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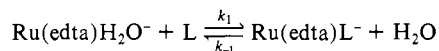
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Properties and Reactivities of Pentadentate Ethylenediaminetetraacetate Complexes of Ruthenium(III) and -(II)

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The reaction of the pentadentate edta complex of ruthenium(III) with various entering ligands L has been studied as a function of pH, temperature, and L at 0.2 M ionic strength in aqueous solution. Over the pH range 0.8-8.5, the species $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ is the sole form reactive in the substitution processes. Both forward (k_1) and reverse (k_{-1}) rate constants



have been determined, as well as activation parameters for the complexation (k_1) process (L, k_1 in $\text{M}^{-1} \text{s}^{-1}$ (25 °C), k_{-1} in s^{-1} (25 °C), ΔH_1^\ddagger in kcal mol^{-1} , ΔS_1^\ddagger in $\text{cal deg}^{-1} \text{mol}^{-1}$): acetonitrile, 30 ± 7 , 3.2 ± 0.2 , 8.3 ± 0.5 , -24 ± 4 ; thiocyanate, 270 ± 20 , 0.5 ± 0.1 , 8.9 ± 0.5 , -18 ± 3 ; pyridine, 6300 ± 500 , 0.061 ± 0.002 ; isonicotinamide, 8300 ± 600 , 0.7 ± 0.2 , 6.6 ± 0.5 , -19 ± 3 ; pyrazine, 20000 ± 1000 , 2.0 ± 0.5 , 5.7 ± 0.5 , -20 ± 3 . Forward rate constants for the analogous substitution reaction for $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ (25 °C, 0.2 M ionic strength) are as follows: thiocyanate, $2.7 \pm 0.2 \text{ M}^{-1} \text{s}^{-1}$; acetonitrile, $13 \pm 1 \text{ M}^{-1} \text{s}^{-1}$; isonicotinamide, $30 \pm 15 \text{ M}^{-1} \text{s}^{-1}$. The substitution reactions of $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ proceed by an associative mechanism, while those of $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ appear to be dissociative in nature. Spectra and reduction potentials for the $\text{Ru}(\text{edta})\text{L}^{-/2-}$ complexes are reported.

Introduction

Although ethylenediaminetetraacetate (edta) complexes of Ru(III) have been known for more than a decade,¹⁻³ knowledge of the chemistry of these systems is quite limited. Electrochemical studies⁴ have shown that electron transfer is rapid and reversible for the $\text{Ru}(\text{edta})\text{H}_2\text{O}^{-/2-}$ couple and that $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ is oxidized by perchlorate ion. Recently, Shimizu⁵ has reported the reaction of $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ with formate ion to form the carbonyl complex $\text{Ru}^{\text{II}}(\text{edta})\text{CO}^{2-}$ at an appreciable rate. Oyama and Anson⁶ have accomplished the attachment of the edta complex of Ru(III) to a graphite electrode surface through the uncoordinated carboxylate group of edta and reported electrochemical data for several $\text{Ru}(\text{edta})\text{L}^{-/2-}$ couples.

We have found that it is possible to generate an extensive series of substituted pentadentate edta complexes of both ruthenium(III) and ruthenium(II) ($\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$ and $\text{Ru}^{\text{II}}(\text{edta})\text{L}^{2-}$) in which L ranges from water to N aromatic heterocycles.⁷ Analogous series have been characterized for $\text{Ru}(\text{NH}_3)_5\text{L}^{3+}$ and $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$.^{8,9} Comparison of the properties of this edta series with those of the amines may provide insight concerning the role of the ligands in determining the reactivity and properties of the metal center. Further, since the substituted species $\text{Ru}(\text{edta})\text{L}$ may be generated for both Ru(III) and Ru(II), the role of the metal oxidation state may be systematically explored for this series as has been done for the amines.¹⁰⁻¹²

In preliminary studies, we discovered similarities in the properties of $\text{Ru}^{\text{II}}(\text{edta})\text{L}^{2-}$ and $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$. When L is an aromatic N heterocycle, the visible metal-to-ligand charge-transfer spectra are very similar. Studies of the rates of formation of such complexes revealed, however, that the reactivities of the edta complexes toward substitution differ dramatically from those of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$.^{9,13-19}

In this report we present the results of studies of the substitution reactions of $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ and $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$, as well as spectral and electrochemical properties of the $\text{Ru}(\text{edta})\text{L}^{-/2-}$ complexes.

Experimental Section

Materials. The pentadentate ethylenediaminetetraacetate (edta) complex of ruthenium(III), $\text{Ru}(\text{Hedta})\text{H}_2\text{O} \cdot 4\text{H}_2\text{O}$, was prepared according to the literature procedure.¹ Electronic and infrared spectra of this complex agreed well with the reported values.¹ The complex was also characterized by titration with a standard sodium hydroxide solution in 0.2 M potassium trifluoromethanesulfonate (Ktfms).

The complex anion $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ was prepared in situ in acetate buffer solution by the reduction of $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ with zinc amalgam under argon or with molecular hydrogen at a platinum-black surface.

Commercial trifluoromethanesulfonic acid (Htfms, 3 M Co.) was purified by distillation under reduced pressure (bp 54 °C (8 torr)). The initial and final 10% aliquots were discarded and the middle 80% fraction was collected. Ktfms was obtained by neutralizing a warm aqueous Htfms solution with potassium carbonate. All other reagents were the highest purity commercially available and were used without further purification. Triply distilled water was used throughout.

