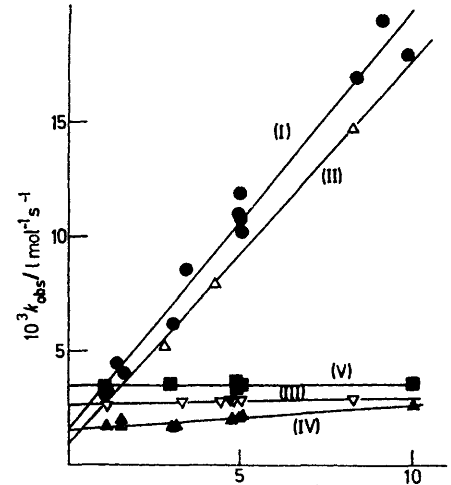


FIGURE 1 The hydrogen-ion dependence of rate constants for the Cr^{2+} reduction of complexes (I)–(V) at 25 °C, I = 1.0M(LiClO$_4$)

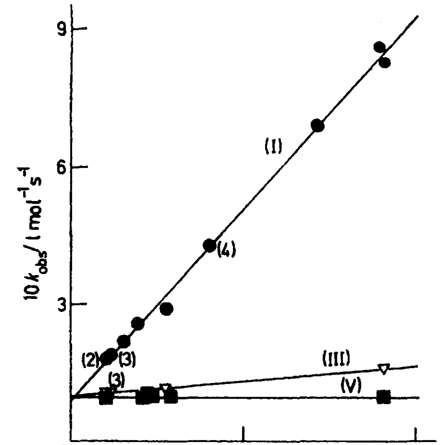


FIGURE 2 The hydrogen-ion dependence of rate constants for the V^{2+} reduction of complexes (I), (III), and (V) at 25 °C, I = 1.0M(LiClO$_4$). Number of runs which have been averaged indicated in parentheses

TABLE 4

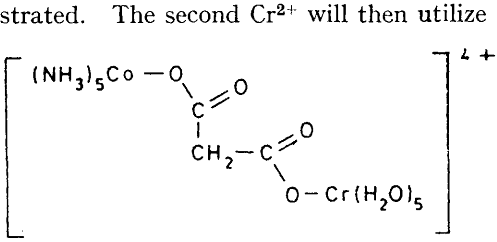
Summary of rate constants (25 °C) for the Cr^{2+} and V^{2+} reductions of complexes (I)—(V), I = 1.00M(LiClO$_4$)

Complex	10^3k_{Cr}	$10k_V$	k_{Cr}/k_V
$[H^+]$-independent rate constants k_1(l mol^{-1} s^{-1}) [a]			
(I)	1.6 ± 0.5	0.8 ± 0.1	0.020
(II)	1.0 ± 0.3	*b*	
(III)	2.65 ± 0.05	1.0 ± 0.01	0.027
(IV)	1.5 ± 0.06	*b*	
(V)	3.57 ± 0.03	1.0 ± 0.03	0.036
$[H^+]^{-1}$-dependent rate constants k_2(s^{-1}) [a]			
(I)	1.8 ± 0.1	0.84 ± 0.03	0.021
(II)	1.6 ± 0.06	*b*	
(III)	0.026 ± 0.009	0.066 ± 0.002	0.004
(IV)	0.108 ± 0.014	*b*	

[a] Cr^{2+} rate constant referred to as k_{Cr} and V^{2+} rate constant as k_V. [b] Not studied.

All five reactions give a k_1 term and values at 25 °C lie within the narrow range (1—3.6) × 10^{-3} l mol^{-1} s^{-1}. The magnitude of the rate constants suggests an outer-sphere mechanism, and this assignment gains support from the V^{2+} studies and the k_{Cr}/k_V ratios of 0.020 for (I), and 0.027 for (III) (Table 4). The ratio for (V) of 0.036 we find less acceptable and will return to later.

