

dismutase proteins. Whether the mechanism suggested by eq 10 is relevant to those for the proteins is unknown, but the absence of electron transfer from their metal centers to $O_2^{\cdot-}$ is a reasonable expectation.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-8516247. We are grateful to the Robert A. Welch Foundation for the award of a Predoctoral Fellowship to P.K.S.T.

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Influence of the Pendant Group on the Substitution Lability of N-Substituted Ethylenediaminetriacetate Complexes of Ruthenium(III) in Aqueous Solution

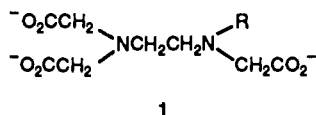
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Received July 13, 1989

Following earlier studies on the substitution behavior of ethylenediaminetetraacetate and related complexes of Ru(III), the series has now been extended to include data for the *N*-methylethylenediaminetriacetate complex. Substitution reactions of the aqua and hydroxo complexes with thiocyanate and thiourea exhibit remarkably different activation volumes, which suggest that the substitution mechanism may change over from I_a to A for the aqua and hydroxo complexes, respectively. These data enable an overall discussion of the influence of the pendant group on the substitution lability of such ruthenium(III) complexes. It is suggested that when the pendant group contains a carboxylate moiety, the syn lone pair of electrons on the carboxylate oxygen may interact effectively with the coordinated water molecule and so account for the extreme lability observed in the case of the ethylenediaminetetraacetate complex.

Introduction

The extreme lability of the $Ru(edta)H_2O^-$ complex (*edta* = ethylenediaminetetraacetate) has attracted significant attention from kineticists in recent years.²⁻⁶ In these studies it is generally accepted that *edta* is coordinated as a pentadentate ligand with the sixth coordination site being occupied by a water molecule. Protonation of the pendant carboxylate group (i.e. $R = CH_2COO^-$ in **1**) or deprotonation of the coordinated water molecule results



in a substantial decrease in the lability of the $Ru(edta)H_2O^-$ complex.³⁻⁶ It is especially the role of the pendant R group that has stimulated interesting research in this area.⁶⁻⁸

We recently reported a detailed study of the substitution behavior of $Ru(edta)H_2O^-$ with a series of anionic and neutral ligands.⁶ The reported activation parameters, especially ΔV^\ddagger , support the operation of an I_a mechanism in which the pendant carboxylate moiety significantly assists $Ru-OH_2$ bond breakage. We concluded that hydrogen bonding between the carboxylate oxygen and the coordinated water molecule could account for the increased lability. This could result in a weakening of the $Ru-OH_2$ bond and/or in the creation of an open area and accessible site for associative ligand attack. In order to gain more insight into the influence of the pendant R group in **1**, we performed a kinetic study of the substitution behavior of $Ru(hedtra)H_2O$, where *hedtra*

= *N*-(hydroxyethyl)ethylenediaminetriacetate (i.e. $R = CH_2C-H_2OH$ in **1**).⁷ In this way, the suggested effect of hydrogen bonding could be reduced and the protonation of the pendant R group could be excluded. The results demonstrated a decrease of approximately 2 orders of magnitude in the substitution rate constant of the aqua complex as compared to the *edta* analogue. The activation parameters underline the operation of an I_a mechanism.

In the present study, we have replaced R in **1** by methyl in order to even further decrease the possible effect of hydrogen bonding between R and the coordinated water molecule. The results of this investigation, along with those reported before,^{6,7} enable us to comment on the intimate nature of the pendant labilization effect and to reveal mechanistic differences between the substitution behavior of $Ru(\text{medtra})H_2O$ and $Ru(\text{medtra})OH^-$, where *medtra* = *N*-methylethylenediaminetriacetate.