Physical Measurements. UV and visible spectral measurements were carried out with Cary 14 and 17 spectrometers. For the binding of $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ to acetonitrile, equilibrium constants were calculated from slope-to-intercept ratios of plots of $(\Delta A)^{-1}$ vs. $[\text{L}]^{-1}$, where ΔA is the absorbance change accompanying complexation and $[\text{L}]$ is the molar concentration of the ligand.²⁰ The electronic spectral band maxima and molar absorptivities of $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$ and $\text{Ru}^{\text{II}}(\text{edta})\text{L}^{2-}$ were measured for equilibrated solutions in which more than 90% of the Ru species was complexed with a single L. This procedure was necessary since a second molecule of L may coordinate at high concentrations of L.

Rates of rapid reactions were measured with a Durrum-Gibson stopped-flow instrument which was modified as previously described.²¹ Slower reaction rates were measured with Cary 14, 16, and 17 spectrometers. The substitution kinetics were studied in the presence of at least tenfold excess ligand. The redox processes were studied

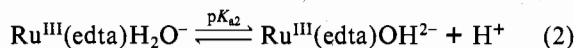
with $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^{2-}$ in at least tenfold excess over $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$. Transmittance vs. time curves were monitored in the charge-transfer wavelength region of the products where large transmittance changes were expected. For $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$, this was usually in the range 300–400 nm and for $\text{Ru}^{\text{II}}(\text{edta})\text{L}^{2-}$ in the range 300–500 nm depending on the ligand. Pseudo-first-order rate constants (k_{obsd}) were calculated from the semilogarithmic plots of absorbance change ($A_t - A_\infty$) vs. time.

Cyclic voltammetric measurements were carried out with a Princeton Applied Research Model 176 potentiostat-galvanostat and a Model 175 universal programmer. Voltammograms were recorded on a Hewlett-Packard Model 7000A X-Y recorder. The electrochemical cell used was a conventional three-electrode type with an aqueous saturated calomel electrode (SCE) as a reference electrode and a piece of platinum wire as the auxiliary electrode. Three types of working electrodes, a hanging drop mercury electrode (HDME), a platinum button electrode (PBE), and a pyrolytic graphite electrode (PGE)²² were used. The reversibility of the electrode reactions decreased in the order HDME > PBE > PGE. Therefore, the HDME was used in most measurements, and the formal reduction potentials were calculated by using the midpoint of the anodic and cathodic peaks of reversible cyclic voltammograms. Formal reduction potentials reported here are all vs. the normal hydrogen electrode (NHE). The errors due to junction potentials and the difference in diffusion coefficients between the oxidized and reduced forms of the complexes have been neglected, and the potentials are reported to ± 0.010 V.

pH Measurements were carried out with a Beckman Research pH meter which was calibrated with commercial standard buffers at room temperature. All kinetic, spectral, and electrochemical measurements were carried out at 25.0 ± 0.2 °C except when the effect of temperature was studied. Acetate, phosphate, and borate buffers were used at pHs above 3.5, and Htms was used at pHs below 3. The ionic strengths of all the solutions were adjusted to 0.2 M with Ktms.

Results

Alkalimetric titration of $\text{Ru}(\text{Hedta})\text{H}_2\text{O}\cdot 4\text{H}_2\text{O}$ in 0.2 M Ktms gave two pH inflections. The volume ratio of the sodium hydroxide solution to the second and first equivalent points was 2.00, and the equivalent weight of the complex was calculated to be 239 ± 1 . This was consistent with the molecular weight 480.4 calculated for $\text{Ru}(\text{Hedta})\text{H}_2\text{O}\cdot 4\text{H}_2\text{O}$. The $\text{p}K_{\text{a}}$ values of these two protonation-deprotonation processes were calculated from the titration curve to be 2.37 and 7.63, consistent with values reported earlier.¹ The more acidic $\text{p}K_{\text{a}1}$ value corresponds to the deprotonation of the uncoordinated carboxylic acid group of edta ligand, and the more basic $\text{p}K_{\text{a}2}$ corresponds to that of coordinated water.



Both $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ and $\text{Ru}(\text{edta})\text{H}_2\text{O}^{2-}$, when mixed with excess L in pH ~ 5 aqueous solutions, undergo substitution reactions with L. Depending on the concentration and nature of L, complexes containing one, two, or more molecules of L per ruthenium may be obtained. For example, solid samples obtained from the overnight reaction of $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ with pyrazine contain two molecules of pyrazine per Ru(II). When $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ is mixed with 1 M thiocyanate ion, visible spectral changes associated with the binding of one and two thiocyanate ions are resolvable, while over a period of several hours, further changes corresponding to the binding of a third, and perhaps a fourth, thiocyanate ion can be observed. At the other extreme of conditions, i.e., when $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ or $\text{Ru}(\text{edta})\text{H}_2\text{O}^{2-}$ is in excess over L, complications may be encountered with bifunctional ligands such as pyrazine and thiocyanate. These groups may bind simultaneously to two metal centers and so give rise to binuclear complexes. These potential complications were taken into account in designing the experiments from which the electrochemical and spectral properties of the monosubstituted edta complexes were obtained.

