References and Notes

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pH-Jump-Induced Intramolecular Electron Transfer within the $(NH_3)_5RuOV(HEDTA)^+$ Binuclear Ion

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A series of Ru(II)–V(IV) oxo-bridged binuclear complexes, $(NH_3)_5RuOVL^{4-n}$ (L = EDTA, $n = 4$; L = HEDTA, $n = 3$; L = EDDA, $n = 2$), have been formed in solution from $(NH_3)_5RuOH_2^{2+}$ and the corresponding VOL^{2-n} complex. The formation rate constant, k_1, for $(NH_3)_5RuOV(HEDTA)^+$ (I) is 2.83 ± 0.37 M^{-1} s^{-1} (25.0 °C, $\mu = 0.10$ NaCl, pH 6.86), indicative of substitution of the monovalent anion complex $VO(HEDTA)^-$ on Ru(II). The $(NH_3)_5RuOVL^{4-n}$ complexes exhibit a MLCT band near 605 nm which gives their characteristic dark green color. This band is assigned to the Ru(II) $d_{xy}(B_2) \rightarrow VO^{2+}\ \pi^*(E)$ transition similar to the MLCT spectra observed for $(NH_3)_5Ru(II)$–X complexes (X = an aromatic N heterocyclic ligand, N_2, nitriles, etc.). The $(NH_3)_5RuOVL^{4-n}$ complexes exhibit an eight-line ESR spectrum characteristic of a localized V(IV) oxidation state ($A_{iso} = 100.9$ G for I compared to 102.1 G for $VO(HEDTA)^-$ in 50:50 vol % propylene glycol–water). The MLCT bands and ESR spectra are bleached under proton-jump conditions; the products are observed to be Ru(III) and V(III) monomer complexes. The rate law for this process is given by $-d(I)/dt = (k_2 + k_3[H_3O^+]^2)[I]$ with $k_2 = 0.11 \pm 0.04$ s^{-1}, $k_3 = (3.55 \pm 0.04) \times 10^3$ M^{-2} s^{-1} (25.2 °C, $\mu = 0.10$ NaCl/HCl). The activation parameters for the k_3 path of intramolecular electron transfer are $\Delta H_3^{\ddagger} = 6.86 \pm 0.24$ kcal/mol and $\Delta S_3^{\ddagger} = -19.2 \pm 0.8$ eu. Regeneration of the Ru(II)–V(IV) binuclear complexes can be achieved under pH-jump conditions by recombination of Ru(III) and V(III) monomers, $(NH_3)_5RuOH^{2+}$ and $VL(OH)^{2-n}$. The regeneration reaction proceeds by the inner-sphere path. The second-order rate constant for regeneration of I, k_4, is 1.32×10^6 M^{-1} s^{-1} (25.3 °C, $\mu = 0.10$) and exhibits activation parameters of $\Delta H_4^{\ddagger} = 12.1 \pm 0.5$ kcal/mol and $\Delta S_4^{\ddagger} = 9.4 \pm 1.6$ eu. The $(NH_3)_5RuOV(EDDA)^{2+}$ complex undergoes competitive intramolecular electron transfer and H_3O^+ catalyzed loss of EDDA. At pH 2.4 the ligand dissociation pathway consumes 57% of the initial Ru(II), forming $(NH_3)_5RuOV(H_2O)_4^{4+}$ which does not undergo proton-promoted intramolecular electron transfer for $[H_3O^+] \leq 0.35$ M. Mechanisms are proposed which involve cis OH^-, H_2O coordination positions at the V(IV) center for the $[H_3O^+]^2$ promoted bleaching process of I. A related cis OH^-, OH^- orientation is proposed for the recombination of Ru(III) and V(III) monomers in the pH-jump-induced regeneration of I. Regeneration rates are modestly sensitive to specific interactions between phosphate, Tris, and 2,6-lutidine buffer species and $(NH_3)_5RuOH^{2+}$. This effect is described in terms of unstructured and structured ion pairs or ion-dipole pairs between $(NH_3)_5RuOH^{2+}$ and the buffers.

Introduction

The redox chemistry of transition-metal centers is often modified dramatically by a chelating environment relative to the simple aquo species. These effects are usually due to ligand field factors which restrict the labilities, or spin state of the central ion, or due to the existence of low-lying unfilled ligand orbitals which are available to promote the electron-transfer process. Much less attention has been given to the effect of concerted structural changes which may be coupled to redox events. Recently coordination-controlled electron-transfer processes have been detected in the cross reactions of $VO(HEDTA)^-/V(HEDTA)^-$[1,2] and $VO(HEDTA)^-/Mn(EDTA)(H_2O)^-$.[3] The rearrangement factor is transmitted to the observed rate constant in terms of an additional activation entropy, $\Delta S_{CR}^{\ddagger}$.[2,3] Rate-limiting rearrangements are slow enough to allow the detection of the $V^{II}V^{IV}O(HEDTA)_2^{2-}$

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binuclear ion which precedes intramolecular electron transfer. By comparison, no evidence is available for detection of a (II, IV) precursor complex in the $V(H_2O)_6^{2+}/VO(H_2O)_5^{2+}$ cross reaction[4] or the $Cr(H_2O)_6^{2+}/VO(H_2O)_5^{2+}$ reaction[5] or any other system where the inner-sphere component utilizes a single atom bridging unless a spin-state change controls the rate as in the $Cu(I)/Co(en)_2(SCH_2CH_2CO_2)^{2+}$ reaction.[3,6] Outer-sphere reactions are also subject to rearrangement controls imposed by chelation. The oxidation of $VO(H_2O)_5^{2+}$ by $Mn(EDTA)(H_2O)^-$ follows a dominant $1/[H_3O^+]$ dependence and may be inner sphere.[4,7] Complexation of VO^{2+} by $HEDTA^{3-}$ or $EDTA^{4-}$, but not NTA^{3-}, removes all equatorial H_2O sites of VO^{2+}. Oxidation of $VO(HEDTA)^-$ or $VO(EDTA)^{2-}$ by $Mn(EDTA)(H_2O)^-$ is outer sphere. The rate law exhibits elimination of the $1/[H_3O^+]$ path with the rate law changed to a first-order $[H_3O^+]$ dependence. This is suggestive of ring opening at the VO^{2+}–chelate site.[4] These systems have important implications for the structural-redox control balance which may be achieved by locking-in the chelating environment of a metal center, perhaps by allosteric effects for a metalloprotein redox process.[3]

Equally important in terms of potential biological control mechanisms for redox processes is the question of coupling redox-structural changes to an altered proton gradient. This question is frequently contested as a means of biochemical control in the as-yet-unelucidated mechanism of oxidative phosphorylation.[8,9] DeMaeyer et al. have reported the preparation of the relatively rare oxo-bridged heterobinuclear complex $(NH_3)_5RuOV(H_2O)_4^{4+}$.[10] The VO^{2+} unit may be viewed as a soft ligand toward Ru(II) in much the same way as N_2 or the aromatic N heterocycles interact with t_{2g}^6 configuration of Ru(II) via empty π^* orbitals.[10] The oxidation-state assignment of Ru(II)–V(IV) is made on the basis of a charge-transfer band at 625 nm ($\epsilon \sim 2.0 \times 10^3\ M^{-1}\ cm^{-1}$), the presence of the V═O stretching frequency at 975 cm^{-1} for the sulfate salt, and an ESR resonance at $g = 1.98$.[10] The $(NH_3)_5RuOV(H_2O)_4^{4+}$ complex is unchanged over the hydrogen ion range of 0.02–0.35 M. The lower limit (0.02 M) is established by the hydrolysis of the V(IV) aquo component of this species. We have generated a related series of complexes $(NH_3)_5RuOVL^{4-n}$ (L = EDTA, $n = 4$; L = HEDTA, $n = 3$; L = EDDA, $n = 2$) by means of the direct combination of $(NH_3)_5RuH_2O^{2+}$ and the corresponding VOL^{2-n} complex or by indirect means from Ru(III) and V(III) monomers under appropriate pH conditions. The observations which we report here establish the oxidation states in the binuclear $(NH_3)_5RuOVL^{4-n}$ complexes to be Ru(II)–V(IV). However, in marked contrast to the DeMaeyer ion, these systems can be reversibly driven between Ru(II)–V(IV) and Ru(III)–V(III) oxidation states by means of adjustment in the hydrogen ion environment. The DeMaeyer ion can also be generated from $(NH_3)_5RuCl^{2+}$ and $V(H_2O)_6^{3+}$, but the pathway proceeds by outer-sphere production of $(NH_3)_5RuOH_2^{2+}$ and $VO(H_2O)_5^{2+}$ which combine with loss of coordinated H_2O at Ru(II) rather than by intramolecular electron-transfer events.[10] We report in this paper the several interesting properties and dissimilar reactivities brought about by chelation at the VO^{2+} end of the $(NH_3)_5RuOV(H_2O)_4^{2+}$ ion.

