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Titanium(III) Reduction of Axially Substituted Metal–Metal-Bonded Diruthenium Complexes

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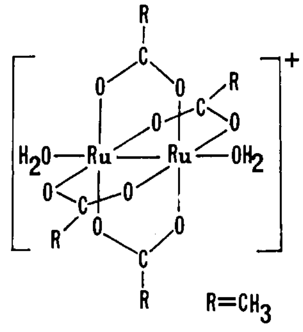
The metal–metal-bonded cationic complex tetrakis(μ-acetato)diaquadiruthenium(II,III) ($Ru_2(OAc)_4(H_2O)_2^+$) undergoes rapid successive axial ligations with Cl^- to form $Ru_2(OAc)_4Cl(H_2O)$ and $Ru_2(OAc)_4Cl_2^-$. The formation constants K_1 and K_2 for these chloro complexes at 25 °C were calculated to be 15 M^{-1} and 3.7 M^{-1}. The dimeric complexes exhibit quasi-reversible one-electron redox cycles with reduction potentials 0.007, −0.015, and −0.055 V vs SCE for the diaqua, monochloro, and dichloro complexes in 0.01 M H^+. Titanium(III) reduces $Ru_2(OAc)_4Cl_2^-$ in acidic chloride media through an outer-sphere electron-transfer mechanism in which both hexaaquatitanium(III) and its conjugate base are the reactive reducing agents. The rate constants for the $Ti(H_2O)_6^{3+}$ and $Ti(H_2O)_5OH^{2+}$ reductions were found to be 75 and 1.1×10^3 M^{-1} s^{-1} at 23 °C. The larger reactivity of $Ti(H_2O)_6^{3+}$ toward this metal–metal-bonded complex as compared to saturated amine complexes of Ru(III) and Co(III) and to Ni(II) macrocycles is perhaps due to greater electronic coupling between the redox partners as a result of a larger radial extension of the molecular orbitals of the metal–metal-bonded complex.

Introduction

Metal–metal-bonded diruthenium complexes have received a great deal of attention recently.[2–11] A large body of work is devoted mainly to structural characterization and an understanding of the electronic structures of multiple metal–metal bonds. Metal–metal-bonded diruthenium(II,III) complexes such as the tetrakis(μ-acetato)diruthenium(II,III) cation (I) have a bond order of 2.5 and contain three unpaired electrons in π^* and δ^* molecular orbitals.[4,7–9] The solution chemistry, especially substitution and redox mechanisms of these "electron-rich" complexes, remains largely unexplored.[12] Here we report equilibrium and electrochemical studies of axially substituted tetrakis(μ-acetato)diruthenium(II,III) complexes and the mechanism of electron-transfer reaction using Ti(III) as a reductant.



I

Experimental Section

Materials. The ruthenium complexes tetrakis(μ-acetato)diruthenium(II,III) chloride and potassium tetrakis(μ-acetato)dichlorodiruthenate(II,III) were prepared by following literature methods.[13,14] The former complex was recrystallized from 1.0 M CH_3COOH. Sodium chloride was of primary standard grade material (Thorn Smith) and was dried at 110 °C before use. Titanium(III) stock solutions were prepared from titanium trichloride (Aldrich) in 1 M HCl under N_2. These solutions were standardized either by a spectrophotometric[14] method or by a dichromate titration.[15] Hydrogen ion concentrations in these stock solutions were determined by NaOH titration following the method of Davies and Earley.[16] Ionic strength was maintained at 2.0 M by using $NaClO_4$–NaCl for the equilibrium studies and at 1.0 M by using LiCl for the redox reactions involving Ti(III). Desired acidities were maintained by adding appropriate amounts of $HClO_4$ or HCl.

Physical Measurements. A computer-interfaced double-beam (Varian DMS 100) spectrophotometer was employed for UV–visible spectroscopic measurements. The cell compartment was thermostated at desired temperatures (±0.2 °C). Cyclic voltammograms were recorded on a potentiostat-galvanostat (PAR 362) connected to an X-Y recorder (Houston 2000). Electrochemical measurements were performed in an H-cell using a saturated calomel electrode (reference), a glassy-carbon electrode (working), and a platinum wire (auxiliary). Solutions were purged with N_2 that was scrubbed through two Cr(II) towers. Rate measurements were carried out on a stopped-flow instrument (Durrum 110). The reproducibility of the absorbance–time traces was checked by accumulating three successive curves, which were displayed on an oscilloscope.

