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Kinetics of the Reaction of Titanium(III) with (3-Cyano-2,4-pentanedionato-*N*)pentaamminecobalt(III): Intramolecular Electron Transfer between Cobalt(III) and Titanium(III)

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The reaction of Ti(III) with $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$, where NCacac = 3-cyano-2,4-pentanedionate, proceeds in two separate stages. The first stage corresponds to the rapid reversible formation of a stable binuclear precursor complex. The second slower reaction involves intramolecular electron transfer in the Co(III)-Ti(III) precursor complex. This reaction shows saturation behavior with respect to total Ti(III) concentration and implies an equilibrium between uncomplexed Co(III) and Ti(III). The reaction is also inversely dependent on $[\text{H}^+]^2$ and supports the structure $[(\text{NH}_3)_5\text{Co}(\text{NCacac})\text{Ti}(\text{OH})(\text{OH}_2)_3]^{4+}$ for the precursor complex. The kinetic data allow an estimate of $\sim 6 \text{ s}^{-1}$ for the intramolecular electron-transfer rate. The results are compared to Ti(III) reactions with Ru(III) complexes.

Introduction

Mechanistic studies of the reduction of cobalt(III) amine complexes by titanium(III) have demonstrated the diverse reactivity patterns of $[\text{Ti}(\text{OH}_2)_6]^{3+}$ in electron-transfer reactions.¹⁻⁶ The assessment of inner- vs. outer-sphere mechanisms has been accomplished by application of linear free energy relationships,⁴⁻⁶ hard-soft acid-base concepts,⁴ and the complexity of the dependence of the rate constants on acid concentration.⁷ Gould and others have shown that an inner-sphere pathway is favored when the oxidant contains a potential bridging ligand capable of chelation of the reductant by "hard" oxygen donor atoms.^{1,5,7} The rate expressions obtained for many of these types of oxidants can only be derived by invoking the formation of binuclear precursor complexes prior to the electron-transfer step.^{7,8} However, as yet, no physical evidence for precursor complex formation has been obtained in Ti(III)-Co(III) systems.

In this paper we wish to report the titanium(III) reduction of a cobalt(III) complex containing a pendant β -diketone moiety,⁹ $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$. For this reaction, reduction occurs via a two-step process: formation of a Ti(III)-Co(III) precursor complex followed by intramolecular electron transfer mediated by the β -diketonato group.

Experimental Section

Materials. Lithium chloride and hydrochloric acid solutions for use in kinetic studies were prepared from reagents purchased from G. Frederick Smith Chemical Co. and were standardized by standard methods. Solutions of Ti(III) were prepared by dissolving 3 g of Ti metal (Alfa) under argon in 75 mL of a 3 mol L⁻¹ HCl solution at 60 °C. This stock solution was stored under argon at 5 °C. Solutions of Ti(III) for use in kinetic runs were prepared by transferring an aliquot of the stock solution to a volume of degassed doubly distilled water with standard syringe techniques. Ionic strength and acid concentration were adjusted by adding aliquots of standardized lithium chloride and hydrochloric acid solutions. Concentration of Ti(III) was determined by reaction with excess standard ferric ammonium sulfate solution followed by determination of excess iron(III) by iodometric titration with standard sodium thiosulfate.

Concentrations of acid in the Ti(III) solutions were determined by charging an aliquot of the Ti(III) solution onto a degassed column of Amberlite IR-120(H) cation exchange resin. The amount of acid liberated was determined via titration and used to calculate the original concentration of acid in the Ti(III) solutions.

The ligand 3-cyano-2,4-pentanedione (NCacacH) and (3-cyano-2,4-pentanedionato-*N*)pentaamminecobalt(III) perchlorate, $[(\text{NH}_3)_5\text{Co}(\text{NCacac})](\text{ClO}_4)_2$, were prepared as described previously.⁹

Kinetic measurements were carried out with a thermostated Durrum Model D-110 stopped-flow spectrophotometer interfaced to a DASAR data storage and retrieval system. Rate constants were obtained directly from the exponential decay traces by matching the trace with a curve generated by an exponential curve simulator.

