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Slow Intramolecular Electron Transfer in a Ru(III)-Ti(III) Redox Intermediate Having a Dianion Derived from a Dihydroxyquinone as Bridging Ligand

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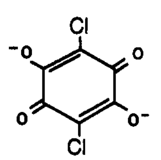
Slow intramolecular electron transfer (ET) has been observed in the binuclear intermediate of a Ti(III)-Ru(III) redox reaction that involves a dianion derived from a dihydroxyquinone as bridging ligand; this indicates that this ligand provides small but significant cross-bridge Ru(III)-Ti(III) electronic interaction. A Ti(III)-Co(III) reaction with a similar bridging ligand follows a different intimate mechanism (formation of a quinone radical ion), but intramolecular Co(III)-Ti(III) ET through squarate as bridging ligand is so slow that much of the overall redox change is accomplished by a competing outer-sphere reaction of that intermediate with $TiOH^{2+}$. A two-phase reaction was observed for the Ti(III) reduction (in M LiCl at 25 °C) of $Co(en)_2SQ^+$ (en is ethylenediamine; SQ^{2-} is the dianion of squaric acid). Relatively rapid formation of a binuclear intermediate is followed by competition between outer-sphere attack of $TiOH^{2+}$ on the deprotonated intermediate and intramolecular ET within that deprotonated species: $Ti^{3+} \rightleftharpoons TiOH^{2+} + H^+$ (K_a); $Co(en)_2SQ^+ + Ti^{3+} \rightleftharpoons Co(en)_2(SQ)Ti^{4+}$ (K_1); $Co(en)_2(SQ)Ti^{4+} \rightleftharpoons Co(en)_2(SQ)TiOH^{3+} + H^+$ (K_2); $Co(en)_2(SQ)TiOH^{3+} \rightarrow$ products (k_3); $Co(en)_2(SQ)TiOH^{3+} + TiOH^{2+} \rightarrow$ products (k_4). Here, $k_4K_1K_2K_a = 14\ s^{-1}$ and $k_3K_1K_2 = 0.8\ s^{-1}$. Reduction of $Co(trien)Q^+$ (trien is triethylenetetramine, and Q^{2-} is the dianion of 2,5-dihydroxy-1,4-benzoquinone) by Ti(III) (in M LiCl at 25 °C) also involves formation of a dinuclear complex between Ti^{3+} and the oxidant ($K_1' = 4.5 \times 10^2\ M^{-1}$) followed by further reaction of that complex by two competing paths. One path is intramolecular ET within the intermediate ($k_3' < 0.5\ s^{-1}$); the other path is reaction between a second $TiOH^{2+}$ and the preassembled (not deprotonated) intermediate ($k_4' = 1.3 \times 10^3\ s^{-1}\ M^{-1}$). Reduction of $Ru(trien)CQ^+$ (CQ^{2-} is the dianion of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone) by Ti^{3+} also involves formation of an intermediate ($K_1'' = 6 \times 10\ M^{-1}$). Intramolecular ET within that intermediate has a rate constant of $1.1 \times 10^2\ s^{-1}$, and $\Delta H^* = -16$ kJ/mol and $\Delta S^* = -150$ J/(deg mol). Intramolecular ET in this kinetic intermediate is many orders of magnitude slower than that in analogous pyrazine-bridged mixed-valence diruthenium systems; electronic coupling between donor and acceptor orbitals is smaller in the dihydroxyquinonate-bridged species than in the pyrazine-bridged dimers due to orbital symmetry mismatch in the former case.

Introduction

Being able to adjust rates of intramolecular electron transfer (ET) between metal ions would be of fundamental interest, and might even be useful (in applications such as molecular electronics[1]). Control of intramolecular ET should most readily be achieved when electron-donor and electron-acceptor orbitals are rather weakly coupled. In such cases, orbital symmetry considerations would be expected to be important in determining rates.[2] Much attention has been devoted to stable mixed-valence binuclear species,[3] but measurement of rate constants for intramolecular ET in such molecules is rarely straightforward.[4] When fairly rapid formation of an intermediate is followed by relatively slow intramolecular ET, rate constants for the latter process can be measured.[5] In some Ti(III) redox reactions, such as the one reported here, the specific rate for the ET event can be separated from the preceding substitution process.