Equilibrium Studies. Axial ligations to the tetrakis(μ-acetato)diaquadiruthenium(II,III) cation, $Ru_2(OAc)_4(H_2O)_2^+$, by chloride were monitored spectrophotometrically. Ruthenium solutions (5.0×10^{-4} M) were mixed with chloride solutions of variable concentrations (0–2.0 M). Acidity was maintained at 0.1 M. UV–visible spectra of the ruthenium complex were recorded in the wavelength region 900–250 nm. The absorbance values as a function of $[Cl^-]$ can be adequately described by

$$D = \frac{[Ru_2]_t}{1 + K_1[Cl^-] + K_1K_2[Cl^-]^2}(\epsilon_1 + \epsilon_2K_1[Cl^-] + \epsilon_1\epsilon_2K_1K_2[Cl^-]^2) \quad (1)$$

where $[Ru_2]_t$ is the total ruthenium concentration in solution, K_1 and K_2 are the equilibrium constants for the formation of monochloro and dichloro complexes, and ϵ_1 through ϵ_3 are the molar absorptivities of the diaqua-, monochloro-, and dichlorodiruthenium(II,III) complexes.

The molar absorptivities ϵ_1 and ϵ_3 were obtained at $[Cl^-] = 0$ and at high chloride concentration when no further changes in the absorption spectra were apparent. The values of K_1, K_2, and ϵ_2 were evaluated by utilizing an iterative nonlinear least-squares computer program.[17] In this fitting routine, the known parameters are kept invariant, and the others are allowed to float until a good agreement between the observed and calculated absorbances is achieved and the convergence criterion is satisfied.

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Table I. Observed and Calculated Absorbances of $Ru_2(OAc)_4(H_2O)_2^+$ As a Function of $[Cl^-]$ ($[Ru_2]$ = 0.50 mM)

$[Cl^-]$, M	obsd abs	calcd abs[a]	$[Cl^-]$, M	obsd abs	calcd abs[a]
0.0	0.55	0.55	0.40	1.22	1.25
0.01	0.60	0.59	0.50	1.31	1.31
0.05	0.75	0.73	0.60	1.38	1.35
0.09	0.80	0.85	0.70	1.38	1.39
0.10	0.89	0.87	0.80	1.42	1.41
0.20	1.07	1.06	0.90	1.42	1.43
0.30	1.20	1.18	1.50	1.44	1.43

[a] Values were calculated from eq 1 at 290 nm by using ϵ_1, ϵ_2, and ϵ_3 as 1.1×10^3, 1.62×10^3, and 3.29×10^3 M^{-1} cm^{-1}; $K_2 = 3.7$ M^{-1}, and $K_1 = 15$ M^{-1}.

Rate Measurements. Titanium(III) reduction of the tetrakis(μ-acetato)dichlorodiruthenate(II,III) anion was carried out in 1.0 M LiCl–HCl following a decrease in absorbance at 450 nm. The rate constants were evaluated by using the expression

$$D = (D_0 - D_\infty)e^{-k_0 t} + D_\infty \quad (2)$$

under pseudo-first-order conditions using excess Ti(III). Under second-order conditions, using a 2–3-fold excess of Ti(III), eq 3 was used.

$$D = D_0 + \frac{k_2B(D_\infty - D_0)[e^{-(k_2B-k_2A)t} - 1]}{k_2Be^{-(k_2B-k_2A)t} - k_2A} \quad (3)$$

In these expressions, D_0, D, and D_∞ are the absorbances at $t = 0$, at time t, and at infinite time. The first- and second-order rate constants are denoted by k_0 and k_2. In eq 3, A and B refer to the concentrations of $[Ru_2]$ and [Ti(III)].

Stoichiometry of Ti(III) Reduction of the Diruthenium Complex. Solutions of $Ru_2(OAc)_4Cl_2^-$ (2.0×10^{-3} M) in 0.1 M HCl–1.9 M LiCl were mixed with Ti(III) solutions of variable concentrations ($(0.5–5.0) \times 10^{-3}$ M) in the same electrolyte. Spectra of the products were recorded immediately after mixing (~30 s) in the wavelength range 600–400 nm. Plots of changes in absorbance (ΔD) vs molar ratio, $[Ti(III)]/[Ru_2]$, exhibited break points near unit molar ratio.

Table II. Electrochemical Parameters for $Ru^{II}Ru^{III}/Ru^{II}Ru^{II}$ Redox Couples[a]

$[Ru_2(OAc)_4(H_2O)_2]^+$, mM	$[Cl^-]$, M	ΔE,[b] mV	$E_{1/2}$,[c,d] V
1.0	0.0	80	+0.007
1.0	0.2	75	−0.024
1.0	0.8	75	−0.043
1.0	1.5	80	−0.053
2.0	2.0	75	−0.055

[a] An acidity of 0.01 M $HClO_4$ was always maintained. [b] Scan rate was 100 mV/s; E was found to be 68 mV at a 20 mV/s sweep rate. [c] No effect of sweep rate on $E_{1/2}$ was observed. [d] Potentials are with respect to SCE.