Table I. Electronic Spectra of $\text{Ru}(\text{edta})\text{L}$ Complexes^a

| complex | λ_{max} , nm | ϵ_{max} , $\text{M}^{-1} \text{cm}^{-1}$ |
|---|-----------------------------|--|
| $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ | 350 sh 280 | 680 ± 30 sh 2800 ± 50 |
| $\text{Ru}^{\text{III}}(\text{edta})\text{NCS}^{2-}$ | 460 358 282 | 1010 ± 50 974 ± 50 2990 ± 100 |
| $\text{Ru}^{\text{III}}(\text{edta})\text{isn}^-$ | <i>b</i> | |
| $\text{Ru}^{\text{III}}(\text{edta})\text{pz}^-$ | <i>c</i> | |
| $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ | 282 427 | 2900 ± 100 260 ± 15 |
| $\text{Ru}^{\text{II}}(\text{edta})\text{NCS}^{3-}$ | <i>c</i> | |
| $\text{Ru}^{\text{II}}(\text{edta})\text{py}^{2-}$ | 382 | 6760 ± 600 |
| $\text{Ru}^{\text{II}}(\text{edta})\text{isn}^{2-}$ | 460 | $11\,000 \pm 1000$ |
| $\text{Ru}^{\text{II}}(\text{edta})\text{pz}^{2-}$ | 463 | $11\,600 \pm 1000$ |
| $\text{Ru}^{\text{II}}(\text{edta})\text{CH}_3\text{pz}^-$ | 558 | $19\,400 \pm 1500$ |

^a Measured in acetate buffer, pH 5.5, $\mu = 0.2$ M (Ktms); 25.0 °C; pz = pyrazine, isn = isonicotinamide, CH_3pz^+ = *N*-methylpyrazinium ion. ^b No peaks or shoulders were observed at $\lambda \geq 300$ nm. ^c No peaks or shoulders were observed at $\lambda \geq 320$ nm.

Table II. Formal Reduction Potentials of $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-/\text{Ru}^{\text{II}}(\text{edta})\text{L}^{2-}$ Couples^d

| L | E_f , V | ΔE_p , V ^a |
|-----------------|--------------------|-------------------------------|
| water | -0.01 ± 0.01^b | 0.070 |
| thiocyanate | $+0.07 \pm 0.01^b$ | 0.065 |
| pyridine | $+0.10 \pm 0.01^b$ | 0.060 |
| imidazole | $+0.10 \pm 0.01^c$ | 0.060 |
| isonicotinamide | $+0.16 \pm 0.01^b$ | 0.060 |
| pyrazine | $+0.24 \pm 0.01^b$ | 0.060 |
| acetonitrile | $+0.26 \pm 0.01^b$ | 0.060 |

^a Separation between the anodic and cathodic peaks of the cyclic voltammogram. ^b Acetate buffer, pH 5.5, $\mu = 0.2$ M (Ktms). ^c Imidazole buffer, pH 7.0, $\mu = 0.2$ M (Ktms). ^d At 25.0 °C.

Electronic Spectra of $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$ and $\text{Ru}^{\text{II}}(\text{edta})\text{L}^{2-}$. The electronic spectra of the edta complexes of Ru(III) and Ru(II), measured in pH 5.1–5.5 acetate buffer ($\mu = 0.2$ M (Ktms), 25.0 °C), are summarized in Table I. No characteristic peaks or shoulders were observed for L = isonicotinamide and pyrazine at wavelengths longer than 300 and 320 nm, respectively, for the $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$ species; however, the molar absorptivity in the UV range was significantly larger than that of $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$. Only when thiocyanate or iodide was coordinated, were well-defined visible bands observed for the Ru(III) complexes.

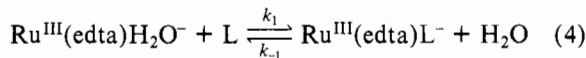
By contrast, the isonicotinamide (isn) and pyrazine complexes of Ru(II) exhibited intense bands in the visible region. Although the molar absorptivity of the acetonitrile complex of $\text{Ru}^{\text{II}}(\text{edta})^{2-}$ was larger than that of $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ in the UV range, the spectrum of the acetonitrile complex lacked in characteristic features.

Formal Potentials of $\text{Ru}(\text{edta})\text{L}^{-/2-}$ Couples. The formal electrode potentials were measured in acetate buffer at pH 4.5 for the $\text{Ru}(\text{edta})\text{L}^{-/2-}$ couples (eq 3). A 10^{-3} M solution

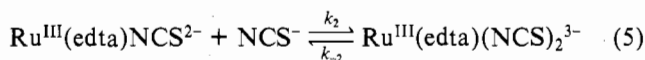


of $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ was titrated with ligand. (For L = pyrazine, 10^{-3} M pyrazine was titrated with $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$.) In the absence of L the single reversible cyclic voltammogram of $\text{Ru}(\text{edta})\text{H}_2\text{O}^{-/2-}$ was seen. After the addition of 0.5 equiv of L, a second reversible couple was observed. After the addition of 1 equiv of L, the original voltammogram of the $\text{Ru}(\text{edta})\text{H}_2\text{O}^{-/2-}$ couple disappeared. This final voltammogram was used to evaluate the formal potential of $\text{Ru}(\text{edta})\text{L}^{-/2-}$. The reduction potentials measured are listed in Table II. The potentials of the $\text{Ru}(\text{edta})\text{H}_2\text{O}^{-/2-}$ and $\text{Ru}(\text{edta})\text{isn}^{-/2-}$ couples are in good agreement with values reported by other workers.^{4,6}