We now report a kinetic study of Ti(III) reduction of $Ru(trien)CQ^+$, where CQ^{2-} is the dianion of chloranilic acid, $C_6Cl_2O_4^{2-}$ (A). Ti(III) reductions of $Co(trien)Q^+$ and $Co(en)_2SQ^+$, where Q^{2-} and SQ^{2-} are the dianions of 2,5-dihydroxy-1,4-benzoquinone, $C_6H_2O_4^{2-}$, and squaric acid, $C_4O_4^{2-}$ (B and D, respectively), were also studied. (C represents NQ^{2-}, the anion of 5,8-dihydroxy-1,4-naphthoquinone: some comparisons with compounds involving this ion will be made.) As bridging ligands, tetraoxo derivatives of small rings do not allow rotation about the bridge axis; dihydroxyquinones have frontier orbitals that are similar in energy to the t_{2g} orbitals of ruthenium.[6]



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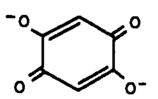

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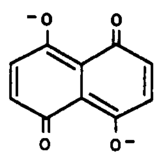

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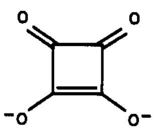

D

Quite different rate laws were observed for Ti(III) reductions of the two cobalt(III) oxidants, due to differences in reducibility of the two bridging ligands. The rate of intramolecular ET within the intermediate of the Ti(III) reduction of $Ru(trien)CQ^+$ was found to be 6 orders of magnitude less than the corresponding rate observed for pyrazine-bridged diruthenium ions. This major difference indicates that metal-metal interaction is much less across a dihydroxyquinone bridge than across a bridging pyrazine.

Experimental Section

The Ti(III) solution was prepared and standardized under nitrogen as described.[7] Cyclic voltammograms were obtained in 1.0 M LiCl, $1.0 < pH < 3.0$, at 24 ± 0.4 °C, at carbon-paste electrodes. Squaric acid

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(H_2SQ), chloranilic acid (H_2CQ), 2,5-dihydroxy-1,4-benzoquinone (H_2Q), and triethylenetetramine (trien) were purchased from Aldrich Chemical Co. and used as supplied. $[Co(en)_2CO_3]Cl$, *cis*-$[Co(trien)Cl_2]Cl$, and *cis*-$[Ru(trien)Cl_2]Cl$ were prepared as described.[8]

$[Co(trien)Q]Cl\cdot 2H_2O$. H_2Q (0.23 g, 1.6 mmol) was dissolved in 20 mL of water, and 2 M KOH was added to adjust the pH to 6; 0.50 g (1.6 mmol) of *cis*-$[Co(trien)Cl_2]Cl$ was added with stirring at ca. 50 °C. After 20 min, the color of the solution had changed from violet to yellow-brown. A small undissolved residue was filtered off, and the solution was evaporated under vacuum to 3 mL. Ethanol was carefully added: a brown powder formed. This powder was filtered off and washed with cold ethanol. The product was redissolved in a minimum quantity of warm (50 °C) water, and ethanol was added. The recrystallized product was collected, washed with cold ethanol and ether, and dried in air (yield 40%). Anal. Found[9] (calc for $[Co(trien)Q]Cl\cdot 2H_2O$): Co, 14.40 (14.21); C, 32.62 (34.75); N, 13.31 (13.51); Cl, 8.98 (8.55); H_2O, 8.2 (8.7). Wavelengths of maximum absorption, nm (extinction coefficients, log (ϵ, cm^{-1} M^{-1})): 510 (2.7), 364 (3.8), 306 (3.5). Irreversible cyclical voltammograms gave a reduction potential at half-peak height of −65 mV vs NHE.

$[Co(en)_2SQ]Cl\cdot 2.5H_2O$. H_2SQ (0.17 g, 1.5 mmol) was dissolved in a solution of 0.4 g (1.5 mmol) $[Co(en)_2CO_3]Cl$[10] in 15 mL of water. The solution was heated at 70 °C for 30 min with stirring. CO_2 evolved during the process, and the color of the solution changed from red-pink to brown. The solution was evaporated under vacuum to 3 mL. Acetone was carefully added: a brown crystalline solid deposited. This solid was filtered off, washed with ethanol, and dried in air (yield 80%). Anal. Found (calc for $[Co(en)_2SQ]Cl\cdot 2.5H_2O$): Co, 15.93 (15.86); C, 26.20 (25.86); N, 15.37 (15.08); Cl, 9.87 (9.54); H_2O, 11.3 (12.1). Wavelengths of maximum absorption, nm (log ϵ): 540 (2.1), 382 (3.3). Irreversible cyclical voltammograms gave a reduction potential at half-peak height of 50 mV vs NHE.