Experimental Section

Chemicals and Methods. $VO(ClO_4)_2$ was prepared by the method of Rossotti and Rossotti.[11] $VO(SO_4)\cdot 2H_2O$ was obtained from Fisher Scientific Co. and purified as described by Johnson and Shepherd.[12] $(NH_3)_5RuCl_3$ was prepared by the method of Vogt, Katz, and Wiberley[13] via $(NH_3)_6RuCl_3$ recrystallized from acetone.[14] $(NH_3)_5RuOH_2^{2+}$ solutions were prepared by reduction of $(NH_3)_5RuCl^{2+}$ in Ar-flushed solutions over Zn/Hg chips. Reduction time of 30 min was allowed for $\sim 10^{-4}$ M Ru(III) solutions. Zn/Hg chips are prepared from the amalgamation of Zn by $HgCl_2$ solution in HCl ($\sim$0.1 M). The chips are washed with copious amounts of distilled deionized water to remove contaminants before the chips are air-dried. $(NH_3)_5RuOH_2^{2+}$ solutions were analyzed by complexation with 2-methylpyrazine and spectrophotometric determination of $(NH_3)_5Ru(2\text{-}CH_3pz)^{2+}$ at 467 nm ($\epsilon\ 1.36 \times 10^4\ M^{-1}\ cm^{-1}$).[15] Ar was scrubbed through Cr(II) towers and supplied to glass vessels via an all-glass manifold. Solutions were manipulated using gastight syringes. Spectrophotometric cells were preflushed with Ar and sealed with rubber septa (or glass stopcocks for prolonged exposure in cells). Titration and pH adjustments were carried out by addition of appropriate HCl or NaOH solutions via Gilmont microburets into purging vessels equipped with a single combination pH probe, precalibrated with commercial buffer standards. pH readings were obtained on an Orion 601 or 701 digital pH meter. NaCl replaced KCl in the pH probe to avoid precipitation problems of $KClO_4$.

VCl_3 was prepared by reduction of V_2O_5 by S_2Cl_2.[16] Workup procedures were carried out in anhydrous conditions within glovebags. Purity of samples was checked for V(IV) by means of presence or absence of the ESR eight-line VO^{2+} resonance. VCl_3 was stored in a vacuum desiccator to prevent oxidation of the solid in air.

$Na_2H_2EDTA\cdot 2H_2O$ (Baker Analyzed Reagent Grade), $H_3(HEDTA)$ (Aldrich), H_2EDDA (Sigma), H_3NTA (Aldrich), 2-methylpyrazine (99%, Aldrich), NaCl (analytical grade), pH 6.86 phosphate buffer (Fisher), and pH 9.18 borate buffer (Fisher) were used as supplied from the manufacturer. 2,6-Lutidine (Matheson Coleman and Bell; practical grade) was distilled from CaH_2. *p*-Toluenesufonic acid (Eastman Chemical) was treated by activated carbon in aqueous solution, filtered, and standardized by titration. Chloride ion was removed from solutions of $(NH_3)_5RuCl^{2+}$, prepared by dissolving weighed amounts of $(NH_3)_5RuCl_3$, by stoichiometric titration with Ag^+. Solutions were first reduced to Ru(II) to labilize Cl^-. Weighed amounts of Ag_2O were prepared by dissolving the solid in a minimum of trifluoroacetic acid (HFTA). The Ag(TFA) solution was added to the $(NH_3)_5RuOH_2^{2+}/3Cl^-$ solution to precipitate AgCl. The Ru(II) solution was then filtered in air to remove AgCl and to rapidly oxidize the sample to $(NH_3)_5RuH_2O^{3+}$.

Spectral and Kinetic Studies. All electronic spectra were recorded on a Varian-Cary 118C spectrophotometer with a thermostated cell compartment and a repetitive scan attachment. ESR spectra were recorded on a Varian E-4 X-band instrument. Aqueous solutions at room temperature were obtained in an Ar-flushed quartz flat cell. Low-temperature spectra (77 K) were recorded for a frozen glass containing the complex in a 50:50 vol % mixture of propylene glycol and water.[17] Slow kinetic processes were followed at fixed wavelength or by repetitive scan on the Varian-Cary 118C unit. Stopped-flow experiments were monitored on a Durrum D-110 spectrophotometer. Initially, absorbance–time data were extracted from photographs of oscilloscopic traces. Acquisition of a DECLAB 1103 computer system, with programs stored on floppy disks, permitted later experiments to be analyzed in an on-line fashion. Rates determined by the off-line and computer procedures for equivalent or identical experiments gave identical constants, within experimental error. Least-squares analysis was carried out with the computer system.[17]

Results and Observations

Spectra of Binuclear Complexes. When $(NH_3)_5RuOH_2^{2+}$ is combined under Ar with $VO(H_2O)_5^{2+}$, $VO(HEDTA)^-$, $VO(EDTA)^{2-}$, and VO(EDDA), a green species is obtained if the pH is above a critical value (eq 1). The green binuclear

$$(NH_3)_5RuOH_2^{2+} + VO(L)^{2-n} \rightleftarrows (NH_3)_5RuOV(L)^{4-n} + H_2O \quad (1)$$

L = EDTA, $n = 4$, pH >4.5
L = HEDTA, $n = 3$, pH >3.5
L = EDDA, $n = 2$, pH >3.0 (see text)
L = $(H_2O)_4$, $n = 0$, pH $\gtrsim$1

complex appears to be fully formed under the following conditions: EDTA, pH $\sim$7.0; HEDTA, pH $\sim$6.0; EDDA, pH $\sim$5.0, $(H_2O)_4$, pH $\gtrsim$1. Each of the resultant $(NH_3)_5RuOV(L)^{4-n}$ complexes has a spectrum similar to the electronic spectrum reported by DeMaeyer for $(NH_3)_5RuOV(H_2O)_4^{4+}$. Bands are observed near 600 nm attributed to $d_{xy}(B_2)$ Ru(II) → $\pi_a^*(E)$ VO^{2+} transition and in the near-UV ($\sim$398 nm) attributed to $\pi_b(E)$ Ru^{2+} → $\pi_a^*(E)$ VO^{2+} transition.[10] The spectral parameters are given