Substitution Reactions of the edta Complex of Ru(III). The addition of potassium thiocyanate to an acetate buffer solution containing the pentadentate edta complex of Ru(III) gave an almost instantaneous color change to dark red. Purple developed when potassium iodide was added to the same starting solution. These color changes represent the ligand-substitution reactions shown in eq 4 where $L^- = I^-$ or SCN^- . Preliminary



study of the reaction with $L =$ thiocyanate in acetate buffer (thiocyanate in tenfold excess) indicated the presence of two consecutive reactions. The absorbance change vs. time curve monitored at 470 nm could be analyzed in terms of two exponential decays. The absorbance change due to the initial step was more than 80% of the total change, and the observed pseudo-first-order rate constant (k_{obsd}) was at least 10 times greater than that of the second step. The second step most likely represents the coordination of second thiocyanate ion to form the quadridentate edta complex as shown in eq 5.



The kinetic study of this slower second step in the thiocyanate reaction was carried out in detail under pseudo-first-order conditions in acetate buffer solutions. After the rapid first stage the absorbance change vs. time curves monitored in the 470–510-nm range were exponential for at least 4 half-lives. The observed pseudo-first-order rate constants were independent of monitoring wavelength. A plot of the observed rate constants vs. thiocyanate concentration was linear with slope $(2.8 \pm 0.5) \times 10^{-3} M^{-1} s^{-1}$ and intercept $(1.6 \pm 0.2) \times 10^{-3} s^{-1}$. The spectrophotometric determination of the equilibrium constant for this process (K_2) with the use of the absorbance changes at 470 nm gave $1.5 \pm 0.3 M^{-1}$ for the formation of $Ru^{III}(edta)(NCS)_2^{3-}$. This is in good agreement with the slope/intercept value $1.8 \pm 0.4 M^{-1}$ obtained from the plots of k_{obsd} vs. $[SCN^-]$. The agreement between the spectrophotometric K_2 and the slope/intercept ratio demonstrated that the slope and intercept correspond to k_2 and k_{-2} , respectively, in eq 5. At 0.05 M SCN^- , k_{obsd} was independent of the acetate buffer concentration ($0.01 M \leq [OAc^-] \leq 0.15 M$) and the complex concentration ($5 \times 10^{-5} M \leq [Ru^{III}(edta)H_2O^-] \leq 7 \times 10^{-4} M$); however, it was dependent on pH, decreasing from $(1.7 \pm 0.1) \times 10^{-3} s^{-1}$ at pH 5.1 to less than $10^{-4} s^{-1}$ at pH 1.1. These observations clarified the nature of the second step which might interfere in the analysis of the kinetic data for the first step.

The stopped-flow kinetics of the initial rapid reactions (eq 4) were studied in acetate buffer in the pH range 5.1–5.5 under pseudo-first-order conditions. The transmittance vs. time curves were monitored in the 280–350-nm range for $L =$ pyrazine, pyridine, isonicotinamide, acetonitrile, and imidazole and in the 470–510-nm range for $L =$ thiocyanate. In all cases, the plots of the absorbance change vs. time were exponential for at least 2 half-lives. The long-time deviations from exponential behavior were ascribed to the secondary reactions (vide supra) which were responsible for up to 20% of the total absorbance changes. There was a ca. 10% rate increase when the acetate buffer concentration decreased from 0.15 to 0.01 M. Since this effect was relatively small, the rate variation due to the buffer concentration was neglected, and the data were collected in the 0.05–0.10 M buffer concentration range. The pseudo-first-order rate constants thus obtained were proportional to the concentration of the incoming ligand;⁷ data for $L^- = SCN^-$ are summarized in Table III.²³ The ratio of intercept to slope for $L =$ acetonitrile was in good agreement with the slope-to-intercept ratio (K_1) obtained from a plot of $(\Delta A)^{-1}$ vs. $[L]^{-1}$ (Figure 1). Therefore, the slopes and in-

Table III. Observed Pseudo-First-Order Rate Constants (k_{obsd}) for the Reaction of the edta Complex of Ru(III) with $L =$ Thiocyanate Ion^a

