Electron Transfer Reactions between Penta-ammine(nitrilotriacetato)-cobalt(III) and Chromium(II) and between Acetatopenta-amminecobalt(III) and *N*-Methyliminodiacetato-chromium(II)

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The complex $[Co(NH_3)_5(H_2nta)]^{2+}$ (nta^{3-} = nitrilotriacetate) reacts with Cr^{II} with the rate law $-d[Co^{III}]/dt = k'[Co(NH_3)_5(H_2nta)^{2+}][Cr^{2+}]a_H^{-2}$ with k' = 2.45 mol dm^{-3} s^{-1} at 25 °C and ionic strength 1.0 mol dm^{-3} ($Na[ClO_4]$). A binuclear intermediate $[Co(NH_3)_5(nta)Cr]^{2+}$ is proposed and the specific rate of internal electron transfer is estimated to be *ca.* 600 s^{-1}. The rate of reaction of $[Co(NH_3)_5(O_2CMe)]^{2+}$ with Cr^{II} is enhanced by the presence of *N*-methyliminodiacetic acid (H_2mida). The rate law is $-d[Co^{III}]/dt = k_2'[Co(NH_3)_5(O_2CMe)^{2+}][Cr^{2+}][HL^-]a_H^{-1}$ with k_2' = 0.24 dm^3 mol^{-1} s^{-1} at 25 °C, and ionic strength 1.0 mol dm^{-3} ($Na[ClO_4]$). The specific rate for the bimolecular reaction $[Co(NH_3)_5(O_2CMe)]^{2+}$ + [Cr(mida)] is estimated to be 18 dm^3 mol^{-1} s^{-1}. The results are discussed in relation to the analogous reactions involving Fe^{II} as reductant.

IN previous papers we have reported the kinetics of electron transfer between cobalt(III) and iron(II) by two mechanisms: a unimolecular process[1] involving a complex with cobalt and iron linked by a short carbon chain [equation (1), M = Fe]; and a bimolecular process[2] between Co^{III} and Fe^{II} in separate complexes, but with the same inner-sphere ligand environments as in the unimolecular case [equation (2), M = Fe]. Here we

$$[Co^{III}(NH_3)_5\{O_2CCH_2N(CH_2CO_2)_2\}M]^{2+} \xrightarrow{k_1^M} Co^{II} + M^{III} \quad (1)$$

$$[Co^{III}(NH_3)_5(O_2CMe)]^{2+} + M[(O_2CCH_2)_2NMe] \xrightarrow{k_2^M} Co^{II} + M^{III} \quad (2)$$

describe studies of the corresponding systems with chromium(II) as reductant in place of Fe^{II}, in which we have found evidence for the same two mechanisms [equations (1) and (2), M = Cr].

RESULTS AND INTERPRETATION

All reactions were carried out with Cr^{II} in sufficiently large excess over Co^{III} to give pseudo-first-order kinetics [equation (3)]. Rate constants $k_{obs.}$ were obtained by fitting data to equation (4), where A_0, A, and A_∞ denote absorbances at times 0, t, and ∞ respectively.

$$-d[Co^{III}]_T/dt = k_{obs.}[Co^{III}]_T \quad (3)$$

$$\ln (A - A_\infty) = \ln (A_0 - A_\infty) - k_{obs.}t \quad (4)$$

The Reaction $[Co^{III}(NH_3)_5(O_2CMe)]^{2+} + Cr^{2+}$.—As a preliminary to the present study a few experiments were conducted with $[Co^{III}(NH_3)_5(O_2CMe)]^{2+}$ and Cr^{2+} in the absence of *N*-methyliminodiacetic acid (H_2mida). In perchloric acid media the reaction is[3] as in (5) and three experiments

$$[Co(NH_3)_5(O_2CMe)]^{2+} + 5H^+ + Cr^{2+} \longrightarrow Co^{2+} + 5[NH_4]^+ + [Cr(O_2CMe)]^{2+} \quad (5)$$

at $[H^+]$ = 0.080 mol dm^{-3} and $[Cr^{2+}] = 8.2 \times 10^{-3}$—$1.72 \times 10^{-2}$ mol dm^{-3} conformed to the rate law (6), with $k_0 = (0.30 \pm 0.02)$ dm^3 mol^{-1} s^{-1} at 25 °C and ionic strength

$$-d \ln[Co^{III}]_T/dt = k_0[Cr^{II}]_T \quad (6)$$

1.0 mol dm^{-3} ($Na[ClO_4]$). The value of k_0 is similar to that of 0.35 dm^3 mol^{-1} s^{-1} obtained by Barrett *et al.*[3] in lithium perchlorate media at the same ionic strength. In glycine buffer ($glyO^-$ = glycinate) there was some enhancement in rate (Figure 1) according to the rate law (7), with k' =