Table I. Electronic Spectra of $(NH_3)_5RuOV(L)^{4-n}$ Complexes at 25 °C

complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	ref
$(NH_3)_5RuOV(EDTA)$	398 ((1.2 ± 0.1) × 10^4)	This work
	605 ((3.0 ± 0.3) × 10^3)	This work
$(NH_3)_5RuOV(HEDTA)^+$	398 ((1.2 ± 0.1) × 10^4)	This work
	605 ((3.2 ± 0.3) × 10^3)	This work
$(NH_3)_5RuOV(EDDA)^{2+}$	392 ((1.2 ± 0.1) × 10^4)	This work
	600 ((2.7 ± 0.3) × 10^3)	This work
$(NH_3)_5RuOV(H_2O)_4{}^{4+}$	378 (1.3 ×10^4)	10
	625 (2.0 × 10^3)	10

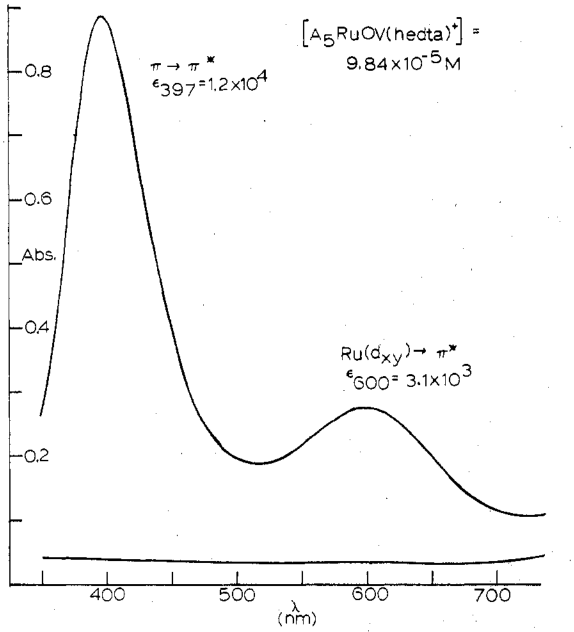


Figure 1. Visible spectrum of $(NH_3)_5RuOV(HEDTA)^+$: $T = 25.4$ °C, $\mu = 0.10$ (phosphate), [Ru(II)] = 9.85×10^{-5} M, $[VO(HEDTA)]_{tot} = 9.85 \times 10^{-4}$ M.

in Table I. The spectrum of $(NH_3)_5RuOV(HEDTA)^+$ is shown in Figure 1. At pH 8.0 the $(NH_3)_5RuOV(HEDTA)^+$ exhibits a well-resolved ESR spectrum indicative of a V(IV) localized unpaired electron (Figures 2a and 2b).

pH-Dependent Formation. Below pH 1.3 if $(NH_3)_5RuOH_2{}^{2+}$ is combined with $VO(HEDTA)^-$ at equal concentrations no green binuclear species accumulates with time. Because the substitution reaction of ligand on $(NH_3)_5RuOH_2{}^{2+}$ is slow,[18] and because an outer-sphere oxidation of Ru(II) by V(IV) may be possible, an analysis for Ru(II) as a function of time was carried out. 2-Methylpyrazine is known to scavenge $(NH_3)_5RuOH_2{}^{2+}$; the resultant $(NH_3)_5Ru(2\text{-}CH_3pz)^{2+}$ is more resistive to oxidation because of a shift in reduction potential of about 0.4 V.[19] Injection of 2-methylpyrazine into identical solutions at 3.0, 20.0, and 63.0 min after initially combining equal concentrations of $(NH_3)_5RuOH_2{}^{2+}$ and $VO(HEDTA)^-$ showed successive consumption of $(NH_3)_5RuOH_2{}^{2+}$ as monitored at 525 nm for the amount of $(NH_3)_5Ru(2\text{-}CH_3pz)H^{3+}$ present.[22] The disappearance of Ru(II) obeys a second-order rate law as shown by the 2-methylpyrazine rapid quench method (two trials) in Figure 3. The analysis was carried out at $[2\text{-}CH_3pz] = 1$ M. Under these conditions scavenging of $(NH_3)_5RuOH_2{}^{2+}$ is complete in about 1 s. The specific second-order rate constant, which is determined by the slope of Figure 3, is found to be 2.29 ± 1.06 M^{-1} s^{-1}. This value is in reasonable agreement with data, to be described below, which were obtained for the substitution of $VO(HEDTA)^-$ upon $(NH_3)_5RuOH_2{}^{2+}$ under pH conditions where the resultant binuclear species is stable. With pseudo-first-order conditions in $VO(HEDTA)^-$ where $[V(IV)]_{tot}:[Ru(II)]_{tot} =$ 15:1, substitution of VO(HEDTA) is complete in 20 min at pH 1.3. For these experiments the amount of $(NH_3)_5RuOH_2{}^{2+}$ was also determined by the 2-methylpyrazine analysis. But no binuclear complex is detectable at this pH. The specific second-order rate constant for the loss of Ru(II) as determined by the 2-methylpyrazine quench method at

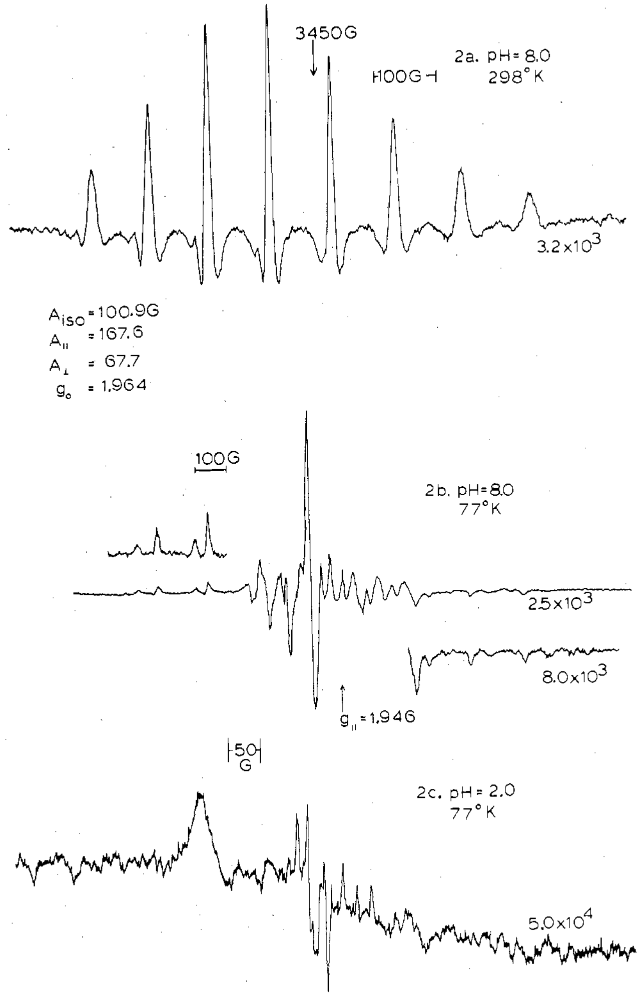


Figure 2. ESR spectra of solutions containing $(NH_3)_5RuOV(HEDTA)^+$ prior to pH adjustments: (a) pH 8.0, $T = 298$ K, 5.0 G modulation amplitude, 50 mW, 8.0 min scan, 9.479 GHz, second derivative mode; (b) pH 8.0, $T = 77$ K, 0.5 mW, first derivative mode, 9.024 GHz, other settings as 2a; (c) pH 2.0, $T = 77$ K, other settings as 2b; all spectra are obtained in 50%:50% v/v propylene glycol–water with initial binuclear concentration = 3.1×10^{-3} M (excess [Ru(II)] = 1.0×10^{-4} M).

