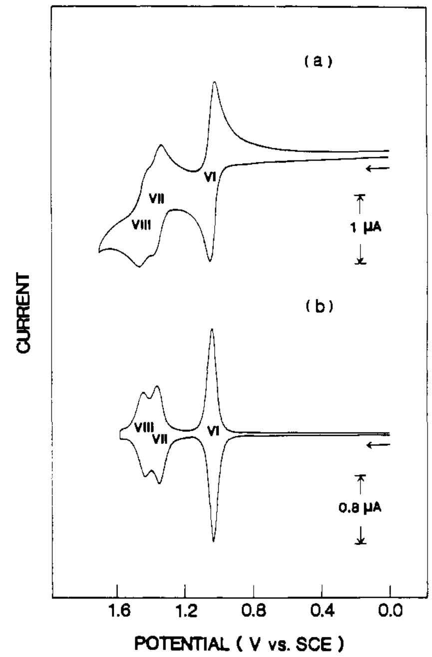

Figure 6. (a) Cyclic voltammogram and (b) differential pulse voltammogram of $[(TPP)RhCl]_2bpy$ in CH_2Cl_2, 0.2 M TBAP at −72 °C.

volve two overlapping one-electron-transfer processes. A normal pulse voltammogram of $[(TPP)RhCl]_2bpy$ is depicted in Figure 5c and shows the number of electrons involved in each oxidation step to be two, one, and one. All of these reversible oxidations involve the intact Rh(III) dimer and not decomposition products from the original material. This is also demonstrated by the cyclic voltammogram for oxidation of $[(TPP)RhCl]_2bpy$ in CH_2Cl_2 at −72 °C. This voltammogram is shown in Figure 6a and is similar to the voltammogram obtained at room temperature.

The differential pulse voltammogram of $[(TPP)RhCl]_2bpy$ at −72 °C (Figure 6b) also demonstrates the reversibility of each electron-transfer process. The data indicate that the two porphyrin rings of $[(TPP)RhCl]_2bpy$ are equivalent, but this is not the case for $[[(TPP)RhCl]_2bpy]^{2+}$, which shows an interaction across the bridging nitrogen heterocycle. Similar behavior was not found for the other three bridging-ligand systems, and an overall oxidation mechanism of $[(P)RhCl]_2L$ is shown in Scheme II.

In summary, the data in this study indicate that the presence of a bridging ligand between two rhodium porphyrin units does not substantially alter the electrochemical behavior of the individual rhodium(III) complexes. The initial reductions of $[(P)RhCl]_2L$ are all metal-centered and are followed by a rapid chemical reaction that leads to a Rh(II) monomer and the ultimate formation of $[(P)Rh]_2$ in THF. The oxidations are all porphyrin ring centered and lead to π cation radicals. However, this study does clearly demonstrate that an interaction between two bridged porpyrin units is possible for complexes that contain a nitrogen-heterocycle bridging ligand and a porphyrin central metal other than iron.

In principle, the reduction of $[(P)RhCl]_2L$, where L = bpy or BPE, generates a short-lived mixed-valence complex. If one assumes that reduction process Ib is due to the intact dimer, an equilibrium constant for formation of the mixed-valence state can be calculated. However, process Ib may be due to the reduction of monomeric (P)RhCl(L) formed by decomposition of the monoanion, $[[(P)RhCl]_2L]^-$. A distinction between the two cases is only possible if the monoanion can be stabilized. This is not the case for the present series of compounds.

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Registry No. bpy, 553-26-4; BPE, 13362-78-2; BPA, 4916-57-8; TMDP, 17252-51-6; $[(TPP)RhCl]_2bpy$, 114550-19-5; $[(TPP)RhCl]_2BPE$, 114533-28-7; $[(TPP)RhCl]_2BPA$, 114533-29-8; $[(TPP)RhCl]_2TMDP$, 114533-30-1; $[(OEP)RhCl]_2bpy$, 106468-35-3; $[(OEP)RhCl]_2BPE$, 114550-16-2; $[(OEP)RhCl]_2BPA$, 114550-17-3; $[(OEP)RhCl]_2TMDP$, 114550-18-4; $[(TPP)Rh]_2$, 88083-37-8; $[(OEP)Rh]_2$, 63439-10-1; (TPP)RhCl, 77944-60-6; (OEP)RhCl, 36670-30-1; (OEP)RhI, 69509-36-0; THF, 109-99-9; Rh, 7440-16-6; Pt, 7440-06-4; CH_2Cl_2, 75-09-2.

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Nonbridging Ligand Effects as Mechanistic Probes in Ruthenium(III)-Titanium(III) Electron-Transfer Reactions

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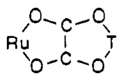
Rates of reduction of $Ru(NH_3)_5(pyridine)^{3+}$ by Ti(III) complexes of pentanedione (at 25.0 °C and 1.0 M LiCl) are as predicted from redox potentials of the complexes and the rate-potential relationship followed by Ru(III)-Ti(III) reactions that involve outer-sphere mechanisms. Intermediates, corresponding to an inner-sphere mechanism, are observed for reductions of $Ru_2(CH_3COO)_2(C_2O_4)_2^-$ by Ti^{3+} and by $TiC_2O_4^+$. No intermediate is observable for the reaction of $Ti(C_2O_4)_2^-$ with that oxidant, but the rate indicates an inner-sphere mechanism for the reaction. Nonbridging oxalate ligands on Ti(III) reduce the stability of the intermediate. The rate of electron transfer within the intermediate is significantly increased by the second oxalate added. Stability constants (at 25.0 °C and 1.0 M LiCl) for $TiC_2O_4^+$ and $Ti(C_2O_4)_2^-$ were found to be 8.5×10^5 M^{-1} and 2.5×10^5 M^{-1}.