$$-d \ln[Co^{III}]_T/dt = (k_0 + k'[glyO^-]_T)[Cr^{II}]_T \quad (7)$$

2.5 dm^6 mol^{-2} s^{-1} at 25 °C, pH 2.35, and ionic strength 1.0 mol dm^{-3} ($Na[ClO_4]$).‡ Presumably the effect of glycine is to co-ordinate with Cr^{2+} and so stabilise the chromium(III) product. The quotient k'/k_0 = 8.3 dm^3 mol^{-1} may then be compared with analogous 'non-bridging

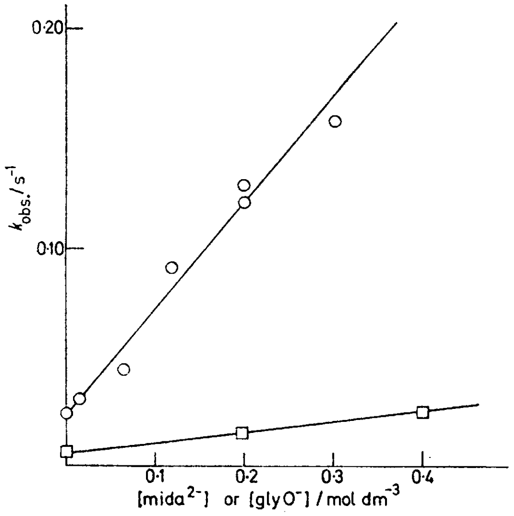

FIGURE 1 Reactions $[Co(NH_3)_5(O_2CMe)]^{2+} + Cr^{II}$: (□), glycine dependence in the absence of *N*-methyliminodiacetic acid; (○), *N*-methyliminodiacetic acid dependence in the presence of glycine, $[glyO^-]_T$ = 0.40 mol dm^{-3}.† In all experiments, $[Cr^{II}]_T = 1.92 \times 10^{-2}$ mol dm^{-3}, pH 2.35, 25 °C, and ionic strength 1.0 mol dm^{-3} ($Na[ClO_4]$)

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† The expression $[glyO^-]_T$ refers to *total* stoicheiometric concentration of glycine, as distinguished from the *species* concentration; $[mida]_T$ has a similar significance.

‡ In calculating ionic strength, 1 mole of the zwitterion glycine was taken as 1 mole of a 1 : 1 electrolyte, as also was 1 mole of glycinium perchlorate (see A. Albert and E. P. Serjeant, 'Ionisation Constants of Acids and Bases,' Methuen, London, 1962, p. 119).

[1] (*a*) R. D. Cannon and J. Gardiner, *J. Amer. Chem. Soc.*, 1970, **92**, 3800; (*b*) *Inorg. Chem.*, 1974, **13**, 390.

[2] R. D. Cannon and J. Gardiner, *J.C.S. Dalton*, 1972, 887.

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

ligand effects ',[4] for example $k'/k_0 = 0.59$ dm^3 mol^{-1} for the effect of chloride ion on the same reaction at 25 °C and ionic strength 1.47 mol dm^{-3}.[5]

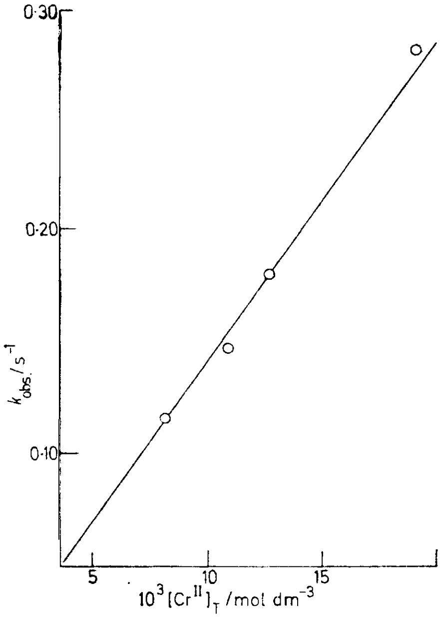

FIGURE 2 Chromium(II) dependence of the reaction $[Co(NH_3)_5(O_2CMe)]^{2+} + Cr^{II}$ in *N*-methyliminodiacetic acid buffer. $[mida^{2-}]_T = 0.40$ mol dm^{-3}, $[glyO^-]_T = 0$, pH 2.35, 25 °C, and ionic strength 1.0 mol dm^{-3} (Na[ClO$_4$])