| pH | [Ru(III)], M | [L], M | k_{obsd} , s ⁻¹ |
|-------------------|----------------------|--------|------------------------------|
| 0.94 | 9.3×10^{-5} | 0.05 | 0.8 ± 0.1 |
| 0.98 | 1.0×10^{-4} | 0.05 | 0.71 ± 0.02 |
| 0.98 | 1.0×10^{-4} | 0.025 | 0.36 ± 0.01 |
| 0.98 | 1.0×10^{-4} | 0.01 | 0.15 ± 0.01 |
| 0.98 | 1.0×10^{-4} | 0.005 | 0.08 ± 0.01 |
| 1.13 | 1.0×10^{-4} | 0.05 | 1.0 ± 0.1 |
| 1.42 | 9.3×10^{-5} | 0.05 | 1.5 ± 0.1 |
| 1.72 | 9.7×10^{-5} | 0.05 | 2.6 ± 0.1 |
| 2.10 | 1.1×10^{-4} | 0.05 | 4.7 ± 0.1 |
| 2.40 | 1.0×10^{-4} | 0.05 | 6.7 ± 0.2 |
| 2.82 | 1.0×10^{-4} | 0.05 | 11.7 ± 0.1 |
| 2.94 | 1.0×10^{-4} | 0.05 | 12.2 ± 0.1 |
| 4.16 | 9.9×10^{-5} | 0.05 | 13.6 ± 0.1 |
| 4.50 | 8.1×10^{-5} | 0.1 | 26.1 ± 0.2 |
| 4.50 | 9.5×10^{-5} | 0.05 | 14.7 ± 0.1 |
| 4.50 | 9.6×10^{-5} | 0.025 | 6.8 ± 0.2 |
| 4.50 | 9.6×10^{-5} | 0.01 | 3.4 ± 0.2 |
| 4.50 | 9.6×10^{-5} | 0.005 | 1.8 ± 0.2 |
| 4.64 ^b | 1.0×10^{-4} | 0.05 | 11.7 ± 0.2 |
| 4.64 ^c | 1.0×10^{-4} | 0.05 | 13.7 ± 0.5 |
| 4.64 ^d | 1.0×10^{-4} | 0.05 | 14.3 ± 0.3 |
| 4.64 ^e | 1.0×10^{-4} | 0.05 | 16.0 ± 0.5 |
| 5.50 ^f | 1.0×10^{-4} | 0.005 | 1.10 ± 0.01 |
| 5.50 ^f | 1.0×10^{-4} | 0.003 | 0.76 ± 0.01 |
| 5.50 ^f | 1.0×10^{-4} | 0.001 | 0.46 ± 0.01 |
| 5.50 ^g | 1.0×10^{-4} | 0.01 | 0.82 ± 0.02 |
| 5.50 ^g | 1.0×10^{-4} | 0.005 | 0.42 ± 0.01 |
| 5.50 ^g | 1.0×10^{-4} | 0.003 | 0.27 ± 0.01 |
| 5.50 ^g | 1.0×10^{-4} | 0.001 | 0.112 ± 0.004 |
| 6.12 | 1.0×10^{-4} | 0.05 | 13.5 ± 0.2 |
| 6.56 | 1.0×10^{-4} | 0.05 | 12.4 ± 0.2 |
| 7.07 | 1.0×10^{-4} | 0.05 | 9.8 ± 0.2 |
| 7.74 | 1.0×10^{-4} | 0.1 | 11.0 ± 0.1 |
| 7.74 | 1.0×10^{-4} | 0.05 | 5.4 ± 0.1 |
| 7.74 | 1.0×10^{-4} | 0.03 | 3.4 ± 0.1 |
| 7.74 | 1.0×10^{-4} | 0.01 | 1.0 ± 0.1 |
| 8.58 | 1.0×10^{-4} | 0.1 | 3.2 ± 0.1 |
| 8.58 | 1.0×10^{-4} | 0.05 | 1.7 ± 0.1 |
| 8.58 | 1.0×10^{-4} | 0.03 | 0.95 ± 0.01 |

^a Unless otherwise stated the rate constants were measured in buffer solutions with $\mu = 0.2 M$ (Ktfms) and at 25.0 °C. ^b $[HOAc] = [KOAc] = 0.15 M$. ^c $[HOAc] = [KOAc] = 0.10 M$. ^d $[HOAc] = [KOAc] = 0.05 M$. ^e $[HOAc] = [KOAc] = 0.02 M$. ^f 15.0 °C. ^g 3.3 °C.

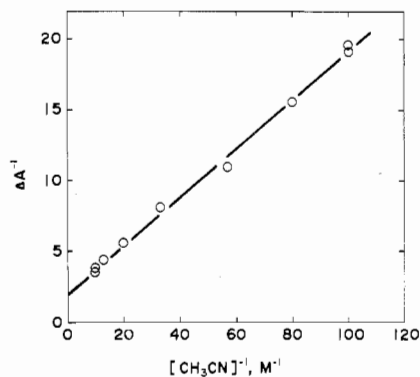


Figure 1. Plot of the reciprocal absorbance change (ΔA^{-1}) monitored at 310 nm vs. the reciprocal incoming ligand concentration for the reaction $Ru^{III}(edta)H_2O^- + CH_3CN \rightleftharpoons Ru^{III}(edta)CH_3CN^- + H_2O$; pH 5.5 (acetate buffer), $\mu = 0.2 M$ (Ktfms), 25.0 °C.

tercepts of the k_{obsd} vs. $[L]$ plot were interpreted as the forward (k_1) and reverse (k_{-1}) rate constants, respectively (Table IV). The activation parameters for reaction 4 were obtained from the temperature dependence of k_1 (and for SCN^- and CH_3CN , k_{-1} , as well) over the temperature range 3–25 °C and are given in Table V.

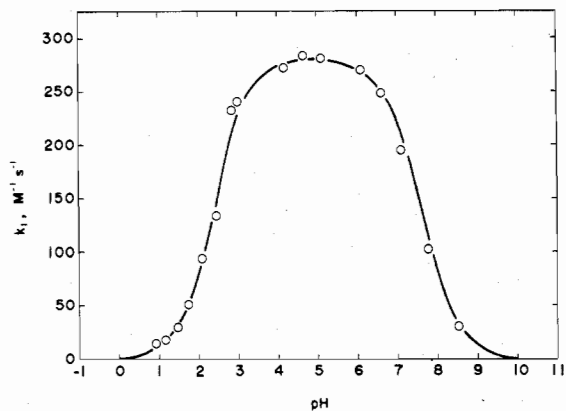


Figure 2. Plot of the second-order rate constant (k_1) vs. pH for the reaction of thiocyanate ion with the edta complex of Ru(III): $\mu = 0.2$ M (Ktfs), 25.0 °C.