Reactions were followed by measuring the change in absorbance of the reaction mixtures at 428 and 480 nm. All reactions were carried out under pseudo-first-order conditions (Ti(III) in >10-fold excess over Co(III)) at an ionic strength of 1.0 mol L⁻¹ (LiCl). Electronic spectra were recorded on a Beckman Acta CIII UV-visible spectrophotometer. The acid dissociation constant of the cobalt(III) complex was determined spectrophotometrically under conditions identical with those employed in kinetic runs.¹⁰

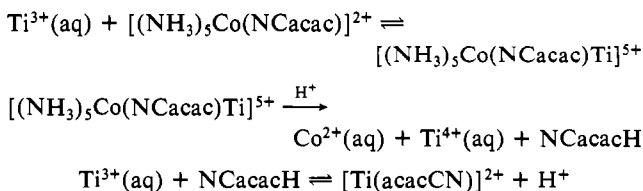
Cobalt(II) present in reaction mixtures was detected by reaction with thiocyanate ion in mixed acetone-water solutions.¹¹

Results and Discussion

The reaction of titanium(III) with $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$ occurs in two distinct steps. Addition of $\text{Ti}^{3+}(\text{aq})$ to a solution of the cobalt(III) complex (equimolar amounts) results in an initial rapid increase in absorbance with absorbance maxima at 428 and 480 nm, followed by a slower bleaching of this solution (Figure 1). When an excess of Ti(III) is used, the bleaching is not complete and the final red-orange solution exhibits maxima at 428 and 480 nm. Tests for the presence of Co(III) indicate that no reduction of the complex occurs during the initial absorbance increase. It was shown that the second slower reaction resulted in formation of cobalt(II), with a 1:1 stoichiometry as determined by spectrophotometric methods.

This behavior (Scheme I) can be tentatively attributed to the rapid formation of a Ti(III)-Co(III) precursor complex followed by intramolecular electron transfer to yield $\text{Co}^{2+}(\text{aq})$, $\text{Ti}^{4+}(\text{aq})$, and NCacacH. In the presence of excess Ti(III), a complete bleaching does not occur due to the reaction of Ti(III) with free ligand formed during reduction of the cobalt(III) complex. This postulated behavior was examined by studying the reaction of $\text{Ti}^{3+}(\text{aq})$ with free ligand 3-cyano-2,4-pentanedione.

Scheme I



Reaction of $\text{Ti}^{3+}(\text{aq})$ with NCacacH. Addition of excess $\text{Ti}^{3+}(\text{aq})$ to a solution of NCacacH results in the rapid formation of a red-orange solution with absorption maxima identical with those found for the product of the reduction of $[(\text{NH}_3)_5\text{Co}$

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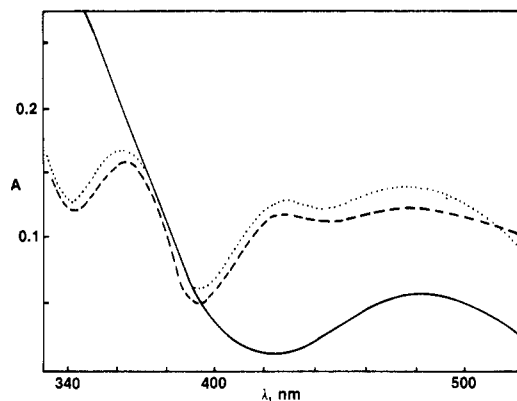


Figure 1. Visible spectrum for the reaction of titanium(III) with $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$: (—) before addition of Ti^{3+} ; (···) 60 s after addition of Ti^{3+} ; (---) 5 min after addition of Ti^{3+} . $[\text{Co}(\text{III})] = 2.5 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{Ti}^{3+}] = 0.011 \text{ mol L}^{-1}$.

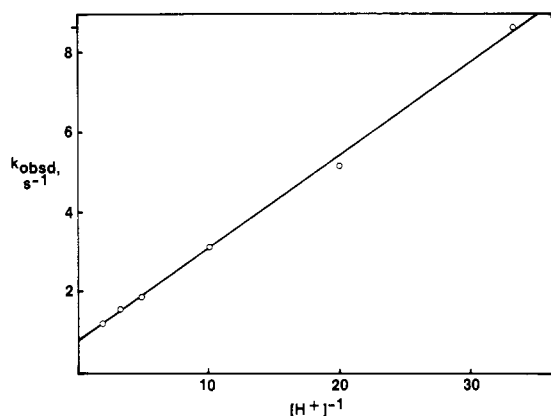


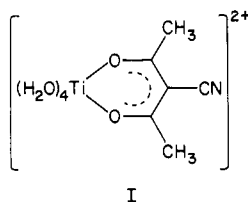
Figure 2. Acid dependence for the reaction of titanium(III) with 3-cyano-2,4-pentanedione. $[\text{Ti}^{3+}] = 0.00680 \text{ mol L}^{-1}$, $T = 25.0 \text{ }^\circ\text{C}$, $I = 1.00 \text{ mol L}^{-1}$ (LiCl).