Experimental Section

Materials. An aqueous concentrated solution of $Na_3\text{medtra}$ was prepared as described elsewhere⁹ by the reaction of *N*-methylethylenediamine with monochloroacetic acid. Since the ligand could not be readily isolated, this solution was used in the subsequent synthetic work. A portion of this solution (2.0 mmol) acidified to pH 4 with concentrated HCl was added to 0.75 g (2.0 mmol) of $K_2[RuCl_5H_2O]$, and the mixture was refluxed for 2 h. During this time, the solution became greenish yellow. It was reduced in volume on a water bath, followed by the addition of cold ethanol to precipitate the complex. The precipitate was filtered off, washed with cold ethanol/water (9:1), and dried under vacuum. The yield based on $K_2[RuCl_5H_2O]$ was 45%. Chemical analysis¹⁰ for $K[Ru(\text{medtra})Cl] \cdot 2H_2O$ (theoretical values): C, 24.18 (23.66); H, 3.86 (3.72); N, 5.66 (6.13). All other chemicals were of analytical reagent grade, and deionized water (Millipore) was used throughout this study. Acetate, citrate, phosphate, and borate buffers were used to control the pH of the test solutions.¹¹ Na_2SO_4 was used to adjust the ionic strength.

Measurements. The substitution reactions were followed spectrophotometrically in the wavelength range 360-600 nm with a Shimadzu UV 250 spectrophotometer and a Durrum D 110 stopped-flow instrument. Kinetic measurements at elevated pressure were performed on a

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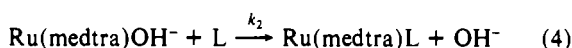
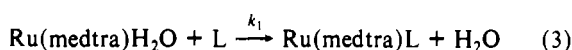
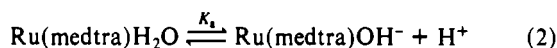
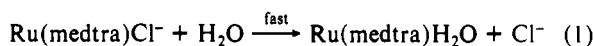
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homemade high-pressure stopped-flow unit.¹² All the mentioned instruments were thermostated to ± 0.1 °C for the kinetic measurements. The absorbance-time plots were analyzed with the aid of a data acquisition system,¹³ and the corresponding first-order plots were linear for at least 2–3 half-lives of the reaction. pH measurements were carried out with a Radiometer PHM 64 instrument, which was calibrated with standard buffer solutions at the desired temperature.

Results and Discussion

The isolated $\text{K}[\text{Ru}(\text{medtra})\text{Cl}]$ complex shows a characteristic IR band at 1642 cm^{-1} , which can be assigned to the coordinated carboxylate groups. A similar band was observed for the corresponding edta and hedtra complexes.^{6,7}

A series of experiments were performed to investigate the nature and reactivity of the $\text{Ru}(\text{medtra})\text{Cl}^-$ complex in solution. The UV-vis spectrum is characterized by absorbance shoulders at 290 nm ($\epsilon = 2400\text{ M}^{-1}\text{ cm}^{-1}$) and 380 nm ($\epsilon = 920\text{ M}^{-1}\text{ cm}^{-1}$), which are in close agreement with those reported for $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ and $\text{Ru}(\text{hedtra})\text{H}_2\text{O}$.^{6,7} On dissolution of $\text{K}[\text{Ru}(\text{medtra})\text{Cl}]$, the complex undergoes rapid aquation to produce $\text{Ru}(\text{medtra})\text{H}_2\text{O}$ (eq 1). Addition of a large excess of a chloride salt to the solution causes a decrease in the absorbance at 290 nm and the formation of a band at 300 nm, which can be associated with the formation of the chloro complex. The formation constant of the chloro complex was estimated on the basis of the observed spectral changes to be $1.0 \pm 0.1\text{ M}^{-1}$. This small value accounts for the observation that the isolated chloro complex immediately aquates on dissolution. A potentiometric titration of the aqua complex resulted in a $\text{p}K_a$ value of 6.30 ± 0.05 at 25 °C and 0.20 M ionic strength (see eq 2). This $\text{p}K_a$ value is ca. 1 unit lower than that of $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ (viz. 7.6⁶) and significantly higher than that of $\text{Ru}(\text{hedtra})\text{H}_2\text{O}$ (viz. 4.9⁷). These trends can be accounted



for in terms of the negative charge on the edta complex, which will inhibit deprotonation, the higher stability of the $\text{Ru}-\text{OH}_2$ bonds in the hedtra and medtra complexes, which will be accompanied by a decrease in the O–H bond strength, and the different electron-donating capabilities of the pendant CH_3 and $\text{CH}_2\text{CH}_2\text{OH}$ groups. In addition, hydrogen bonding between the hydroxyethyl group in hedtra and the coordinated water molecule may account for the very low $\text{p}K_a$ value reported for the $\text{Ru}(\text{hedtra})\text{H}_2\text{O}$ complex.⁷ It follows that the medtra complex exhibits behavior similar to that of the edta and hedtra complexes in solution.

