Kinetics of the Electron-transfer Reaction of Penta-ammine(nitrilotriacetato)cobalt(III) and Titanium(III): Evidence for a Binuclear Intermediate †

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The reaction $[Co(NH_3)_5(H_2L)]^{2+}$ + Ti^{III}, where $L^{3-} = N(CH_2COO)_3{}^{3-}$, has been studied in aqueous acidic media. The kinetics are consistent with the stepwise mechanism $[Co(NH_3)_5(HL)]^+ + Ti^{III} \overset{*K_1}{\rightleftharpoons} [Co(NH_3)_5LTi]^{3+} + H^+$ followed by $[Co(NH_3)_5LTi]^{3+} \xrightarrow{k} Co^{II} + Ti^{IV}$ with $k = a/(b + [H^+])$. At 25 °C, log $^*K_1$ = 1.60 ± 0.18 and 1.73 ± 0.21 at ionic strength 1.0 mol dm^{-3} ($LiClO_4$ and NaCl respectively), a = 0.046 ± 0.005 (NaCl) and 0.055 ± 0.010 ($LiClO_4$) mol dm^{-3} s^{-1}, and a/b = 1.0 ± 0.1 s^{-1} (NaCl). The formation of the binuclear intermediate is confirmed by rapid-scan spectroscopy. The mechanism of the intramolecular electron-transfer reaction is discussed.

The complex $[Co(NH_3)_5(Hnta)]^+$ [$nta^{3-} = N(CH_2COO)_3{}^{3-}$] has been shown to form binuclear complexes with various metal ions, and the electron-transfer reaction with iron(II) was found to involve a Co^{III}–Fe^{II} precursor complex [equations (1) and (2)].[1] The combination of a high stability constant

$$[Co(NH_3)_5(Hnta)]^+ + Fe^{2+} \overset{*K_{Fe}}{\rightleftharpoons} [Co(NH_3)_5(nta)Fe]^{2+} + H^+ \qquad (1)$$

$$[Co(NH_3)_5(nta)Fe]^{2+} \xrightarrow{k} Co^{II} + Fe^{III}(nta) \qquad (2)$$

$^*K_{Fe}$ and low electron-transfer rate constant k made it possible to observe the binuclear complex in solution, the equilibrium (1) being driven significantly to the right within the range of iron(II) and acid concentrations used. In the case of the analogous reaction with Cr^{2+} in place of Fe^{2+}, the complex $[Co(NH_3)_5(nta)Cr]^{2+}$ could not be detected in this way, but the electron-transfer rate constant was estimated[2] as k_{Cr} = 600 s^{-1}.

From a consideration of typical stability constants and reaction rates of titanium(III) complexes, it appeared to us that a Co^{III}–Ti^{III} complex might be detectable, and this has proved to be the case. Here we report the kinetics of the reaction (3). Our results support the mechanism in equations (4) and (5), but in contrast to the previous systems the electron-transfer reaction (5) is strongly base-catalysed, and is not an elementary step.

$$[Co(NH_3)_5(H_2nta)]^{2+} + Ti^{3+} + 3H^+ \longrightarrow Co^{2+} + 5NH_4{}^+ + Ti^{IV}(nta)^+ \qquad (3)$$

$$Co^{III} + Ti^{III} \overset{K}{\rightleftharpoons} Co^{III}{\cdot}Ti^{III} \qquad (4)$$