Table I. Kinetic Data for the Reaction of Titanium(III) with 3-Cyano-2,4-pentanedione^a

$[\text{H}^+]$, mol L^{-1}	$10^3[\text{Ti}^{3+}]$, mol L^{-1}	$10^4[\text{NCacacH}]$, mol L^{-1}	k_{obsd} , s^{-1}
0.03	6.80	4.85	6.01
0.05	6.80	4.85	4.74
0.10	6.80	4.85	2.96
0.20	6.80	4.85	1.90
0.20	10.50	7.75	3.02
0.20	21.0	7.75	5.80
0.20	31.5	7.75	8.53
0.20	42.0	7.75	11.5
0.30	6.80	4.85	1.60
0.50	6.80	4.85	1.30

^a $T = 25 \text{ }^\circ\text{C}$, and $I = 1.0 \text{ mol L}^{-1}$ (LiCl); the reaction was studied at 450 nm.

$(\text{NCacac})^{2+}$ with excess $\text{Ti}^{3+}(\text{aq})$. The kinetics of the complexation reaction were studied over a wide range of $\text{Ti}^{3+}(\text{aq})$ and H^+ concentrations (Table I) with $\text{Ti}^{3+}(\text{aq})$ in large excess over free ligand to ensure that only the 1:1 complex, postulated as I, would be formed.



At constant acid concentration, a plot of k_{obsd} vs. $[\text{Ti}^{3+}]$ is linear with a near-zero intercept, indicating a small degree of reversibility

in the complexation reaction. The uncertainty associated with the small value of the intercept precluded a quantitative determination of the reverse reaction rate. The dependence of k_{obsd} on $[\text{H}^+]$ is indicative of an acid-dependent and acid-independent pathway for complexation (Figure 2). The data yields a rate law of the general form

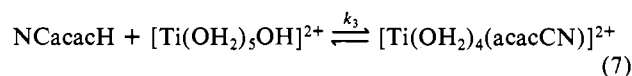
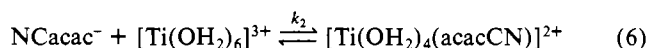
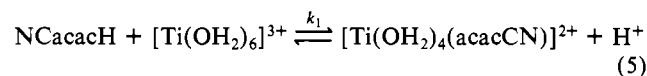
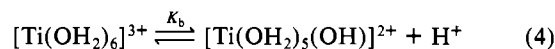
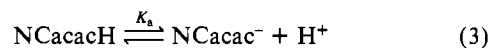
$$k_{\text{obsd}} = (a + b[\text{H}^+]^{-1})[\text{Ti}(\text{III})] \quad (1)$$

Since both Ti^{3+} and the free ligand NCacacH exhibit acid-base behavior ($K_b(\text{Ti}^{3+}) = 4 \times 10^{-3} \text{ mol L}^{-1}$; $K_a(\text{NCacacH}) = 2.2 \times 10^{-4} \text{ mol L}^{-1}$), the involvement of either of the deprotonated species can account for the observed acid-dependent term and presents a proton ambiguity.¹³ The possible reacting partners are shown in Scheme II. This mechanism leads to the rate law 2 where k_A

$$k_{\text{obsd}} = \left[\frac{k_1[\text{H}^+] + k_A}{(K_a + [\text{H}^+])(K_b + [\text{H}^+])} \right] [\text{Ti}^{3+}] \quad (2)$$

$= k_2K_a$ or k_3K_b depending on whether NCacac^- or TiOH^{2+} , respectively, is responsible for the acid dependence. A fit of the experimental data to eq 2 yields values of $k_1 = 1.2 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_2 = 1.6 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_3 = 9.0 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$. Since the pathways are kinetically indistinguishable, other criteria must be used to differentiate between them.

Scheme II



The mechanism involving attack of Ti^{3+} on the neutral and deprotonated forms of the free ligand (eq 5 and 6) was favored for two main reasons. (1) The rate of substitution of NCacac^- on Ti^{3+} was determined to be $1.6 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$, and this value compares favorably with the rate obtained by Diebler for the complexation reaction of Ti^{3+} with the oxalate anion HC_2O_4^- ($k = 3.9 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ at $10 \text{ }^\circ\text{C}$ ¹⁴). Since both reactions involve complexation of a bidentate oxygen donor anion with Ti^{3+} , the similarity in rates seems to favor reaction of Ti^{3+} rather than TiOH^{2+} . (2) If the acid-dependent pathway were due to reaction of TiOH^{2+} with NCacacH , one would also expect a contribution from the reaction of TiOH^{2+} with NCacac^- , with a rate constant equal to and probably greater than $k_3 = 9 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ due to the electrostatic enhancement.¹⁴ The absence of experimental evidence for this pathway (no inverse $[\text{H}^+]^2$ dependence) leads us to favor the mechanism as shown in eq 3–6.