Table IV. Rate Constants for the Substitution Reactions of $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ at 25.0 °C

| ligand | $k_1, \text{M}^{-1} \text{s}^{-1}$ | k_{-1}, s^{-1} | $k_1/k_{-1}, \text{M}^{-1}$ |
|------------------------------|------------------------------------|-------------------------|-----------------------------|
| acetonitrile ^a | 30 ± 7 | 3.2 ± 0.2 | $9 \pm 3, 11 \pm 2^c$ |
| thiocyanate ^a | 270 ± 20 | 0.5 ± 0.1 | 540 ± 100 |
| imidazole ^b | 1860 ± 100 | | |
| pyridine ^c | 6300 ± 500 | 0.061 ± 0.002 | $100\,000 \pm 30\,000$ |
| isonicotinamide ^a | 8300 ± 600 | 0.7 ± 0.2 | $12\,000 \pm 3000$ |
| pyrazine ^a | $20\,000 \pm 1000$ | 2.0 ± 0.5 | $10\,000 \pm 3000$ |

^a Acetate buffer, pH 5.1–5.5, $\mu = 0.2$ M (Ktfs). ^b Imidazole buffer, pH 7.2, $\mu = 0.2$ M (Ktfs). ^c Pyridine buffer, pH 5.2, $\mu = 0.2$ M (Ktfs). ^d K_1 determined spectrophotometrically at 310 nm.

The effect of pH on the observed rate constant was relatively small in acetate buffer solutions; however, a very large effect of pH was observed outside the acetate buffer region (Table III). Figure 2 shows the effect of pH on the second-order rate constant (k_1) of the reaction with thiocyanate. A maximum value was obtained in the acetate buffer region $4 < \text{pH} < 6$, and the second-order rate constant decreased at both sides of this pH range. The second-order rate constant dropped to half of the maximum value at pH 2.4 and 7.6, the pH values which correspond to the $\text{p}K_a$'s of $\text{Ru}^{\text{III}}(\text{Hedta})\text{H}_2\text{O}$. This pH dependence of k_1 may be analyzed in terms of reaction pathways a–c

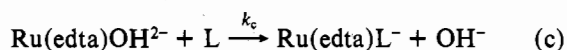
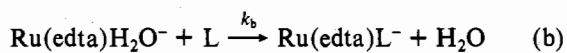
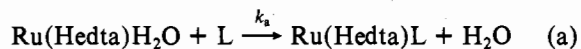


Table V. Temperature Dependence of the Substitution Reactions of $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$

| ligand | $T, ^\circ\text{C}$ | $k_1, \text{M}^{-1} \text{s}^{-1}$ | k_{-1}, s^{-1} | $\Delta H^\ddagger, \text{kcal mol}^{-1}$ | $\Delta S^\ddagger, \text{eu}$ | $\Delta H^\circ, \text{kcal mol}^{-1}$ | $\Delta S^\circ, \text{eu}$ |
|-----------------|---------------------|------------------------------------|-------------------------|---|--------------------------------|--|-----------------------------|
| acetonitrile | 25.0 | 30 ± 7 | 3.2 ± 0.2 | 8.3 ± 0.5 | -24 ± 4 | -10.0 ± 2.5 | -30 ± 8 |
| | 15.0 | 15 ± 1 | 1.4 ± 0.1 | | | | |
| | 4.5 | 10 ± 1 | 0.4 ± 0.1 | | | | |
| thiocyanate | 25.0 | 270 ± 20 | 0.5 ± 0.1 | 8.9 ± 0.5 | -18 ± 3 | -12.5 ± 2.5 | -28 ± 8 |
| | 15.0 | 145 ± 15 | 0.3 ± 0.1 | | | | |
| | 3.3 | 77 ± 3 | 0.4 ± 0.1 | | | | |
| isonicotinamide | 25.0 | 8300 ± 600 | 0.7 ± 0.2 | 6.6 ± 0.5 | -19 ± 3 | | |
| | 15.0 | 5100 ± 300 | | | | | |
| | 3.3 | 3200 ± 100 | | | | | |
| pyrazine | 25.0 | $20\,000 \pm 1000$ | 2.0 ± 0.5 | 5.7 ± 0.5 | -20 ± 3 | | |
| | 15.0 | $14\,400 \pm 600$ | | | | | |
| | 3.8 | 8400 ± 300 | | | | | |

^a Acetate buffer, pH 5.1–5.5, $\mu = 0.2$ M (Ktfs).