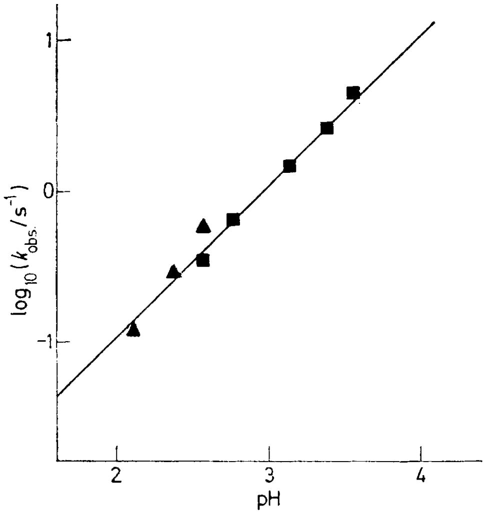

FIGURE 3 Hydrogen-ion dependence of the reaction $[Co(NH_3)_5(O_2CMe)]^{2+} + Cr^{II}$ in *N*-methyliminoacetic acid buffer. $[H_2mida]_T = 0.40$ mol dm^{-3}, $[Cr^{II}]_T = 1.92 \times 10^{-2}$ mol dm^{-3}, 25 °C, ionic strength 1.0 mol dm^{-3} (Na[ClO$_4$]). Initial cobalt(III) concentration: 1.0×10^{-3} (▲); 2.0×10^{-3} mol dm^{-3} (■). The straight line is drawn with gradient 1.0

The Reaction $[Co(NH_3)_5(O_2CMe)]^{2+} + [Cr^{II}(mida)]$.—This was studied in glycine buffer, at 410 nm, where the principal absorbing species is the chromium(III) chelated product. Good pseudo-first-order rate plots were obtained. At constant pH, rates were first order in the concentrations of the chelating agent (Figure 1) and of Cr^{II} (Figure 2), and over the pH range 2.0—3.5 had an inverse first-order dependence on hydrogen-ion concentration (Figure 3). Since it is known that under these conditions the predominant form of the ligand is the ion Hmida$^-$, these data may be summarised in the rate law (8), where $k_2' = 0.24 \pm 0.02$ dm^3 mol^{-1} s^{-1} at 25 °C and ionic strength 1.0 mol dm^{-3} (Na[ClO$_4$]), and a_H denotes the hydrogen-ion activity. This is consistent with the mechanism in (9) and (10) provided

$$-d[Co^{III}]_T/dt = k_2'[Cr^{II}]_T[Hmida^-]a_H^{-1} \qquad (8)$$

$$Cr^{2+} + Hmida^- \xrightleftharpoons{K_s^*} [Cr(mida)] + H^+ \qquad (9)$$

$$[Co(NH_3)_5(O_2CMe)]^{2+} + [Cr(mida)] \xrightarrow{k_2} \text{Products} \qquad (10)$$

that equilibrium (9) is established rapidly and that the extent of complexation of Cr^{II} remains small. Then we have $k_2' = k_2K_s^* = k_2K_sK_a'$ where K_s is the stability constant of [Cr(mida)] and K_a' is the acid-dissociation constant of Hmida$^-$. Using p$K_a' = 9.27$ as found previously,[2] we calculate $k_2K_s = (4.5 \pm 0.4) \times 10^8$ dm^6 mol^{-2} s^{-1}. The ' non-bridging ligand effect ' defined by $k_2K_s/k_0 = 1.5 \times 10^9$ dm^3 mol^{-1} may be compared with the corresponding value of 4.2×10^9 dm^3 mol^{-1} found for the reduction of $[Cr(OH)]^{2+}$ by [Cr(mida)] at the same temperature and ionic strength.[6]

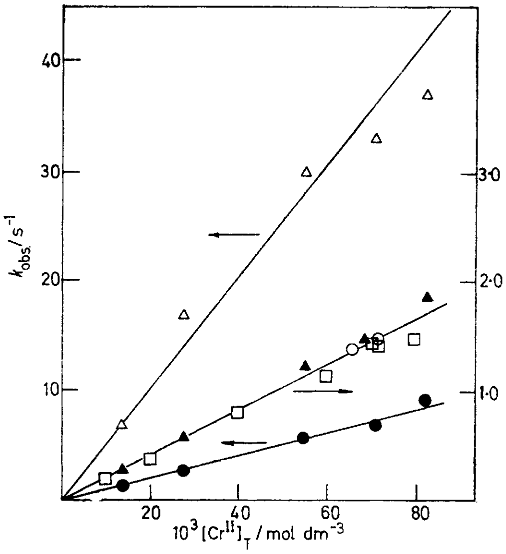

FIGURE 4 Chromium(II) dependence of the reaction $[Co(NH_3)_5(H_2nta)]^{2+} + Cr^{II}$ in perchloric acid–sodium perchlorate media at 25 °C and ionic strength 1.0 mol dm^{-3} (Na[ClO$_4$]). $[H^+] = 5 \times 10^{-2}$ (△), 0.2 (▲), and 0.1 mol dm^{-3} (●). $[Zn^{2+}] = 0.117$ mol dm^{-3} (○) or $\frac{1}{2}[Cr^{II}]_T$ (□)