The μ-amido-complexes (I) and (II) both give large k_2 contributions; clearly acid dissociation of the methylene hydrogens of (I) is not a possible explanation. Product analyses for the Cr^{2+} reduction of complex (I) were carried out on reactant solutions, $[H^+]$ = 0.05M, at which value >95% of the reaction proceeds by k_2. The k_2 path cannot be a conventional outer-sphere type of process in view of the high yield of $[Cr(H_2O)_5(O_2CCH_2CO_2H)]^{2+}$. Attachment of the Cr^{2+} at the pendant or remote carboxylate must therefore occur. The product of the first stage is most probably a Co^{III}–Cr^{III} complex as illustrated. The second Cr^{2+} will then utilize one or both of the unco-ordinated O-atoms in a relatively rapid inner-sphere process. Two primary binuclear Cr^{III} products are possible. The *ca.* 3 h duration of experiments for which product analyses were carried out, and the low $[H^+]$ of 0.05M, are presumably sufficient to permit



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* At $[H^+]$ = 0.05M, I = 1.00M (LiClO$_4$), we confirm that the products from the Cr^{2+} reduction of $[Co(NH_3)_5(O_2CCH_2CO_2H)]^{2+}$ are $[Cr(H_2O)_4(O_2CCH_2CO_2]^{+}$ (88%) and $[Cr(H_2O)_5(O_2CH_2CO_2H)]^{2+}$ (12%).

[12] G. Svatos and H. Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 4172.

[13] R. D. Butler and H. Taube, *J. Amer. Chem. Soc.*, 1965, **87**, 5597.

[14] C. Lavallee and E. Deutsch, *Inorg. Chem.*, 1972, **12**, 3133.

decomposition of such binuclear species to mononuclear complexes.

The slopes in Figures 2 and 3 corresponding to k_2 are small for (III) and (IV). It is assumed that values obtained are real and not due to medium effects since, if the latter were the case, they would also be expected for (V). No k_2 term is obtained for (V). The mechanism by which electron transfer is achieved for k_2 must, therefore, account for the relatively high values of k_2 for the μ-amido-complexes (I) and (II) as compared with the di-μ-hydroxo-complexes (III) and (IV). We note that for k_2 the k_{Cr}/k_V ratio of 0.021 for (I) at least (Table 4) is consistent with an outer-sphere process. If the reaction were conventional inner-sphere then the Cr^{2+} reduction would generally be much more favourable relative to that for V^{2+}. We suggest, therefore, that the Cr^{2+} and V^{2+} first become attached to the unprotonated remote carboxylate, where the geometry of the malonate is such that close approach of the reductant to one of the cobalt(III) centres occurs. An examination of models has indicated that, assuming a non-planar ring for (I) and (II),[15] closer approach is possible for (I) and (II) than for (III) and (IV). This mechanism is we feel best described as one involving precursor complex formation with outer-sphere electron transfer. On less strong grounds the same mechanism was proposed for the $[H^+]^{-1}$-dependent path in the Cr^{2+} reduction of the di-μ-hydroxo-μ-*o*-phthalato-complex.[16]

TABLE 5

I.r. bands for complexes (I)—(V)

Complex	Bridging CO_2 group ν_{as}(C–O)	ν_s(C–O)	$\Delta\nu$	Other bands
(I) (unprotonated)	1 575 (vs)	1 425 (m)	150	1 730 (s) [a]
(I) (unprotonated)	1 570 (vs)	1 450 (w)	120	1 610 (s) and 1 350 (s) [b]
(II) (unprotonated)	1 575 (vs)	1 415 (m)	160	1 718 (s) [a]
(III) (unprotonated)	1 581 (vs)	1 437 (m)	144	1 720 (s) [a]
(IV) (unprotonated)	1 570 (vs)	1 420 (m)	150	1 715 (s) [a]
(V)	1 580 (vs)	1 420 (m)	160	
$[Co(CH_2C_2O_4)_3]^{3-}$ [d,e]	1 595 (vs, b) [f]	1 365 (s) [g]		
$[Co(NH_3)_4(CH_2C_2O_4)]^+$ [d,h]	1 600 (vs, b)	1 375 (s) [g]	225	

[a] ν(C=O) of pendant CO_2H group. [b] ν_{as}(C–O) and ν_s(C–O) respectively of pendant CO_2^- group. [c] Ref. 19. [d] Examples of chelated malonato-complexes in which each carboxylato-group is unidentate. [e] N. C. Kneten and S. T. Spees, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2437. [f] ν(C=O). [g] ν(C–O). [h] Ref. 11.

