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# Titanium(III) Reductions of Binuclear and Tetranuclear μ-Carboxylato Cobalt(III)–Ammine Complexes. Evidence for Remote Attack of Titanium(III) at an Unprotonated Carboxylate

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The kinetics of the reductions of a series of binuclear and tetranuclear cobalt(III)–ammine complexes containing μ-carboxylato bridging ligands by $TiOH^{2+}$ have been studied at 25 °C in aqueous *p*-toluenesulfonate media. Outer-sphere mechanisms have been assigned when the oxidants do not have sites for inner-sphere precursor complex formation with the reductant available. From comparison of rate constants with those for outer-sphere $V^{2+}$ and $Cr^{2+}$ reductions of the same complexes, linear free energy relationships are obtained ($\log k_{TiOH} = 0.66 \log k_V - 0.64$ and $\log k_{TiOH} = 0.57 \log k_{Cr} + 0.35$). For the $TiOH^{2+}$ reductions of the unprotonated forms of the binuclear μ-oxalato and μ-fumarato complexes **4** and **5**, inner-sphere mechanisms with attack of the reductant at the remote uncomplexed carboxylate are tentatively assigned. The corresponding protonated forms are reduced via outer-sphere mechanisms.

## Introduction

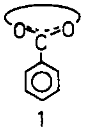
Kinetic studies of electron-transfer reactions with $[Ti(OH_2)_6]^{3+}$ as reducing agent for cobalt(III)–ammine complexes containing "inorganic" ligands ($N_3^-$, $NCS^-$, $SO_4^{2-}$, $F^-$, $Cl^-$, $Br^-$, $I^-$) have appeared during the last 3–4 years.[1-5] Ti(III) reductions of a variety of pentaamminecobalt(III) complexes containing coordinated carboxylic acids have also been studied.[6,7] Apart from experimental difficulties (e.g., $ClO_4^-$ and $NO_3^-$ are reduced by Ti(III)), a major problem of these studies is the unambiguous assignment of inner-sphere or outer-sphere mechanisms. Thompson and Sykes[3] have assessed bridging ligands for inner-sphere electron transfer by means of hard and soft acid–base theory. They have established linear free energy relationships between outer-sphere reductions of mononuclear cobalt(III) complexes with $TiOH^{2+}$, $[Ru(NH_3)_6]^{2+}$, and $[V(OH_2)_6]^{2+}$. Martin and Gould[6] have demonstrated that Ti(III) reductions of carboxylatopentaamminecobalt(III) complexes occur by inner-sphere mechanisms with attack of the reductant at the adjacent carbonyl oxygen (with and without chelation).

This paper investigates the possibility of inner-sphere Ti(III) reductions with attack of the reductant at a remote, uncomplexed carboxylic group and transfer of an electron through the organic ligand to coordinated Co(III). Binuclear μ-carboxycarboxylato(*O,O′*)-di-μ-hydroxo-bis[triamminecobalt(III)] complexes **4**, **5**, and **6** are used as oxidants because inner-sphere mechanisms with adjacent attack or adjacent attack with chelation of the reductant cannot be operative when both oxygen atoms of one carboxylate group are coordinated to Co(III) ions.[8-10]

## Experimental Section

**Reagents.** Binuclear and tetranuclear Co(III)–ammine complexes containing symmetrical μ-carboxylato(*O,O′*) bridges were prepared as perchlorate salts as described previously.[11-14] Titanium hydride (Fluka) was dissolved in HCl or *p*-toluenesulfonic acid (HOTs) at 50 °C (~60 h) in air-free conditions. The concentration of Ti(III) was determined by titration with dichromate[15] and subsequent standardizations were carried out spectrophotometrically using a molar absorption coefficient 3.97 $dm^3\ mol^{-1}\ cm^{-1}$ at 502 nm. The $H^+$ concentration was determined from a titration with 0.1 mol $dm^{-3}$ NaOH after passing aliquot portions down a column of Amberlite IR-120(H) cation-exchange resin. Solutions of chromium(II) perchlorate, vanadium(II) perchlorate, and $LiClO_4$ were prepared as described previously.[14] Sodium toluenesulfonate (NaOTs) was prepared by neutralization of HOTs with NaOH and was used as supporting electrolyte to adjust the ionic strength to 1.0 mol $dm^{-3}$.