$[Ru(trien)CQ]Cl\cdot 2H_2O$. H_2CQ (0.11 g, 0.5 mmol) was dissolved in 20 mL of water, and 2 M KOH was added to bring the solution to pH 5; 0.20 g (0.5 mmol) of *cis*-$[Ru(trien)Cl_2]Cl$ was added, with stirring, at 40 °C. After 10 min, the color of the solution had changed from red to green. A small undissolved residue was filtered off, and the solution was evaporated under vacuum to 6 mL. Ethanol was carefully added: a green powder formed. This was recovered by filtration, washed with ethanol and ether, and dried in air (yield <30%). Anal. Found (calc for $[Ru(trien)CQ]Cl\cdot 2H_2O$): Ru, 18.16 (19.21); C, 28.51 (27.41); N, 10.44 (10.75); H_2O, 6.54 (6.84). Wavelengths of maximum absorption, nm (log ϵ): 304 (4.3), 456 (3.7), 640 (4.1) nm. Quasireversible cyclical voltammograms gave the reduction potential for $Ru(trien)CQ^+$ as −40 mV vs NHE.

Ion-exchange experiments[11] indicate that the cations of the three complexes are monopositive in dilute acid (0.7 < pH < 3.0). Spectrophotometric titration indicated 1/1 (within 15%) stoichiometry for each reaction.[12] Subsequent kinetic experiments were carried out under pseudo-first-order conditions with Ti(III) in at least 15-fold excess. Rates of reactions were measured by monitoring the decrease in absorbance at an absorbance peak of the oxidant (376, 380, and 640 nm, respectively). Kinetic measurements were made on a computer-linked Durrum stopped-flow spectrophotometer at 25.0 ± 0.2 °C and ionic strength 1.0 M (LiCl). Absorbance–time curves were adequately fitted using single or (in the case of $Co(trien)Q^+$) double exponentials. Values of first-order rate constants for each kinetic run were calculated using least-squares techniques. Listed[13] values of k_{obsd} are averages of three or more determinations. Precision is generally 5%.

Results

For reduction of $Co(en)_2SQ^+$ by Ti(III) at 25 °C, values of k_{obsd} increase as the concentrations of Ti(III) increase and decrease as the concentrations of H^+ increase. The data are consistent with the rate law

$$k_{obsd} = a\frac{[Ti(III)]_t^{\,2}}{[H^+]^2} + b\frac{[Ti(III)]_t}{[H^+]} \qquad (1)$$

where $a = (1.4 \pm 0.2) \times 10\ s^{-1}$ and $b = (8.0 \pm 0.6) \times 10^{-1}\ s^{-1}$.

In the Ti(III) reduction of $Co(trien)Q^+$, two rate constants (k_f' and k_s', precise to 10%), corresponding to a faster absorbance decrease followed by a slower absorbance decrease, were obtained.[14] The values of k_f' are linearly dependent on $[Ti(III)]_t$ but independent of acidity. The values of k_s' are linearly dependent on $[Ti(III)]_t$ and on $[H^+]^{-1}$. The data obtained at 25 °C are consistent with the rate laws

$$k_f' = a'[Ti(III)]_t + b' \qquad (2)$$

$$k_s' = c' + d'\frac{[Ti(III)]_t}{[H^+]} \qquad (3)$$

with $a' = (4.9 \pm 0.5) \times 10^3\ s^{-1}\ M^{-1}$, $b' = 11 \pm 1\ s^{-1}$, $c' = 0.49 \pm 0.04\ s^{-1}$, and $d' = 5.2 \pm 0.1\ s^{-1}$.

The value of k_{obsd}'' for reduction of $Ru(trien)CQ^+$ by Ti(III) is independent of acidity and proportional to $[Ti(III)]_t$ at low $[Ti(III)]_t$. As $[Ti(III)]_t$ increases, the slope of the k_{obsd}'' vs $[Ti(III)]_t$ curve decreases. The data are consistent with the rate law

$$k_{obsd}'' = \frac{a''[Ti(III)]_t}{1 + b''[Ti(III)]_t} \qquad (4)$$

with $a'' = (6.6 \pm 0.5) \times 10^3\ s^{-1}\ M^{-1}$ and $b'' = (5.9 \pm 0.2) \times 10\ M^{-1}$ at 25.0 °C. The values of b'' decreased slightly as temperature increased from 10 to 33 °C, but that decrease was within experimental error (b'' was effectively constant over the temperature range studied). The value of a'' showed small but significant increase over the same temperature range (Table I).