The substitution reactions indicated in (3) and (4) were studied under pseudo-first-order conditions (excess of L) for $\text{L} = \text{SCN}^-$ and $\text{SC}(\text{NH}_2)_2$. The observed first-order rate constant increases linearly with increasing $[\text{L}]$ with no significant intercept, as demonstrated for two typical examples in Figure 1. When a large excess of L ($\geq 0.50\text{ M}$) is used, a subsequent slow reaction is observed, which is presumably due to the formation of a 1:2 complex. The substitution reactions exhibit a characteristic pH dependence, as demonstrated in Figure 2, which is in line with reactions 3 and 4. The rate law in (5) predicts a sigmoid-shaped

$$k_{\text{obs}} = \{k_1[\text{H}^+] + k_2K_a\}[\text{L}]/\{[\text{H}^+] + K_a\} \quad (5)$$

curve for the plot of k_{obs} versus pH with limiting values of $k_{\text{obs}} = k_1[\text{L}]$ and $k_{\text{obs}} = k_2[\text{L}]$ at low and high pH, respectively. An appropriate fit of the data results in $k_1 = 2.3 \pm 0.1$, $k_2 = 0.15 \pm 0.04\text{ M}^{-1}\text{ s}^{-1}$, and $\text{p}K_a = 6.25 \pm 0.05$ for $\text{L} = \text{SC}(\text{NH}_2)_2$ and

Table I. Summary of k_{obs} as a Function of Temperature and Pressure for the Reaction $\text{Ru}^{\text{III}}(\text{medtra})(\text{H}_2\text{O}/\text{OH}^-) + \text{L} \rightarrow \text{Ru}^{\text{III}}(\text{medtra})\text{L} + \text{H}_2\text{O}/\text{OH}^-$

ligand	[ligand], M	temp, °C	press., MPa	$10^2 k_{\text{obs}}$, s ⁻¹
thiocyanate ^a	0.025	25.0	0.1	0.59 ± 0.01
		30.0		0.73 ± 0.03
		35.0		0.91 ± 0.02
		40.0		1.08 ± 0.02
	0.10	25.0	5	2.16 ± 0.01
			25	2.38 ± 0.06
			50	2.57 ± 0.08
			75	2.69 ± 0.10
			100	2.89 ± 0.18
thiourea ^a	0.10	25.0	0.1	24.2 ± 1.0
		30.0		29.5 ± 1.1
		35.0		36.4 ± 1.5
		40.0		44.8 ± 2.0
	0.020	25.0	5	5.1 ± 0.1
			25	5.4 ± 0.1
			50	5.8 ± 0.2
			75	6.1 ± 0.2
			100	6.5 ± 0.1
thiocyanate ^b	0.10	25.0	0.1	0.45 ± 0.03
		30.0		0.59 ± 0.01
		35.0		0.74 ± 0.08
		40.0		0.92 ± 0.06
		25.0	5	0.55 ± 0.02
		25		0.62 ± 0.02
		50		0.76 ± 0.05
		75		0.88 ± 0.02
		100		0.99 ± 0.01
thiourea ^b	0.10	25.0	0.1	1.07 ± 0.01
		30.0		1.29 ± 0.06
		35.0		1.58 ± 0.08
		40.0		1.94 ± 0.07
		25.0	5	1.25 ± 0.04
		25		1.44 ± 0.06
		50		1.59 ± 0.05
		75		1.67 ± 0.05
		100		1.81 ± 0.11
thiocyanate ^c	0.10	25.0	5	0.52 ± 0.02
			25	0.62 ± 0.03
			50	0.74 ± 0.04
			75	0.80 ± 0.03
			100	0.96 ± 0.05
thiourea ^c	0.050	25.0	5	0.51 ± 0.03
			25	0.53 ± 0.02
			50	0.61 ± 0.02
			75	0.66 ± 0.01
			100	0.71 ± 0.03