**Kinetic Measurements.** The reductions of complexes **1–9** were studied by conventional spectrophotometric methods using a Unicam SP 1700 spectrophotometer at 524 nm (absorption maximum of binuclear and tetranuclear complexes) and at 25 ± 0.1 °C. The faster runs of the Ti(III) reduction of $[(NH_3)_4CoC_2O_4]^+$ were followed on a Durrum stopped-flow spectrophotometer, Model 110, at 505 nm. The reactants were mixed using standard syringe techniques under an argon or nitrogen atmosphere. Great care was exercised to avoid prolonged contacts of the reaction mixtures with the rubber serum caps of the optical cells.[16] All reactions were first order in both [Co(III)] and $[Ti(III)]_t$, respectively. Kinetic runs were carried out under pseudo-first-order conditions with at least tenfold excess of reductant. Reactions were followed for 5 half-lives. Absorbance changes at 524 nm were in good agreement with calculated values for complete reduction of two Co(III) atoms (complexes **1–6**) or four Co(III) atoms (**7–9**), respectively, and show the reductions of the first Co(III) atom of each complex to be the rate-determining step. In all cases only a single stage of the reaction was observed (decrease in absorbance). First-order rate constants were evaluated from gradients (×2.303) of plots of log $(A_t - A_\infty)$ against time, where $A_t$ is the absorbance at time *t* and $A_\infty$ that after the reaction is complete. Since the perchlorate salts of complexes were reduced ([complex] = $(0.5–1.0) \times 10^{-3}$ mol $dm^{-3}$), the plots obtained were only linear to 70–80% completion of the reaction due to the reduction of perchlorate by Ti(III).[17]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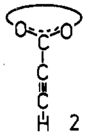
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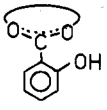
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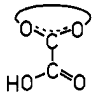
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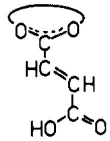
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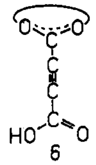
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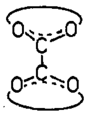
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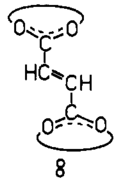
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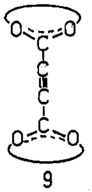
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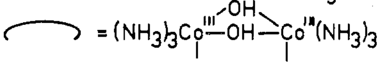

## Results

**(a) Ti(III) Reduction of the μ-Benzoato Complex 1.** Kinetic data of the reduction of **1** by $[Ti(OH_2)_6]^{3+}$, 0.028–0.084 mol $dm^{-3}$, in aqueous HCl–LiCl media ($\mu$ = 1.0 mol $dm^{-3}$) at 25 °C, $[H^+]$ = 0.05–0.66 mol $dm^{-3}$, using pseudo-first-order conditions (excess reductant) are summarized in Table I

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**Table II.** Summary of Rate Constants for the Ti(III) Reductions of Cobalt(III) Complexes at 25 °C, $\mu = 1.0$ mol dm$^{-3}$

| Complex | $k_1$,[a] s$^{-1}$ | Ref |
|---|---|---|
| **1**, $\mu$-benzoato | $(0.19 \pm 0.05) \times 10^{-4}$ [b] | This work |
| **2**, $\mu$-propiolato | $(1.26 \pm 0.2) \times 10^{-4}$ | This work |
| **3**, $\mu$-salicylato | $(0.86 \pm 0.1) \times 10^{-4}$ | This work |
| **7**, $\mu_4$-oxalato | $(0.95 \pm 0.2) \times 10^{-4}$ | This work |
| **8**, $\mu_4$-fumarato | $(2.05 \pm 0.2) \times 10^{-4}$ | This work |
| **9**, $\mu_4$-acetylenedicarboxylato | $(1.74 \pm 0.2) \times 10^{-4}$ | This work |
| $[Co(NH_3)_4C_2O_4]^+$ | $0.12 \pm 0.03$ | This work |
| $[Co(NH_3)_6]^{3+}$ | $0.3 \times 10^{-4}$ | 3 |
| $[Co(bpy)_3]^{3+}$ | $4.4 \times 10^{-2}$ | 3 |

[a] Equation 2. [b] $k_1$ from eq 1.

(supplementary material). Under these conditions $[Ti(OH_2)_6]^{3+}$ is the predominant Ti(III) species and no significant buildup of chloro complexes has been reported.[18] No effect on the rate was observed when the chloride medium was replaced by $p$-toluenesulfonate. Dependencies on $[H^+]$ and the total Ti(III) concentration, $[Ti(III)]_t$, conform to the rate law (1). $k_0$ was evaluated graphically (intercept/$[H^+]$) from

$$-d[\text{complex}]/dt = \left(k_0[H^+] + \frac{k_1}{[H^+]}[Ti(III)]_t\right)[\text{complex}] \quad (1)$$

a plot of the observed pseudo-first-order rate constants, $k_{obsd}$, measured at constant $[H^+]$ as a function of $[Ti(III)]_t$ (Figure 1): $k_0 = (0.8 \pm 0.3) \times 10^{-5}$ dm$^3$ mol$^{-1}$ s$^{-1}$. A plot of $(k_{obsd} - k_0[H^+])/[Ti(III)]_t$ against $[H^+]^{-1}$ is reasonably linear (Figure 2). The straight line passes within experimental error through the origin; $k_1$ was evaluated from the slope according to eq 1 ($(1.92 \pm 0.1) \times 10^{-5}$ dm$^3$ mol$^{-1}$ s$^{-1}$). As has been shown previously for the slow outer-sphere $Cr^{2+}$ reduction of **1**, OH-bridge cleavage processes make a contribution.[9] This is also found when Ti(III) is the reductant: Ti(III) scavenges the product of the bridge cleavage which is therefore independent of $[Ti(III)]_t$. The $[H^+]$-catalyzed bridge cleavage is the rate-determining step. Thus the numerical value obtained for $k_0$ from the $Cr^{2+}$ reduction of **1** in acidic perchlorate media at 25 °C, $0.88 \times 10^{-5}$ dm$^3$ mol$^{-1}$ s$^{-1}$, is identical with the one obtained from the Ti(III) reduction.