The Reaction $[Co(NH_3)_5(H_2nta)]^{2+} + Cr^{2+}$.—This was studied in perchloric acid–sodium perchlorate media, at 410 nm where again the principal absorbing species is the chelated chromium(III) product. In all cases good pseudo-first-order plots were obtained, conforming to equation (4) for up to three half-lives of reaction. Rates were first order in [Cr^{II}] (Figure 4) and inverse second order in hydrogen-ion

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[4] J. E. Earley, *Progr. Inorg. Chem.*, 1970, **13**, 243.

[5] P. V. Manning and R. G. Jarnagin, *J. Phys. Chem.*, 1963, **67**, 2884.

[6] R. D. Cannon and J. E. Earley, *J. Chem. Soc.* (*A*), 1968, 1102.

concentration over the range $[H^+] = 0.030$—0.200 mol dm^{-3} (Figure 5). It has been shown [1b] that under these conditions the predominant form of the cobalt complex is $[Co(NH_3)_5(H_2nta)]^{2+}$ (nta = nitrilotriacetato), hence the rate law may be expressed as in (11) where $k_1' = 10^{0.39\pm0.1} \approx 2.45$ mol dm^{-3} s^{-1} at 25 °C and ionic strength 1.0 mol dm^{-3} ($Na[ClO_4]$).

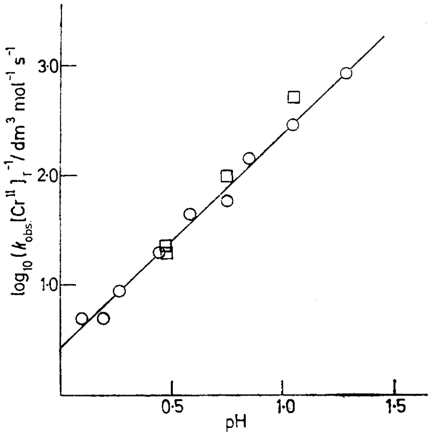

FIGURE 5 Hydrogen-ion dependence of the reaction $[Co(NH_3)_5(H_2nta)]^{2+} + Cr^{II}$ in perchloric acid–sodium perchlorate media at 25 °C and ionic strength 1.0 mol dm^{-3} ($Na[ClO_4]$). (○), $[Cr^{II}]_T = 3.98 \times 10^{-2}$ mol dm^{-3}; (□), from chromium(II)-dependence data (Figure 4). The line is drawn with gradient 2.0

$$-d[Co^{III}]_T/dt = k_1'[Co(NH_3)_5(H_2nta)^{2+}][Cr^{II}]_T a_H^{-2} \quad (11)$$

$$[Co(NH_3)_5(H_2nta)]^{2+} + Cr^{2+} \overset{K_{Cr}^*}{\rightleftharpoons} [Co(NH_3)_5(nta)Cr]^{2+} + 2H^+ \quad (12)$$

$$[Co(NH_3)_5(nta)Cr]^{2+} \xrightarrow{k_1} \text{Products} \quad (13)$$

This is consistent with the mechanism in equations (12) and (13), again provided that equilibrium (12) is established rapidly and that the quotient $[Co(NH_3)_5(nta)Cr^{2+}]/[Co(NH_3)_5(H_2nta)^{2+}]$ remains small. Thus we have $k_1' = k_1K_{Cr}^* = k_1K_{Cr}K_{a1}K_{a2}$, where K_{Cr} is the stability constant of $[Co(NH_3)_5(nta)Cr]^{2+}$ and K_{a1} and K_{a2} are the successive acid-dissociation constants of $[Co(NH_3)_5(H_2nta)]^{2+}$. An equivalent form of the rate law would be (14), with $k_1'' = k_1K_S$.