The much lower rate of substitution of the neutral ligand NCacacH on Ti^{3+} ($k_1 = 120 \text{ L mol}^{-1} \text{ s}^{-1}$) as compared to the deprotonated ligand ($k_2 = 1.6 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$) is consistent with an associative mechanism, as has been proposed for other substitutions on $\text{Ti}(\text{III})$.^{14,15} The protonated ligand is expected to be a much weaker nucleophile than NCacac^- due to the charges involved. Since nucleophilic strength is an important factor in associative substitution reactions,¹⁶ the large decrease in rate upon going from the anion to the neutral ligand is not too surprising. Other workers have also indicated that substitution on $\text{Ti}(\text{III})$ involves $[\text{Ti}(\text{OH}_2)_6]^{3+}$ rather than $[\text{Ti}(\text{OH}_2)_5(\text{OH})]^{2+}$.¹⁷

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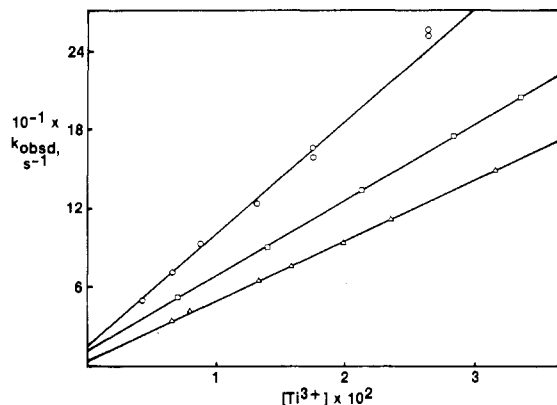
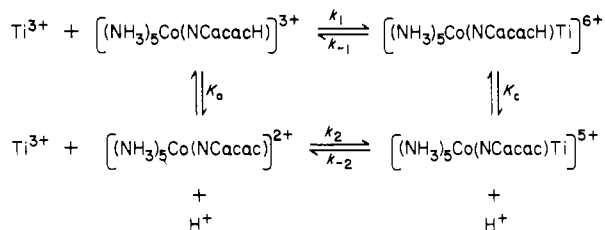


Figure 3. Plot of k_{obsd} vs. $[\text{Ti}^{3+}]$ for the complexation reaction of Ti(III) with $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$. $T = 19.4$ (Δ), 25.0 (\square), 31.6 (\circ) $^\circ\text{C}$; $[\text{H}^+] = 0.200$ mol L^{-1} , $I = 1.00$ mol L^{-1} (LiCl).

Scheme III



Finally, no reduction of free ligand by Ti(III) was evident during the complexation reactions, and solutions of the $[\text{Ti}(\text{OH}_2)_4(\text{acacCN})]^{2+}$ complex were stable for long periods of time (>5 h).

Reaction of $\text{Ti}^{3+}(\text{aq})$ and $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$. The first fast reaction in the titanium(III) reduction of $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$ was studied by following the absorbance increase at 428 or 480 nm (Table II). This reaction, corresponding to formation of a Ti(III)–Co(III) precursor complex, was complete before the second slow reaction had progressed to any extent. Plots of the observed rate constants vs. $[\text{Ti}^{3+}]$ were linear with a finite intercept at a given acid concentration (Figure 3), obeying eq 8. This behavior

$$k_{\text{obsd}} = k_f[\text{Ti}^{3+}] + k_r \quad (8)$$

is indicative of a reversible reaction, and the forward and reverse rates were obtained from the slopes and intercepts of kinetic plots. The acid dependence of the forward and reverse reactions yielded rate laws 9 and 10.

$$k_f = \frac{a + b[\text{H}^+]}{c + [\text{H}^+]} \quad (9)$$

$$k_r = \frac{d + e[\text{H}^+]}{f + [\text{H}^+]} \quad (10)$$

A mechanism consistent with the data is shown in Scheme III. This mechanism leads to rate law 11 where K_a and K_b are the acid dissociation constants for $[(\text{NH}_3)_5\text{Co}(\text{NCacacH})]^{3+}$ and $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, respectively ($K_a = 0.0653$ mol L^{-1}). A nonlinear least-squares fit of the experimental data to eq 11 gave rate

$$k_{\text{obsd}} = \frac{(k_1[\text{H}^+] + k_2K_a)[\text{Ti}^{3+}]_T}{([\text{H}^+] + K_a)(1 + K_b[\text{H}^+])} + \frac{k_{-1}[\text{H}^+] + k_{-2}K_c}{[\text{H}^+] + K_c} \quad (11)$$