^a $[\text{Ru}(\text{III})] = 2.5 \times 10^{-4}\text{ M}$; $\text{pH} \approx 2.5$; citric acid/NaOH buffer, 0.10 M; ionic strength = 0.20 M (Na_2SO_4). ^b $[\text{Ru}(\text{III})] = 5.0 \times 10^{-4}\text{ M}$; $\text{pH} \approx 8.0$; HCl/borate buffer, 0.025 M; ionic strength = 0.20 M (Na_2SO_4). ^c $[\text{Ru}(\text{III})] = 5.0 \times 10^{-4}\text{ M}$; $\text{pH} \approx 9.0$; 3-(cyclohexylamino)ethanesulfonic acid (CHES) buffer, 0.10 M; ionic strength = 0.20 M (Na_2SO_4).

Table II. Summary of Rate Parameters for the Reaction^a $\text{Ru}^{\text{III}}(\text{medtra})(\text{H}_2\text{O}/\text{OH}^-) + \text{L} \rightarrow \text{Ru}^{\text{III}}(\text{medtra})\text{L} + \text{H}_2\text{O}/\text{OH}^-$

ligand	pH	$k(25\text{ °C})$, $\text{M}^{-1}\text{ s}^{-1}$	ΔH^\ddagger , kJ mol^{-1}	ΔS^\ddagger , $\text{J K}^{-1}\text{ mol}^{-1}$	ΔV^\ddagger , $\text{cm}^3\text{ mol}^{-1}$
thiourea	≈ 2.5	2.34 ± 0.10	29.4 ± 1.0	-139 ± 2	-6.1 ± 0.7
	≈ 8.0	0.15 ± 0.04	31.5 ± 1.0	-158 ± 4	-8.9 ± 1.1
	≈ 9.0	0.11 ± 0.03			-9.7 ± 1.2^b
thiocyanate	≈ 2.5	0.28 ± 0.02	29.8 ± 1.4	-157 ± 4	-7.7 ± 0.5
	≈ 8.0	0.05 ± 0.01	32.0 ± 2.0	-163 ± 6	-15.4 ± 1.5
	≈ 9.0	0.05 ± 0.01			-15.1 ± 1.5^b

^a Citric acid/NaOH buffer, 0.10 M, for $\text{pH} \approx 2.5$; HCl/borate buffer, 0.025 M, for $\text{pH} \approx 8.0$; ionic strength = 0.20 M (Na_2SO_4). ^b CHES buffer; $\Delta V^\ddagger = 1.2 \pm 0.2\text{ cm}^3\text{ mol}^{-1}$.¹⁴

$k_1 = 0.28 \pm 0.02$, $k_2 = 0.04 \pm 0.01\text{ M}^{-1}\text{ s}^{-1}$, and $\text{p}K_a = 6.5 \pm 0.1$ for $\text{L} = \text{SCN}^-$. These $\text{p}K_a$ values are in good agreement with the value determined potentiometrically.

The temperature and pressure dependences were investigated under conditions where the reactions are independent of pH, i.e.