$$-d[Co^{III}]_T/dt = k_1''[Co(NH_3)_5(nta)][Cr^{2+}] \quad (14)$$

Using pK_{a1} 1.82 and pK_{a2} 7.96 as found previously,[1b] we calculate $k_1'' = 10^{10.17} \approx 1.5 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. This is close to the diffusion-controlled limit for bimolecular processes, and very much in excess of the highest previously reported secord-order rate constants for reduction by Cr^{II}.* Clearly, therefore, equation (14) does not imply a bimolecular process with specific rate k_1''. A plausible sequence of steps would be as in (15)—(17) followed by (13), where $[Co(NH_3)_5(Hnta)Cr]^{3+}$ denotes a complex with Cr^{II} attached to one or two carboxyl groups but not to the tertiary nitrogen atom, and all three equilibria are attained rapidly.†‡

$$[Co(NH_3)_5(H_2nta)]^{2+} \rightleftharpoons [Co(NH_3)_5(Hnta)]^+ + H^+ \quad (15)$$

$$[Co(NH_3)_5(Hnta)]^+ + Cr^{2+} \rightleftharpoons [Co(NH_3)_5(Hnta)Cr]^{3+} \quad (16)$$

$$[Co(NH_3)_5(Hnta)Cr]^{3+} \rightleftharpoons [Co(NH_3)_5(nta)Cr]^{2+} + H^+ \quad (17)$$

Effect of added non-reducing metal ions. At the highest acidities, the inclusion of zinc ion in the solution had no effect on the rate (Figure 4), but at lower acidities both Zn^{2+} and Co^{2+} inhibited the electron-transfer reaction. Introducing the equilibria (18), where M = Co or Zn, and again using equations (12) and (13) we obtain (19) and hence (20), where $[M]_T = [M^{2+}] + [Co(NH_3)_5(nta)M^{2+}]$, $K_M = K_M^*K_{a1}^{-1}K_{a2}^{-1}$, and $k^0_{obs.}$ is the value of $k_{obs.}$ obtained in the absence of added M^{2+} ion. As shown in Figure 6, the data conform to this equation with $K_{Zn}/k_1K_{Cr} = 1.03 \times 10^{-2}$ s and $K_{Co}/k_1K_{Cr} = 1.40 \times 10^{-3}$ s, whence log $K_{Zn} = 8.2 \pm 0.4$ and log $K_{Co} = 7.3 \pm 0.3$. These values may be

$$[Co(NH_3)_5(H_2nta)]^{2+} + M^{2+} \overset{K_M^*}{\rightleftharpoons} [Co(NH_3)_5(nta)M]^{2+} + 2H^+ \quad (18)$$

$$-\frac{d[Co^{III}]}{dt} = \frac{k_1K_{Cr}^*[Co^{III}]_T[Cr^{II}]_T a_H^{-2}}{1 + K_M^*[M]_T a_H^{-2}} \quad (19)$$

$$\frac{[Cr^{II}]_T}{k_{obs.}} = \frac{[Cr^{II}]_T}{k^0_{obs.}} + \frac{K_M[M]_T}{k_1K_{Cr}} \quad (20)$$

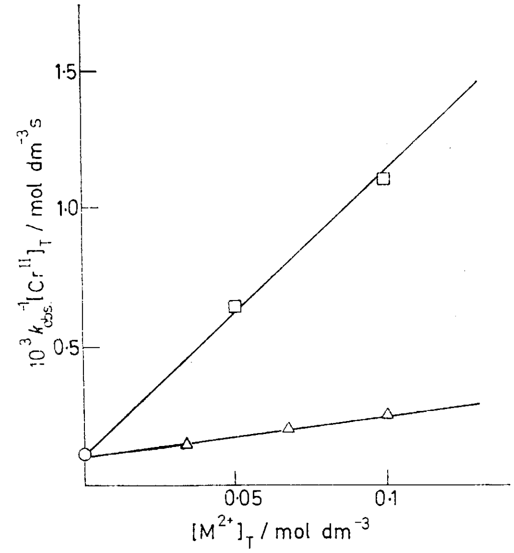

FIGURE 6 Effect of non-reducing metal ions on the reaction $[Co(NH_3)_5(H_2nta)]^{2+} + Cr^{II}$ [*cf.* equation (20)] at $[H^+] = 1 \times 10^{-2}$ mol dm^{-3}, 25 °C, and ionic strength 1.0 mol dm^{-3} ($Na[ClO_4]$). (□), $M^{2+} = Zn^{2+}$ (each point represents the average of three determinations); (△), $M^{2+} = Co^{2+}$; (○), no added metal ion (value of $k^0_{obs.}$ extrapolated from Figure 5)

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* For example, for $[CoBr(NH_3)_5]^{2+} + Cr^{2+}$, $k = 1.4 \times 10^6$ dm^3 mol^{-1} s^{-1} (J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, 1964, **86**, 1019).