$$Co^{III}{\cdot}Ti^{III} \xrightarrow{k} Co^{II} + Ti^{IV} \qquad (5)$$

Experimental

Materials.—The perchlorate salt of $[Co(NH_3)_5(H_2nta)]^{2+}$ was prepared as previously described.[1b] Titanium(III) solutions in aqueous chloride media at low acid concentration were prepared, handled, and analysed by published methods.[3] An alternative convenient source was the complex $[Ti(urea)_6]^{3+}$.[4] The perchlorate salt was prepared as follows. Titanium metal crushed sponge (10 g) was dissolved in concentrated hydrochloric acid (100 cm^3) under a nitrogen atmosphere. The deep purple solution was decanted away from any undissolved metal. Urea (72 g) was added, followed by saturated aqueous sodium perchlorate. The pale blue crystalline product was collected, washed with water, and purified by re-precipitation (1 l water, 20 g urea, followed by saturated $NaClO_4$ until precipitation was complete) (Found: C, 10.0; H, 3.60; N, 22.8. Calc.: C, 10.2; H, 3.40; N, 23.75%). The salt could be stored in air without apparent decomposition. It is sparingly soluble in water when sufficient urea is present to suppress aquation, but in the absence of added urea it can easily be dissolved at room temperature to give solutions up to 0.1 mol dm^{-3}, with pH ≈ 1.9. The chloride salt $[Ti(urea)_6]Cl_3{\cdot}xH_2O$ was obtained by slow evaporation of a solution of $TiCl_3$ and urea in HCl. The large dark blue crystals, slightly deliquescent, could be stored in an air-tight jar, but after a few weeks they became coated with an ink-black surface layer, presumably of some mixed-valence species.

Other reagents were of AnalaR or equivalent grades.

Measurements.—Single-wavelength kinetic studies were performed with an Aminco-Morrow stopped-flow apparatus, modified for temperature control,[5] and with a Durrum D-130 stopped-flow apparatus combined with a Zeiss Jena SPM 2 monochromator. Rapid-scanning measurements were made with a Multiplex stopped-flow spectrophotometer as previously described.[6]

Results

Spectral Observations.—Using the Multiplex stopped-flow instrument, spectra of the cobalt(III) + titanium(III) reaction mixture, in acid solution, were obtained over the range 500—890 nm, at 0.5-s intervals. In each experiment, the spectrum immediately after mixing was similar to a superposition of the spectra of $[Co(NH_3)_5(H_2nta)]^{2+}$ and Ti^{III} in the medium used [Figure 1(*a*), (*b*); spectra 1]. The next spectrum showed an increase in absorbance across the range measured [Figure 1(*a*), (*b*); spectra 2], while subsequent spectra showed progressive changes corresponding to the kinetics of the electron-

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† Taken from the Ph.D. Theses of R. Marčec, University of Zagreb, 1977, and J. A. Wray, University of East Anglia, 1983. Presented in part at the 20th International Conference on Co-ordination Chemistry, Calcutta, December 1979.