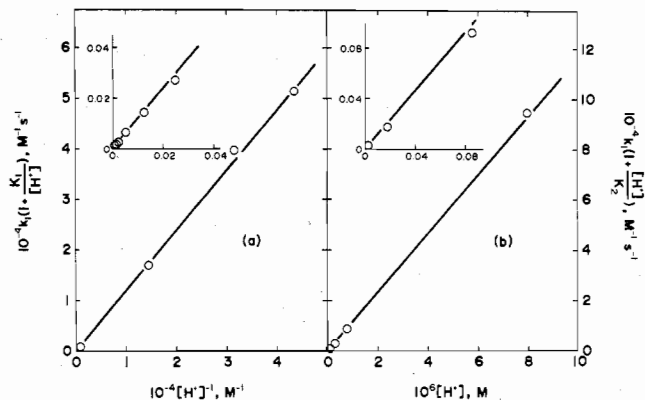


Figure 3. (a) Plot of the function $k_1(1 + K_1/[\text{H}^+])$ vs. $[\text{H}^+]^{-1}$ and (b) plot of the function $k_1(1 + [\text{H}^+]/K_2)$ vs. $[\text{H}^+]$ for the reaction of the edta complex of Ru(III) with thiocyanate: $\mu = 0.2$ M (Ktfs), 25.0 °C.

where the equilibria among the reactants may be expressed as

$$K_{a1} = \frac{[\text{Ru}(\text{edta})\text{H}_2\text{O}^-][\text{H}^+]}{[\text{Ru}(\text{Hedta})\text{H}_2\text{O}]} = 4.27 \times 10^{-3} \text{ M}$$

$$K_{a2} = \frac{[\text{Ru}(\text{edta})\text{OH}^{2-}][\text{H}^+]}{[\text{Ru}(\text{edta})\text{H}_2\text{O}^-]} = 2.34 \times 10^{-8} \text{ M}$$

Then the rate of formation of products is given by

$$\frac{d}{dt} \{ [\text{Ru}(\text{Hedta})\text{L}] + [\text{Ru}(\text{edta})\text{L}^-] \} = [\text{L}] \times \{ k_a[\text{Ru}(\text{Hedta})\text{H}_2\text{O}] + k_b[\text{Ru}(\text{edta})\text{H}_2\text{O}^-] + k_c[\text{Ru}(\text{edta})\text{OH}^{2-}] \}$$

which leads to the following expression for the observed second-order rate constants:

$$k_1 = \frac{k_c K_{a1} K_{a2} + k_b K_{a1} [\text{H}^+] + k_a [\text{H}^+]^2}{K_{a1} K_{a2} + K_{a1} [\text{H}^+] + [\text{H}^+]^2}$$

In order to simplify the data treatment we note that, from the shape of Figure 2 and in particular from the very low values of k_{obsd} at pH 1 and at pH 8.5, it is evident that $k_b \gg k_a$ or k_c . Thus it is reasonable to neglect contributions from path c at high $[\text{H}^+]$ (pH < 5) and from path a at low $[\text{H}^+]$ (pH > 5); the approximations

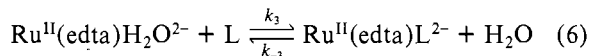
$$k_1 \approx \left(k_a + \frac{k_b K_{a1}}{[\text{H}^+]} \right) \left(1 + \frac{K_{a1}}{[\text{H}^+]} \right)^{-1} \quad \text{at pH} < 5$$

$$k_1 \approx \left(k_c + \frac{k_b [\text{H}^+]}{K_{a2}} \right) \left(1 + \frac{[\text{H}^+]}{K_{a2}} \right)^{-1} \quad \text{at pH} > 5$$

are then obtained. These relationships are tested in Figure 3. Figure 3a has a slope of $1.19 \pm 0.08 \text{ s}^{-1} = k_b K_{a1}$ from which $k_b = 279 \pm 18 \text{ M}^{-1} \text{ s}^{-1}$. The intercept of Figure 3a is $<10 \text{ M}^{-1} \text{ s}^{-1}$ which may be identified with k_a . Figure 3b has a slope of $(1.16 \pm 0.06) \times 10^{10} \text{ M}^{-2} \text{ s}^{-1} = k_b/K_{a2}$ from which $k_b = 272 \pm 14 \text{ M}^{-1} \text{ s}^{-1}$, in good agreement with the value obtained from Figure 3a. The intercept of Figure 3b is $<10 \text{ M}^{-1} \text{ s}^{-1} = k_c$. In summary, values of k_b obtained from data in both acid and base are in good agreement, while k_a and k_c are found to be negligible compared to k_b . This being the case, substitution by thiocyanate proceeds through path b throughout the entire pH range studied. The observed value of the forward rate constant is determined simply by k_b and the fraction of the Ru(III) complex present as $\text{Ru}(\text{edta})\text{H}_2\text{O}^+$; at pH 5 the measured forward rate constant k_1 equals k_b .

Similar rate vs. pH profiles were observed for all the incoming ligands studied. In all cases, the second-order rate constants became half of the maximum values at pH values around 2.4 and 7.6. When the values of k_1 were plotted as in Figure 3, linear plots were again obtained for both acidic and basic regions for pyrazine and acetonitrile and in the basic region for isonicotinamide. Furthermore, in all cases the intercepts were zero within experimental error so that the reactivity of $\text{Ru}(\text{Hedta})\text{H}_2\text{O}$ and $\text{Ru}(\text{edta})\text{OH}^{2-}$ must be at least 2 orders of magnitude less than that of $\text{Ru}(\text{edta})\text{H}_2\text{O}^+$ for these ligands as well. Although detailed study was not carried out, it must be noted that the ratios k_1/k_{-1} were somewhat dependent on pH. The ratios k_1/k_{-1} were relatively constant from pH 0.7 to pH about 6, but became smaller as the pH increased above 8.5, e.g., for L = thiocyanate, the value of k_1/k_{-1} was 540 M^{-1} at pH 5.50 and 32 M^{-1} at pH 8.58. A similar trend was observed for L = isonicotinamide and pyrazine, although the magnitude of the decrease in k_1/k_{-1} values in basic media was less than that observed for thiocyanate.