constants $k_1 = (2.26 \pm 0.05) \times 10^4$ L mol $^{-1}$ s $^{-1}$, $k_2 = (4.0 \pm 2) \times 10^2$ L mol $^{-1}$ s $^{-1}$, $k_{-1} = 5 \pm 4$ s $^{-1}$, $k_{-2} = 50 \pm 20$ s $^{-1}$, and $K_c = 0.08 \pm 0.04$ mol L^{-1} . The small magnitude and large uncertainty in the values of the intercepts ($k_r = 8\text{--}40$ s $^{-1}$) precludes a more accurate determination of the terms k_{-1} , k_{-2} , and K_c relating to the reverse reaction, dissociation of the binuclear complexes. The activation parameters for k_1 and k_2 were also determined: $\Delta H_1^\ddagger = 24 \pm 5$ kcal mol $^{-1}$, $\Delta H_2^\ddagger = 8.2 \pm 1.0$ kcal mol $^{-1}$, $\Delta S_1^\ddagger = 22 \pm 8$ eu and $\Delta S_2^\ddagger = -13 \pm 3$ eu.

Table II. Kinetic Data for the Reaction of Titanium(III) with $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$ at 25 $^\circ\text{C}$ ^a

$[\text{H}^+]$, mol L^{-1}	$[\text{Ti}^{3+}]$, mol L^{-1}	k_{obsd} , s $^{-1}$	k_{obsd}^1 , s $^{-1}$
0.200	0.00705	52.4	0.0180
0.200	0.0141	90.9	0.0320
0.200	0.02115	135.1	0.0442
0.200	0.0282	175.4	0.0561
0.200	0.0336	202.4	0.0667
0.030	0.00705	103.7	0.357
0.050	0.00705	93.6	0.166
0.100	0.00705	71.6	
0.200	0.00705	51.3	0.021
0.300	0.00705	40.0	0.011
0.500	0.00705	30.0	0.006
0.050	0.00645	85.0	0.161
0.050	0.0129	167	0.254
0.050	0.0258	314	0.426
0.050	0.03225	348	0.494
0.100	0.00645	66.4	0.051
0.100	0.0129	121	0.086
0.100	0.01935	184	0.119
0.100	0.0258	237	0.151
0.100	0.03225	289	0.182
0.200	0.00645	48.8	0.016
0.200	0.0129	81.6	0.028
0.200	0.01935	125	0.039
0.200	0.0258	173	
0.200	0.03225	206	0.058
0.200	0.0067	51.2	0.0164
0.200	0.0134	85.4	0.0289
0.200	0.0201	132.6	0.0398
0.200	0.0268	174	0.051
0.200	0.0335	216	0.0625
0.050	0.0067	104	0.138
0.050	0.0134	174	0.250
0.050	0.0201	244	0.341
0.050	0.0268	313	0.426
0.100	0.0134	134	0.087
0.100	0.0067	73	0.049
0.100	0.0201	194	0.123
0.100	0.0268	253	0.156

^a $I = 1.00$ mol L^{-1} (LiCl); $[\text{Co(III)}] = 2 \times 10^{-4}$ mol L^{-1} .

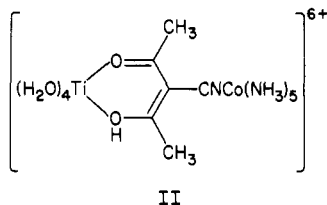
The observed acid dependency can also be explained by a mechanism involving attack of both Ti^{3+} and TiOH^{2+} on the protonated oxidant $[(\text{NH}_3)_5\text{Co}(\text{NCacacH})]^{3+}$, analogous to the proton ambiguity of the free ligand complexation reaction. However, the mechanism as shown is favored for reasons entirely analogous to those given for the free ligand reaction.

The rate of substitution of the deprotonated oxidant on Ti^{3+} (2.2×10^4 L mol $^{-1}$ s $^{-1}$) is comparable to the current upper limit for substitution reactions involving Ti^{3+} and metal complexes with bridging ligands¹⁸ ($k \sim 3 \times 10^4$ L mol $^{-1}$ s $^{-1}$ for $[(\text{NH}_3)_4\text{Ru}(\text{OOCOO})]^{2+}$). The substitution rate for the protonated oxidant (~ 400 L mol $^{-1}$ s $^{-1}$) is much less than k_1 and falls within the range of rates (50–500 L mol $^{-1}$ s $^{-1}$) for precursor complex formation in Ti(III)–Co(III) redox systems (obtained from mechanistic arguments^{5,7} involving the acid dependence of the overall reduction rate). The large rate enhancement for $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$ may be due primarily to the fact that the coordination site (for Ti^{3+}) is at a remote location from the tripisite cobalt(III) center and possesses a negative charge. A favorable electrostatic attraction would account for the rate increase, assuming the Ti^{3+} ion "sees" only the uninegative β -diketonate moiety. This is supported by the results for the Ti(III) complexation with NCacac $^-$. Therefore, the delocalized negative charge on the diketone function, rather than chelate formation, is responsible for the rate increase. Chelate formation with (salicylato)pentamminecobalt(III) does not result in larger rates for precursor complex formation.⁵