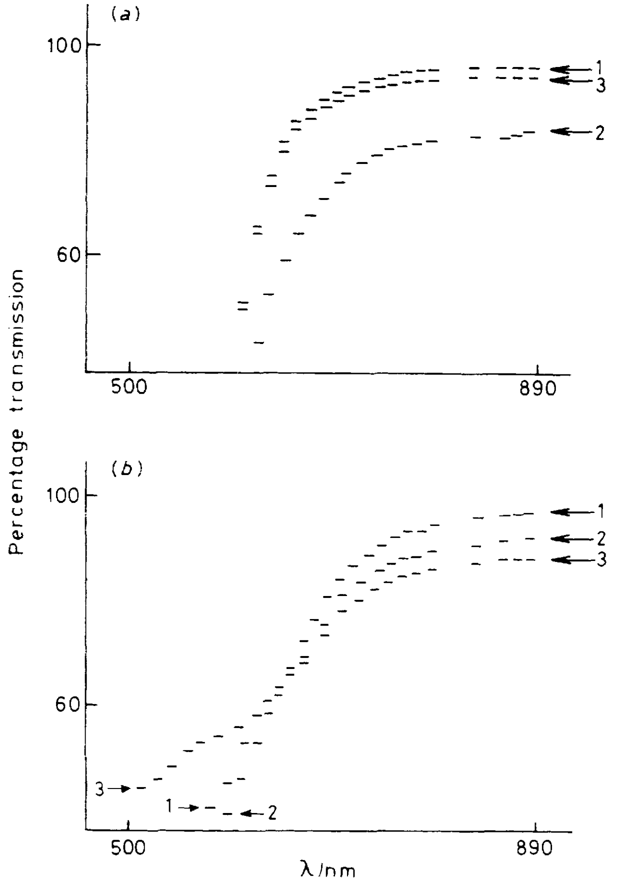


Figure 1. Rapid-scan spectra of reaction (3) at $[H^+] = 0.1$, $I = 1.0$ mol dm^{-3} (NaCl), 18 °C, and pathlength 1 cm. Initial concentrations (mmol dm^{-3}) after mixing: (*a*) Ti, 12; Co, 28; (*b*) Ti, 34; Co, 6. Each horizontal bar corresponds to a wavelength range of 10 nm. Scan time for each spectrum, 10^{-4} s. Spectra: 1, immediately after mixing (*i.e.* after dead-time of *ca.* 10 ms); 2, 0.5 s after mixing; 3, final spectrum, after 15 s

transfer reaction. The progressive changes differed according to the ratio of reagents in the mixture. With cobalt in excess over titanium the absorbance decreased with time over the whole wavelength range, corresponding to the disappearance of the titanium(III) peak at 540 nm [Figure 1(*a*), *cf.* spectra 2 and 3]. With titanium in excess over cobalt there was an isosbestic point at *ca.* 675 nm: at lower wavelengths the absorbance decreased in agreement with the disappearance of cobalt(III), but at higher wavelengths it increased slightly [Figure 1(*b*), spectra 2 and 3]. The increase may have been due to the formation of a Ti^{III}–Ti^{IV} mixed-valence species. It was not investigated further.

Under the conditions of these scanning experiments, the half-life of the overall reaction (3) was *ca.* 5 s, hence spectrum 2 in each experiment was taken to be that of the equilibrium mixture of reactants and intermediate [equation (4)] with relatively little change due to the electron-transfer reaction (5). The absorbances recorded in a series of experiments with ([Co] + [Ti]) = constant, and varying [Co]/[Ti] ratio, are shown in Figure 2. The pronounced maximum at [Co]/[Ti] ≈ 1 confirms the formation of the Co^{III}–Ti^{III} complex.

Kinetics.—Single-wavelength measurements were carried out at λ = 502 nm. With titanium in sufficiently large excess over cobalt, pseudo-first-order kinetics were observed [equation (6); A_0, A, and A_∞ = absorbances at times 0, t, and

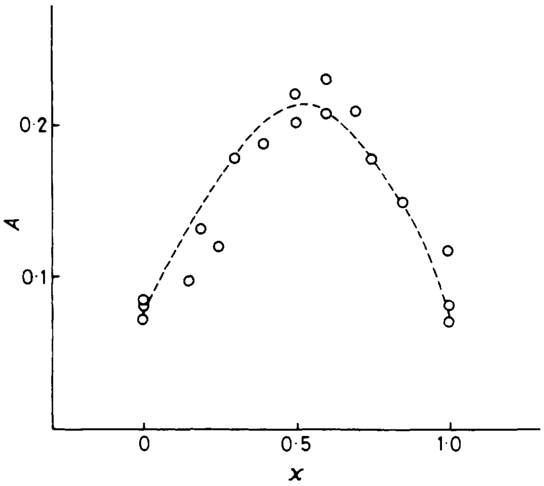


Figure 2. Absorbance A at time $t = 0.5$ s (*cf.* Figure 1, spectra 2) as a function of the ratio $x = [Ti^{III}]/a$, where $a = [Co^{III}] + [Ti^{III}]$; λ = 690 nm, pathlength 1 cm, $[H^+] = 0.1$, $I = 1.0$ mol dm^{-3} (NaCl), 18 °C, and $a = 40$ mmol dm^{-3}. The broken curve is that calculated with the equation $A = A_0x - A_1(1 - x) + \Delta\varepsilon\{1 + Ka - [(1 + Ka)^2 - 4K^2a^2x(1 - x)]^{\frac{1}{2}}\}/2K$, where A_0 and A_1 are the absorbances at $x = 0$ and 1, $K = 200$ dm^3 mol^{-1}, and $\Delta\varepsilon = 11.5$ dm^3 mol^{-1} cm^{-1}