The rate constant for reduction of $Ru(NH_3)_5py^{3+}$ by $Ti(OH)^{2+}$ falls on a linear free energy relationship (between redox rate constant and reaction free energy) along with rate constants for other Ru(III)-Ti(III) reactions that follow outer-sphere electron-transfer (hereafter ET) mechanisms.[1] Rate constants[2] for Ti(III) reduction of both $Ru(NH_3)_4C_2O_4^+$ and $Ru(NH_3)_5C_2O_4^+$ are 10^4 faster than expected on the basis of that linear free energy relationship. The reductant attacks at the carbonyl oxygen adjacent to the metal atom. ET through structure I is rapid. In



I

contrast, the redox reaction between $Ru_2(CH_3COO)_2(C_2O_4)_2^-$ and Ti(III) occurs by an inner-sphere mechanism with attack of the reductant at a remote, uncomplexed carboxylic group, but an

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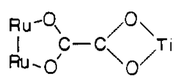
observable trinuclear intermediate (structure II) is involved.[3]



II

Oxalate as a nonbridging ligand significantly increases the rate of inner-sphere reductions of oxalato complexes of Co(III) and Ru(III).[4] We now report results of a study of the influence of oxalate ion as a nonbridging ligand on the rate of reduction of $Ru_2(CH_3COO)_2(C_2O_4)_2^-$ by Ti(III) (an inner-sphere reaction with observable intermediate) and of pentane-2,4-dione (hereafter pd) as a nonbridging ligand on the rate of reduction of $Ru(NH_3)_5py^{3+}$ by Ti(III) (an outer-sphere reaction). Comparison of these two sets of experiments leads to a conclusion relative to the detailed mechanism of ET in the $Ru_2(CH_3COO)_2(C_2O_4)_2^-$–Ti(III) reaction.

Experimental Section

Ti(III) solutions were prepared and standardized under nitrogen as described.[1] Absorbance of the Ti(III) solutions at 300 nm was negligible, indicating absence of Ti(IV).[5] Kinetic measurements were made on a computer-linked Durrum stopped-flow spectrophotometer at 25.0 ± 0.2 °C and ionic strength of 1.0 M (LiCl). Added ligand was equilibrated with Ti(III) prior to initiation of redox reactions. Symbols M, L, and so on, refer to Ti^{3+}, pd^- or $C_2O_4^{2-}$, etc.

$[Ru(NH_3)_5py](ClO_4)_3$ was prepared as described by Gaunder and Taube.[6] The spectrum of the ruthenium complex was in good agreement with literature values [λ, nm (ε, cm^{-1} M^{-1}): 262 (4.63×10^3), 256 (4.71×10^3), 248 (4.67×10^3)]. The color of $Ru(NH_3)_5py^{3+}$ (hereafter Ru-py) solutions changed from light green to deep yellow after mixing, under N_2, with Ti(III) solutions, or with Ti(III) preequilibrated with pd. Spectrophotometric titration showed that 1.0 ± 0.1 mol of oxidant was consumed for each mole of Ti(III) added, both in the presence of added pd and in its absence. Absorbance increase accompanying the reduction of Ru-py was followed at 408 nm at 25.0 ± 0.2 °C. The reaction followed first-order kinetics for more than 3 half-times. Values of k_{obsd}, determined by using linear least-squares techniques, were generally reproducible within 5%. Data are shown in Table I and II. Polarographic (DME) measurements were made by using an IBM Model EC/225 voltammetric analyzer with a saturated calomel reference electrode in 1.0 M LiCl media at 24.0 ± 0.2 °C.

$Ru_2(CH_3COO)_2(C_2O_4)_2^-$ was prepared in solution as described.[3] Wavelengths (nm) of maximum absorption (extinction coefficients, M^{-1} cm^{-1}) are 375 (3.5×10^3) and 475 (1×10^3), as reported. Free oxalate concentrations in $Ru^{II}Ru^{III}$ solutions are less than 0.05 mM. The color of $Ru_2(CH_3COO)_2(C_2O_4)_2^-$ solution changed from brown to light yellow after mixing with Ti(III) solutions or with Ti(III) solutions preequilibrated with additional oxalate ion. Spectrophotometric titration showed that 1 mol of oxidant was consumed for each mole of Ti(III) added, both in the presence of added oxalate and in its absence. Kinetic experiments were carried out, with Ti(III) at least 10-fold in excess, at 476 nm (an absorbance maximum of the oxidant).

When Ti(III) solutions were mixed with the $Ru^{II}Ru^{III}$ solution, at low concentrations of added oxalate, a two-phase reaction, involving a maximum in absorbance, was observed.[7] Kinetic data were adequately fitted by a double-exponential function. The rate constant for the absorbance increase was designated k_f and that for the final absorbance decrease designated k_s. A linear least-squares program was used to evaluate k_s from kinetic data taken on the decreasing slope. Values of k_s were generally reproducible to better than 10%. Data are shown in Tables III and IV. At higher oxalate concentrations, when more than 95% of the Ti(III) is complexed, the maximum is not observed, but only a single exponential absorbance decrease occurs (Figure 1). In these cases the rate constant was determined by a linear least-squares procedure.

Formation constants of (oxalato)titanium(III) complexes were measured under the conditions used for the kinetic experiments. Spectra observed were corrected for absorption due to uncomplexed Ti(III). As reported,[8] the wavelength of maximum absorption was 370 nm for the corrected spectra taken at low ligand/metal ratios and the wavelength of maximum absorption shifted to 400 nm at high ligand/metal ratios.

Table I. Kinetics of Reduction of $Ru(NH_3)_5py^{3+}$ by Ti(III) at 25.0 °C in 1.0 M LiCl[a]

$[H^+]$, mM	[Ti(III)], mM	k_{obsd}, s^{-1}	10^2k_1[b], M^{-1} s^{-1}	$10k$,[c] s^{-1}
40.1	4.84	3.23	6.7	2.7
60.2	4.84	2.12	4.4	2.6
100	1.21	0.30	2.5	2.5
100	2.42	0.63	2.6	2.6
100	4.84	1.42	2.9	2.9
100	9.68	2.82	2.9	2.9
100	18.2	5.55	3.0	3.0
121	4.84	1.08	2.2	2.7
151	4.84	0.85	1.8	2.7
198	4.84	0.64	1.3	2.6
				av 2.7 ± 0.2

[a] [Ru-py] = 6.9×10^{-5} M. [b] $k_1 = k_{obsd}$ [Ti(III)]. [c] $k = k_1[H^+]$.

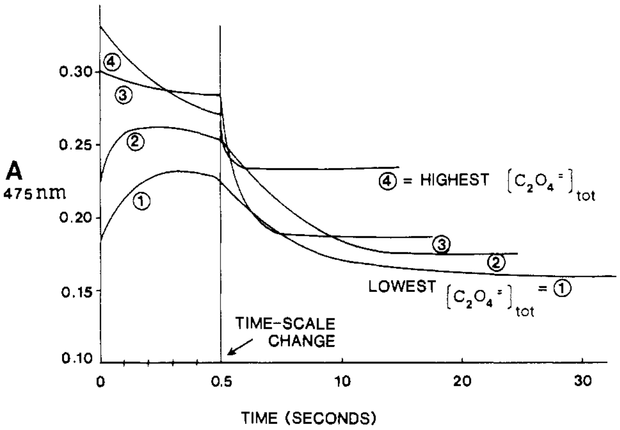


Figure 1. Traces of absorbance at 475 nm vs time for the reduction of $Ru_2(CH_3COO)_2(C_2O_4)_2^-$ by oxalato–Ti(III) complexes with $[Ti(III)]_t$ = 1.2 mM and $[H^+]$ = 100 mM: $[C_2O_4^{2-}]_t$ = 1.0 (1), 4.0 (2), 10 (3), 30 mM (4).