† Similar comments may be applied to the reaction $[Co(NH_3)_5(HPO_4)]^+ + Cr^{2+}$, which has a rate term $k[Co(NH_3)_5(PO_4)][Cr^{2+}]$ with $k = 4.8 \times 10^9$ dm^3 mol^{-1} s^{-1} (J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, 1964, **86**, 1019).

‡ A further possibility would be to replace equation (17) by (17a), so that $k_1' = k_{OH}K_WK_{Cr}'K_{a1}$ where K_{Cr}' is the equilibrium constant for equation (16) and K_W is the ionic product of water. However, this requires an unacceptably high value of k_{OH}: using $K_W = 10^{-14}$ mol^2 dm^{-6} and estimating $K_{Cr}' \leqslant 10^2$ dm^3 mol^{-1}, we calculate $k_{OH} \geqslant 10^{14}$ dm^3 mol^{-1} s^{-1}.

$$[Co(NH_3)_5(Hnta)Cr]^{3+} + OH^- \xrightarrow{k_{OH}} [Co(NH_3)_5(nta)Cr]^{2+} + H_2O \quad (17a)$$

compared with those obtained in the study of the $[Co(NH_3)_5(H_2nta)]^{2+} + Fe^{2+}$ reaction [1b] using glycine buffer media at the same temperature and ionic strength, *i.e.* $\log K_{Zn} = 7.57 \pm 0.17$ and $\log K_{Co} = 7.26 \pm 0.17$ respectively.

DISCUSSION

The equilibrium constants K_s and K_{Cr} are not known but they may be estimated from other data. In the series of complexes [M(mida)] [7] with different bivalent transition metals, and in the analogous series $[Co(NH_3)_5(nta)M]^{2+}$,[1b] stability constants follow the well known Irving–Williams sequence. On comparing with similar sequences for other ligands, where a value for Cr^{II} is also known, we estimate $\log K_s = 7.4 \pm 1.0$ and $\log K_{Cr} = 7.5 \pm 0.5$ at 25 °C and ionic strength 1.0 mol dm^{-3}.* The latter figure combined with our kinetic data gives the order of magnitude of the specific rate of electron transfer in the precursor complex, *viz.* k_1 *ca.* 600 s^{-1}. It also implies that in the pH range 2—3, and at the higher chromium(II) concentrations used, equilibrium (12) should be displaced appreciably to the right, with consequent modification of the chromium(II) dependence as in equation (21). We did find such a chromium(II)

$$k_{obs.} = k_1K_{Cr}{}^*[Cr^{II}]_Ta_H{}^{-2}/(1 + K_M{}^*[M]_Ta_H{}^{-2} + K_{Cr}{}^*[Cr^{II}]_Ta_H{}^{-2}) \quad (21)$$

dependence, in a series of experiments in glycine buffer at pH 1.66, implying k_1 in the range 80—300 s^{-1}; and in further experiments with a variety of buffer media we have confirmed that the rate of reaction remains within the stopped-flow time scale over the pH range 1.5—6. There are, however, small differences in rate depending on the buffer, and reproducibility is poor owing to the instability of Cr^{II} under these conditions.

Comparison of iron(II) and chromium(II) reduction rates [a]

Rate term [b]	Rate constant	M = Fe	M = Cr
$[Co(NH_3)_5(O_2CMe)^{2+}][M^{2+}]$	k_0/dm^3 mol^{-1} s^{-1}	$\leqslant 10^{-6}$ [c]	3.0×10^{-1} [d]
$[Co(NH_3)_5(nta)][M^{2+}]$	k_1K_M/dm^3 mol^{-1} s^{-1}	1.3×10^5 [e]	1.5×10^{10} [d]
$[Co(NH_3)_5(nta)M^{2+}]$	k_1/s^{-1}	1.2×10^{-1} [e]	6×10^2 [f]
$[Co(NH_5)_5(O_2CMe)^{2+}][M^{2+}][mida^{2-}]$	k_2K_s/dm^6 mol^{-2} s^{-1}	1.5×10^3 [c]	4.5×10^8 [d]
$[Co(NH_3)_5(O_2CMe)^{2+}][M(mida)]$	k_2/dm^3 mol^{-1} s^{-1}	1.5×10^{-3} [c]	1.8×10^1 [g]

[a] At 25 °C and ionic strength 1.0 mol dm^{-3} (Na[ClO$_4$]). [b] Symbols as defined in text. [c] Ref. 2. [d] This work. [e] Ref. 1*b*. [f] Assuming $K_M = 3 \times 10^7$ dm^3 mol^{-1}. [g] Assuming $K_s = 2.5 \times 10^7$ dm^3 mol^{-1}.