An estimate * of the acid dissociation constant of the protonated μ-malonato-ligand is that it is about the same as the first acid dissociation constant of malonic acid (pK_a *ca.* 2.74).[17] Rate constants (k_2/K_a) for the Cr^{2+} reduction of unprotonated complexes (I) and (II) are accordingly *ca.* 1.0 l mol^{-1} s^{-1}. This is significantly faster than for conventional outer-sphere reaction by k_1.

Acid dissociation of the OH group of the μ-glycolato-ligand is not effective and no [H$^+$]-dependence is expected (or observed) in the Cr^{2+} and V^{2+} reductions of (V). It is, nevertheless, possible that the precursor complex outer-sphere mechanism may contribute to k_1, and this could in some part be responsible for the high k_{Cr}/k_V ratio of 0.036. The Cr^{2+} reduction of $[Co(NH_3)_5(O_2CCH_2OH)]^{2+}$ has been studied previously, and yields the chelated complex $[Cr(H_2O)_4(O_2CCH_2OH)]^{2+}$.[13]

To summarize, the reaction sequence most consistent with our experiments is shown in equations (3) and (4) for k_1 (which is outer-sphere), and equations (5)—(7) for k_2. The $Cr^{III}X$ product in (4) is known to be >85% chelated. Reactions (6) and (7) yield both unidentate and chelated $Cr^{III}X$.

$$Cr^{2+} + (Co^{III})_2X \xrightarrow{k_1} Co^{III}X + Cr^{III} + Co^{2+} \quad (3)$$

$$Cr^{2+} + Co^{III}X \xrightarrow{\text{fast}} Cr^{III}X + Co^{2+} \quad (4)$$

$$Cr^{2+} + (Co^{III})_2X \xrightarrow{k_2} Co^{III}XCr^{III} + Co^{2+} \quad (5)$$

$$Cr^{2+} + Co^{III}XCr^{III} \xrightarrow{\text{fast}} (Cr^{III})_2X + Co^{2+} \quad (6)$$

$$(Cr^{III})_2X \xrightarrow{\text{fast}} Cr^{III}X + Cr^{III} \quad (7)$$

EXPERIMENTAL

The preparation of the di-μ-hydroxo-μ-malonato-bis[triammine-cobalt(III)] complex, $[(NH_3)_3Co\cdot\mu(OH,OH,O_2CCH_2CO_2H)\cdot Co(NH_3)_3][ClO_4]_3\cdot\frac{2}{3}NaClO_4\cdot H_2O$(III) has been described previously.[18] Other complexes studied were prepared as described below.

μ-Amido-μ-malonato-bis[tetra-amminecobalt(III)] *Perchlorate* (I).[19]—Malonic acid (G.P.R. Grade) was recrystallized from hot water until it gave a melting point of 135 ± 1 °C. The product (6 g) was dissolved in water (20 ml) at 50 °C, and μ-amido-μ-chloro-bis[tetra-amminecobalt(III)] chloride (1 g) was added slowly with stirring to the solution; it was maintained at 50 °C for 1 h and then filtered. The filtrate was evaporated to dryness under reduced pressure at 40—50 °C. The residue was worked up with ethanol and then diethyl ether; it was dissolved in a minimum of 0.1M-$HClO_4$ (*ca.* 3 ml) at 40 °C, filtered, and sodium perchlorate crystals (1 g) were added to the solution. After being set aside overnight at 5 °C the solution was filtered and the crystals washed with ethanol and ether. The crystals were

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* See measured values for other complexes in refs. 4 and 16.

[15] See *e.g.* details for μ-amido-μ-sulphato-structure, U. Thewalt, *Acta Cryst.*, 1971, **B27**, 1744.