Discussion

The third-order rate law term observed for the Ti(III) reduction of $Co(en)_2SQ^+$ is unusual—it indicates that *two* Ti(III) species are involved in the reduction:

$$Ti^{3+} \overset{K_a}{\rightleftharpoons} TiOH^{2+} + H^+ \qquad (5)$$

$$Co(en)_2SQ^+ + Ti^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(en)_2(SQ)Ti^{4+} \qquad (6)$$

$$Co(en)_2(SQ)Ti^{4+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co(en)_2(SQ)TiOH^{3+} + H^+ \qquad (7)$$

$$Co(en)_2(SQ)TiOH^{3+} \xrightarrow{k_3} \text{products} \qquad (8)$$

$$Co(en)_2(SQ)TiOH^{3+} + TiOH^{2+} \xrightarrow{k_4} \text{products} \qquad (9)$$

If the steady-state approximation is applied to the intermediates $Co(en)_2(SQ)Ti^{4+}$ and $Co(en)_2(SQ)TiOH^{3+}$, and it is assumed

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(9) Analyses by E + R Microanalytical Laboratory, Inc.

(10) Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1967**, *6*, 787.

(11) Ion-exchange experiments were made with Dowex 50W-X8 strongly acidic cation-exchange resin purchased from Baker. The resin was allowed to swell in water before packing the column with the resin slurry. The column was cleaned by elution with 2 M HCl and then with distilled water. An aliquot solution of the oxidant to be examined was loaded into the column and eluted with distilled water. The H^+ concentration of the eluent was then determined by titration with standard NaOH.

(12) Titration data are given in the supplementary material.

(13) Observed rate constants are listed in the supplementary material.

(14) Several recrystallized samples, resulting from different preparations, gave consistent results: the biphasic character of these rate plots seems to be due to characteristics of the reaction, rather than to the presence of an impurity.

Table I. Rate Constants as a Function of Temperature for the Reaction of Ru(trien)CQ$^+$ with Ti(III)

			$\ln (k_3''/T)$	
T, K	K_1'', M^{-1}	$10^{-3}\,k_3''$, s^{-1} M^{-1}	obsd	calc[a]
283	62	4.1	−1.456	−1.406
290	60	5.3	−1.193	−1.238
298	59	6.5	−0.997	−1.055
306	57	6.9	−0.936	−0.882

[a] Values of $\ln (k_3''/T)_{\text{calc}}$ were calculated with $\Delta H_a^* = 16$ kJ/mol and $\Delta S_a^* = -150$ J/(deg mol).

that $(k_3 + k_4[\text{TiOH}^{2+}]) \ll k_{-2}[\text{H}^+]$, this mechanism yields

$$k_{\text{obsd}} = k_4K_1K_2K_a\frac{[\text{Ti(III)}]^2}{[\text{H}^+]^2} + k_3K_1K_2\frac{[\text{Ti(III)}]}{[\text{H}^+]} \qquad (10)$$

where $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$. Thus $k_4K_1K_2K_a = a = 14$ s^{-1}, $k_3K_1K_2 = b = 0.8$ s^{-1}, and $k_3 = (b/a)K_ak_4 = (2.3 \times 10^{-4}\ \text{M})k_4$. This mechanism involves a competition between intramolecular ET from Ti(III) to Co(III) within the preassembled intermediate on the one hand and outer-sphere attack of TiOH^{2+} on that dinuclear complex on the other hand. The intramolecular rate is so slow that the bimolecular path predominates if [Ti(III)] > 10 mM.

The biphasic kinetics observed for the reduction of Co(trien)Q$^+$ by Ti(III) indicates that an intermediate of some stability is involved in that reaction. Since k_f' does not depend on acid concentration, formation of that intermediate involves Ti^{3+}, rather than TiOH^{2+}, as reactant. Since the rate law for k_s' has two terms, one independent of both acidity and Ti(III) concentration and the other dependent on both acid and Ti(III) concentrations, decay of that intermediate proceeds through two competing paths, one involving the intermediate alone and another in which a second TiOH^{2+} ion acts as a reactant.