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Table III. Summary of Rate and Activation Parameters for the Reaction^a

$$\text{Ru}^{\text{III}}(\text{N/O})(\text{H}_2\text{O}/\text{OH}^-) + \text{L} \xrightarrow{k} \text{Ru}^{\text{III}}(\text{N/O})\text{L} + \text{H}_2\text{O}/\text{OH}^-$$

L	complex ^b	$k(25^\circ\text{C}), \text{M}^{-1} \text{s}^{-1}$	$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$\Delta S^\ddagger, \text{J K}^{-1} \text{mol}^{-1}$	$\Delta V^\ddagger, \text{cm}^3 \text{mol}^{-1}$	ref
SC(NH ₂) ₂	Ru(edta)H ₂ O ⁻	2970 ± 50	22 ± 1	-105 ± 5	-6.8 ± 0.6	6
	Ru(hedtra)H ₂ O	22.6 ± 1.0	34 ± 1	-105 ± 2	-4.1 ± 0.7	7
	Ru(medtra)H ₂ O	2.3 ± 0.1	29 ± 1	-139 ± 2	-6.1 ± 0.7	c
	Ru(hedtra)OH ⁻	2.8 ± 0.5			-7.1 ± 0.5	7
	Ru(medtra)OH ⁻	0.15 ± 0.04	31 ± 1	-158 ± 4	-8.9 ± 1.1	c
SC(NHMe) ₂	Ru(edta)H ₂ O ⁻	1450 ± 25	25 ± 1	-107 ± 4	-8.8 ± 0.2	6
	Ru(hedtra)H ₂ O	9.4 ± 2.0	37 ± 4	-99 ± 13	-6.2 ± 0.5	7
	Ru(edta)OH ²⁻	75 ± 5				6
SC(NMe ₂) ₂	Ru(edta)H ₂ O ⁻	154 ± 5	29 ± 3	-107 ± 11	-12.2 ± 0.5	6
	Ru(hedtra)H ₂ O	2.0 ± 0.2	39 ± 2	-108 ± 5	-10.4 ± 1.0	7
SCN ⁻	Ru(edta)H ₂ O ⁻	270 ± 27	37 ± 2	-75 ± 5	-9.6 ± 0.3	6
	Ru(hedtra)H ₂ O	6.8 ± 0.3	39 ± 2	-100 ± 7	-7.3 ± 0.6	7
	Ru(medtra)H ₂ O	0.28 ± 0.02	30 ± 1	-157 ± 4	-7.7 ± 0.5	c
	Ru(hedtra)OH ⁻	1.1 ± 0.1	40 ± 2	-105 ± 5	-10.8 ± 0.7	7
	Ru(medtra)OH ⁻	0.04 ± 0.01	32 ± 2	-163 ± 6	-15.4 ± 1.5	c
N ₃ ⁻	Ru(edta)H ₂ O ⁻	2070 ± 97	26 ± 3	-94 ± 10	-9.9 ± 0.5	6
	Ru(hedtra)H ₂ O	18.5 ± 2.6	38 ± 1	-92 ± 2		7
	Ru(edta)OH ²⁻	75 ± 10				6
	Ru(hedtra)OH ⁻	2.6 ± 0.1	45 ± 1	-86 ± 3	-14.1 ± 1.2	7

^aThe abbreviation N/O in the reaction represents the N- and O-bonded chelates. ^bThe data are presented in such a way that the reactivity of the different aqua and hydroxo complexes can be compared. ^cThis work.

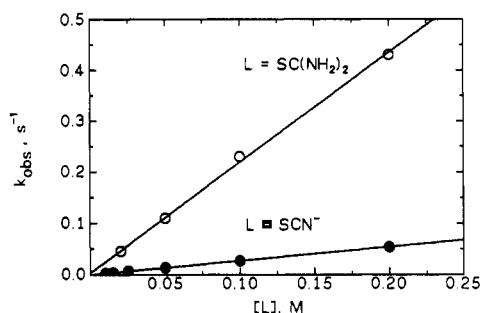


Figure 1. Dependence of k_{obs} on $[\text{L}]$ for the reaction of Ru(medtra)H₂O with thiourea and thiocyanate: $[\text{Ru}(\text{III})] = 5.0 \times 10^{-4} \text{ M}$; pH = 3.0 (citrate buffer, 0.10 M); ionic strength = 0.20 M (Na₂SO₄); temperature = 25.0 °C; open points, thiourea; closed points, thiocyanate.