Table III. Rate Data for the Ti(III) Reduction of $Ru_2(OAc)_4Cl_2^-$ at Various $[H^+]$ (μ = 1.0 M LiCl, T = 23 °C)[a]

$[H^+]$, mM	$10^{-2}k_o$, M^{-1} s^{-1}	$10^{-2}k_c$, M^{-1} s^{-1}	$[H^+]$, mM	$10^{-2}k_o$, M^{-1} s^{-1}	$10^{-2}k_c$, M^{-1} s^{-1}
98	0.82	0.98	50	1.28	1.20
78	1.01	1.03	30	1.71	1.48
50	1.32	1.20	15	2.6	2.1
50	1.37	1.20	6.0	3.3	3.6

[a] k_o and k_c are the observed and calculated second-order rate constants; calculated values are based on eq 10 for $a = 75$ M^{-1} s^{-1}, $b = 2.5$ s^{-1}, and $c = 2.3 \times 10^{-3}$ M.

Results and Discussion

Axial Anation Reaction. The diruthenium(II,III) complex tetrakis(μ-acetato)diruthenium(II,III) chloride exists as a zigzag polymer in which chloride bridges two dimeric units.[4] In aqueous solution, water molecules are coordinated to the two axial sites, replacing chloride bridges.[6,9] The electronic spectrum of the diaqua complex exhibits bands at 960 (ϵ = 60 M^{-1} cm^{-1}), 425 (ϵ = 705 M^{-1} cm^{-1}), and 310 (sh) nm. Bathochromic shifts for the 425-nm band were observed as Cl^- was added to the diaqua complex. The shoulder at 310 nm concomitantly disappeared. Two isosbestic points were observed at 820 and 390 nm. No detectable changes in the absorption spectra (800–290 nm) were observed at $[Cl^-] > 1.5$ M, and each spectrum exhibited a band at 450 nm under these conditions. The electronic absorption spectra of the tetrakis(μ-acetato)diaquadiruthenium(II,III) cation and the tetrakis(μ-acetato)dichlorodiruthenate(II,III) anion in 0.9 M NaCl–0.1 M HCl are identical. Therefore, the spectral changes as a function of $[Cl^-]$ are not due to the formation of an outer-sphere complex between the diaqua complex and chloride ion. The absorbance as a function of $[Cl^-]$ can be described by a pair of reactions of successive anation by Cl^- at the two axial sites:[18]

$$Ru_2(OAc)_4(H_2O)_2^+ + Cl^- \overset{K_1}{\rightleftharpoons} Ru_2(OAc)_4(H_2O)Cl \quad (4)$$

$$Ru_2(OAc)_4(H_2O)Cl + Cl^- \overset{K_2}{\rightleftharpoons} Ru_2(OAc)_4Cl_2^- \quad (5)$$

The values of K_1 and K_2 were evaluated to be 15 ± 1 M^{-1} and 3.7 ± 0.3 M^{-1} at several wavelengths by utilizing eq 1. Table I compares calculated and observed absorbances at 300 nm.

The cyclic voltammograms of the diaqua complex in the chloride media each exhibited a reduction and an oxidation wave. Reduction and oxidation peaks are separated by 70–80 mV at the scan rate 20–100 mV/s. The ratios of the anodic to cathodic peak currents were very nearly unity (0.95–1.02). No systematic deviation of this ratio as a function of scan rate was observed. Pertinent electrochemical parameters as obtained from cyclic voltammograms as a function of $[Cl^-]$ are listed in Table II. Both the oxidation and reduction waves showed a cathodic shift with an increase of $[Cl^-]$ initially, and no appreciable change in the peak potentials was observed above 1.5 M Cl^-. The two limiting $E_{1/2}$ values corresponding to the reductions of the diaqua and dichloro complexes can be evaluated as 0.007 and −0.055 V vs SCE from the voltammograms at $[Cl^-] = 0$ and $[Cl^-] = 2.0$ M. If the reduction potential at a given $[Cl^-]$ is taken as the contributions from diaqua, aqua chloro, and dichloro complexes that exist in equilibrium, reduction potentials for the three forms then can be evaluated as

$$Ru_2(OAc)_4(H_2O)_2^+ + e^- \xrightleftharpoons{E_{1/2} = 0.007\text{ V}} Ru_2(OAc)_4(H_2O)_2 \quad (6)$$

$$Ru_2(OAc)_4(H_2O)Cl + e^- \xrightleftharpoons{E_{1/2} = -0.015\text{ V}} Ru_2(OAc)_4Cl(H_2O)^- \quad (7)$$

$$Ru_2(OAc)_4Cl_2^- + e^- \xrightleftharpoons{E_{1/2} = -0.055\text{ V}} Ru_2(OAc)_4Cl_2^{2-} \quad (8)$$