$$\text{Ti}^{3+} \overset{K_a}{\rightleftharpoons} \text{TiOH}^{2+} + \text{H}^+ \qquad (11)$$

$$\text{Co(trien)Q}^+ + \text{Ti}^{3+} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} \text{Co(trien)(Q)Ti}^{4+} \qquad (12)$$

$$\text{Co(trien)(Q)Ti}^{4+} \xrightarrow{k_3'} \text{products} \qquad (13)$$

$$\text{Co(trien)(Q)Ti}^{4+} + \text{TiOH}^{2+} \xrightarrow{k_4'} \text{products} \qquad (14)$$

If formation of Co(trien)(Q)Ti^{4+} involves a relatively rapid equilibrium, and the initial spectral change (k_f') corresponds to the approach to that equilibrium, then

$$k_f' = k_1'[\text{Ti(III)}] + k_{-1}' \qquad (15)$$

under conditions[15] where [Ti(III)] ≫ [Co(trien)(Q)Ti^{4+}], so that $k_1' = a' = 4.9 \times 10^3$ s^{-1} M^{-1} and $k_{-1}' = b' = 11$ s^{-1}. The equilibrium constant for reaction 12 can be calculated as $K_1' = k_1'/k_{-1}' = 4.5 \times 10^2$ M^{-1}.

The rate expression for k_s' is

$$k_s' = \left[k_3' + \frac{k_4'K_a[\text{Ti(III)}]}{[\text{H}^+]}\right]\frac{K_1'[\text{Ti(III)}]}{1 + K_1'[\text{Ti(III)}]} \qquad (16)$$

When K_1'[Ti(III)] > 1, this reduces to

$$k_s' = k_3' + \frac{k_4'K_a[\text{Ti(III)}]}{[\text{H}^+]} \qquad (17)$$

So that $k_3' = c' = 0.49$ s^{-1} and $k_4' = d'/K_a = 1.3 \times 10^3$ s^{-1} M^{-1}.

Even though the rate laws observed for the two Co(III) systems are quite different, both reactions involve the same overall mechanism—a competition between intramolecular ET in a binuclear intermediate and outer-sphere reduction of that intermediate by TiOH^{2+}. The difference in rate law between the reduction of Co(en)$_2$SQ$^+$ and that of Co(trien)Q$^+$ indicates that the intermediate does not undergo deprotonation when Q^{2-} is the bridging ligand but that deprotonation does occur when SQ^{2-} is the bridging ligand. The best explanation for this difference is that the intimate mechanism in the Co(trien)(Q)Ti^{4+} case involves the "chemical" (radical-ion) mechanism—rapid transfer of an electron to the bridging ligand rather than to the oxidant metal ion and relatively slow progress of the electron from that ligand to its ultimate location on the cobalt atom.[16] On this basis, Co(trien)(Q)Ti^{4+} contains a *reduced* form of the bridging ligand.[17] The rate-limiting steps in the inferred mechanism are substitution on Ti^{3+} for k_f', ET from the one-electron-reduced bridging ligand to the cobalt(III) center for k_3', and outer-sphere reduction of the intermediate by TiOH^{2+} for k_4'.

Since formation of the binuclear complex by reaction between Ti^{3+} and Co(trien)Q$^+$ is followed by fast ET from Ti(III) to the bridging ligand, deprotonation of coordinated Ti does not influence the kinetics. In the case of reduction of Co(en)$_2$SQ$^+$, deprotnation of Ti occurs before ET. The difference in intimate mechanism between the reductions of the two cobalt oxidants ultimately derives from the difference in the reduction potentials of the two bridging ligands: 2,5-dihydroxy-1,4-benzoquinone can be reduced by Ti(III), but squaric acid is not reduced by Ti(III).[18]

The acid-independent rate law observed for the Ti(III) reduction of Ru(trien)CQ$^+$ indicates[19] that Ti^{3+}, rather than TiOH^{2+} is the reductant.

$$\text{Ru(trien)CQ}^+ + \text{Ti}^{3+} \overset{K_1''}{\rightleftharpoons} \text{Ru(trien)(CQ)Ti}^{4+} \qquad (18)$$

$$\text{Ru(trien)(CQ)Ti}^{4+} \xrightarrow{k_3''} \text{products} \qquad (19)$$

If formation of the intermediate is relatively rapid

$$k_{\text{obsd}}'' = \frac{k_3''K_1''[\text{Ti(III)}]_t}{1 + K_1''[\text{Ti(III)}]_t} \qquad (20)$$

so that, at 25 °C, $K_1'' = b'' = 5.9 \times 10$ M^{-1} and $k_3'' = a''/b'' = 1.1 \times 10^2$ s^{-1}. The temperature dependence of redox rates indicates that K_1'' has $\Delta H°$ near zero: variation of limiting rate, k_3'', with temperature leads to $\Delta H^* = 16 \pm 8$ kJ/mol and $\Delta S^* = -150 \pm 40$ J/(deg mol).[20]