**(b) Ti(III) Reductions of Binuclear Complexes 2 and 3 and Tetranuclear Complexes 7, 8, and 9.** All Ti(III) reductions of complexes **2**, **3**, **7**, **8**, and **9** conform to the simple rate law (2). Plots of $k_{obsd}/[Ti(III)]_t$ against $[H^+]^{-1}$ are linear over

$$-d[\text{complex}]/dt = \frac{k_1}{[H^+]}[Ti(III)]_t[\text{complex}] \quad (2)$$

the $[H^+]$ range investigated (0.05–0.90 mol dm$^{-3}$). Kinetic data are given in Table I ($k_{obsd}$) and Table II ($k_1$). With the possible exception of complex **3**, none of the complexes contains acidic protons. Therefore, the inversely $[H^+]$-dependent path is believed to stem—at least in large part—from the participation of a deprotonated form of $[Ti(OH_2)_6]^{3+}$. This has been observed previously for the outer-sphere Ti(III) reduction of $[Co(NH_3)_6]^{3+}$, $[Co(bpy)_3]^{3+}$,[3] and $[(NH_3)_5CoDMN]^{3+}$[6] which also exhibit an $[H^+]^{-1}$ path. Martin and Gould[6] reported a good fit to their data using a dissociation constant for $[Ti(OH_2)_6]^{3+}$ of $1.6 \times 10^{-3}$ mol dm$^{-3}$ in 1.0 mol dm$^{-3}$ $OTs^-$ media. Somewhat higher values have been reported for chloride[19] or bromide[20] media. In this study, true rate constants $k_{TiOH}$ for the reaction of $TiOH^{2+}$ were determined from $k_1/K_a$ using the numerical value of Martin and Gould for $K_a$ (Table III).

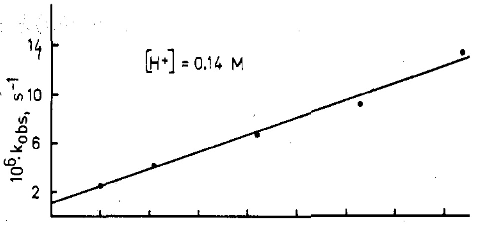

**Figure 1.** $TiOH^{2+}$ reduction of the $\mu$-benzoato complex **1**: dependence of pseudo-first-order rate constant $k_{obsd}$ (excess reductant) on titanium(III) concentration $[Ti(III)]_t$ at constant $[H^+]$, 25 °C, and $\mu = 1.0$ mol dm$^{-3}$ (NaOTs).

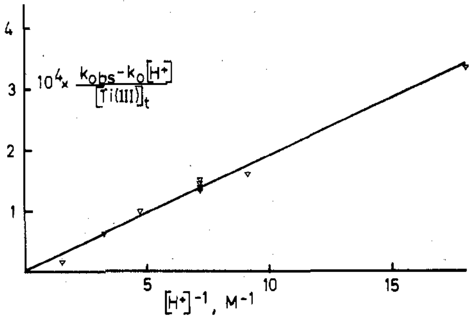

**Figure 2.** $TiOH^{2+}$ reduction of complex **1**: dependence of $(k_{obsd} - k_0[H^+])/[Ti(III)]_t$ on $[H^+]^{-1}$ according to eq 1.

In the case of the $\mu$-salicylato complex **3** Ti(III) reduction of the form deprotonated at the phenolic OH group may contribute. However, reductions of this complex by $[Cr(OH_2)_6]^{2+}$ and $[V(OH_2)_6]^{2+}$ at 25 °C ($\mu = 1.0$ mol dm$^{-3}$ ($LiClO_4$)) conform to the simple rate law (3) which is in-

$$-d[2]/dt = k_{Red}[\text{reductant}][2] \quad (3)$$

dependent of $[H^+]$ (0.02–0.9 mol dm$^{-3}$). Values of $k_{Cr}$ and

**Table III.** Compilation of Second-Order Rate Constants for the Reductions of Protonated ($k_{aH}$, dm$^3$ mol$^{-1}$ s$^{-1}$) and Unprotonated ($k_a$, dm$^3$ mol$^{-1}$ s$^{-1}$) Forms of Co(III) Complexes at 25 °C, $\mu = 1.0$ mol dm$^{-3}$