Results

Four equilibria are involved in complex formation between Ti(III) and pd.

$$M + L \rightleftarrows ML \qquad K_i = \frac{[ML]}{[M][L]} \tag{1}$$

$$ML + L \rightleftarrows ML_2 \qquad K_{ii} = \frac{[ML_2]}{[ML][L]} \tag{2}$$

$$ML_2 + L \rightleftarrows ML_3 \qquad K_{iii} = \frac{[ML_3]}{[ML_2][L]} \tag{3}$$

$$HL \rightleftarrows H + L \qquad K_a = \frac{[H][L]}{[HL]} \tag{4}$$

Values of K_i, K_{ii}, K_{iii}, and K_a have been determined[9] to be 2.51×10^{10} M^{-1}, 2.51×10^8 M^{-1}, 1.26×10^6 M^{-1}, and 1.26×10^{-9} M under the conditions of our experiments.

In the absence of added pd, polarography in 0.1 M HCl–0.9 M LiCl gave a half-wave potential of 0.04 ± 0.01 V vs NHE for the oxidation of Ti^{3+}, in agreement with prior reports.[10] At low concentration of pd added, the values of the half-wave potential shift in the cathodic direction as pd concentration increases and becomes constant at 0.00 ± 0.01 V vs NHE. At higher ligand concentration ($[pd]_t$ > 100 mM), the half-wave potential becomes

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Table II. Kinetics of Reduction of $Ru(NH_3)_5py^{3+}$ by Ti(III)–Pentane-2,4-dione Complexes at 25.0 °C in 1.0 M LiCl[a]

$[HL]_t$, mM	$[H]_t$, mM	$10^3[Ti(III)]_t$, mM	$10^8[L]_f$, mM	$[H]_f$, mM	$10^3[M]_f$, mM	$10^3[ML]_f$, mM	$10^3[ML_2]_f$, mM	$10^6[ML_3]_f$, mM	k_{obsd}, s^{-1}	k_{calcd},[b] s^{-1}
0.5	200	823	0.28	200	769	54.3	0.04	0.00	0.12	0.12
1.0	201	823	0.57	200	721	102	0.15	0.00	0.12	0.12
2.0	202	823	1.14	200	639	183	0.53	0.01	0.14	0.14
3.0	203	823	1.73	200	573	249	1.08	0.02	0.15	0.15
4.0	204	823	2.32	200	519	303	1.77	0.05	0.17	0.17
5.0	205	823	2.9	200	473	347	2.55	0.09	0.18	0.18
10.0	210	823	6.0	21	327	489	7.31	0.55	0.29	0.29
30.0	230	823	18.4	201	141	652	30.1	6.96	0.70	0.71
70.0	270	823	43.4	201	63	685	74.6	40.8	1.48	1.52
100	300	823	62.2	201	43	674	105	82.4	1.97	2.07
10.0	110	823	11.7	101	204	601	17.7	2.61	0.53	0.51
10.0	160	823	7.9	151	272	540	10.7	1.06	0.40	0.37
10.0	260	823	4.8	250	371	447	5.4	0.32	0.22	0.24
10.0	310	823	4.0	300	408	411	4.1	0.21	0.19	0.20
10.0	210	1070	5.86	201	427	628	9.24	0.68	0.34	0.37
10.0	210	1450	5.70	201	592	848	12.1	0.87	0.47	0.49
10.0	210	2180	5.43	201	915	1250	17.0	1.16	0.81	0.71
10.0	209	2900	5.19	201	1250	1630	21.3	1.39	0.97	0.92

[a] [Ru-py] = 4.6×10^{-5} M. Tabulated concentrations are calculated from initial total concentrations (subscript t) with use of an iterative computer program and the values $K_1 = 2.51 \times 10^{10}$ M^{-1}, $K_2 = 2.51 \times 10^8$ M^{-1}, $K_3 = 1.26 \times 10^6$ M^{-1}, and $K_a = 1.26 \times 10^{-9}$ M. [b] k_{calcd} is defined by eq 5 and computed from the concentrations given in the table and the values of $k = 2.7 \times 10$ s^{-1}, $k' = 2.3 \times 10^2$, and $k'' = 1.8 \times 10^4$ M^{-1} s^{-1}.

Table III. Kinetics of Reduction of $Ru_2(CH_3COO)_2(C_2O_4)_2^-$ by Ti^{3+} at 25 °C in 1.0 M LiCl[a]

$[H^+]$, mM	[Ti(III)], mM	k_s, s^{-1}	$[H^+]$, mM	[Ti(III)], mM	k_s, s^{-1}
30	2.00	0.18	100	7.00	0.20
60	2.00	0.20	100	10.00	0.20
100	2.00	0.16	120	2.00	0.19
100	1.20	0.17	150	2.00	0.16
100	5.00	0.16	200	2.00	0.19
					av 0.18 ± 0.02

[a] $[Ru^{II}Ru^{III}]_T = 1.13 \times 10^{-4}$ M.

less cathodic and a second (much smaller) anodic wave develops. The half-wave potentials for the second anodic wave are unchanged at −0.15 ± 0.05 V as the ligand concentration goes up to 1.0 M. We interpret the wave at 0.00 ± 0.01 V as corresponding to oxidation of TiL^{2+}, and the wave at −0.15 ± 0.05 V as corresponding to oxidation of TiL_2^+.