An oxidation and a reduction were always observed although the ruthenium complexes are partitioned into three forms at the chloride concentrations investigated here.[19] Separate oxidation and reduction peaks for the individual complexes may not be detected, since $E_{1/2}$ values for the three complexes span only 60 mV. The electrode reactions are quasi-reversible, and therefore a faster ligand exchange (as compared to the heterogeneous electron-transfer reaction) may also result in the formation of a single pair of redox waves. Attempts were made to measure the rates of the chloride anation reaction. More than 95% of the reaction was over within the mixing time (~4 ms) of the stopped-flow experiment using 0.5 M Cl^- and 1.0×10^{-3} M di-

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(18) The large absorbance change (ΔD = 0.88 at 290 nm for 5.0×10^{-4} M ruthenium complex) cannot be adequately described by monochlorodiruthenium(III) complex formation. This change, in part, due to the change in anionic environment in the secondary coordination sphere for which we kept μ = 2.0 M ($[Cl^-] + [ClO_4^-]$) can also be ruled out, since a mixture of sulfate and perchlorate (μ = 1.0 M with $[SO_4^{2-}]$ = 0.1–0.5 M) did not change the absorption spectra. Moreover, the synthesis and X-ray structural characterization of the dichloro complex have already been documented.[4b]

(19) Two oxidation and two reduction waves were observed for tetrakis(μ-butyrato)diruthenium(II,III) chloride in CH_2Cl_2,[4c] which were ascribed to electrode reactions of mono- and dichloro complexes in solution. The same compound exhibits an oxidation and a reduction wave in other coordination solvents such as DMSO and acetonitrile.

ruthenium complex. The lower limit for the second-order rate constant can be estimated as 10^4 M^{-1} s^{-1} by using less than 1 ms as the half-life of the reaction. We were also unable to measure the rates of axial ligation by other ligands such as thiocyanate and pyridine. With the former reaction, $Ru_2(OAc)_4SCN{\cdot}H_2O$ precipitated, whereas with the latter, the metal–metal-bonded complex suffered decomposition, probably to monomeric Ru(II) and Ru(III) complexes.

Titanium(III) Reduction. Titanium(III) reduction of the diruthenium complex was carried out in 1.0 M Cl^- in the acidity range (100–6.0) × 10^{-3} M maintained by HCl. In this range of chloride concentrations the diruthenium complex predominantly exists as the tetrakis(μ-acetato)dichlorodiruthenate(II,III) anion. The spectrophotometric titration data support 1:1 stoichiometry according to

$$Ru^{II}Ru^{III}Cl_2^- + Ti^{III} \rightarrow Ru^{II}Ru^{II}Cl_2^{2-} + Ti^{IV} \qquad (9)$$

The diruthenium(II) complex exhibits a band at 465 nm. The absorption spectrum of $Ru_2(OAc)_4(H_2O)_2$ exhibits a band at 438 nm in aqueous solution.[20] This bathochromic shift in the absorption band in the presence of chloride perhaps indicates that chloride is coordinated to the diruthenium(II). We were unable to obtain equilibrium constants for the chloro complexes of the diruthenium(II) because of slow decomposition ($t_{1/2} \sim 15$ min) of the dimeric complex. This decomposition, however, did not complicate redox kinetics, for which half-lives were in milliseconds.

The redox reaction is first-order with respect to each reactant. The second-order rate constants at various hydrogen ion concentrations follow the rate law

$$k_0 = \frac{a[H^+] + b}{c + [H^+]} \qquad (10)$$

The values of a and b obtained form a nonlinear least-squares treatment were $a = 75 \pm 4$ M^{-1} s^{-1} and $b = 2.5 \pm 0.1$ s^{-1}, with $c = 2.3 \times 10^{-3}$ M. This is consistent with the following mechanism ($a = k_1$, $b = k_2K_a$, $c = K_a$):

$$Ti(H_2O)_6^{3+} + H_2O \xrightleftharpoons{K_a = 2.3 \times 10^{-3}\ M} Ti(H_2O)_5OH^{2+} + H_3O^+ \qquad (11)$$

$$Ti(H_2O)_6^{3+} + Ru_2(OAc)_4Cl_2^- \xrightarrow{k_1 = 75\ M^{-1}\ s^{-1}} \text{products} \qquad (12)$$

$$Ti(H_2O)_5OH^{2+} + Ru_2(OAc)_4Cl_2^- \xrightarrow{k_2 = 1.1 \times 10^3\ M^{-1}\ s^{-1}} \text{products} \qquad (13)$$