The observed behavior, in which Ti^{3+} forms a relatively stable precursor complex with the oxidant, has not been observed before in Ti(III)–Co(III) redox systems, although evidence of long-lived

intermediates has been exhibited in Ti(III)–Ru(III) systems.¹⁸

According to Scheme III, the complexation reaction results in the formation of two precursor complexes, which are related by the acid dissociation constant, K_a , determined kinetically to be $\sim 0.08 \text{ mol L}^{-1}$. Additional evidence for this equilibrium was obtained from the change in absorbance of solutions of the precursor complex with acid concentration. These changes were used to obtain an estimate of the formation constant K_p (k_f/k_r) at $[\text{H}^+] = 0.20 \text{ mol L}^{-1}$ of $\sim 560 \text{ L mol}^{-1}$. The kinetically determined value is 500 L mol^{-1} . Up to this point it has been assumed that the precursor complex involves chelation of the Ti^{3+} (as opposed to monodentate coordination) by the free acac pendant. However, the value of K_c (0.08 mol L^{-1}) does not support a chelated structure such as II for the protonated precursor complex.



The equilibrium constant for proton loss in II would be expected to be much higher than the K_a for the complex $[(\text{NH}_3)_5\text{Co}(\text{NCacacH})]^{3+}$, but it is only marginally so. Also, K_c is too large to be attributed to hydrolysis of coordinated water in II. For the latter, the equilibrium constant would be expected to be slightly less than that for $[\text{Ti}(\text{OH}_2)_6]^{3+}$ ($4 \times 10^{-3} \text{ mol L}^{-1}$)^{19,20} due to the electronegativity of the oxygen donor atom on the diketone moiety. Finally, the data for the subsequent reduction of the precursor complex argue for equilibrium constants K_1 and K_2 , which are not of the same value as k_1/k_{-1} and k_2/k_{-2} for the complexation reaction. This implies that K_1 and K_2 relate to equilibria of the chelated precursor complexes whereas the complexation rate constants refer to monodentate complexes. A small absorbance increase is observed in the time following the complexation reaction and the beginning of the redox process. Kinetic data could not be obtained for this process but can be interpreted as ring closure to yield the chelated precursor complexes.

The second phase observed in the titanium(III) reaction with $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$ corresponded to a decrease in absorbance at peak maxima of the binuclear Ti(III)–Co(III) complex. Formation of a quantitative amount of Co(II) was detected, and this process was assigned as reduction of the precursor complex.

Observed rate constants tended towards a less than first-order dependence on $[\text{Ti}^{3+}]$ as the titanium concentration was increased. Plots of $k^1_{\text{obsd}}^{-1}$ vs. $[\text{Ti}^{3+}]$ were linear with finite intercepts (Figure 4). The slopes and intercepts of these plots were found to be strongly dependent on the acid concentration, and the data were best fit by a rate law of the general form

$$k^1_{\text{obsd}} = \frac{a[\text{Ti}^{3+}]}{[\text{H}^+]^2 + b[\text{H}^+] + c + d[\text{H}^+][\text{Ti}^{3+}]} \quad (12)$$

The saturation-type behavior as reductant concentration was increased implies an equilibrium between uncomplexed oxidant and Ti(III), and the precursor complexes as shown in Scheme IV. The inverse $[\text{H}^+]^2$ dependence also necessitates the loss of two protons in the formation of the redox-active species. Since electron transfer is slow relative to the formation of the species, the various equilibria can be assumed to be rapidly established. A mechanism consistent with all the data is given in Scheme IV. This leads to rate law 13, which is of the same form as (12) when $K_2K_a[\text{H}^+]$

$$k^1_{\text{obsd}} = \frac{k_{\text{et}}K_2K_aK^*[\text{Ti}^{3+}]}{([\text{H}^+] + K_b)([\text{H}^+] + K_a) + (K_1[\text{H}^+]^2 + K_2K_a[\text{H}^+])[\text{Ti}^{3+}]} \quad (13)$$