In the Table the rate parameters reported here are compared with reactions involving Fe^{II} in place of Cr^{II}. As discussed previously,[1b] the ratio of second- to first-order rate constants, $k_2{}^{Cr}/k_1{}^{Cr} \approx 3 \times 10^{-2}$ dm^3 mol^{-1}, can be regarded as an estimate of the formation constant $K_{ip}{}^{Cr}$ of the precursor complex $[Co(NH_3)_5(O_2CMe)^{2+}\cdot Cr(mida)]$, relative to the reactants $[Co(NH_3)_5(O_2CMe)]^{2+}$ and [Cr(mida)]. It is of the same order of magnitude as the corresponding value for the reactions of Fe^{II}, $K_{ip}{}^{Fe} \approx k_2{}^{Fe}/k_1{}^{Fe} = 1.25 \times 10^{-2}$ dm^3 mol^{-1}.† It follows

$$[Co(NH_3)_5(O_2CMe)]^{2+} + [Cr(mida)] \xrightleftharpoons{K_{ip}{}^{Cr}} [Co(NH_3)_5(O_2CMe)^{2+}\cdot Cr(mida)] \quad (22)$$

$$[Co(NH_3)_5(O_2CMe)]^{2+} + [Fe(mida)] \xrightleftharpoons{K_{ip}{}^{Fe}} [Co(NH_3)_5(O_2CMe)^{2+}\cdot Fe(mida)] \quad (23)$$

that if we compare the rates of reduction by Cr^{II} and by Fe^{II}, the ' work terms ', *i.e.* the values of K_{ip}, will approximately cancel, and the ratio will be a true measure of the relative stabilities of the transition states as defined in the quasi-equilibrium expression (24) with $K_2{}^{\dagger} \approx k_2{}^{Cr}/k_2{}^{Fe} \approx 10^4$. For the unimolecular reaction we may write (25) directly, with $K_1{}^{\dagger} \approx k_1{}^{Cr}/k_1{}^{Fe} \approx 5 \times 10^3$.

$$[Co(NH_3)_5(O_2CMe)^{2+}\cdot Fe(mida)]^{\ddagger} + [Co(NH_3)_5(O_2CMe)^{2+}\cdot Cr(mida)] \xrightleftharpoons{K_2{}^{\ddagger}} [Co(NH_3)_5(O_2CMe)^{2+}\cdot Fe(mida)] + [Co(NH_3)_5(O_2CMe)^{2+}\cdot Cr(mida)]^{\ddagger} \quad (24)$$

$$\{[Co(NH_3)_5(nta)Fe]^{2+}\}^{\ddagger} + [Co(NH_3)_5(nta)Cr]^{2+} \xrightleftharpoons{K_1{}^{\dagger}} [Co(NH_3)_5(nta)Fe]^{2+} + \{[Co(NH_3)_5(nta)Cr]^{2+}\}^{\ddagger} \quad (25)$$

The analogous reactions $[Co(NH_3)_5(O_2CMe)]^{2+} + M^{2+}$ show much greater sensitivity to the nature of M, with a lower limit $k_0{}^{Cr}/k_0{}^{Fe} \geqslant 3 \times 10^5$. An equivalent statement is that the effect of chelation of the reductant is greater for Fe^{II} than for Cr^{II}. This can be understood in terms of the Marcus theory of electron transfer.[8] In a series of reactions between the same pair of metal ions, with the same bridging group, rate constants k are expected to vary with the equilibrium constants K according to equation (26),‡ where k_0 is the rate constant observed when $K = 1$ and Z is the specific rate for collisions between the reacting species at the same mean separation distance as in the transition state. Thus for small changes in log K the change in log k may be obtained by differentiating equation (26) to give (27).

$$\log k = \log k_0 + \tfrac{1}{2}\log K + \frac{(\log K)^2}{16 \log(k_0/Z)} \quad (26)$$

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* For details see R. D. Cannon, *J. Inorg. Nuclear Chem.*, in the press.

† In ref. 1*b*, the notation for the formation constant of the precursor complex $[Co(NH_3)_5(O_2CMe)^{2+}\cdot Fe(mida)]$ was $k_2'/k_1 = K_{IV}K_V$.

‡ Equation (26) was first developed for outer-sphere electron-transfer reactions, but has since been shown to be of more general application (see, for example, R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891; A. O. Cohen and R. A. Marcus, *ibid.*, p. 4249; R. A. Marcus, *J. Amer. Chem. Soc.*, 1969, **91**, 7224).

[7] ' Stability Constants of Metal–Ion Complexes,' eds. A. E. Martell and L. G. Sillén, (*Special Publ.* Nos. 17 and 25), The Chemical Society, London, 1964 and 1975.