In the absence of added pd, the reaction of Rupy with Ti(III) follows the rate law

$$k_{obsd} = k[Ti^{3+}][H^+]^{-1}$$

where $k = 2.7 \times 10$ s^{-1}, in agreement with the prior report.[1]

Table IV. Kinetics of Reduction of $Ru_2(CH_3COO)_2(C_2O_4)_2^-$ by Oxalato Complexes of Ti(III) at 25 °C in 1.0 M LiCl[a]

$[H^+]_t$, mM	$[C_2O_4^{2-}]_t$, mM	$[Ti(III)]_t$, mM	$[H^+]_f$, mM	$10^3[C_2O_4^{2-}]_f$, mM	$10[Ti^{3+}]$, mM	$10[TiC_2O_4^+]$, mM	$10[Ti(C_2O_4)_2^-]$, mM	k_s(obsd), s^{-1}	k_s(calcd),[b] s^{-1}
38	7.0	1.20	32	43	0.03	1.0	11.0	1.1	1.2
55	20.0	1.20	33	156	0.00	0.3	11.7	3.1	3.3
64	4.0	1.20	61	8.1	0.56	3.8	7.7	0.33	0.35
68	7.0	1.20	61	18.7	0.13	2.1	9.8	0.64	0.61
71	10.0	1.20	60	31.0	0.05	1.4	10.6	0.92	0.87
85	20.0	1.20	60	70.0	0.01	0.75	11.3	1.6	1.6
99	30.0	1.20	60	109	0.00	0.42	11.6	2.5	2.6
113	40.0	1.20	60	148	0.00	0.31	11.7	3.3	3.3
101	0.5	1.20	101	0.35	9.1	2.7	0.23	0.18	0.18
101	1.0	1.20	100	0.76	6.9	4.3	0.82	0.19	0.19
102	2.0	1.20	101	1.76	3.9	5.6	2.5	0.20	0.20
105	4.0	1.20	101	4.41	1.4	5.1	5.6	0.27	0.26
110	7.0	1.20	102	9.21	0.46	3.5	8.0	0.40	0.37
115	10.0	1.20	103	14.3	0.22	2.6	9.2	0.47	0.48
131	20.0	1.20	104	31.7	0.05	1.3	10.6	0.83	0.87
148	30.0	1.20	105	48.3	0.02	0.92	11.1	1.2	1.3
165	40.0	1.20	107	64.3	0.01	0.70	11.3	1.6	1.6
181	50.0	1.20	108	80.6	0.01	0.57	11.4	1.8	1.8
104	4.0	2.00	101	3.1	3.6	9.3	7.1	0.20	0.23
113	10.0	2.00	103	11.9	0.49	4.9	14.6	0.48	0.43
101	4.0	5.00	100	1.2	22.3	21.5	6.2	0.21	0.19
108	10.0	5.00	104	5.2	4.6	19.8	25.6	0.35	0.28
101	4.0	7.00	100	0.79	39.3	25.7	5.1	0.16	0.19
105	10.0	7.00	102	3.13	12.4	32.3	25.3	0.30	0.23
100	4.0	10.00	100	0.53	66.7	29.4	3.9	0.12	0.18
103	10.0	10.00	101	1.82	31.3	47.2	21.5	0.23	0.21
140	7.0	1.20	132	6.4	0.81	4.3	6.9	0.30	0.31
163	20.0	1.20	135	21.2	0.11	1.9	10.0	0.81	0.64
170	7.0	1.20	161	4.7	1.25	4.9	5.8	0.29	0.27
193	20.0	1.20	165	15.3	0.20	2.4	9.4	0.60	0.51

[a] $[Ru^{II}Ru^{III}]_T = 1.05 \times 10^{-4}$ M. Concentrations of H^+, Ti^{3+}, $TiC_2O_4^+$, and $Ti(C_2O_4)_2^-$ are calculated from initial total concentrations (subscript t) with use of an iterative computer program and the values $K_1 = 0.09$ M, $K_2 = 4 \times 10^{-4}$ M, $K_3 = 8.3 \times 10^5$ M^{-1}, and $K_4 = 2.5 \times 10^5$ M^{-1}. $[C_2O_4^{2-}]$ in the oxidant solution is less than 0.05 mM, which is negligible in calculation. [b] k_s(calcd) is defined by eq 32 and computed from the concentrations given in the table and the values of $k_{et} = k'_{et} = 0.18$ s^{-1}, $k''_{et} = 50$ s^{-1}, $K = 8.5 \times 10^5$, $K' = 2.0 \times 10^5$, and $K'' = 4 \times 10^2$ M^{-1}.

The observed first-order rate constant (k_{obsd}) for reduction of Ru-py with Ti(III) increases as pd concentration increases and decreases as acidity increases. The data are adequately fitted by the rate law

$$k_{\text{obsd}} = k[\text{Ti}^{3+}][\text{H}^+]^{-1} + k'[\text{TiL}^{2+}] + k''[\text{TiL}_2^+] \qquad (5)$$

where k' and k'' are second-order rate constants for the reactions of TiL^{2+} and TiL_2^+ with the oxidant. From eq 1–4

$$k_{\text{obsd}} = (k[\text{H}]^{-1} + k'K_1[\text{L}] + k''K_1K_2[\text{L}]^2)[\text{M}] \qquad (6)$$

This can be rearranged to

$$\frac{(k_{\text{obsd}}/[\text{M}]) - (k/[\text{H}])}{K_1[\text{L}]} = k' + k''K_2[\text{L}] \qquad (7)$$

A linear plot was obtained using zero-time concentrations computed iteratively and the values of k, k_{obsd} and K_1. This yielded the values $k' = 2.3 \times 10^2$ M^{-1} s^{-1} and $k'' = 1.8 \times 10^4$ M^{-1} s^{-1}.

Several equilibria are involved in complex formation between Ti(III) and oxalic acid.

$$\text{H}_2\text{C}_2\text{O}_4 \rightleftarrows \text{HC}_2\text{O}_4^- + \text{H}^+ \qquad K_1 = \frac{[\text{H}^+][\text{HL}]}{[\text{H}_2\text{L}]} \qquad (8)$$

$$\text{HC}_2\text{O}_4^- \rightleftarrows \text{C}_2\text{O}_4^{2-} + \text{H}^+ \qquad K_2 = \frac{[\text{H}^+][\text{H}]}{[\text{HL}]} \qquad (9)$$

$$\text{Ti}^{3+} + \text{C}_2\text{O}_4^{2-} \rightleftarrows \text{TiC}_2\text{O}_4^+ \qquad K_3 = \frac{[\text{ML}]}{[\text{M}][\text{L}]} \qquad (10)$$

$$\text{TiC}_2\text{O}_4^+ + \text{C}_2\text{O}_4^{2-} \rightleftarrows \text{Ti(C}_2\text{O}_4)_2^- \qquad K_4 = \frac{[\text{ML}_2]}{[\text{ML}][\text{L}]} \qquad (11)$$

$$\text{Ti(C}_2\text{O}_4)_2^- + \text{C}_2\text{O}_4^{2-} \rightleftarrows \text{Ti(C}_2\text{O}_4)_3^{3-} \qquad K_5 = \frac{[\text{ML}_3]}{[\text{ML}_2][\text{L}]} \qquad (12)$$

$$\text{Ti}^{3+} + \text{HC}_2\text{O}_4^- \rightleftarrows \text{Ti(HC}_2\text{O}_4)^{2+} \qquad K_6 = \frac{[\text{MHL}]}{[\text{M}][\text{HL}]} \qquad (13)$$

Values of K_1 and K_2 have been determined[11] to be 0.09 and 4 × 10^{-4} M under conditions of our experiments. Chaudhuri and Diebler[8] measured K_3 and K_4 (in 1.0 M NaCl) as 3 × 10^6 M^{-1} and 1 × 10^6 M^{-1}, but at 10 °C rather than 25 °C.