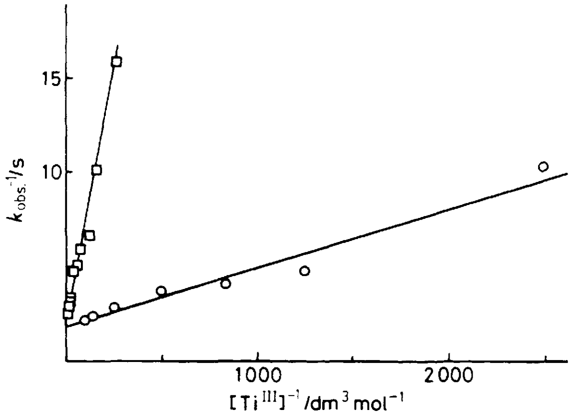


Figure 3. Evaluation of k and kK [see text, equation (7)], from plots of $k_{obs.}^{-1}$ against $[Ti^{III}]^{-1}$: (□), 1 mol dm^{-3} LiClO$_4$ medium, $[H^+] = 0.15$ mol dm^{-3}; (○), 1 mol dm^{-3} NaCl medium, $[H^+] = 0.036$ mol dm^{-3}

$$A - A_\infty = (A_0 - A_\infty)\exp(-k_{obs.}t) \qquad (6)$$

∞). Plots of $\log(A - A_\infty)$ against time were typically linear for 3—4 half-lives. At high acid and low titanium(III) concentrations, the dependence of $k_{obs.}$ on $[Ti^{III}]$ was first order, but at $[H^+] < 0.1$ mol dm^{-3} and $[Ti^{III}] > 0.01$ mol dm^{-3}, significant deviations were observed consistent with an equilibrium saturation effect [equation (7)]. Plots of $k_{obs.}^{-1}$ against $[Ti^{III}]^{-1}$

$$k_{obs.} = kK[Ti^{III}]/(1 + K[Ti^{III}]) \qquad (7)$$

(Figure 3) and also of $[Ti^{III}]/k_{obs.}$ against $[Ti^{III}]$ were used to obtain the parameters kK and k (Table). Plots of $\log(kK)$, $\log k$ and $\log K$ against $-\log[H^+]$ gave the order of the hydrogen-ion dependence of each parameter in the range studied, namely, kK between -3 and -2, K between -2 and -1, and k between -1 and zero, with curvature toward the less negative orders with decreasing $[H^+]$. The variation of K is consistent

Table. Kinetic parameters for the reaction $[Co(NH_3)_5(H_2nta)]^{2+} + Ti^{3+} \longrightarrow Co^{II} + Ti^{IV}$ [a]

$[H^+]$ / mol dm^{-3}	$10^3[Ti^{III}]$ / mol dm^{-3}	No. of data	kK [b] / dm^3 mol^{-1} s^{-1}	k [b] / s^{-1}	log(K/ dm^3 mol^{-1})[c]
(*a*) Perchlorate medium [d]					
1.0	7—124	3	0.20 [e]		
0.2	13—96	15	7.4 (8.7)	0.33 (0.28)	1.42
0.15	4—84	10	19 (19)	0.48 (0.46)	1.61
0.1	4—72	8	32 (31)	0.48 (0.49)	1.81
0.095	8—280	14	37 (46)	0.48 (0.44)	1.95
0.045	2.5—75	6	108 (91)	0.91 (1.04)	2.01
(*b*) Chloride Medium [f]					
0.7	0.4—11	7	0.40 [e]		
0.1	0.4—25	8	68 (64)	0.31 (0.33)	2.31
0.036	0.4—10	7	322 (322)	0.54 (0.51)	2.79
0.017	0.25—4	4	990 (830)	0.66 (0.77)	3.10
0.01	0.25—4	5	1 240 (1 170)	0.94 (0.97)	3.10
0.007 35	0.25—2	4	3 030 (2 540)	0.70 (0.75)	3.58
0.006 67	0.25—3	5	3 360 (2 890)	0.91 (0.96)	3.52