Scheme IV

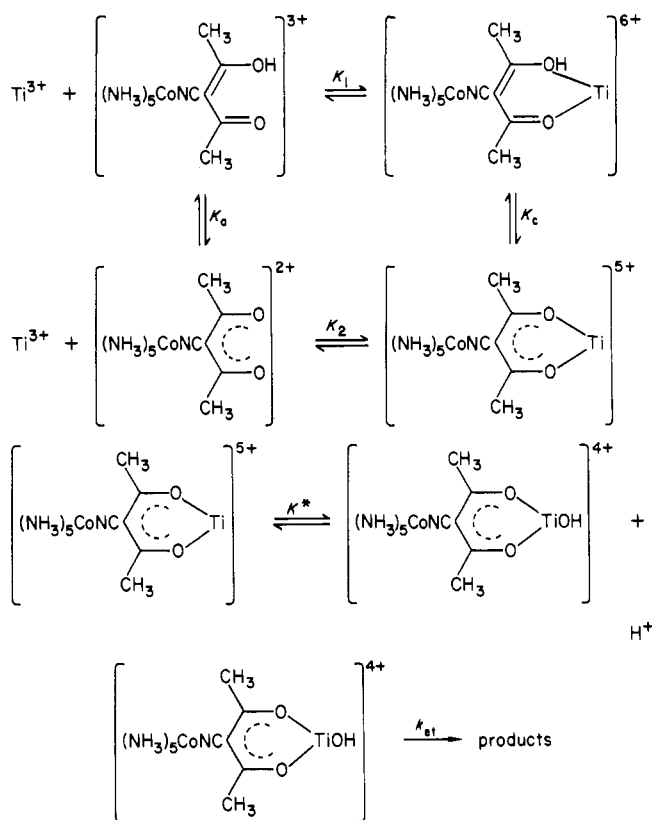


Table III. Comparison of Observed and Calculated Rate Constants for the Titanium(III) Reduction of $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$ at 25°C^a

$[\text{H}^+]$, mol L ⁻¹	$[\text{Ti}^{3+}]$, mol L ⁻¹	k^1_{obsd} , s ⁻¹	k^1_{calcd} , s ⁻¹	
0.050	0.0067	0.138	0.137	
	0.0129	0.254	0.244	
	0.0134	0.250	0.252	
	0.01935	0.346	0.339	
	0.0201	0.341	0.349	
	0.0258	0.426	0.421	
	0.0268	0.426	0.433	
	0.03325	0.494	0.492	
	0.100	0.0067	0.0485	0.0499
		0.0129	0.0865	0.0886
0.0134		0.0872	0.0918	
0.01935		0.119	0.124	
0.0201		0.123	0.127	
0.0258		0.151	0.154	
0.0268		0.156	0.158	
0.03225		0.182	0.180	
0.200		0.00645	0.0156	0.0154
		0.0067	0.0164	0.0159
	0.00705	0.0180	0.0167	
	0.0129	0.0277	0.0284	
	0.0134	0.0289	0.0293	
	0.0141	0.0320	0.0306	
	0.01935	0.0385	0.0396	
	0.0201	0.0398	0.0408	
	0.02115	0.0442	0.0425	
	0.0268	0.0511	0.0508	
0.0282	0.0561	0.0527		
0.03225	0.0577	0.0580		
0.0335	0.0625	0.0595		

^a $I = 1.00 \text{ mol L}^{-1}$ (LiCl); $[\text{Co(III)}] = 2 \times 10^{-4} \text{ mol L}^{-1}$. ^b k^1_{calcd} was obtained from a non-linear least-squares fit of the data to eq 13.

$\gg K_1[\text{H}^+]^2$. From the measured value of K_a along with approximate values of the rate constants from slopes and intercepts of plots of $k^1_{\text{obsd}}^{-1}$ vs. $[\text{Ti}^{3+}]^{-1}$, values for K_1 , K_2 , and $k_{\text{et}}K^*$ were refined by using a nonlinear least-squares fit of the data to eq 13. The values obtained were $K_1 = 12 \pm 3 \text{ L mol}^{-1}$, $K_2 = 20 \pm 2 \text{ L mol}^{-1}$ and $k_{\text{et}}K^* = 0.06 \pm 0.01 \text{ mol L}^{-1} \text{ s}^{-1}$. The goodness of fit

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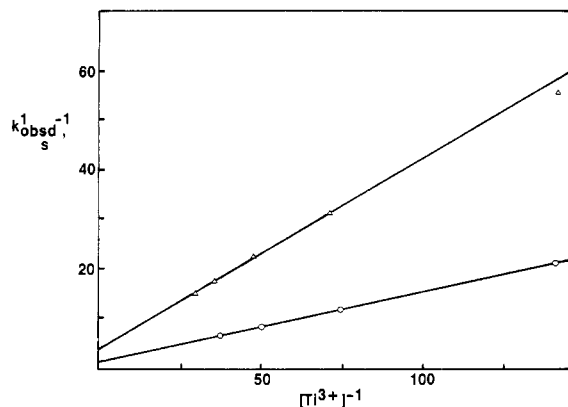