Chloride does not serve as a bridging ligand for Ti(III) reductants, and therefore an inner-sphere mechanism can be ruled out.[21] Outer-sphere titanium(III) reductions[22] occur primarily through $Ti(H_2O)_5OH^{2+}$. For example, rate data for titanium(III) reductions of Ru(III),[23] Co(III),[24-28] Ni(III),[29] and Cr(V)[30] complexes can be adequately described without the k_1 term although $Ti(H_2O)_5OH^{2+}$ enjoys only 0.2-V potential advantage over its $Ti(H_2O)_6^{3+}$ counterpart.[31,32] By application of the Marcus[33] model of outer-sphere electron transfer and utilization of available electrochemical data,[31,32] it can be shown that[34] $k_2 \leq 35k_1$. The ratio k_2/k_1 for the dichlorodiruthenium complex is 20 as predicted from Marcus' correlation. The same ratio was found to be within 15–50 for Os^{III}bpy (bpy = bipyridyl),[31] $Ru_2(OAc)_4(H_2O)_2^+$, and $Ru(acac)_3$ (acac = 2,4-pentanedionate)[12b] complexes. However, k_1 is smaller than expected for a large number of Co(III), Ru(III), Cr(V), and Ni(III) complexes.[23-30]

Since the rates of Ti(III) reduction of these dimeric ruthenium complexes correlate well with the Marcus model for outer-sphere electron-transfer reactions, electronic couplings (H_{12}) for these complexes must be sufficiently large to allow adiabatic electron transfer.[35,36] Large radical extensions of the molecular orbitals of all of these complexes are perhaps responsible for the larger H_{12} values. On the other hand, sluggish reactions of Co(III) and Ru(III) saturated amine complexes and macrocyclic Ni(III) complexes with aquatitanium(III) reductant are largely due to nonadiabatic electron-transfer reactions.[37] It remains to be seen, however, whether calculation of H_{12} values will lead to satisfactory correlations of non-Marcusian redox reactions.

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(34) It can be shown that

$$\frac{k_2}{k_1} = \left(\frac{k_{11}}{k_{11}'}\right)^{1/2} e^{-nF\Delta E^\circ/2RT}$$

where k_{11}' and k_{11} are the rate constants for the $Ti(H_2O)_6^{4+/3+}$ and $Ti(H_2O)_5(OH)^{3+/2+}$ self-exchange reactions and ΔE° represents the difference of the reduction potentials of the Ti(IV)/Ti(III) redox couples. In this derivation it is assumed that $(f_{12}/f_{12}')^{1/2}$ is very close to unity, where $\log f_{12} = (\log K_{12})^2/(4 \log (k_{11}k_{22}/Z^2))$.

(35) The electron transmission probability κ can be expressed by[36]

$$\kappa = \frac{2H_{12}^2}{h}\left(\frac{\pi^3}{E_{op}RT}\right)^{1/2} e^{-\Delta G_\lambda^*/RT}$$

where H_{12} is the electronic coupling matrix element, E_{op} ($=E_{in} + E_{out}$) is the potential energy associated with the optical electron transfer, and G^* ($=\Delta G^*_{out} + \Delta G^*_{in}$) is the free energy necessary to reorganize the reactants prior to electron transfer. Both activation energy terms contain outer- and inner-sphere contributions as designated by the subscripts "in" and "out".

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(37) Apparent discrepancies between the reactivities of the hexaaquatitanium(III) cation toward two categories of complexes, viz. (i) Co(III) and Ru(III) saturated amine complexes and Ni(II) macrocycles and (ii) dimeric ruthenium complexes, may not be due to anharmonicity and (or) tunneling factors, neither of which is embodied in the classical electron-transfer theory.[33,36] Contributions from these factors, if appreciable, should be comparable for both categories. For example, Sutin and co-workers[36] demonstrated that about 5% deviation in activation energy from the classical model can be accounted for by nonparabolic potential energy surfaces for the $Fe(H_2O)_6^{3+/2+}$ self-exchange reaction. Such a small deviation in activation energy should be reflected in a negligible change in rate constant.