The LUMO of bridging ligand mixes effectively with Ru(III) t_{2g} orbitals so that ET to the ligand is not distinguishable from ET to ruthenium and the chemical (radical-ion) mechanism does not obtain. For most inner-sphere Ru(III)–Ti(III) ET reactions previously reported,[21] bridging ligands are so efficient in mediating ET that these reactions are substitution-limited. Activation parameters measured for such substitution-limited redox reactions are similar to those reported for water exchange in Ti(H$_2$O)$_6^{3+}$: $\Delta H^* \approx 43$ kJ/mol and $\Delta S^* \approx 1$ J/(deg mol).[22] The temperature

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(15) The value of k_1' is determined by the intercept obtained by extrapolation to zero [Ti(III)]. The lowest [Ti(III)] employed was 25 times larger than the concentration of oxidant. If one were to make measurements at lower [Ti(III)], observed rates would be expected to fall below the line obtained by extrapolation of the high-[Ti(III)] data, once pseudo-first-order conditions no longer obtained.

(16) Purcell, W. *Polyhedron* **1989**, *8*, 563.

(17) The intermediate heretofore referred to as Co(trien)(Q)Ti^{4+}, would better be designated as [Co$^{\text{III}}$(trien)(Q$^-$)Ti$^{\text{IV}}$]$^{4+}$.

(18) The redox potentials of Ti(III) and the bridging ligand are ≈0.03 V for Ti$^{4+/3+}$ and ≈0.2 V for Q$^{-/2-}$, both versus NHE. Although the squarate ligand can be oxidized readily (Schmidt, A. H. *Synthesis* **1980**, 961–994), that ligand cannot be reduced at these potentials.

dependence measured for the high-[Ti(III)] limiting rate of Ti(III) reduction of Ru(trien)CQ$^+$ is much less than that characteristic of Ti(III) substitution reactions (the activation energy is less than half as great). This indicates that the reaction rate is not substitution-limited and that rate is controlled by the ET process. Rates of substitution-limited Ru(III)–Ti(III) reactions are controlled by the charge type of the oxidant, as is consistent with the associative character found for Ti(III) substitution reactions in many studies. Reactions of oxidants of the same charge type as the oxidant of present interest have rate constants[22b] of about 3×10^4 M^{-1} s^{-1}; formation of the intermediate is much faster than the limiting rate measured here. The rate constant k_3 is identified as the rate constant for intramolecular ET.

The entropy of activation now reported has a large negative value, as do entropies of activation for intermolecular electron transfers in which rate is dominated by assembly of like-charged redox partners. In contrast, Fischer, Tom, and Taube[23] measured low values of entropy of activation (±3 J/(deg mol)) for a series of intramolecular ET reactions mediated by 4,4′-bipyridine and related bridging groups; in these cases, a quite constant Franck–Condon barrier, modulated by small differences in adiabaticity, determines the ET rate. If the slow rate of the Ti(III) reduction of Ru(trien)CQ$^+$ does not result from a Frank–Condon barrier, but rather arises from weak electronic coupling of donor and acceptor orbitals,[24] the value of the Arrhenius preexponential factor[25] would be low, and a more unfavorable entropy of activation would be obtained for this intramolecular ET than is observed for the intramolecular reactions involving bridging 4,4′-bipyridine and related bridging ligands. The interpretation that the rate-limiting step in the Ti(III) reduction of Ru(trien)CQ$^+$ is slow ET through bridging CQ^{2-} within a preassembled intermediate and the inference that the barrier to ET is the relatively small degree of effective overlap between donor and acceptor orbitals are consistent with our results.

The rate constant now reported for intramolecular ET in the Ti(III) reduction of Ru(trien)CQ$^+$ ($k_3'' = 10^2$ s^{-1}) is 10^6 times smaller than the rate constant calculated[26] for intramolecular ET in the Creutz–Taube ion and measured[27] for intramolecular ET in other pyrazine-bridged diruthenium mixed-valence species that are closely related to that ion ($k_3 > 10^8$ s^{-1}).