Figure 4. Plot of k_{obsd}^{-1} vs. $[\text{Ti}^{3+}]^{-1}$ for the second reaction in the Ti(III) reduction of $[(\text{NH}_3)_5\text{Co}(\text{NCacac})]^{2+}$. $T = 25.0^\circ\text{C}$, $I = 1.00\text{ mol L}^{-1}$ (LiCl); $[\text{H}^+] = 0.20\text{ mol L}^{-1}$ (Δ); $[\text{H}^+] = 0.10\text{ mol L}^{-1}$ (\circ).

of the rate equation to experimental data is demonstrated in Table III, which contains calculated and experimental observed rate constants for the reduction process.

The rate of electron transfer in the precursor complex, k_{et} , can be estimated by assuming an upper limit of $\sim 10^{-2}\text{ mol L}^{-1}$ for the acid dissociation constant for coordinated water on titanium(III)¹⁸ in $[(\text{NH}_3)_5\text{Co}(\text{NCacac})\text{Ti}(\text{H}_2\text{O})_4]^{5+}$. This yields a value of at least 6 s^{-1} for the intramolecular electron-transfer rate.

The mechanism proposed, formation of a binuclear intermediate followed by electron transfer within the conjugate base of the intermediate, has been suggested, on the basis of kinetic evidence, for several Co(III)–Ti(III) reactions (in these systems the binuclear intermediate has not been detected).^{21,22} In the (fpd)-Ru^{III}–Ti(III) reaction this mechanism yields an intramolecular electron-transfer rate constant of $\geq 10^4\text{ s}^{-1}$.¹⁷ The large rate in the latter case has been explained in terms of effective overlap of donor–acceptor orbitals that are of the same symmetry (t_{2g} – t_{2g}). Thus, the relatively slow rate observed in the Co(III)–Ti(III) system under study can be rationalized in part on the basis of the symmetry mismatch (t_{2g} – e_g). Further work will be necessary in order to arrive at a better understanding of the intramolecular electron-transfer between Co(III) and Ti(III). The high affinity of Ti^{3+} for oxygen chelates shown here and elsewhere^{7,18} implies that the rapid formation of a relatively stable precursor complex might be observed in related systems presently being developed in our laboratories.

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Oxidation–Reduction and the Electrocatalytic Ligand Substitution of Tetracobalt Clusters

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The capacity of polynuclear clusters to undergo multiple oxidation and reduction is probed with a series of bicapped tetracobalt carbonyls derived from the phenylphosphinidene-bridged $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$ (I). The redox behavior of I and its derivatives $\text{Co}_4(\text{CO})_{10-x}(\mu_4\text{-PPh})_2\text{L}_x$, where L is a mono- or diphosphine, is initially examined by a combination of electrochemical methods including cyclic voltammetry, linear sweep microvoltammetry, and polarography. All the techniques reveal a consistent trend for the oxidation of the tetracobalt cluster to be increasingly facilitated upon successive phosphine substitution ($x = 0, 1, 2, 3$, and 4); but reduction follows the opposite trend. The anion radical derived from the 0/–1 redox couple of the tetracobalt cluster I is shown to be substitutionally labile. The latter allows a facile ligand substitution to occur under mild conditions when a small cathodic current is passed through a solution of the cluster I containing various phosphorus(III) nucleophiles. The mechanism of the electrocatalytic process is discussed in the light of electron-transfer catalysis applicable to other mononuclear and polynuclear metal carbonyls.

Introduction

Transition-metal clusters are under active investigation as potential catalysts, particularly the utilization of carbon monoxide.^{1–5} Their virtue undoubtedly lies in the possibility of multiple coordination sites and the ready access to various oxidation levels that are allowed by the presence of contiguous metal centers. Indeed these two facets of catalytic activity may be coupled. Thus, there is recent evidence that ligand substitution of the coordinated carbon monoxide in diamagnetic bi- and trimetallic complexes of cobalt is induced by electron accession.^{6–9} The greatly enhanced

lability of the carbonylmetal anion radicals to substitution has also been observed in various carbonylmetal cation radicals.¹⁰ Such studies suggest that the chemical reactivity of metal clusters may generally be enhanced by deliberate reduction and/or oxidation.

Unfortunately, the relevant data relating to the redox properties of metal carbonyl clusters are limited—certainly in comparison

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