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

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

[19] K. L. Scott, Ph.D. Thesis, University of Leeds, 1972.

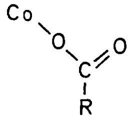
dissolved in water (3 ml) at 40 °C and concentrated $HClO_4$ (3 ml) was added. When the solution was allowed to cool slowly to room temperature red crystals were obtained; these were collected, washed with ethanol and ether, and dried by suction (yield 0.66 g) {Found: C, 4.8; H, 3.8; Cl, 18.6; N, 16.4. Calc. for $[(NH_3)_4Co{\cdot}\mu(NH_2,O_2CCH_2CO_2H){\cdot}Co(NH_3)_4][ClO_4]_4$: C, 4.7; H, 3.8; Cl, 18.4; N, 16.4%}. The u.v.–visible spectrum gave peaks at 515 nm (ε 365 l mol^{-1} cm^{-1}) and 366 (ε 623). A sample of unprotonated 3+ complex was isolated as the perchlorate salt from a solution containing NaOH. I.r. bands for this and other complexes are given in Table 4.

μ-Amido-μ-dimethylmalonato-bis[tetra-amminecobalt(III)] *Perchlorate* (II).—Dimethylmalonic acid (3 g) was dissolved in 0.5M-perchloric acid (10 ml) at 60 °C and μ-amido-μ-chloro-bis[tetra-amminecobalt(III)] (1 g) was added in small amounts to the solution with stirring. The temperature was maintained at 65 °C for 45 min, after which the solution was cooled to 0 °C and concentrated $HClO_4$ (5 ml) was added followed by solid $NaClO_4{\cdot}H_2O$ to near saturation. When the solution was set aside for *ca.* 10 min at 0 °C unchanged dimethylmalonic acid and some μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] perchlorate were precipitated. These were filtered off and the solution kept at 0 °C for a few hours. Very slowly red crystals of the desired product were obtained. The product is extremely soluble in water and is difficult to recrystallize without using sodium perchlorate {Found: C, 4.3; H, 3.1; Cl, 21.35; N, 10.3. Calc. for $[(NH_3)_4Co{\cdot}\mu(NH_2,O_2CC(CH_3)_2CO_2H){\cdot}Co(NH_3)_4][ClO_4]_4{\cdot}4NaClO_4{\cdot}2H_2O$: C, 4.5; H, 2.7; Cl, 21.4; N, 9.5%}. The u.v.–visible spectrum gave peaks at 517 (ε 366 l mol^{-1} cm^{-1}) and 368 nm (ε 610).

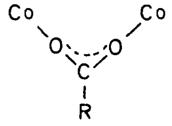
Di-μ-hydroxo-μ-dimethylmalonato-bis[triamminecobalt(III)] *Perchlorate* (IV).—Dimethylmalonic acid (0.7 g) was dissolved in 0.5M-$HClO_4$ (20 ml) at 60 °C. Tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate dihydrate (3.0 g) was added in small amounts with stirring to the solution and the temperature was maintained at 60 °C for 15 min. Perchloric acid (2 ml; 10M) was added to the solution which was then saturated with $NaClO_4{\cdot}1H_2O$. When the solution was cooled to 0 °C for *ca.* 2 h red crystals were obtained. These were filtered off and washed with ether. The complex is extremely soluble in water, ethanol, methanol, and acetone but is insoluble in diethyl ether. Perchloric acid and sodium perchlorate were again used to induce crystallization from a minimum amount of water at 30 °C {Found: C, 8.0; H, 4.2; Cl, 15.5; N, 12.24; H_2O, 4.8% (over P_2O_5 *in vacuo*). Calc. for $[(NH_3)_3Co{\cdot}\mu(OH,OH,O_2CC(CH_3)_2CO_2H){\cdot}Co(NH_3)_3][ClO_4]_3{\cdot}2H_2O$: C, 8.34; H, 4.3; Cl, 14.8; N, 11.7; H_2O, 5.0%}. The u.v.–visible spectrum gave peaks at 524 nm (ε 101 l mol^{-1} cm^{-1}) and 300 (ε 2.6 × 10^3) and a shoulder at 370 (ε 250).