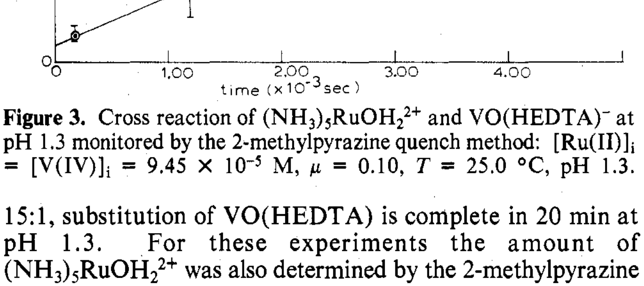


Figure 3. Cross reaction of $(NH_3)_5RuOH_2{}^{2+}$ and $VO(HEDTA)^-$ at pH 1.3 monitored by the 2-methylpyrazine quench method: $[Ru(II)]_i = [V(IV)]_i = 9.45 \times 10^{-5}$ M, $\mu = 0.10$, $T = 25.0$ °C, pH 1.3.

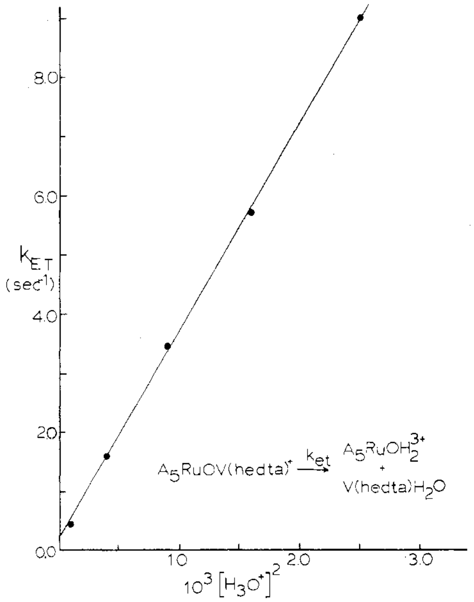


Figure 4. $[H_3O^+]$ dependence of $(NH_3)_5RuOV(HEDTA)^+$ bleaching reaction: $[(NH_3)_5RuOV(HEDTA)^+]_i = 1.40 \times 10^{-4}$ M, $\mu = 0.10$ (NaCl/HCl), $T = 25.4$ °C.

120.0, 220.0, and 330.0 s after mixing of $(NH_3)_5RuOH_2^{2+}$ and $VO(HEDTA)^-$ at pH 1.3 is 3.11 ± 0.13 M^{-1} s^{-1} assuming that the available V(IV) pool for reaction is the total analytical concentration of $VO(HEDTA)^-$ in these experiments. The absence of the binuclear species at pH 1.3 will be shown later to be due to proton-promoted electron transfer which converts every $(NH_3)_5RuOV(HEDTA)^+$ formed via substitution into Ru(III) and V(III) products. Hence no Ru(II) is found at the end of the reaction under either first-order or second-order conditions and no binuclear complex accumulates.

Under higher pH conditions with the $(NH_3)_5RuOV(HEDTA)^+$ fully formed, injection of 2-methylpyrazine produces no $(NH_3)_5Ru(2\text{-}CH_3pz)^{2+}$ in the same analysis time. This experiment shows that dissociation of $(NH_3)_5RuOV(HEDTA)^+$ is very slow. A similar result was obtained by DeMaeyer when $(NH_3)_5RuOV(H_2O)_4^{4+}$ was purged with N_2 and no $(NH_3)_5RuN_2^{2+}$ was detected via dissociation. At pH 6.86 $(NH_3)_5RuOH_2^{2+}$ and $VO(HEDTA)^-$ combine to form the binuclear complex (eq 1). The binuclear formation under pseudo-first-order conditions in $VO(HEDTA)^-$ was monitored in spectrophotometric cells at the 398-nm maximum. The rate law corresponds to eq 2 with $k_1 = 2.83 \pm 0.37$ M^{-1} s^{-1} at 25.0 °C, $\mu = 0.10$ (NaCl). The value determined for substitution on $(NH_3)_5RuOH_2^{2+}$ is the proper rate estimated for monovalent anions.[18,19]

$$d[(NH_3)_5RuOV(HEDTA)^+]/dt = k_1[(NH_3)_5RuOH_2^{2+}][VO(HEDTA)^-] \quad (2)$$

Proton-Dependent Intramolecular Electron Transfer. If a solution containing $(NH_3)_5RuOV(HEDTA)^+$ or $(NH_3)_5RuOV(EDTA)$, fully formed at a buffered pH, is suddenly adjusted into the acidic domain, both the CT band at 605 nm and the ESR resonance are bleached. That the pH-jump experiment does not represent a simple dissociation of the binuclear ions into $(NH_3)_5RuOH_2^{2+}$ and $VO(L)^{2-n}$ species is supported by two observations. The ESR spectrum in frozen solution at pH 1.0 no longer shows the presence of V(IV). The $VO(HEDTA)^-$ species would be ESR active as the monomer (Figure 2c) ($(NH_3)_5RuOH_2^{2+}$ is diamagnetic and should not destroy the $VO(HEDTA)^-$ resonance). Also, when the acid-bleached solution is treated with 2-methylpyrazine less than 3% of the total [Ru] is detectable as $(NH_3)_5Ru(2\text{-}CH_3pz)H^{3+}$.[22] Therefore, intramolecular electron transfer between the Ru(II) and V(IV) centers in the $(NH_3)_5RuOV(L)^{n-4}$ complexes (L = EDTA or HEDTA) is implicated, rather than an acid-induced dissociation which would have liberated $(NH_3)_5RuOH_2^{2+}$, detectable with 2-methylpyrazine.

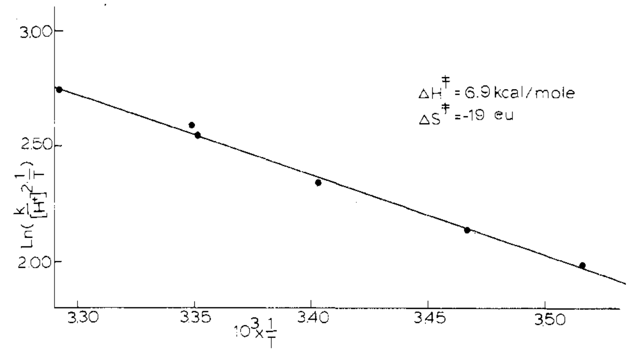


Figure 5. Temperature dependence for bleaching $(NH_3)_5RuOV(HEDTA)^+$: $[H_3O^+] = 0.030$ M, $[(NH_3)_5RuOV(HEDTA)^+] = 1.40 \times 10^{-4}$ M, $\mu = 0.10$ (NaCl/HCl).

Table II. Temperature Dependence for Bleaching $(NH_3)_5RuOV(HEDTA)^+$ at $\mu = 0.10$

T, K	$10^3/T$	$10^{-3}k_3$, M^{-2} s^{-1}	ln (k_3/T)
303.8	3.292	4.73	2.745
298.6	3.349	3.97	2.589
298.4	3.351	3.82	2.550
293.9	3.403	3.06	2.343
288.4	3.467	2.46	2.144
284.4	3.516	2.08	1.990

Table III. Second-Order Binuclear Complex Formation from $(NH_3)_5RuOH^{2+}$ and V(HEDTA), $\mu = 0.10$, $T = 25$ °C

pH, $[\text{buffer}]_{\text{tot}}$	$10^{-5}k_{\text{obsd}}$, M^{-1} s^{-1}	$k_{\text{calcd}}/k_{\text{obsd}}$^{b}
6.86 ± 0.03, [phosphate] = 0.051	5.64 ± 0.40	1.29
7.50, [Tris] = 0.127	7.47^a	1.50
6.87, [lutidine] = 0.051	5.33^a	1.37

^{a} Single determination. ^{b} k_{calcd} from data in Figure 5.