Under our conditions, at low ligand/metal concentration ratios, the absorbance, A, of an oxalato–titanium(III) solution should be

$$A = \epsilon_3[\text{ML}] + \epsilon_6[\text{MHL}] \qquad (14)$$

where ϵ_3 and ϵ_6 are the molar absorptivities of TiC_2O_4^+ and $\text{TiHC}_2\text{O}_4^{2+}$. It can be shown that[11]

$$\frac{A}{[\text{M}]} = [\text{L}]_t\frac{\epsilon_3K_3 + \epsilon_6K_6[\text{H}]/K_2}{\alpha} - \frac{A(K_3 + K_6[\text{H}]/K_2)}{\alpha} \qquad (15)$$

where

$$\alpha = 1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1K_2} \qquad (16)$$

Since $[\text{M}]_t \gg [\text{L}]_t$, [M] was approximated by $[\text{M}]_t$ to obtain an initial estimate of the formation constant, which was then refined by iteration. At constant $[\text{L}]_t$ and [H], plots of A/[M] vs A should give straight lines with negative slopes, S, defined by

$$S = \frac{K_3 + K_6[\text{H}]/K_2}{\alpha} \qquad (17)$$

Plots for several acidities are shown in Figure 2. From the intercept, the molar absorptivity of TiC_2O_4^+ was evaluated as $\epsilon_3 = 71 \pm 5$ M^{-1} cm^{-1}. Setting $\beta = \alpha K_2/[\text{H}^+]$

$$\beta S = K_6 + K_3K_2/[\text{H}^+] \qquad (18)$$

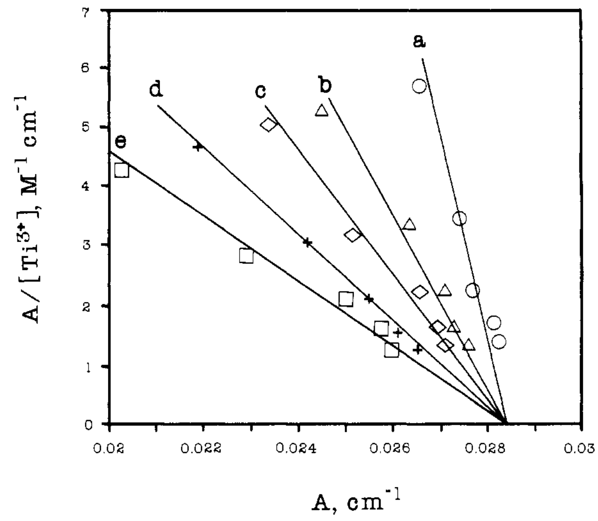

Figure 2. A/[Ti^{3+}] vs A (at 370 nm) at 25 °C, 1.0 m LiCl, and cell length = 10.0 cm: [H$^+$] = 60 (a), 100 (b), 130 (c), 160 (d), 200 mM (e). $[\text{C}_2\text{O}_4^{2-}]_t$ = 4.0 × 10^{-4} M; [Ti(III)] = (4.5–21) × 10^{-3} M.

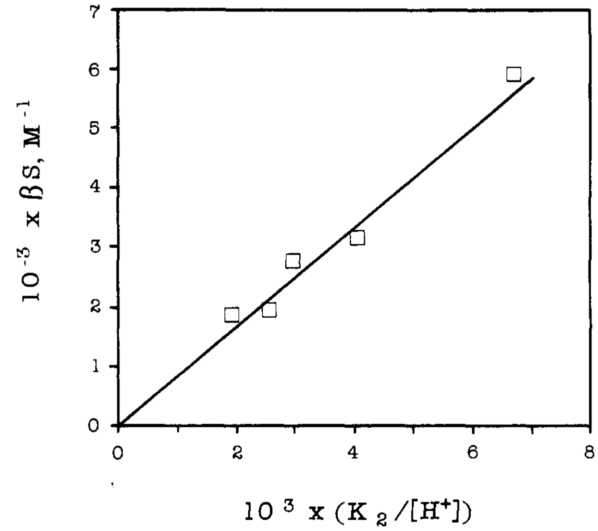

Figure 3. βS vs K_2/[H$^+$] (eq 18). The slope of the line is K_3, and the intercept is K_6.

Values of βS are plotted against K_2/[H$^+$] in Figure 3. The zero intercept of the straight line obtained indicates that [MHL] is negligible under our conditions ($K_6 < 300$ M^{-1}). The slope gives K_3 = (8.5 ± 0.5) × 10^5 M^{-1} (1.0 M LiCl and 25.0 °C).

Protonated complexes are generally not important[8,11] at high ligand/metal conditions, so that

$$A = \epsilon_3[\text{ML}] + \epsilon_4[\text{ML}_2] + \epsilon_5[\text{ML}_3] \qquad (19)$$

where ϵ_4 and ϵ_5 are molar absorptivities of ML_2 and ML_3. It can be shown that[12]

$$\frac{[\text{M}]_t}{A} = \frac{1 + K_5[\text{L}]}{\epsilon_4 + \epsilon_5K_5[\text{L}]} + \frac{f(\text{L})}{K_3K_4(\epsilon_4 + \epsilon_5K_5[\text{L}])} \qquad (20)$$

where

$$f(\text{L}) = \frac{1}{[\text{L}]^2} + \frac{K_3}{[\text{L}]} + \frac{[\text{M}]_t\epsilon_3K_3}{A[\text{L}]} \qquad (21)$$

Chaudhuri and Diebler[8] and also Pecsok[13] have sought, but not found, evidence that Ti(III) forms a tris(oxalato) complex. The formation constant (K_5) for the tris(oxalato)titanium(III) is small.

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(11) Moorehead, E. G.; Sutin, N. *Inorg. Chem.* **1966**, *5*, 1866.
(12) McConnell, H.; Davidson, N. *J. Am. Chem. Soc.* **1950**, *72*, 3164.
(13) Pecsok, R. L. *J. Am. Chem. Soc.* **1951**, *73*, 1304.