| | $TiOH^{2+}$ | | | | $[Cr(OH_2)_6]^{2+}$ | | | | $[V(OH_2)_6]^{2+}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Complex | $k_a$ | | $k_{aH}$ | | $k_a$ | | $k_{aH}$ | | $k_a$ | | $k_{aH}$ | | Ref |
| $[Co(NH_3)_4C_2O_4]^+$ | 75 | i.s. | | | $2 \times 10^5$ | i.s. | | | 45 | i.s. | | | 30 |
| $[Co(NH_3)_5C_2O_4]^+$ | $8.6 \times 10^4$ | i.s. | | | $4.6 \times 10^4$ | i.s. | 100 | i.s. | 45 | i.s. | 12.5 | i.s. | 31 |
| $[Co(NH_3)_6]^{3+}$ | 0.019 | o.s. | | | $8.9 \times 10^{-5}$ | o.s. | | | 0.0037 | o.s. | | | 3, 32 |
| $[Co(bpy)_3]^{3+}$ | 27.8 | o.s. | | | 23.1[a] | o.s. | | | $1.1 \times 10^3$ | o.s. | | | 3, 33 |
| 1 | 0.012 | o.s. | | | 0.0015[b] | o.s. | | | 0.050 | o.s. | | | 9 |
| 2 | 0.080 | o.s. | | | 0.0044 | o.s. | | | 0.24 | o.s. | | | 14 |
| 3 | 0.054 | o.s. | | | 0.0028 | o.s. | | | 0.14 | o.s. | | | |
| 4 | 4.8 | i.s. (?) | 0.62 | o.s. | 131 | i.s. | 4.7 | i.s. | 28 | i.s. | 1.55 | o.s. | 22 |
| 5 | 8.6 | i.s. (?) | 0.092 | o.s. | Not detected | | 2.64 | i.s. | 3.6 | i.s. | 0.12 | o.s. | 24, 23 |
| 6 | 0.3 | o.s. (?) | 0.18 | o.s. | 0.13 | i.s. | 0.67 | i.s. | 7.5 | i.s. | 0.94 | o.s. | 14, 23 |
| 7 | 0.061 | o.s. | | | 0.0036 | o.s.[c] | | | 0.21 | o.s. | | | 10 |
| 8 | 0.13 | o.s. | | | 0.0024 | o.s. | | | 0.10 | o.s. | | | |
| 9 | 0.11 | o.s. | | | 0.011 | o.s. | | | 0.55 | o.s. | | | 14 |

[a] Calculated from the equation $k_{Cr} = 0.021 k_V$. [b] Measured at 30 °C. [c] $\mu = 0.2$ mol dm$^{-3}$ ($LiClO_4$).

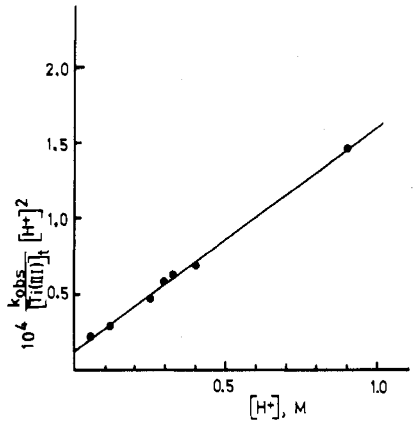

**Figure 3.** $TiOH^{2+}$ reduction of the μ-fumarato complex **5**: dependence of $k_{obsd}[Ti(III)]_t^{-1}[H^+]^2$ on $[H^+]$ at 25 °C, $\mu = 1.0$ mol dm$^{-3}$ (eq 5).

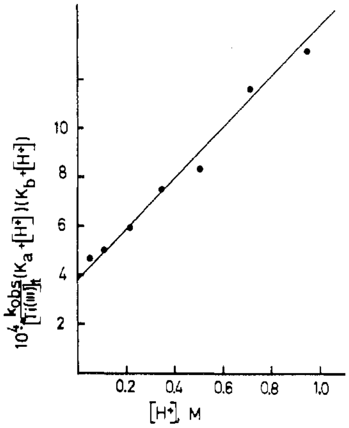

**Figure 4.** $TiOH^{2+}$ reduction of the μ-oxalato complex **4**: dependence of $k_{obsd}[Ti(III)]_t^{-1}(K_a + [H^+])(K_b + [H^+])$ on $[H^+]$ at 25 °C, $\mu$ = 1.0 mol dm$^{-3}$ (NaOTs) (eq 4) ($K_a = 1.58 \times 10^{-3}$ mol dm$^{-3}$, $K_b = 5.03 \times 10^{-2}$ mol dm$^{-3}$).

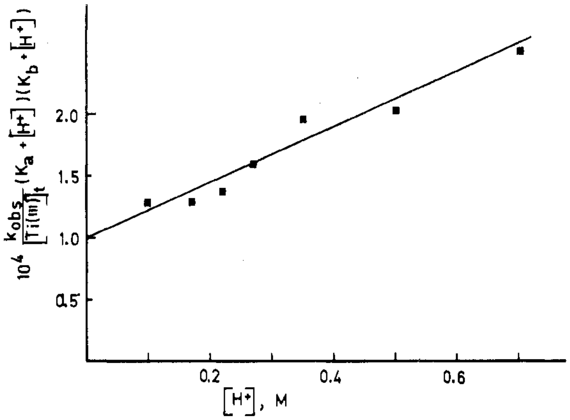

**Figure 5.** $TiOH^{2+}$ reduction of the μ-carboxyacetylenecarboxylato complex **6**: dependence of $k_{obsd}[Ti(III)]_t^{-1}(K_a + [H^+])(K_b + [H^+])$ on $[H^+]$ at 25 °C, $\mu$ = 1.0 mol dm$^{-3}$ (NaOTs) (eq 4) ($K_a = 1.58 \times 10^{-3}$ mol dm$^{-3}$, $K_b$ = 0.11 mol dm$^{-3}$).