The rate of intramolecular electron transfer for the $(NH_3)_5RuOV(HEDTA)^+$ was followed by the proton-jump procedure using a stopped-flow instrument. The hydrogen ion range 0.01–0.05 M was studied at $\mu = 0.10$ (NaCl/HCl), 25.2 °C. The observed rate law (eq 3) is demonstrated by the linearity in k_o vs. $[H_3O^+]^2$ (Figure 4). The values are $k_2 = 0.11 \pm 0.04$ s^{-1} and $k_3 = (3.55 \pm 0.04) \times 10^3$ M^{-2} s^{-1}.

$$-d[(NH_3)_5RuOV(HEDTA)^+]/dt = (k_2 + k_3[H_3O^+]^2)[(NH_3)_5RuOV(HEDTA)]_{\text{tot}} \quad (3)$$

The temperature dependence of the proton-promoted intramolecular electron transfer was studied from 11.2 to 30.6 °C at $\mu = 0.10$ (NaCl/HCl) for the k_3 path. The activation parameters were obtained by means of the usual Eyring plot (+ln(k/T) vs. $1/T$) shown in Figure 5. The tabular data are listed in Table II. pH-jump-induced electron transfer within $[(NH_3)_5RuOV(HEDTA)^+]$ occurs with $\Delta H_3^\ddagger = 6.86 \pm 0.24$ kcal/mol and $\Delta S_3^\ddagger = -19.2 \pm 0.8$ eu.

Re-formation of the Binuclear Complex. The binuclear $(NH_3)_5RuOV(HEDTA)^+$ complex can be prepared by the combination of Ru(III) and V(III) monomers. $(NH_3)_5RuOH^{2+}$ solutions were prepared as described in the Experimental Section (in the absence of Cl^-) and adjusted with appropriate buffers. The $V(HEDTA)(H_2O)$ complex was prepared at a pH below the range of competitive $[(V(HEDTA))_2O^{2-}]$ binuclear formation[20] (pH <4.0) but low enough in $[H_3O^+]$ to be accommodated by the buffering action

Table IV. pH-Jump Recovery of $(NH_3)_5RuOV(HEDTA)^+$ from Monomer Complexes Prepared by Acid Bleaching of the Binuclear Complex

$10^8[H_3O^+]$, M	buffer[a]	$10^{-6}k_{obsd}$, M^{-1} s^{-1}	$10^7/k$, M s
0.417	T	1.31	7.63
0.447	T	1.32	7.58
0.617	T	1.29	7.75
0.676	T	1.29	7.75
1.62	T	1.13	8.85
1.62	T	1.23	8.13
(3.16)[b]	(T)	(0.747)	(13.4)
3.47	T	1.31	7.63
3.55	T	1.09	9.17
5.62	T	0.920	10.9
7.76	L	0.861	11.6
9.33	L	0.862	11.6
9.33	L	0.848	11.8
11.5	T	0.750	13.3
(13.4)[b]	(L)	(0.533)	(18.8)
13.5	L	0.733	13.6
(13.8)[b]	(P)	(0.564)	(17.7)
14.5	L	0.708	14.1
15.1	P	0.814	12.3
15.1	L	0.715	14.0
15.1	P	0.852	11.7
16.2	P	0.867	11.5
17.4	P	0.848	11.8
24.0	L	0.561	17.8
29.5	L	0.447	22.4
33.9	P	0.539	18.6

[a] Key: T = Tris buffer, L = 2,6-lutidine, P = phosphate buffer. [b] Values in parentheses are those of combining separately prepared monomer complexes with the Ru(III) monomer equilibrated with buffer as described for Table III.

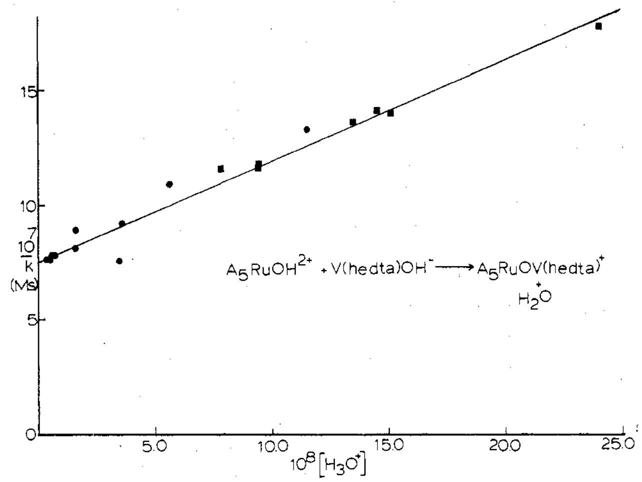


Figure 6. pH-jump regeneration at $(NH_3)_5RuOV(HEDTA)^+$: T = 25.4 °C, μ = 0.10 ($NaClO_4$/buffers), $[(NH_3)_5RuOH^{2+}]$ = [V(HEDTA)(H_2O)] = 6.30×10^{-5} M, [Tris buffer]$_{tot}$ = 0.127 M, ●, [2,6-lutidine] = 0.103 M, ■.

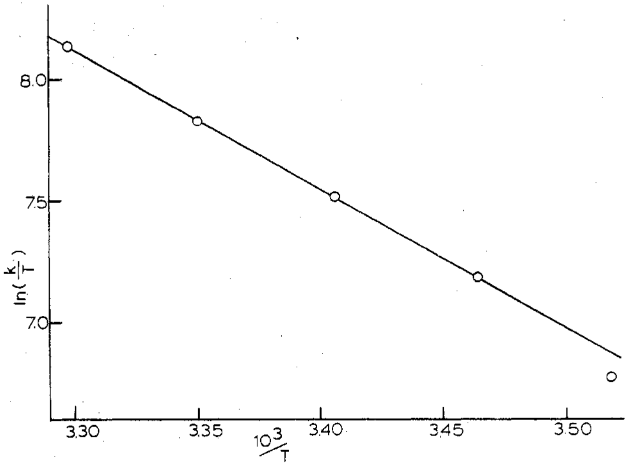


Figure 7. Temperature dependence for pH-jump regeneration reaction at pH 6.71: $[(NH_3)_5RuOH^{2+}]_i$ = $[V(HEDTA)(H_2O)]_i$ = 6.10×10^{-5} M, μ = 0.10 ($NaClO_4$/phosphate).

Table V. pH-Jump Regeneration of $(NH_3)_5RuOV(HEDTA)^+$ from Proton Bleached Solutions of the Ru(II)-V(IV) Binuclear ion

T, K	$10^3/T$	$10^{-5}k_4$, M^{-1} s^{-1}	$\ln(k_4/T)$
303.2	3.298	10.4	8.140
298.5	3.350	7.49	7.828
293.5	3.407	5.40	7.518
288.6	3.465	3.83	7.191
284.2	3.519	2.48	6.772

of the buffer in the $(NH_3)_5RuOH^{2+}$ solution. These solutions were mixed by the stopped-flow technique and the generation of $(NH_3)_5RuOV(HEDTA)^+$ was followed at 398 nm. The accumulated data are given in Table III. Under these conditions all of the Ru(III) is present as $(NH_3)_5RuOH^{2+}$ which has a pK_a ~4.[21] Solutions prepared in this manner gave modestly lower values for the rate constant for regeneration (k_{obsd}) of the Ru(II)-V(IV) binuclear complex than is obtained for pH-jump experiments conducted on acid-bleached solutions which previously contained the green binuclear species (cf. Tables III and IV). In the latter case acid-bleached solutions were mixed with buffers in the stopped-flow cuvette. Hence the buffer effect deals with the time available for buffer ions, presumably the free base form, to interact specifically with Ru(III). However, both methods gave $k_{obsd} \sim 10^6$ M^{-1} s^{-1} rather than diffusion-controlled recovery of the Ru(II)-V(IV) chromophore. This is added evidence that the products of the original H_3O^+ promoted bleaching process are monomers and not a Ru(III)-V(III) binuclear complex. The pH-jump, prebleached, solutions gave second-order recovery of $(NH_3)_5RuOV(HEDTA)^+$ according to eq 4. The reactive

$$d[(NH_3)_5RuOV(HEDTA)^+]/dt = k_{obsd}[(NH_3)_5RuOH^{2+}][V(HEDTA)]_{tot} \quad (4)$$