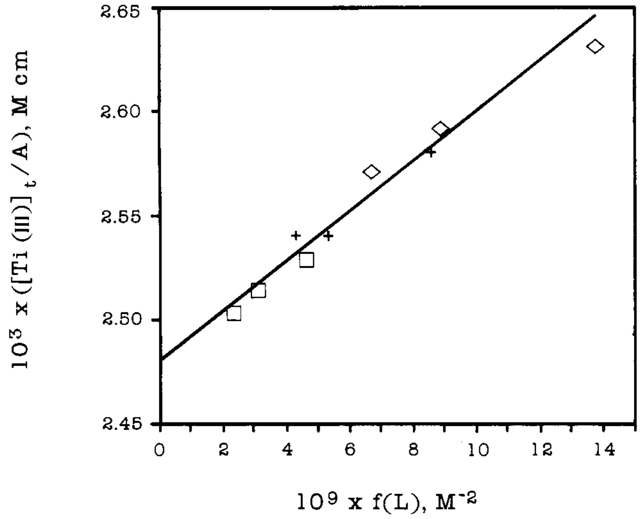

Figure 4. $[\mathrm{Ti(III)}]_t/A$ vs $f(\mathrm{L})$ (eq 9) (400 nm) at 25 °C, $I = 1.0$ M, and cell length = 0.20 cm: $[\mathrm{H}^+] = 100$ (□), 150 (+), 200 mM (◇). $[\mathrm{Ti(III)}]_t = 7.47$ mM; $[\mathrm{C_2O_4}^{2-}]_t = 80$–160 mM.

Since $\epsilon_4 \gg \epsilon_3$ we assume that $\epsilon_5 \gg \epsilon_4$ and then, provisionally, that $\epsilon_5 K_5[\mathrm{L}] \ll \epsilon_4$. Equation 20 can then be reduced to

$$\frac{[\mathrm{M}]_t}{A} = \frac{1}{\epsilon_4} + \frac{f(\mathrm{L})}{\epsilon_4 K_3 K_4} \tag{22}$$

A plot of $[\mathrm{M}]_t/A$ vs $f(\mathrm{L})$ using absorbances at 400 nm ($\epsilon_3 = 76$ M^{-1} cm^{-1}) is shown in Figure 4. The slope and intercept yield $\epsilon_4 = 400 \pm 50$ M^{-1} cm^{-1} at 400 nm and $K_4 = (2.5 \pm 0.5) \times 10^5$ M^{-1}. The fit of the data to a straight line confirms the presumption that $e_5 K_5[\mathrm{L}] \ll \epsilon_4$. On the basis of the assumption that $\epsilon_5/e_4 \cong \epsilon_4/\epsilon_3$, we estimate that $\epsilon_5 \cong 2 \times 10^3$ M^{-1} cm^{-1}, which leads to the conclusion that $K_5 \ll 4 \times 10^2$ M^{-1} (since the highest [L] used was 5×10^{-4} M).

Discussion

The rate law for the reactions of $\mathrm{Ru(NH_3)_5py^{3+}}$ with Ti(III) in the presence of additional pd indicates that the pd-dependent rate law terms are acid independent. That is, that $\mathrm{Ti(pd)^{2+}}$ and $\mathrm{Ti(pd)_2^+}$, rather than their conjugate bases, are the reducing agents. This is what would be expected on the basis of previous results[9b] on reductions of $\mathrm{Ru(pd)_3}$ by Ti(III). The rate constants obtained for the reactions of $\mathrm{Ru(NH_3)_5py^{3+}}$ with $\mathrm{Ti(pd)^{2+}}$ and $\mathrm{Ti(pd)_2^+}$ fit on the linear free energy relationship obtained for Ru(III)–Ti(III) redox reactions,[1] indicating that all three follow the outer-sphere mechanism, as expected in view of the absence of a suitable lead-in group on the oxidant. The rate constant for reaction of $\mathrm{Ti^{3+}}$ and $\mathrm{Ru(NH_3)_5py^{3+}}$ is $k° \leq 1$ M^{-1} s^{-1}. The second-order rate constants, $k° < 1$, $k' = 2.3 \times 10^2$, and $k'' = 1.8 \times 10^4$ M^{-1} s^{-1}, may be taken to indicate the relative reactivity of $\mathrm{Ti^{3+}}$, $\mathrm{TiL^{2+}}$, and $\mathrm{TiL_2^+}$ toward the oxidant. For these outer-sphere reactions, the ratios of rate constants ($k°/k'/k''$) of $<1/10^2/10^4$ correspond directly to the changes in reaction driving force brought about by the nonbridging pd ligands on the redox potential of Ti(III).

In the reduction of $\mathrm{Ru_2(CH_3COO)_2(C_2O_4)_2^-}$ by Ti(III), the maximum in the absorbance–time curve at low oxalate concentration indicates that an intermediate is formed. The extinction coefficient of the intermediate has a maximum at 400 nm, which is the same wavelength at which oxalato–Ti(III) complexes have absorbance maxima.[14] When the oxalate concentration is increased, the values of k_s (the rate constant for disappearance of the intermediate) increase, and at higher oxalate concentrations, no maximum in the absorbance–time curve was observed; only a first-order absorbance decrease occurs (Figure 1). The rate constant for this decrease varies monotonically with added oxalate concentration and smoothly connects with values of k_s. This suggests that the absorbance decrease at high oxalate concentration corresponds to the same reaction as the final absorbance decrease observed at low oxalate concentration. Spectrophotometric titration showed that the redox reaction occurred at any concentration of added oxalate, which leads to the conclusion that the absorbance decrease at high oxalate concentration involves ET. This indicates that absorbance decrease at low oxalate concentration (k_s) also involves the ET step. On this basis, the absorbance increase at low oxalate concentration (k_f) corresponds to formation of the intermediate only, rather than to a combination of substitution and redox processes. We are mainly interested in k_s.

In the absence of added oxalate, k_s is independent of [Ti(III)] as previously reported[3] and also independent of $[\mathrm{H}^+]$.[15] The following mechanism is consistent with our results.[16]

$$\mathrm{Ru_2(CH_3COO)_2(C_2O_4)_2^-} + \mathrm{Ti^{3+}} \xrightleftharpoons{K} \mathrm{Ru_2(CH_3COO)_2(C_2O_4)_2Ti^{2+}} \tag{23}$$

$$\mathrm{Ru_2(CH_3COO)_2(C_2O_4)_2Ti^{2+}} \xrightarrow{k_{et}} \mathrm{P} \tag{24}$$

If formation of the intermediate is relatively rapid, this yields

$$k_s = \frac{k_{et}K[\mathrm{Ti(III)}]_t}{1 + K[\mathrm{Ti(III)}]_t} \tag{25}$$

This is consistent with the observed lack of dependence of rate on [Ti(III)] if $K[\mathrm{Ti(III)}]_t \gg 1$ in the range $0.0012\ \mathrm{M} < [\mathrm{Ti(III)}] < 0.01$ M, so that $k_s = k_{et}$. On this basis, $k_{et} = 0.18 \pm 0.2$ s^{-1}.