at pH ≤ 4 and ≥ 8. The observed rate constants are summarized in Table I, and the corresponding activation parameters, in Table II. The significant difference between k_1 and k_2 is accompanied by a slightly higher value for ΔH^\ddagger and significantly more negative values for ΔS^\ddagger and ΔV^\ddagger . The latter trend especially could point at a substantial mechanistic difference for the two reaction paths. In order to rule out any possible contribution of the buffer toward the observed ΔV^\ddagger at high pH, the work was also repeated in CHES buffer, for which it is known that ΔV^\ddagger for conjugate base formation is almost zero and significantly smaller than for the borate buffer.¹⁴ The mechanistic difference will come out more clearly when the data in Table II are discussed in reference to the data reported before^{6,7} for the closely related edta and hedtra systems summarized in Table III.

The results in Table III underline the significant difference in rate constants for the substitution reactions of the aqua complexes as compared to the hydroxo complexes, i.e. reaction paths k_1 and k_2 in eqs 3 and 4, respectively. Within the series of aqua/hydroxo complexes, the substitution rate constants decrease substantially along the series edta >> hedtra > medtra, which is accompanied by a general increase in ΔH^\ddagger and almost constant ΔS^\ddagger and ΔV^\ddagger . From this trend we conclude that the highest lability is induced by the pendant group when R = CH₂COO⁻, which decreases significantly to R = CH₂CH₂OH and even further to R = CH₃. A decrease in reactivity of 3 orders of magnitude in going from R = CH₂COO⁻ to R = CH₃ must emphasize the important role of the dangling carboxylate group in the lability of the co-

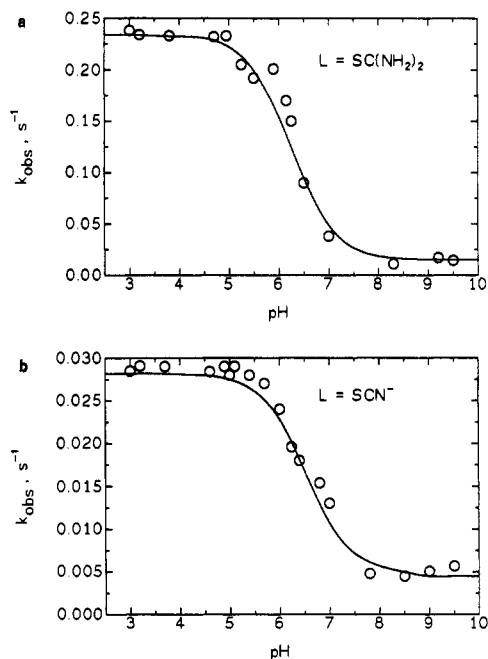


Figure 2. Variation of k_{obs} with pH for the reaction of Ru(medtra)H₂O with L. (a) $[\text{Ru}(\text{III})] = 5.0 \times 10^{-4} \text{ M}$; [thiourea] = 0.10 M; ionic strength = 0.20 M (Na₂SO₄); temperature = 25.0 °C; solid line, calculated by using resolved rate constants; open points, observed rate constants. (b) $[\text{Ru}(\text{III})] = 5.0 \times 10^{-4} \text{ M}$; [thiocyanate] = 0.10 M; ionic strength = 0.20 M (Na₂SO₄); temperature = 25.0 °C; solid line, calculated by using resolved rate constants; open points, observed rate constants.

ordinated water molecule. It is unlikely that hydrogen bonding can account for this lability when it results in deprotonation of the bound water molecule since the corresponding hydroxo species is significantly less labile. Alternatively, it may result in the creation of an open area and accessible site for associative ligand attack, as suggested before.^{3,6} A similar effect may also account for the lability of coordinated hydroxide in the case of the edta complex when the data for L = SC(NH₂)₂ and SC(NHMe)₂ are compared. Protonation of the acetate moiety resulted in a 20-fold decrease in the substitution rate constant,⁶ which is still ca. 6 times larger than for the hedtra ligand (i.e. R = CH₂CH₂OH). It follows that the carbonyl oxygen atom may play a prominent role in the lability process (see further text in Results and Discussion).