V(III) monomer is implicated to be $V(HEDTA)(OH)^-$ rather than V(HEDTA)(H_2O). This effect is shown by the increasing rate with lower $[H_3O^+]$ in Table IV. The data are linear for $1/k_{obsd}$ vs. $[H_3O^+]$ (Figure 6) with a slope of 4.4 ± 0.20 s and intercept of (7.56 ± 0.19) × 10^{-7} M s. Since $(NH_3)_5RuOH^{2+}$ is the only Ru(III) species in this pH range, equilibrium 5 must be responsible for any altering of the rate

$$H_2O + V(HEDTA)(H_2O) \overset{K_a}{\rightleftharpoons} V(HEDTA)OH^- + H_3O^+ \quad (5)$$

with pH. The pK_a for V(HEDTA)(H_2O) is 6.40; K_a = 3.98 × 10^{-7} M,[20] μ = 0.20 ($NaClO_4$). $[V(HEDTA)(OH)^-]$ = $K_a[V(HEDTA)]_{tot}/\{K_a + [H_3O^+]\}$; therefore the observed second-order rate constant for re-forming the binuclear complex is $k_{obsd} = k_4K_a/\{K_a + [H_3O^+]\}$, where k_4 is the second-order rate constant for reaction 6. Reasonable

$$(NH_3)_5RuOH^{2+} + V(HEDTA)OH^- \xrightarrow{k_4} H_2O + (NH_3)_5RuOV(HEDTA)^+ \quad (6)$$

agreement for the value of K_a is obtained using the intercept as $(1/k_4)$; $k_4 = 1.32 \times 10^6$ M^{-1} s^{-1}. The slope equals $(1/k_4)(1/K_a)$. The kinetic value for K_a is then determined as 1.71 × 10^{-7} M (μ = 0.10 NaCl); pK_a = 6.77.

The temperature dependence of the pH-jump regeneration of $(NH_3)_5RuOV(HEDTA)^+$ was examined at pH 6.71. Under this condition $K_a \simeq [H_3O^+]$ such that $k_{obsd} \simeq k_4/2$. The Eyring plot for reaction 6 is shown in Figure 7. The activation parameters are determined to be $\Delta H^{\ddagger}$ = 12.1 ± 0.5 kcal/mol

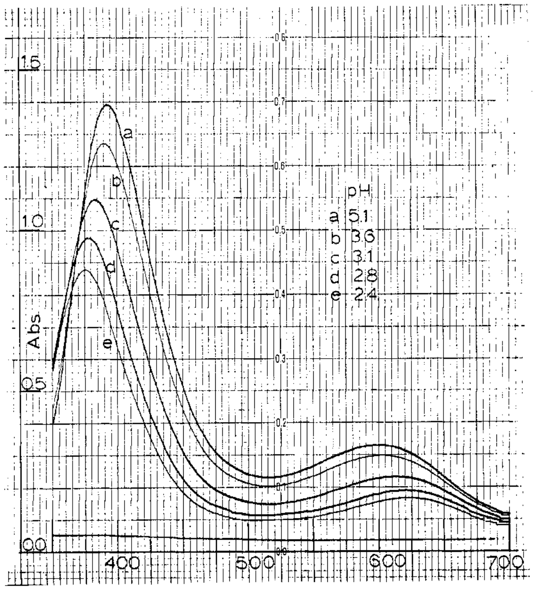


Figure 8. pH-dependent final spectrum for H_3O^+-jump studies of the $(NH_3)_5RuOV(EDDA)^{2+}$ system: 1.2×10^{-3} M, $\mu = 0.10$ (NaCl), $T = 25.2$ °C, 1-cm cell.

and $\Delta S^‡ = +9.4 \pm 1.6$ eu. The rate data are given in Table V.

The $(NH_3)_5RuOV(EDDA)^{2+}$ System. Reaction 1 with L = EDDA is similar to the HEDTA and EDTA cases which have been studied in greater detail as described in the previous section. The stability of VO(EDDA) is less than $VO(HEDTA)^-$ and $VO(EDTA)^{2-}$ due to the lower ligand charge. At high hydrogen ion concentration equilibrium 7 is achieved.

$$VO(L)^{2-n} + 3H_3O^+ \rightleftarrows H_3L^{3-n} + VO(H_2O)_5^{2+} \quad (7)$$

It is therefore anticipated that the EDDA complex, $(NH_3)_5RuOV(EDDA)^{2+}$, behaves differently from $(NH_3)_5RuOV(L)^{4-n}$ for L = HEDTA or EDTA. The product distribution of H_3O^+-jump experiments for the HEDTA and EDTA complexes reveals a steady progression of the decay of both the 605- and 398-nm bands with no shifting of the maxima from pH 8.0 to 2.9. The same pH variation study of the $(NH_3)_5RuOV(EDDA)^{2+}$ system is shown in Figure 8 from pH 5.1 to 2.4. The decay at the 392- and 600-nm bands of the parent complex is also accompanied by a shift toward the 625- and 378-nm maxima of the $(NH_3)_5RuOV(H_2O)_4^{4+}$ complex. At the final value spectrum 57% of the initial complex has been converted to DeMaeyer's ion by loss of EDDA. The remaining 43% has undergone competitive intramolecular electron transfer to form Ru(III) and V(III) monomer species.

Discussion

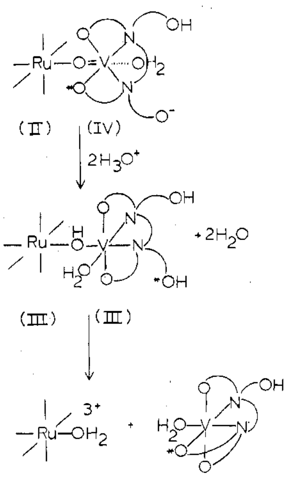
The $(NH_3)_5RuOV(H_2O)_4^{4+}$ complex is not proton promoted into intramolecular electron transfer, at least in the $[H_3O^+]$ range examined for the EDTA family of complexes. However, replacement of four H_2O molecules on the V(IV) site of the binuclear species by a chelating ligand of the EDTA family alters the redox behavior in response to pH adjustment. Depending on the nature of L and the direction of the pH shift, the species $(NH_3)_5RuOVL^{4-n}$ may be induced into intramolecular electron-transfer bleaching of the binuclear ion or caused to re-form from Ru(III) and V(III) monomer complexes. The case with L = EDDA is even more complicated by parallel reactions in which dissociation of the protonated ligand competes with intramolecular electron transfer during a sudden increase in H_3O^+.