In the presence of added oxalate, there is a complex dependence of rate on $[\mathrm{Ti(III)}]_t$. As the concentrations of added oxalate increase, the values of k_s increase and the absorbance increase gradually disappears. The curve of k_s against $[\mathrm{C_2O_4}^{2-}]_t$ is concave upward.

Adding oxalate to Ti(III) solutions produces both $\mathrm{TiC_2O_4^+}$ and $\mathrm{Ti(C_2O_4)_2^-}$. When more than 95% of the Ti(III) is complexed, i.e. when $[\mathrm{Ti(C_2O_4)_2^-}]$ is comparable to $[\mathrm{TiC_2O_4^+}]$, no absorbance increase is observed. We conclude that the trinuclear species formed between the oxidant and $\mathrm{Ti^{3+}}$ or $\mathrm{TiC_2O_4^+}$ has a relatively high formation constant but that involving the oxidant and Ti-

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[14] Olubuyide, O.; Lu, K.; Olayinka, O.; Earley, J. E. *Inorg. Chem.* **1986**, *25*, 4798.

[15] Although $[\mathrm{H}^+]_f$ was carried over a considerable range, we did not observe a dependence of k_s on $[\mathrm{H}^+]_f$. The acid dependence of k_f reported earlier[3] seems likely to be connected with closure of a chelate ring. The initial absorbance decrease reported here[7] corresponds to initial interaction of Ti(III) and coordinated oxidant, probably with formation of a nonchelated complex. The mechanism proposed here could be modified to take these additional stages into account.

[16] Biphasic traces such as we observe can be interpreted in two alternative ways (Alcock, N. W.; Benton, D. J.; Moore, P. *Trans. Faraday Soc.* **1970**, *66*, 2210): either rapid formation and slow decay of an intermediate with a relatively low extinction coefficient or slow formation and rapid decay of an intermediate with a much larger extinction coefficient. In our case the former interpretation is consistent with known rates of formation and extinction coefficients of oxalato–Ti(III) species while the latter interpretation yields values of rate constants and extinction coefficients that are not consistent with prior experience. One should also consider an outer-sphere pathway with dead-end complex formation

$$\mathrm{Ru_2(CH_3COO)_2(C_2O_4)_2^-} + \mathrm{Ti^{3+}} \xrightleftharpoons{K} \mathrm{Ru_2(CH_3COO)_2(C_2O_4)_2Ti^{2+}}$$

$$\mathrm{Ru_2(CH_3COO)_2(C_2O_4)_2^-} + \mathrm{Ti^{3+}} \xrightarrow{k} \mathrm{P}$$

This mechanism yields

$$k_s = \frac{k[\mathrm{Ti(III)}]_t}{1 + K[\mathrm{Ti(III)}]_t}$$

Since k_s is independent of $\mathrm{Ti(III)}_t$ under our experimental conditions, this equation indicates that $k/K = 0.18$ s^{-1}. Bose and Earley[3] presented data that indicate that K is larger than 200 M^{-1}; on this basis, k would be larger than 35 s^{-1} M^{-1}. This is at least 10^2 larger than expected for an outer-sphere reaction between these two reactants; on the basis of the reduction potential measured for $\mathrm{Ru_2(CH_3COO)_2(C_2O_4)_2^-}$ and the rates of authentic outer-sphere reactions,[1] we conclude that the reaction of interest involves a trinuclear intermediate rather than a dead-end complex.

Table V. Second-Order Rate Constants (25 °C) for Oxidations of Ti(III) with Carboxylato Complexes

	k, M^{-1} s^{-1}	
oxidants	M = Co	M = Ru
$M(NH_3)_4C_2O_4^+$	$k_{TiOH^{2+}} = 75$[17]	$k_{Ti^{3+}} = 3.6 \times 10^4$[1,a]
$M(NH_3)_5C_2O_4^+$	$k_{TiOH^{2+}} = 8.6 \times 10^4$[19,a]	$k_{Ti^{3+}} = 2.5 \times 10^4$[1,a]
$M(NH_3)_5CH_3COO^{2+}$	$k_{TiOH^{2+}} = 3$[19]	$k_{Ti^{3+}} = 7 \times 10^2$[1,a]
$M(NH_3)_5SalH^{2+}$	$k_{TiOH^{2+}} = 1 \times 10^2$[20,a,b]	$k_{Ti^{3+}} = 6.3 \times 10^2$[21,a]
$Ru_2(CH_3COO)_2(C_2O_4)_2^-$		$k_{Ti^{3+}} = 1.5 \times 10^5$[c]
$Co_2(OH)_2(NH_3)_6C_2O_4^{2+}$	$k_{TiOH^{2+}} = 4.8$[17]	

[a] Interpreted as being limited by the rate of substitution of Ti^{3+}. [b] This acid-dependent rate constant is interpreted as involving closure of a chelate ring. [c] This work. $k_{Ti^{3+}} = k_{et}K$ (eq 25), where $k_{et} = 0.18$ s^{-1} and $K \cong K_3 = 8.5 \times 10^5$ M^{-1}.

$(C_2O_4)_2^-$ has a relatively low formation constant.

A mechanism that is consistent with our results is

$$Ru_2(CH_3COO)_2(C_2O_4)_2^- + Ti^{3+} \overset{K}{\rightleftharpoons} Ru_2(CH_3COO)_2(C_2O_4)_2Ti^{2+} \tag{26}$$

$$Ru_2(CH_3COO)_2(C_2O_4)_2Ti^{2+} \xrightarrow{k_{et}} P \tag{27}$$

$$Ru_2(CH_3COO)_2(C_2O_4)_2^- + TiC_2O_4^+ \overset{K'}{\rightleftharpoons} Ru_2(CH_3COO)_2(C_2O_4)_2TiC_2O_4 \tag{28}$$

$$Ru_2(CH_3COO)_2(C_2O_4)_2TiC_2O_4 \xrightarrow{k'_{et}} P \tag{29}$$

$$Ru_2(CH_3COO)_2(C_2O_4)_2^- + Ti(C_2O_4)_2^- \overset{K''}{\rightleftharpoons} Ru_2(CH_3COO)_2(C_2O_4)_2Ti(C_2O_4)_2^{2-} \tag{30}$$

$$Ru_2(CH_3COO)_2(C_2O_4)_2Ti(C_2O_4)_2^{2-} \xrightarrow{k''_{et}} P \tag{31}$$

Assuming that formation of the intermediates involves relatively rapid equilibria, this mechanism leads to

$$k_s = (k_{et}K[Ti^{3+}] + k'_{et}K'[TiC_2O_4^+] + k''_{et}K''[Ti(C_2O_4)_2^-])/(1 + K[Ti^{3+}] + K'[TiC_2O_4^+] + K''[Ti(C_2O_4)_2^-]) \tag{32}$$