μ-Glycolato-di-μ-hydroxo-bis[triamminecobalt(III)] *Perchlorate* (V).—To glycolic acid (0.4 g) in 0.5M-perchloric acid (20 ml) at 50 °C, tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate dihydrate (3 g) was added with stirring. The temperature was maintained at 60 °C for 10 min, after which 5M perchloric acid (2 ml) and solid $NaClO_4{\cdot}H_2O$ (*ca.* 30 g) were added to the solution at *ca.* 20 °C. The solution was kept at 0 °C for a few hours to give red crystals which were filtered off and washed with ethanol and ether. Recrystallization induced by addition of perchloric acid and sodium perchlorate was from a minimum of water at 30 °C {Found: C, 3.8; H, 3.4; Cl, 18.6; N, 11.6%. Calc. for $[(NH_3)_3Co{\cdot}\mu(OH,OH,O_2CCH_2OH){\cdot}Co(NH_3)_3][ClO_4]_3{\cdot}\frac{2}{3}NaClO_4$: C, 3.4; H, 3.25; Cl, 18.45; N, 11.9%}. There was no loss in weight when a sample was left *in vacuo* over P_2O_5 for seven days. The u.v.–visible spectrum gave peaks at 524 nm (ε 100 l mol^{-1} cm^{-1}) and 299 nm (ε 2.8 × 10^3), and a shoulder at 370 nm (ε 240).

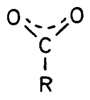
I.r. Spectra.—I.r. spectra of the above compounds (Table 4) are consistent with structures (I)—(V) as displayed. The effect of co-ordination on the C–O stretching frequencies of μ-carboxylato-binuclear cobalt(III) complexes has been discussed previously.[18–21] Siebert and Tremmel [20] have indicated that it is possible to distinguish between unidentate (A) and bidentate (B) carboxylato-groups by comparing the ν_{as}(C–O) stretching frequencies with those of the free carboxylate anion (C). The separation of the symmetric and asymmetric ν(C–O) stretching frequencies (Δν) (Table 5) are indicative of bonding as in (B). Additional ν(C–O) bands are observed in the case of binuclear complexes with dicarboxylic acids. A protonated CO_2H group exhibits a strong ν(C=O) band at *ca.* 1 720 cm^{-1} as observed for the free acid. The unprotonated form of the μ-amido-μ-malonato-complex shows two additional (C–O) frequencies at 1 610 and 1 350 cm^{-1} (Δν = 260 cm^{-1}) which are assigned to the antisymmetric and symmetric ν(C–O) stretching frequency of the unprotonated pendant CO_2^- group.



(A)



(B)



(C)

ν_{as}(C–O)	*ca.* $x + 30$ cm^{-1}	*ca.* $x - 30$ cm^{-1}	x cm^{-1}
Δν	200—260 cm^{-1}	120—180 cm^{-1}	200—230 cm^{-1}

Other Reactants.—Solutions of Cr^{2+} and V^{2+} perchlorates in perchloric and of lithium perchlorate were prepared by procedures as described previously in work from these laboratories.

Kinetic Studies.—The following procedure was adopted. A quantity of solution, containing all components except the reductant, was pipetted into a 4-cm optical cell. Oxygen-free nitrogen was passed through the solution for 20 min whilst the solution was thermostatted to 25 °C. The reaction was started by syringing in the required volume of reductant and mixing for 15 s.

It has previously been shown that hydroxo-bridge cleavage in the di-μ-hydroxo tribridged series of complexes is slow,[3] and makes only a minor contribution alongside outer-sphere Cr^{2+} reduction. Nor is Cr^{2+} able to utilize the lone-pair of electrons of a μ-hydroxo-group for inner-sphere electron transfer.

Product Analyses.—The analyses were carried out using Sephedex SP C-25 columns and different fractions determined as described in reference 16.

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