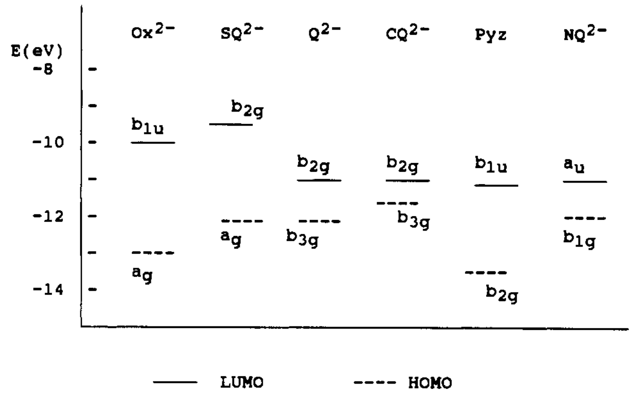

Figure 1. Energy levels and symmetry (in the D_{2h} point group) of frontier orbitals of several bridging ligands. Ox^{2-} oxalate ion ($C_2O_4^{2-}$); SQ^{2-} squarate dianion ($C_4O_4^{2-}$); Q^{2-} = 2,5-dihydroxy-1,4-benzoquinonate dianion ($C_6H_2O_4^{2-}$); NQ^{2-} = 5,8-dihydroxy-1,4-naphthoquinonate dianion ($C_{10}H_4O_4^{2-}$); pyz = pyrazine ($C_4H_4N_2$).

Table II. Magnetic Exchange Parameters for Metal Dimers $M_2(L)_n$(bridge)[a]

complex	J, cm^{-1}	ref
$Ni_2(trien)_2(Ox)^{2+}$	−16	*c*
$Ti_2(Ox)_2(Ox)^{2+}$	−36[b]	*d*
$Ni_2(trien)_2Q^{2+}$	−1	*e,f*
$Ni_2(trien)_2NQ^{2+}$	>−0.1	*g*
$Ru_2(NH_3)_{10}(pyz)^{5+}$	-2×10^3	*h*

[a] Ox^{2-} = oxalate ion ($C_2O_4^{2-}$); Q^{2-} = dianion of 2,5-dihydroxy-1,4-benzoquinone ($C_6H_2O_4^{2-}$); NQ^{2-} = dianion of 5,8-dihydroxy-1,4-naphthoquinone ($C_{10}H_4O_4^{2-}$); pyz = pyrazine ($C_4H_4N_2$). [b] $Ti_2(Ox)_2(Ox)^{2+}$ exists in two forms, a seven-coordinated dimer ((μ-Ox)$Ti_2(Ox)_2(H_2O)_6$) and a mixed seven- and six-coordinated dimer ((μ-Ox)$Ti_2(Ox)_2(H_2O)_5$). The value listed is the average of values measured for the two dimers. [c] Duggan, D. M.; Barefield, E. K.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 985. [d] Wrobleski, J. T.; Brown, D. B. *Inorg. Chim. Acta* **1980**, *38*, 227. [e] Pierpont, C.; Francesconi, L.; Hendrickson, D. *Inorg. Chim. Acta* **1977**, *16*, 3267. [f] Preliminary results indicate that cross-bridge electronic coupling in $(bpy)_2RuQRu(bpy)_2^{5+}$ is small: Earley, J. E.; Olubuyide, O.; Lu, K. *J. Indian Chem. Soc.*, in press. [g] Pierpont, C. G.; Francesconi, L. C.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 3470. [h] Ondrechen, M. J.; Ko, J.; Zhang, L. *J. Am. Chem. Soc.* **1987**, *109*, 1672.

Experimental results on cross-bridge electronic coupling (from magnetic studies of dimeric metal complexes) are listed in Table II. Frontier-orbital energies of several bridging ligands, calculated by us using extended Hückel methods,[28] are shown in Figure 1.