$k_V$ are also listed in Table III. The reductions are slow and from the rate ratio $k_{Cr}/k_V$ of 0.02 outer-sphere mechanisms are assigned. Thus no evidence for the participation of a deprotonated form of **2** has been detected (the dissociation constant is estimated to be about $10^{-10}$ mol dm$^{-3}$ [21]). It is, therefore, concluded that participation of such a species in the Ti(III) reduction in the $[H^+]$ range employed is also not likely.

**(c) Ti(III) Reductions of Binuclear Complexes 4, 5, and 6 and $[(NH_3)_4CoC_2O_4]^+$.** Ti(III) reductions of complexes **4**, **5**, and **6** are very sensitive to acidity. This has been observed previously for the Ti(III) reduction of oxalatopentaamminecobalt(III).[6] All these oxidants have an uncomplexed carboxylato group. A mechanism where the unprotonated ($Co^{III}{}_2L^{2+}$, $k_a$) and protonated ($Co^{III}{}_2LH^{3+}$, $k_{aH}$) forms of the oxidants react via a bimolecular reaction with $TiOH^{2+}$ gives a formal rate law as in eq 4.

$$[Ti(OH_2)_6]^{3+} \overset{K_a}{\rightleftharpoons} [Ti(OH_2)_5OH]^{2+} + H^+$$

$$Co^{III}{}_2LH^{3+} \overset{K_b}{\rightleftharpoons} Co^{III}{}_2L^{2+} + H^+$$

$$Co^{III}{}_2LH^{3+} + TiOH^{2+} \xrightarrow{k_{aH}} \text{products}$$

$$Co^{III}{}_2L^{2+} + TiOH^{2+} \xrightarrow{k_a} \text{products}$$

$$-d[Co^{III}{}_2]_t/dt = \frac{k_{aH}K_a[H^+] + k_aK_aK_b}{(K_a + [H^+])(K_b + [H^+])}[Ti(III)]_t[Co^{III}{}_2]_t \tag{4}$$

$[Ti(III)]_t$ or $[Co^{III}{}_2]_t$ denotes the total concentration of titanium(III) or of cobalt(III) complex. Acidity constants $K_b$ of complexes **4**, **5**, and **6** are known (0.0503,[22] 0.00095,[23] and 0.11[14] at 25 °C, $\mu$ = 1.0 mol dm$^{-3}$ ($LiClO_4$)).

Since $K_a << [H^+]$ *and* $K_b << [H^+]$ hold for complex **5** in the range of $[H^+]$ used (0.05–0.9 mol dm$^{-3}$), expression 4 reduces to eq 5. A plot of $k_{obsd}[Ti(III)]_t^{-1}[H^+]^2$ against $[H^+]$

$$-d[\mathbf{5}]/dt = \frac{k_{aH}K_a[H^+] + k_aK_aK_b}{[H^+]^2}[Ti(III)]_t[\mathbf{5}]_t \tag{5}$$

should be linear where $k_{obsd}$ is the measured pseudo-first-order rate constant (excess reductant, Table I). This is shown in Figure 3. From the intercept ($=k_aK_aK_b$) and slope ($=k_{aH}K_a$), bimolecular rate constants for the reaction of the protonated complex **5** and the unprotonated form with $TiOH^{2+}$ were evaluated (Table III).

A more rigorous test for the applicability of the proposed reaction scheme is encountered by the reductions of complexes **4** and **6** because in these cases $K_b$ is of the same order of magnitude as the experimental $[H^+]$ and the condition $K_b << [H^+]$ does not hold. Now a plot of $k_{obsd}[Ti(III)]_t^{-1}(K_a + [H^+])(K_b + [H^+])$ against $[H^+]$ should give straight lines with intercepts ($=k_aK_aK_b$) and slopes ($=k_{aH}K_a$) using the spectrophotometrically determined dissociation constants $K_b$ for the μ-oxalato complex **4** (0.0503 mol dm$^{-3}$) and the μ-acetylenedicarboxylato analogue **6** (0.11 mol dm$^{-3}$). This is shown in Figure 4 (good linear behavior is observed) and Figure 5 where a reasonable straight line is obtained. Values for $k_{aH}$ and $k_a$ (Table III) were evaluated using a linear least-squares program.