Both Ti^{3+} and $TiC_2O_4^+$ react with the oxidant to form trinuclear species that have relatively large formation constants. The shape of the k_s vs $[C_2O_4^{2-}]_t$ curve indicates that Ti^{3+} and $TiC_2O_4^+$ have similar reactivity ($k_{et}K \cong k'_{et}K'$). At high oxalate concentration, terms containing $[Ti^{3+}]$ can be neglected and $K''[Ti(C_2O_4)_2^-]$ would be smaller than unity, so that

$$k_s = \frac{k'_{et}K'[TiC_2O_4^+] + k''_{et}K''[Ti(C_2O_4)_2^-]}{1 + K'[TiC_2O_4^+]} \tag{33}$$

This can be rearranged to give

$$k_s = k''_{et}K''[Ti(C_2O_4)_2^-] + k'_{et}K'[TiC_2O_4^+] - k_sK'[TiC_2O_4^+] \tag{34}$$

A nonlinear least-squares program was used to solve this equation for k'_{et}, K', and $k''_{et}K''$ by using experimental values of k_s and calculated values of $[Ti(C_2O_4)_2^-]$ and $[TiC_2O_4^+]$. Average values found are $k'_{et} = 0.18$ s^{-1}, $K' = 2.0 \times 10^5$ M^{-1}, and $k''_{et}K'' = 1.9 \times 10^4$ M^{-1} s^{-1}. This entails that $k''_{et} > 50$ s^{-1} (on the basis of the assumption that $K'' \cong K_5 < 4 \times 10^2$ M^{-1}). The value found for k'_{et} is the same as the value found earlier for k_{et}. Since K' is about the same as K_4, we assume that $K \cong K_3$.

On the basis of the linear free energy relationship[1] for outer-sphere Ru(III)–Ti(III) reactions and measurements of the effect of oxalate on the oxidations potentials of Ti(III)[13] (the oxidation potential of $Ti(C_2O_4)_2^-$ is 0.02 V more cathodic than that of Ti^{3+}) the second-order rate constant of an outer-sphere ET reaction between $Ti(C_2O_4)_2^-$ and the oxidant is expected to be 0.02 M^{-1} s^{-1}. The value computed from our results ($k''_{et}K'' = 1.9 \times 10^4 = k''_2$) is 10^6 larger than expected on this basis. The three reactions of present interest involve inner-sphere mechanisms.

The formation constant for the trinuclear intermediate decreases as nonbridging oxalate ligands are added ($K \cong 8.5 \times 10^5$ M^{-1}, $K' = 2.0 \times 10^5$ M^{-1}, $K'' < 400$ M^{-1}), as would be expected on Coulombic grounds. The first added nonbridging oxalate does not have a significant effect on the rate constant for intramolecular ET within the assembled trinuclear intermediate, but the second added nonbridging oxalate increases that rate constant by at least 2 orders of magnitude ($k_{et} = k'_{et} = 0.18$ s^{-1}, $k''_{et} > 50$ s^{-1}). A similar nonbridging ligand effect has been observed[4,14] in inner-sphere reductions of $Co(NH_3)_4C_2O_4^+$ and $Ru(C_2O_4)_3^{3-}$ by Ti(III).

Rates of Ti(III) reductions of (oxalato)amminecobalt(III) and -ruthenium(III) complexes (with attack of the reductant at the carbonyl oxygen adjacent to the oxidant metal center) are several orders of magnitude larger than expected for outer-sphere ET (Table V); in several cases ET is so rapid that these reaction rates are substitution-limited. In contrast, Hery and Wieghardt[17] reported that the rate constant for Ti(III) reduction of $Co_2(OH)_2(NH_3)_6C_2O_4^{2+}$ by an inner-sphere mechanism (with attack of the reductant at a remote, uncomplexed carboxylic group) is nearly the same as the rate constant for the corresponding outer-sphere path, so that both mechanisms are operative in this reaction.[18] The reductions of $Ru_2(CH_3COO)_2(C_2O_4)_2^-$ involve intermediates of a related structure (structure II) and sluggish ET. The rate of ET involving bridging oxalate in structure II is slower than through bridging oxalate in structure I.

The most likely origin of the barrier to ET in structure II is lack of effective interaction between electron-donor and electron-acceptor orbitals, through the bridging oxalate ion.[22] Detailed calculations[23] of the electronic structure of $Ru(CH_3COO)_4^+$ show that the partially filled π^* orbitals of the dimer do not mix with carboxylate $p\pi$ orbitals, but that $p\pi$ orbitals of the carboxylate contribute strongly to the partially filled δ^* orbital of the dimer. The lowest unoccupied molecular orbital of the bridging oxalate[24] has proper symmetry (a_u in D_{2h}) to interact strongly with the δ^* (electron-acceptor) orbital of the diruthenium moiety. The overlap of the oxalate LUMO with the electron-donor orbital (titanium t_{2g}) should be real, but small. The oxalate LUMO involves only the terminal oxygen atoms, not the two carbon atoms.[25] None of the other unfilled ligand orbitals has appropriate symmetry for more effective cross-bridge electronic interaction.[26] The rate constants for intramolecular ET that we observe are not much larger than those observed[27] for the "ligand-bypass" mechanism in $(NC)_5Fe^{II}LCo^{III}(NH_3)_5$ (where L is a nitrogen heterocycle such as imidazole or pyrazine). It seems likely that the ligand-bypass mechanism operates in this case.

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(18) Hery and Wieghart did not observe the formation of an intermediate between Ti(III) and oxidant involving oxalate coordinated to Co^{III}_2. The formation constant of the trinuclear intermediate in our system is much larger than that of the intermediate in the dicobalt system. This is probably connected with a major difference between the diruthenium and the dicobalt oxidants; the former has a single negative charge while the latter has a dipositive charge.

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(21) Bose, R. N.; Earley, J. E. *Inorg. Chem.* **1981**, *20*, 2739.

(22) Another possible contribution to the barrier to ET in structure II is that rotation around a C–C bond is needed for planarity of the bridging oxalate, which, in turn, is required for cross-bridge electronic interaction between electron-donor and electron-acceptor orbitals. Presence of nonbridging oxalate ions on Ti(III) seems likely to impede rotation.

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