[a] At 25 °C, λ = 502 nm. [b] Parameters obtained by least-squares fitting to plots of $k_{obs.}^{-1}$ against $[Ti^{III}]^{-1}$. Values in parentheses were obtained by least-squares fitting to plots of $[Ti^{III}]/k_{obs.}$ against $[Ti^{III}]$. [c] Mean values calculated from the two estimates of kK and k. [d] I = 1.0 mol dm^{-3} ($LiClO_4$). [e] From plots of $k_{obs.}$ against $[Ti^{III}]$. [f] I = 1.0 mol dm^{-3} (NaCl).

with the equilibria (8)—(10) ($^*K_1$ denotes an equilibrium of the type, $M^- + HL \rightleftharpoons ML + H^+$), which lead to expression (11).

$$[Co(NH_3)_5(H_2nta)]^{2+} \xrightleftharpoons{K_a} [Co(NH_3)_5(Hnta)]^{+} + H^+ \quad (8)$$

$$Ti^{3+} \xrightleftharpoons{K_a'} [Ti(OH)]^{2+} + H^+ \quad (9)$$

$$[Co(NH_3)_5(Hnta)]^{+} + Ti^{3+} \xrightleftharpoons{^*K_1} [Co(NH_3)_5(nta)Ti]^{3+} + H^+ \quad (10)$$

$$K = {}^*K_1K_a/\{([H^+] + K_a)([H^+] + K_a')\} \quad (11)$$

Using $K_a = 2.1 \times 10^{-2}$ mol dm^{-3} † and $K_a' = 3.5 \times 10^{-3}$ mol dm^{-3} (ref. 7) the best fit with the experimental points was obtained with log $^*K_1 = 1.60 \pm 0.18$ and 1.73 ± 0.21, at 25 °C in 1 mol dm^{-3} $LiClO_4$ and 1 mol dm^{-3} NaCl, respectively. In the chloride medium, the variation of k is consistent with expression (12). A plot of k^{-1} against $[H^+]$ yielded

$$k = a/(b + [H^+]) \quad (12)$$

$a/b = 1.0 \pm 0.1$ s^{-1} and $a = 0.046 \pm 0.005$ mol dm^{-3} s^{-1}. For the data in the perchlorate medium, only the latter term could be obtained, $a = 0.055 \pm 0.010$ mol dm^{-3} s^{-1}.

Discussion

To explain the hydrogen-ion dependence of k we propose the reactions (13) and (14) where the two formulae in equation (13)

$$\underset{(I)}{[Co(NH_3)_5(nta)Ti]^{3+}} \xrightleftharpoons[k_{-2}]{k_2} \underset{(II)}{\{[Co(NH_3)_5(nta)Ti]^{3+}\}^{\ddagger}} \quad (13)$$

$$\{[Co(NH_3)_5(nta)Ti]^{3+}\}^{\ddagger} \xrightarrow{k_3[h^+]^{-1}} \text{products} \quad (14)$$

denote complexes of different structure and ‡ denotes two intermediates which have the same compositional formula. Applying the steady-state criterion to the intermediate we obtain equation (12), with $a/b = k_2$ and $a = K_2k_3$.

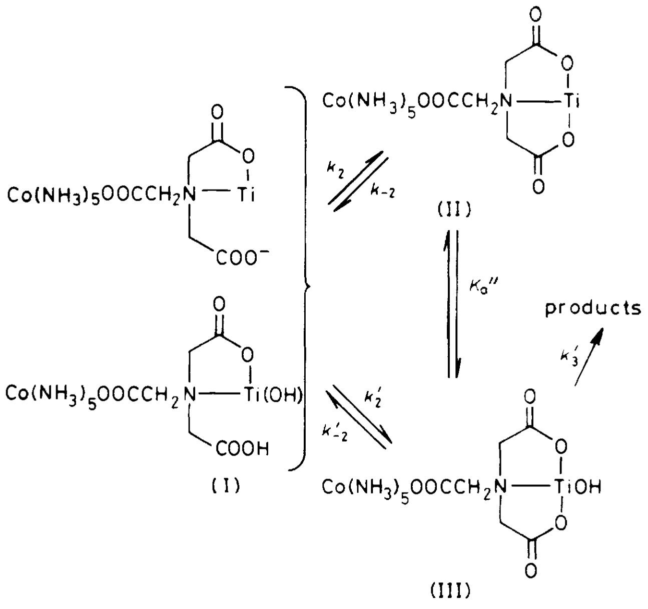
An alternative mechanism, equally consistent with the data, is shown in equations (15) and (16). This also leads to expression (12), the constants k_2' and $K_2'k_3'$ having the same values as k_2 and K_2k_3.