[8] R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1964, **15**, 155.

$$\frac{\Delta \log k}{\Delta \log K} \approx \frac{\mathrm{d} \log k}{\mathrm{d} \log K} = \tfrac{1}{2}\{1 + [\log K/4 \log(k_0/Z)]\} \qquad (27)$$

For two series of reactions involving the reductants Cr^{II} and Fe^{II} corresponding changes in the non-bridging ligands will produce similar changes in the equilibrium constants K^{Cr} and K^{Fe}. Hence for reactions with a common oxidant the variations in rate constant will be related by (28), where ${k_0}^{Cr}$ and ${k_0}^{Fe}$ are analogous to k_0

$$\frac{\Delta \log^{Cr}}{\Delta \log^{Fe}} = \frac{1 + [\log K^{Cr}/4 \log({k_0}^{Cr}/Z)]}{1 + [\log K^{Fe}/4 \log({k_0}^{Fe}/Z)]} \qquad (28)$$

above. The prediction then is that this expression should be less than unity, since ${k_0}^{Cr}$ and ${k_0}^{Fe}$ are less than Z by definition, and $K^{Cr} \gg K^{Fe}$.* This is fulfilled by the experimental data, since we have $\Delta \log k^{Cr}/\Delta \log k^{Fe} = \log({k_2}^{Cr}/{k_0}^{Cr})/\log({k_2}^{Fe}/{k_0}^{Fe})$ and from the Table this is less than or equal to 0.54.

EXPERIMENTAL

Materials.—The complexes $[Co(NH_3)_5(O_2CMe)][ClO_4]_2$ [2] and $[Co(H_2nta)][ClO_4]_2$ [1b] were prepared as described previously. Chromium(II) solutions were prepared by reduction of chromium(III) perchlorate (K. and K. Laboratories, Hollywood, California) in aqueous solution with the requisite concentration of sodium perchlorate to give the desired ionic strength. Two methods of reduction were employed.[6]

(a) *Electrolysis at a mercury cathode*. The product of electrolysis contained hydrogen ion in approximately the same concentration as chromium. This could be estimated by titration with alkali under a nitrogen atmosphere, but only approximately because of oxidation to Cr^{III}.

(b) *Reduction with amalgamated zinc*. This gave a product with very little $HClO_4$, as confirmed by pH measurement, but containing zinc perchlorate of concentration half that of the chromium.

Since the effects of hydrogen and zinc ion were being explicitly studied, either of the two methods was chosen as convenient. The chromium(II) content was determined by injecting aliquot portions into excess of standard dichromate and back titrating with ammonium iron(II) sulphate using Ferroin indicator.

Glycine (B.D.H. reagent grade) and *N*-methyliminodiacetic acid (Aldrich Chemical Company Inc.) were each recrystallised several times from water. Cobalt(II) perchlorate was the Koch–Light product $Co[ClO_4]_2 \cdot 6H_2O$, recrystallised from water. Zinc(II) perchlorate, $Zn[ClO_4]_2 \cdot 6H_2O$, was prepared by dissolving zinc in perchloric acid (both analytical grade) and recrystallising twice.

Measurements. The pH of the buffer was determined with a Vibret model 46A expanded-scale pH meter, with glass and calomel electrodes, standardised at pH 1.09 and 4.00 with 0.100 mol dm^{-3} HCl [9] and with potassium hydrogenphthalate, respectively. In order to compare measurements in the perchloric acid media with those in buffer media, the activity coefficient of H^+ ion was determined by titrating standard alkali and standard acid. This gave $\gamma_H = a_H/[H^+] = 1.76$ at 25 °C and ionic strength 1.0 mol dm^{-3} ($Na[ClO_4]$). Fast reactions were carried out with an Aminco–Morrow stopped-flow apparatus, modified for improved temperature control.[10] Conventional kinetic measurements were made with a Beckman DB spectrophotometer with 10 in chart recorder. All air-sensitive solutions were handled under nitrogen as previously described,[11] except that standard chromium(II) solutions were dispensed from an Agla micrometer syringe which gives improved volumetric accuracy and is adequately airtight.

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* Strictly, the condition for expression (28) to be less than unity is $\log K^{Cr}/(\log Z - \log {k_0}^{Cr}) > \log K^{Fe}/(\log Z - \log {k_0}^{Fe})$.

[9] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' 2nd edn., Butterworths, London, p. 546.

[10] R. D. Cannon and J. S. Stillman, *Inorg. Chem.*, 1975, **14**, 2202, 2207.

[11] R. D. Cannon, *J. Chem. Soc.* (*A*), 1968, 1098.