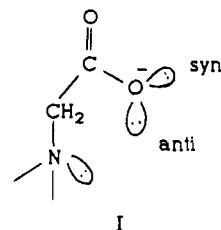
(14) Kitamura, Y.; Itoh, T. *J. Solution Chem.* 1987, 16, 715. CHES = 3-(cyclohexylamino)ethanesulfonic acid.

Another important trend reflected by the data in Table III is the significant decrease in k with increasing steric hindrance on the entering ligand, i.e. in going from thiourea to substituted thiourea. Again this trend is accompanied by an increase in ΔH^\ddagger , almost constant ΔS^\ddagger , and more negative ΔV^\ddagger values. The latter trend reflects the importance of bond formation, since an increase in the size of the entering ligand will be accompanied by an increase in the overlap of the van der Waals radii during bond formation, i.e. a more negative ΔV^\ddagger . This volume decrease will mainly result from intrinsic volume changes for neutral entering ligands but could partially result from charge concentration during the reactions with the anionic ligands. Nevertheless, the latter effect is not overruling when the results are compared for neutral and anionic entering ligands in Table III. Furthermore, for a specific complex the rate constant does depend on the nucleophilicity of the entering ligand but does not vary over more than 1 order of magnitude for the nucleophiles studied. These observations underline the operation of an I_a mechanism in terms of which there is a fine balance between the ability of the ligand to enter the coordination sphere and the induced lability of the leaving water molecule as influenced by the pendant R group.

The increased bond strength in the case of the hydroxo complexes must account for the significantly lower rate constants. In addition, some of these reactions exhibit remarkably negative ΔV^\ddagger values, significantly more negative than would be expected on the basis of electrostriction effects only. For instance, compare the value of $-15.4 \text{ cm}^3 \text{ mol}^{-1}$ for the substitution of $\text{Ru}(\text{medtra})\text{OH}^-$ by SCN^- with a value of $-9.6 \text{ cm}^3 \text{ mol}^{-1}$ for the substitution of $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ by SCN^- . The electrostriction effects should be very similar in both cases, such that the more negative ΔV^\ddagger value observed for the hydroxo complex may indeed indicate that a limiting A mechanism is operative. This means that an increase in the Ru-O bond strength causes a changeover from I_a to A. A similar trend is also observed for the substitution reactions involving the neutral entering ligands: ΔV^\ddagger is throughout more negative for the hydroxo than for the corresponding aquo complexes. Although we ascribed this effect to electrostriction previously,⁷ the data added in this study encourage us to think in terms of a possible changeover in mechanism from I_a to A, depending on the lability of the leaving group. This effect seems to be the strongest for the hedtra and medtra complexes, i.e. where the Ru-O bond strength is of utmost importance.

We now return to the remarkable lability effect of the pendant carboxylate moiety in the $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ complex. The importance of hydrogen bonding to account for such lability effects has also been emphasized for closely related systems.^{15,16}

However, the detailed mechanism of this effect remains unresolved. It was recently reported^{17,18} that the syn lone pair of electrons may be 10^2 – 10^5 times more basic than the anti lone pair of the carboxylate oxygen. This is due to the fact that the anti electrons in an orbital parallel to the carbonyl double bond are partially tied up in that double bond and therefore less available for bonding (see diagram I). It is therefore reasonable to consider the pos-



sibility that the pendant carboxylate group in $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ is positioned in such a way that the syn lone pair can interact with the coordinated water molecule and so account for the extreme lability. This would also account for our recent observation that the rate of this process in D_2O is very similar, within experimental error limits, to that found in water.¹⁹

Finally, this work was originally undertaken in an effort to throw more light on the extreme lability observed in $\text{Fe}^{\text{II/III}}(\text{edta})$ complexes. Our most recent views on the latter system^{20–22} point more in the direction of a seven-coordinate aquo complex in which six coordination sites are occupied by the edta ligand in both oxidation states. This would not allow such a lability effect of the pendant carboxylate group as described above, although a dynamic effect of such a group cannot be ruled out.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Max-Buchner Forschungstiftung, and DAAD for a stipend to H.C.B.

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