$$\underset{(I)}{[Co(NH_3)_5(nta)Ti]^{3+}} \xrightleftharpoons[k_{-2}'[H^+]]{k_2'} \underset{(III)}{[Co(NH_3)_5(nta)Ti(OH)]^{2+}} + H^+ \quad (15)$$

$$[Co(NH_3)_5(nta)Ti(OH)]^{2+} \xrightarrow{k_3'} \text{products} \quad (16)$$

Other mechanisms can also be written, all having the features of two or more rate determining steps, differently catalysed by acid. The two mechanisms cited here are related to each other in the same way as those proposed for the reaction $V^{3+} + Cr^{2+} \longrightarrow V^{2+} + Cr^{3+}$,[8] and other reactions which have been extensively discussed.[9]

We suggest that one of the steps involved in either mechanism is a ring closure, and to accommodate this we propose that the complexes involved have the structures shown in the Scheme below (ionic charges omitted). Complex (I) could have either of the two structures shown, or it could be a mixture of the two in rapid equilibrium. Step k_3 of equation (14)



Scheme.

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† Calculated from the value of K_a reported in ref. 1*b*, using the measured activity coefficient for H^+ of 0.72.

could be written as a direct reaction from (II) to products, but it is more likely to involve the sequence (II) $\longrightarrow$ (III) $\longrightarrow$ products as shown, giving $k_3 = K_a''k_3'$. The conclusion that (II) or (III) rather than (I) is the effective electron-transfer precursor complex is not surprising since the reducing power of Ti^{III} is expected to increase with increased chelation. Deprotonated transition states are also generally characteristic of the electron-transfer reactions of titanium(III).[10]

The two mechanisms are kinetically indistinguishable but it seems likely that the one in equations (13)—(14) will predominate over that in equations (15)—(16) at high acidities, when complex (II) predominates over (III). If the pK_a'' of complex (II) is *ca.* 4, which seems a reasonable estimate,[*] this condition holds throughout the range of acidities in our experiments.

The intramolecular electron-transfer rate constant k_3 can be estimated as follows. From a correlation of stabilities of Ti^{3+} and Fe^{3+} complexes,[†] we obtain $\log(^*K_1K_2) \approx 2$. From our data, $\log(^*K_1K_2K_ak_3) = 0.4$. Hence $\log k_3 \approx 2.4$ and $k_3 \approx 600\ s^{-1}$. Subject to the correct assignment of the mechanism, this appears to be the first quantitative estimate obtained for the rate of an intramolecular $Co^{III}Ti^{III} \longrightarrow Co^{II}Ti^{IV}$ electron transfer.

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[*] Compare the following pK_a values: $Fe^{III}(nta)\ (aq)$, 4.0; $Cr^{III}(nta)\ (aq)$, 5.9; $VO(nta)^-\ (aq)$, 7.2; as correlated with the sequence $Ti^{3+}(aq)$, 2.5; $Fe^{3+}(aq)$, 2.8; $Cr^{3+}(aq)$, 3.9; $VO^{2+}(aq)$, 6.0.[7,11]

[†] We have used $\log K_1\ (M^{3+} + edta^{4-})$ (H_4edta = ethylenediaminetetra-acetic acid) = 21 (Ti), 25 (Fe); $\log K_1\ (M^{3+} + acac^-)$ (Hacac = pentane-2,4-dione) = 8.4 (Ti), 8.4 (Fe); $\log \beta_2(M^{3+} + NC_5H_4CO_2\text{-}2)$ = 11 (Ti), 12.9 (Fe); $\log K_1\ \{Fe^{3+} + [Co(NH_3)_5(nta)]\} = 11.4$; $pK_a\ \{[Co(NH_3)_5(Hnta)]^+ \rightleftharpoons [Co(NH_3)_5(nta)] + H^+\} = 8.0$.[1b,11]

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