Above pH 4 the formation of $(NH_3)_5RuOV(HEDTA)^+$ is complete in 30 min with second-order conditions or 6.5 min under pseudo-first-order conditions in V(IV). The resultant binuclear species is characterizable by its distinct electronic and electron spin resonance spectra. The 2-methylpyrazine quench experiments allow an estimate of the pK_a of VO(HEDTA)H in which the pendant carboxylate functionality may be protonated. The analysis under pseudo-first-order conditions in V(IV) at pH 1.3 exhibits a consumption of Ru(II) equal to the rate of substitution of $VO(HEDTA)^-$ on $(NH_3)_5RuOH_2^{2+}$. The pK_a of $VO(EDTA)H^-$ for the pendant carboxylate group is 3.00 ($\mu = 1.00$, 20 °C)[23] and the pK_a VO(HEDTA)H must be lower by at least one unit based on statistical grounds or charge factors. The first-order rate constant for $VO(HEDTA)^-$ substitution on $(NH_3)_5RuOH_2^{2+}$ is 2.83 ± 0.37 at pH 4 where $VO(HEDTA)^-$ is the only V(IV) species for the monomer. The same rate constant is observed within experimental error for the bleaching of Ru(II) at pH 1.3 under pseudo-first-order conditions in $[VO(HEDTA)^-]_{tot}$ (3.11 ± 0.13 M^{-1} s^{-1}). Since the experiment was conducted at a ratio of V(IV):Ru(II) = 15:1, the amount of $VO(HEDTA)^-$ available for substitution at pH 1.3 must be at least greater than or equal to half of the total if the same rate is to be measured. This conclusion rests on the fact that neutral, uncharged ligands exhibit characteristically slower substitution reactions with $(NH_3)_5RuOH_2^{2+}$ than anions.[18] The uncharged ligands substitute on Ru(II) about 40 times slower; e.g., neutral ligands have k's ~ 0.07 M^{-1} s^{-1} compared to k's ~ 1 M^{-1} s^{-1} for anions. Hence the pK_a for VO(HEDTA)H must be $\lesssim 1.3$. The second-order conditions show a substitution–redox sequence at pH 1.3 as determined by the 2-methylpyrazine quench experiments (Figure 3).

The precision is lower for the second-order experiments due to accumulative errors in side reactions which can interfere in the amount of Ru(II). However, the rate of consumption is still consistent with $VO(HEDTA)^-$ as the dominant substitution reactive species of V(IV) toward $(NH_3)_5RuOH_2^{2+}$ under second-order conditions. This observation reinforces the value of 1.3 for the upper limit for the pK_a of VO(HEDTA)H and probably makes the pK_a of VO(HEDTA)H $\lesssim 0.6$. Hence the dominant reactions are as follows: pH >4, substitution of $VO(HEDTA)^-$ on $(NH_3)_5RuOH_2^{2+}$ forming the stable binuclear complex; pH $\lesssim 1.3$, substitution of $VO(HEDTA)^-$ on $(NH_3)_5RuOH_2^{2+}$ followed by immediate proton-promoted electron transfer which destroys the binuclear complex.

Protonation of the pendant carboxylate site in $(NH_3)_5RuOV(HEDTA)^+$ during the H_3O^+-jump experiments may also be anticipated to occur. The pendant carboxylate group is estimated to have a pK_a ~ 0.6 based on the following electronic effects which are likely to cancel: (1) The remote Ru(II) increases the repulsion upon protonation of the pendant carboxylate group; this is expected to lower the pK_a by approximately 1 log unit relative to the estimated value of 0.6 for VO(HEDTA)H (e.g. to $\sim$0). (2) The Ru(II) back-donation toward V(IV) is expected to reduce the effective charge at the nearer V(IV) center with respect to a protonated carboxylate ligand; this is expected to make the pendant carboxylate more readily protonated, raising the pK_a relative to 0.[26] For the hydrogen ion range examined in the bleaching experiments (0.01–0.05 M) no discontinuity in the rate dependence is observed, which suggests that only one form of $(NH_3)_5RuOV(HEDTA)^+$ is kinetically active throughout the range of $[H_3O^+]$ of 0.01–0.05 M. This is consistent with a pK_a for $(NH_3)_5RuOV(HEDTA)^{2+}$ of $\lesssim 0.6$. One cannot rule out the possibility that one proton of the $[H_3O^+]^2$ dependence might be involved with the initially pendant carboxylate group. However, it remains obscure as to how this protonation would increase the favorability for intramolecular electron transfer in a catalytic way. The more likely conclusion which rests on

Scheme I

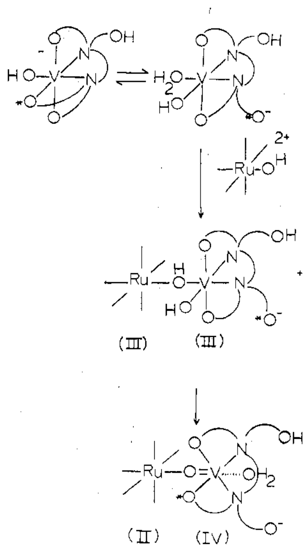


the law of microscopic reversibility and the data for recombination of Ru(III) and V(III) hydroxy monomer complexes to be discussed later assigns the catalytic sites of protonation at two positions: one proton at the bridging oxo ligand and one proton involved in chelate ring opening at a coordinated carboxylate group. Ring opening should allow for reduced strain during the coordination rearrangement which must accompany the change in oxidation state of IV to III and the coordination number from 5 to 6 at vanadium. Protonation at a coordinated carboxylate group to achieve ring opening is further supported by the competitive ligand dissociation and intramolecular transfer events for the EDDA system.

This hypothesis is shown in Scheme I; the rationale for our assignment rests on the principle that $(NH_3)_5RuOH_2^{3+}$ is the leaving group for the H_3O^+-jump experiments. Ligand exchange at Ru(III) is slow. The bridging oxo ligand is certainly retained by the Ru(III) center. Since it is very unlikely that both protons may be bound at the bridging oxo ligand due to the high charge environment of Ru(II), V(IV), and the first H^+, the second H^+ is best located at a cis coordinated carboxylate site. With ring opening, a cis H_2O position relative the protonated bridging ligand is achieved. The cis orientation will be later shown as the most likely orientation for combination of $(NH_3)_5RuOH^{2+}$ with labilized $V(HEDTA)(OH)^-$. A simple proton shift between cis H_2O and the bridging ligand completes the steps required for loss of $(NH_3)_5RuOH_2^{3+}$. These steps are concerted with ligand rearrangements at the vanadium center. The relatively ordered transition state which is required by the protonations described in Scheme I is consistent with the highly negative $\Delta S^{\ddagger} = -19.2 \pm 0.8$ eu determined by the temperature-dependent studies.

The arguments have been made in the previous section to show that the pH-jump-induced recombination of Ru(III) and V(III) monomers occurs with the hydroxy monomer of V(III) as the kinetically active species. At the pH range studied, all of the Ru(III) is initially present as $(NH_3)_5RuOH^{2+}$.[21] The pH dependence must involve changes at the V(III) complex. The substitution inertness of Ru(III) on the time scale of the recombination experiments assures that the Ru(II)–O–V(IV) binuclear species will retain the oxygen of the hydroxy group of $(NH_3)_5RuOH^{2+}$. In contrast to DeMaeyer's study in which $V(H_2O)_6^{3+}$ reacts by an outer-sphere route with $(NH_3)_5RuCl^{2+}$ and the resultant $VO(H_2O)_6^{2+}$ combines with $(NH_3)_5RuOH_2^{2+}$, the EDTA family of ligands do not regenerate the Ru(II)–V(IV) binuclear complexes by outer-sphere electron transfer followed by recombination of Ru(II) and V(IV) fragments. The pH-jump recombination studies exhibit no rate enhancement by the presence of added $VO(HEDTA)^-$. In DeMaeyer's system added $VO(H_2O)_5^{2+}$ is catalytic for generation of $(NH_3)_5RuOV(H_2O)_4^{4+}$ from Ru(III) and V(III) monomers.