The mononuclear oxalatotetraamminecobalt(III) complex does not contain acidic protons. Hence, the simple rate law (2) is observed for the Ti(III) reduction of this species ($k_1$ = 0.119 s$^{-1}$, 25 °C, $\mu$ = 1.0 mol dm$^{-3}$ (NaOTs), $[H^+]$ = 0.05–0.5 mol dm$^{-3}$ (Table I)). The same rate law has been observed for the Ti(III) reduction of the tetranuclear μ-oxalato complex **7** but the observed rate constant $k_1$ is smaller by 3 orders of magnitude ($9.6 \times 10^{-5}$ s$^{-1}$). On the other hand, Ti(III) reduction of the oxalatopentaamminecobalt(III) which contains a monodentate oxalato ligand and therefore has an uncomplexed carboxylic group conforms to a one-term rate law featuring $[H^+]^{-2}$.[6]

## Discussion

The mechanisms of the $Cr^{2+}$ and $V^{2+}$ reductions of binuclear and tetranuclear cobalt(III)–ammine complexes which have no sites available for precursor complex formation with the reductant (complexes **1**, **2**, **7**, **8**, and **9**) have been shown to be of the outer-sphere type.[9,14,10] No enhancement in rate from inner-sphere contributions due to the presence of OH bridges,

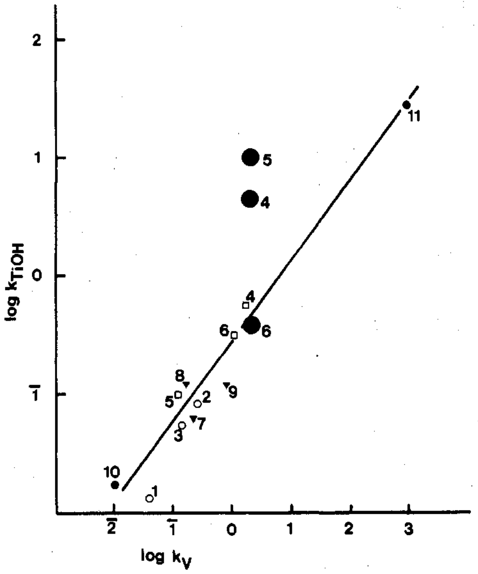

**Figure 6.** Plot of log $k_{TiOH}$ against log $k_V$ for reductions of cobalt(III) complexes by $TiOH^{2+}$ and $V^{2+}$: (•) mononuclear complexes $[Co(NH_3)_6]^{3+}$ (**10**) and $[Co(bpy)_3]^{3+}$ (**11**); (○) binuclear complexes $\mu$-benzoato (**1**), $\mu$-propiolato (**2**), and $\mu$-salicylato (**3**); (▼) tetranuclear complexes $\mu_4$-oxalato (**7**), $\mu_4$-fumarato (**8**), and $\mu_4$-acetylenedicarboxylato (**9**); (□) protonated forms of the complexes $\mu$-oxalato (**4**), $\mu$-fumarato (**5**), and $\mu$-carboxyacetylenecarboxylato (**6**); (●) unprotonated forms of the latter complexes **4**, **5**, and **6** assuming an outer-sphere rate constant for the $V^{2+}$ reduction $\leq 2.0$ dm$^3$ mol$^{-1}$ s$^{-1}$.

a benzene ring as in **1**,[9] or C–C double or triple bonds as in **2**, **8**, or **9**[14,24] was detected. The same behavior is observed when the above complexes are reduced by $TiOH^{2+}$. True rate constants for the reaction of this species with cobalt(III) complexes, $k_{TiOH}$ (dm$^3$ mol$^{-1}$ s$^{-1}$), are given by $k_1/K_a$ and are summarized in Tables II and III using Martin and Gould's value for $K_a$ ($1.58 \times 10^{-3}$ mol dm$^{-3}$).

Thompson and Sykes have shown that a plot of log $k_{TiOH}$ against log $k_V$ is linear for the outer-sphere reductions of mononuclear Co(III) complexes.[3]

$$\log k_{TiOH} = 0.55 \log k_V - 0.55 \qquad (6)$$

This relation holds for the Ti(III) reductions of binuclear (**1**, **2**) and tetranuclear (**7**, **8**, **9**) complexes (Figure 6). A least-squares fit of all data points in Figure 6 including the two points corresponding to the mononuclear complexes $[Co(NH_3)_6]^{3+}$ and $[Co(bpy)_3]^{3+}$ yields

$$\log k_{TiOH} = (0.66 \pm 0.07) \log k_V - (0.64 \pm 0.07) \qquad (7)$$

with a correlation factor of 0.92. A plot of log $k_{TiOH}$ against log $k_{Cr}$ for the same oxidants is shown in Figure 7. Again a reasonably linear correlation is defined.

$$\log k_{TiOH} = (0.57 \pm 0.1) \log k_{Cr} + (0.35 \pm 0.1) \qquad (8)$$

Interestingly, the slope of the latter correlation is ca. 0.5 which appears to be characteristic for log–log plots involving $TiOH^{2+}$ as a reductant[3] (a slope of unity for the corresponding log $k_V$–log $k_{Cr}$ correlation has been reported: log $k_V$ = 1.02 log $k_{Cr}$ + 1.73[22,25]).