In-phase combinations of metal-centered t_{2g} orbitals have lower energy than out-of-phase combinations.[29] The most effective bridging ligand would be expected to be one with a low-energy LUMO of appropriate symmetry to interact with the in-phase combination of the two metal t_{2g} orbitals. The (d_{xz}, d_{yz}) orbitals from the metal ions can form in-phase combinations with b_{1u} or b_{3g} symmetries and out-of-phase combinations with b_{2g} or a_u symmetries, and the d_{xz} orbitals can form an in-phase combination with b_{1u} symmetry. Bridging oxalate and pyrazine have LUMOs with b_{1u} symmetry, appropriate for interaction with the in-phase b_{1g} combination of metal orbitals. Bridging CQ^{2-} has a LUMO with b_{2g} symmetry; bridging NQ^{2-} has a LUMO with a_u symmetry. Neither of these is appropriate for interaction with an in-phase combination of metal orbitals, but each of them has the same symmetry as one of the out-of-phase combinations of metal orbitals. The large magnitude of J observed for $(bpy)_2Ru(pyz)$-

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(19) The rate law observed for the Ti(III) reduction of the oxidant can also be derived from an outer-sphere pathway with "dead-end" complex formation:

$$\text{Ru(trien)CQ}^+ + \text{Ti}^{3+} \overset{K'''}{\rightleftharpoons} \text{Ru(trien)(CQ)Ti}^{4+} \qquad (21)$$

$$\text{Ru(trien)CQ}^+ + \text{Ti}^{3+} \xrightarrow{k'''} \text{products} \qquad (22)$$

This mechanism yields

$$k_{\text{obsd}}'' = \frac{k'''[\text{Ti(III)}]_t}{1 + K'''[\text{Ti(III)}]_t} \qquad (23)$$

At low $[\text{Ti(III)}]_t$, that is, when $K'''[\text{Ti(III)}]_t \ll 1$

$$k_{\text{obsd}}'' = k'''[\text{Ti(III)}]_t \qquad (24)$$

Thus, $k''' = 6.6 \times 10^3$ s^{-1} M^{-1}. On the basis of the linear free energy relationship that applies to outer-sphere Ru(III)–Ti(III) reactions (see Barone and Earley[7]) and the reduction potential measured for Ru(trien)-CQ$^+$, the second-order rate constant of an outer-sphere ET reaction between Ti^{3+} and the oxidant is expected to be <10 s^{-1} M^{-1}. The value computed from the observed rate and eq 24 is more than 10^2 times larger than expected on this basis. This indicates that the reaction proceeds through an inner-sphere mechanism rather than through an outer-sphere pathway with dead-end complex formation.

(20) Overall error was estimated from lines of greatest and least slope that could reasonably be drawn on the Arrhenius plot. The three lower-temperature points indicate that $\Delta H^* = 22$ kJ/mol, but the 35 °C point deviates from that line.

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$Ru(bpy)_2^{5+}$, and rapid rates of intramolecular ET calculated for this ion and observed for related ions, can be understood on the basis that the energy of the LUMO of bridging pyrazine is low and it has appropriate symmetry for overlap with the in-phase metal-orbital combination.[30] CQ^{2-} and NQ^{2-} have nearly the same LUMO energies, higher than that of pyrazine but lower than that of oxalate or squarate—but both CQ^{2-} and NQ^{2-} have LUMOs that require out-of-phase combinations of metal t_{2g} orbitals for effective overlap. This would be expected to give reduced cross-bridge electronic interaction for the dianion bridging ligands derived from dihydroxyquinones[31] and give rise to a slower rate of intramolecular ET for the dihydroxyquinone dianion-bridged intermediate than for the pyrazine-bridged dimers, as is observed.

In this case, a tetraoxo dianion ligand derived from a dihyroxyquinone provides a degree of coupling between metal t_{2g} orbitals that gives rise to slow intramolecular Ru(III)–Ti(III) ET. Systematic variation of such ligands may produce tuning of intramolecular ET rates.

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Supplementary Material Available: Tables of kinetic and titration data (9 pages). Ordering information is given on any current masthead page.

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(30) Hupp has argued that a "hole-transfer" pathway is important in intervalence charge transfer in pyrazine-bridged mixed-valence complexes. Although the LUMO energies are similar for pyrazine and the dihydroxyquinone anions, the HOMO energy for pyrazine is quite different from the HOMO energies of the dihdyroxyquinones. To the extent that hole transfer is important in the pyrazine-bridged case, the difference in HOMO energies may also be significant: Hupp, J. T. *J. Am. Chem. Soc.* **1991**, *112*, 1563–1565.

(31) Symmetry-attenuated electronic coupling between redox sites has been reported in a pentaammineruthenium mixed-valence complex with the 1,4-dicyanamido-2,3,5,6-tetrachlorobenzene dianion as a bridging ligand: Aquino, M. A. S.; Bostock, A. E.; Crutchley, R. J. *Inorg. Chem.* **1990**, *29*, 3641.