Scheme II



The reactivity of $V(HEDTA)OH^-$ for $(NH_3)_5RuOH^{2+}$ has a charge advantage relative to V(HEDTA). In addition the OH^- group can labilize the vanadium(III)–carboxylate bonds via charge repulsion and π donation toward the M(III) center. A cis configuration in the first coordination sphere of V(III) is shown in Scheme II to account for the apparent reactivities. The Ru(III)–V(III) activated complex is at a similar saddle point on the energy surface between Ru(II)–O–V(IV) binuclear species and the Ru(III) plus V(III) monomer species as has been proposed for the pathway in Scheme I. Both proposed intermediates have a labilized carboxylate group which is originally coordinated to the vanadium reactant center and a cis H_2O–OH^- orientation (Scheme I) or a cis OH^-–OH^- orientation (Scheme II). Scheme I reverts to products via a proton shift to convert the Ru(III) center into a good leaving group. It is well-known in the cases of inner-sphere electron transfer that H_2O is a poor bridging ligand between metal centers relative to bridging hydroxide.[24] In Scheme II the cis hydroxide orientation allows for regeneration of the binuclear Ru(II)–V(IV) complex by means of dehydration (a reverse proton shift) and ring closure of the carboxylate ligand at the vanadium center. The internal redox process is also coupled to ligand rearrangement to reverse the oxidation and coordination number changes (III → IV and 6 → 5).

Schemes I and II suitably describe the sequence of kinetic events for the acid-induced intramolecular electron transfer and binuclear ion re-formation for the $(NH_3)_5RuOV(HEDTA)^+$ and $(NH_3)_5RuOV(EDTA)$ systems. With EDDA as the chelating ligand, V–N bond rupture is competitive with dissociation into Ru(III) and V(III) monomers, which is shown as the last step in Scheme I. Re-formation of $(NH_3)_5RuOV(EDDA)^{2+}$ at the comparable pH range used to study the $(NH_3)_5RuOV(HEDTA)^+$ complex is complicated by the hydrolysis of $V(EDDA)(H_2O)_2^+$ at lower pH values than for $V(HEDTA)(H_2O)$ or $V(EDTA)(H_2O)^-$. A scheme represented by II for re-formation of $(NH_3)_5RuOV(EDDA)^{2+}$ is probably inappropriate. For this reason we have been unable to study the process in detail.

A subtle feature has been detected by the two different means of study for the pH-jump regeneration of $(NH_3)_5RuOV(HEDTA)^+$. In both experiment types (A = preequilibration of buffer solution with only $(NH_3)_5RuOH^{2+}$; B = homogeneous formation of buffer and hydroxy monomers from previously fully protonated base forms) the V(III) complex is exposed to the basic buffer species immediately at the time of mixing. The effect must then point to the interaction of $(NH_3)_5RuOH^{2+}$ in a specific way in the pree-

Table VI. Outer-Sphere Dependent Regeneration of $(NH_3)_5RuOV(HEDTA)^+$ Active Buffer[a]

species, K_8 (est)	[active species], M	k_B/k_A	K_9	K_8K_9, M^{-1}
HPO_4^{2-}, 5 M^{-1}	0.025	1.29	2.6	13
2,6-lutidine, 0.15 M^{-1}	0.051	1.37	47	7
Tris, 0.15 M^{-1}	0.026	1.50	127	19

[a] $\mu = 0.10$, $T = 25$ °C.

quilibrated experiments (A) that is not achieved on the time scale of competitive scavenging by $V(HEDTA)(OH)^-$ in pH-jump homogeneous method (B). Outer-sphere associated complexes for both the Ru(III) and V(III) monomers are established at the diffusion limit. If the preequilibrated solutions have a fraction of the $(NH_3)_5RuOH^{2+}$ converted to an unreactive form by the buffer materials, both nonstructured outer-sphere complexes and structured outer-sphere complexes are implicated. The different behavior is defined by the two equilibria 8 and 9. With preequilibration, both the structured

$$(NH_3)_5RuOH^{2+} + B \xrightleftharpoons{K_8} \{(NH_3)_5RuOH^{2+}\cdots B\}_1 \quad (8)$$

$$\{(NH_3)_5RuOH^{2+}\cdots B\}_1 \xrightleftharpoons{K_9} \{(NH_3)_5RuOHB^{2+}\}_2 \quad (9)$$

outer-sphere complex 2 and unstructured complex 1 have time to form. The reactive species $(NH_3)_5RuOH^{2+}$ for the V(III) complexation reaction is reduced by a factor $1/\{1 + K_8[B] + K_8K_9[B]\}$. For the buffer species present in the preequilibrated experiments (A) the strongest $(NH_3)_5RuOH^{2+}$ interactions should occur for HPO_4^{2-} and the free base forms of 2,6-lutidine and Tris, $(HOCH_2)_3CNH_2$. Assuming that the unstructured ion pair (1) is due to the usual dipole–ion interactions, an estimate of K_8 may be made with ~5 for HPO_4^{2-} and 0.15 for the neutral bases.[25] In Table VI we have calculated the apparent value for K_9 and K_8K_9 assuming the dipole–ion estimates for K_8 and the given active species.[27] The values are kinetically established by the ratio of the observed rate constant for formation in the absence of preequilibrium (B) conditions obtained from the data in Figure 5 and the rate constant under preequilibrated (A) conditions. The values calculated for K_9 and K_8K_9 are only of qualitative meaning due to the uncertainties in the validity of the estimate in K_8. However, an interesting trend is suggested by the values of K_8K_9 for the three buffers. The largest interaction with $(NH_3)_5RuOH^{2+}$ is achieved for the buffer ions which may assume a multisite interaction with a face of the octahedron and a tripodal binding of the buffer species. Since the rate of formation of the structured ion (2) cannot be competitive to a great extent with the second-order rate of reaction with the $V(HEDTA)OH^-$ monomer in the (B) type experiments, an estimate of the forward rate k_9 has an upper limit of ~1.0 s^{-1} at 10^{-4} M in Ru(III) and V(III) monomers, similarly the upper limit to $k_{-9} \sim 0.1$ s^{-1} based on the evaluated constants K_9 in Table V. The reason for a tightly ordered outer-sphere complex with 2,6-lutidine is harder to analyze. However, ion-dipole outer-sphere complexes which are formed on mixing (eq 8) may revert to a strongly hydrogen bonded interaction between the hindered N base of 2,6-lutidine and the hydroxyl proton of $(NH_3)_5RuOH^{2+}$. The optimization of a strong, specific interaction of this kind could also be achieved slowly due to the steric effect of adjacent methyl groups of the N base. The free energy changes involved in equilibrium 9 are within a factor of 4 of the thermal energy of the system; with complexation of Ru(III) to V(III) and electron transfer to the Ru(II)–V(IV) binuclear species the Ru(III) will ultimately be converted quantitatively into the binuclear species which has high thermodynamic stability to dissociation into Ru(II) and V(IV). This is evidenced by the absence of conversion of $(NH_3)_5RuOV(HEDTA)^+$ upon addition of 2-methylpyrazine or by N_2 in the case of DeMaeyer's ion. DeMaeyer has estimated a formation constant for $(NH_3)_5RuOV(H_2O)_4^{4+}$ of about 10^7 M^{-1}.[10] The similarity of the spectral properties of the CT bands for the series of binuclear complexes and the 2-methylpyrazine result reported here suggests equally large affinities for $(NH_3)_5RuOV(HEDTA)^+$ and $(NH_3)_5RuOV(EDTA)$.

Acknowledgment. We wish to acknowledge the NSF grant (CHE76-21290) which allowed us to acquire the computer system used in these studies and the Research Corp. for funds which permitted the purchase of the stopped-flow instrument.

Registry No. $(NH_3)_5RuOV(EDTA)$, 67784-71-8; $(NH_3)_5RuOV(HEDTA)^+$, 67784-72-9; $(NH_3)_5RuOV(EDDA)^{2+}$, 67761-85-7.

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(27) K_9 may be calculated from $(k_B/k_A) = \{1 + K_8[B] + K_8K_9[B]\}/\{1 + K_8[B]\}$.
(28) A_{iso} for $(NH_3)_5RuOV(HEDTA)^+$ is 100.9 G compared to 102.1 G for the $VO(HEDTA)^-$ monomer.