From a comparison of rate constants obtained for the $TiOH^{2+}$ reductions of the protonated forms of the $\mu$-fumarato complex **5** and the $\mu$-carboxyacetylenecarboxylato complex **6** with those for the $V^{2+}$ reductions of the same protonated complexes using the above log $k_{TiOH}$–log $k_V$ plot (Figure 6), it is concluded that reductions of these species by $TiOH^{2+}$ occur via outer-sphere mechanisms. This mechanism has been shown previously to be operative for the $V^{2+}$ reductions from measurements of the respective activation parameters.[23] Since data point 4 (Figure 6) obtained for the reductions of the protonated binuclear $\mu$-oxalato complex **4** by $V^{2+}$ and $TiOH^{2+}$ also lies very close to the straight line, outer-sphere mechanisms may be assigned to the reductions by $TiOH^{2+}$ *and* $V^{2+}$,[22] too. The $Cr^{2+}$ reductions of the respective protonated complexes **4**, **5**, and **6**, on the other hand, have been shown to be of the inner-sphere type.[22,24,14] Thus data points 4, 5, and 6 in Figure 7 do not conform to relation 8.

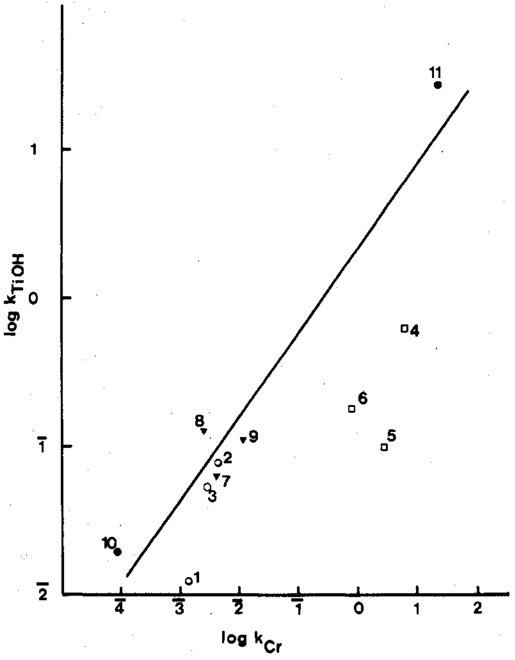

**Figure 7.** Plot of log $k_{TiOH}$ against log $k_{Cr}$ for reductions by $TiOH^{2+}$ and $Cr^{2+}$ of cobalt(III) complexes. Numbering is identical with that of Figure 6.

The assignment of mechanism to the reductions of the unprotonated forms of complexes **4**, **5**, and **6** is more difficult mainly because in these cases the $Cr^{2+}$ and $V^{2+}$ reductions are inner sphere and log–log correlations of the above type cannot be used. However, since the outer-sphere $V^{2+}$ reductions of binuclear $\mu$-carboxylato-di-$\mu$-hydroxo-bis[triamminecobalt(III)] complexes have second-order rate constants which are <2.0 dm$^3$ mol$^{-1}$ s$^{-1}$ at 25 °C (this is true for all known outer-sphere $V^{2+}$ reductions of this type of complex to date), the corresponding points in the log $k_{TiOH}$–log $k_V$ plot (points 4 and 5 in Figure 6) for the reductions of the unprotonated forms of the $\mu$-oxalato and $\mu$-fumarato complexes lie well above the line using $k_{TiOH}$ values from Table III. This is indicative of an inner-sphere mechanism for the $TiOH^{2+}$ reductions of the unprotonated forms of $\mu$-oxalato and $\mu$-fumarato complexes **4** and **5**. In contrast, the $TiOH^{2+}$ reduction of the unprotonated $\mu$-carboxyacetylenecarboxylato analogue (point 6, Figure 6) would—at least in part—be outer-sphere following the above reasoning. Furthermore, a significant acceleration of the $TiOH^{2+}$ reductions occurs in going from the slow outer-sphere reductions of protonated **4** and **5** to the—possibly—inner-sphere reductions of their unprotonated forms, whereas only a marginal enhancement is observed for complex **6**.

It has been pointed out that electron transfer through extended organic bridging ligands from a reducing metal–aquo ion ($[Cr(OH_2)_6]^{2+}$ or $[V(OH_2)_6]^{2+}$) onto cobalt(III) requires intermediate one-electron reduction of the ligand.[26,27] The reducibility of the uncomplexed ligand by the actual reductant is taken as a crude indication for the feasibility of such a mechanism. Uncomplexed fumaric acid[28] and acetylenedicarboxylic acid[29] are reducible by Ti(III) in aqueous acidic solution, succinic acid being the sole organic product. Therefore, inner-sphere electron transfer through the unprotonated forms of complexes **4**, **5**, and **6** would conform to the present picture for this type of mechanism. It is noted that acetylenedicarboxylic acid has been shown to be a less effective electron-mediating structural unit as compared to fumaric acid when the strong reductant $[Cr(OH_2)_6]^{2+}$ is used.[14] It seems plausible that for the weaker reductant $TiOH^{2+}$ the outer-sphere reduction of the unprotonated form of **6** is energetically as favorable as or more favorable than the inner-sphere path.

The presence of two $\alpha$-carbonyl groups suitable for the formation of a chelated precursor complex with the reductant is thought to be responsible for the very high rates of electron transfer in the $Cr^{2+}$ reductions of oxalatotetraamminecobalt(III)[30] and oxalatopentaamminecobalt(III).[31] This was bolstered by the observation of a decrease in the rate of inner-sphere $Cr^{2+}$ reduction by 3–4 orders of magnitude when binuclear $\mu$-oxalato complexes which contain only one remote carbonyl oxygen are the oxidants. Finally, if no carbonyl oxygen is available at all as in the tetranuclear $\mu_4$-oxalato complex **7**, an outer-sphere mechanism has been observed.[10] A very similar pattern emerges from this study when $TiOH^{2+}$ is the reductant. Thus the unprotonated $[Co(NH_3)_5C_2O_4]^+$ is reduced by $TiOH^{2+}$ at a very high rate[6] (Table III), whereas complex **7** is reduced very slowly via an outer-sphere mechanism. Although the inner-sphere $TiOH^{2+}$ reduction of $[(NH_3)_4CoC_2O_4]^+$ is surprisingly slow bearing in mind the $Cr^{2+}$ results, a rate enhancement by a factor of 15 is still observed as compared to the reduction of the unprotonated $\mu$-oxalato complex **4**.

The importance of chelation in inner-sphere electron transfer[6,27] is also demonstrated by the observation that the binuclear $\mu$-salicylato complex **3** is reduced by $Cr^{2+}$, $V^{2+}$, and $TiOH^{2+}$ very slowly via outer-sphere mechanisms, indicating that either the phenolic OH group alone is not suitable for precursor complex formation or electron transfer through the ligand is energetically not favorable (it should be noted that both oxygen atoms of the carboxylate are coordinated to Co(III) and are not available for the reducing aquo ions). In contrast, reduction of the mononuclear salicylatopentaamminecobalt(III) complex by $Cr^{2+}$[21] and $TiOH^{2+}$ (or $[Ti(OH_2)_6]^{3+}$)[7] shows marked enhancement of rates of reduction respectively due to attack of the reductant at the adjacent carbonyl oxygen and chelation at the phenolic hydroxo group.

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**Registry No.** **1**, 52362-69-3; **2**, 61168-69-2; **3**, 52362-75-1; **4**, 65665-32-9; **5**, 58769-41-8; **6**, 61168-66-9; **7**, 41655-88-3; **8**, 52827-96-0; **9**, 61168-68-1; $[Co(NH_3)_4C_2O_4]^+$, 21560-02-1; $Ti(OH_2)_6^{3+}$, 17524-20-8.

**Supplementary Material Available:** Table I showing kinetic data for the reductions of complexes **1–9** and $[Co(NH_3)_4C_2O_4]^+$ by Ti(III) (2 pages). Ordering information is given on any current masthead page.

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# Oxidation–Reduction Reactions between Cobalt(II) and -(III) Chelate and Iron(III) and -(II) Cyanide Complexes. Outer- vs. Inner-Sphere Mechanisms[1]

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Both the forward and reverse reactions for the systems $Co^{II}(chelate) + Fe^{III}(CN)_5X \rightleftharpoons Co^{III}(chelate) + Fe^{II}(CN)_5X$ have been studied at ionic strength 0.26 M, at pH 6.00, and at several temperatures. The chelates were ethylenediaminetetraacetate ion (EDTA), 1,2-propylenediaminetetraacetate ion (PDTA), and *trans*-1,2-cyclohexanediaminetetraacetate ion (CyDTA). The X was either $CN^-$ or triphenylphosphine ($Ph_3P$). Rate data for the forward reactions follow the same pattern as in earlier studies: a rapid formation of a binuclear cyano-bridged complex and a slow formation of mononuclear products. The reverse reactions were studied more extensively. Runs were done in the presence and absence of ascorbic acid (added to drive the reactions to completion). Equilibrium constants for the overall reaction were calculated from data obtained in the absence of ascorbic acid. These values were in good agreement with constants obtained from kinetic data. Trends in rates and activation parameters and comparisons with similar systems lead to the conclusion that the reactions occur by an outer-sphere mechanism. This is the same conclusion Haim reached based on limited studies at 25 °C.

The electron-transfer reaction between cobalt(II)–chelate complexes of the type $Co^{II}Y$ (where Y = EDTA, PDTA, CyDTA, etc.) and iron(III)–cyanide oxidants, $Fe^{III}(CN)_5X$ (where $X = CN^-$, $P(C_6H_5)_3$, etc.) has the overall stoichiometry

$$Co^{II}Y + Fe^{III}(CN)_5X \rightleftharpoons Co^{III}Y + Fe^{II}(CN)_5X \qquad (1)$$

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