Substitution Reactions of $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$. When $\text{Ru}(\text{edta})\text{H}_2\text{O}^{2-}$ in acetate buffer was mixed with an argon-deaerated isonicotinamide solution, an orange solution resulted. The kinetic study of this substitution process (eq 6) was carried



out in acetate buffer solutions. The absorbance change vs. time curves monitored at 460 nm with isonicotinamide in greater than tenfold excess were mixed zeroth and first order and were irreproducible. However, the net absorbance changes were reproducible regardless of the kinetic pattern observed in the complexation process. Such kinetic behavior persisted even when the amalgamated zinc reducing agent was replaced with hydrogen gas at a platinum-black surface. Preliminary study on the reaction of $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ with dioxygen ($[\text{Ru}(\text{edta})\text{H}_2\text{O}^{2-}] = 1 \times 10^{-3} \text{ M}$, $[\text{O}_2] = 1 \times 10^{-4} \text{ M}$, pH 5.5, $\mu = 0.2 \text{ M}$, $25.0 \text{ }^\circ\text{C}$) resulted in apparently clean oxidation to $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^+$ with a second-order rate constant of $30 \pm 4 \text{ M}^{-1} \text{ s}^{-1}$. The behavior of the isonicotinamide substitution kinetics did appear to improve when the reactant solutions were deaerated with argon for a prolonged period of time, and the $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^+$ solution was reduced with amalgamated zinc for 2 h. The kinetic traces obtained from these carefully prepared solutions exhibited an exponential decay for up to 2 half-lives. The observed pseudo-first-order rate constants (Table VI) were proportional to isonicotinamide concentration, and the second-order rate constant (k_3) was calculated to be about $30 \text{ M}^{-1} \text{ s}^{-1}$. The kinetic traces were much better behaved with acetonitrile and thiocyanate. The absorbance change vs. time curves were exponential for at least 3 half-lives (monitored at 250 and 285 nm for acetonitrile and thiocyanate, respectively). For both reactions, the plots of k_{obsd} (Table VI) vs. ligand concentration were linear; however, no well-defined zero intercepts were obtained. The slopes of these plots (k_3) are

Table VI. Observed Pseudo-First-Order Rate Constants (k_{obsd}) for Substitution on the edta Complex of $\text{Ru}(\text{II})^a$

| pH | [Ru(II)], M | [L], M | k_{obsd} , s^{-1} |
|---------------------|----------------------|--------|-------------------------------------|
| L = Thiocyanate | | | |
| 5.50 | 3.2×10^{-5} | 0.002 | 0.0056 ± 0.0002 |
| 5.50 | 3.2×10^{-5} | 0.0015 | 0.0041 ± 0.0002 |
| 5.50 | 3.0×10^{-5} | 0.001 | 0.0029 ± 0.0001 |
| 5.50 | 3.0×10^{-5} | 0.0005 | 0.0011 ± 0.0001 |
| L = Acetonitrile | | | |
| 2.04 | 9.6×10^{-5} | 0.001 | 0.017 ± 0.002 |
| 3.46 | 9.5×10^{-5} | 0.001 | 0.016 ± 0.002 |
| 3.90 | 9.5×10^{-5} | 0.001 | 0.016 ± 0.002 |
| 4.34 | 9.6×10^{-5} | 0.001 | 0.016 ± 0.002 |
| 4.90 | 9.7×10^{-5} | 0.001 | 0.013 ± 0.002 |
| 5.50 | 9.7×10^{-5} | 0.002 | 0.027 ± 0.002 |
| 5.50 | 9.7×10^{-5} | 0.0015 | 0.019 ± 0.001 |
| 5.50 | 9.7×10^{-5} | 0.001 | 0.013 ± 0.002 |
| 5.50 | 9.7×10^{-5} | 0.0005 | 0.007 ± 0.001 |
| L = Isonicotinamide | | | |
| 5.50 | 1.0×10^{-4} | 0.0025 | 0.07 ± 0.02 |
| 5.50 | 1.0×10^{-4} | 0.005 | 0.14 ± 0.05 |
| 5.50 | 1.0×10^{-4} | 0.0075 | 0.32 ± 0.10 |
| 5.50 | 1.0×10^{-4} | 0.01 | 0.40 ± 0.10 |

^a Rate constants were measured in acetate (0.05–0.20 M total) buffer solutions, $\mu = 0.2 \text{ M}$ (Ktfsms), $25.0 \text{ }^\circ\text{C}$.

Table VII. Kinetic and Equilibrium Data for the Substitution Reactions of $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ ^a

| ligand | k_3 , $\text{M}^{-1} \text{ s}^{-1}$ | k_{-3} , s^{-1} ^b | K_3 , M^{-1} ^c |
|-----------------|--|---|--------------------------------------|
| thiocyanate | 2.7 ± 0.2 | $(2.1 \pm 0.5) \times 10^{-4}$ | $(1.3 \pm 0.3) \times 10^4$ |
| acetonitrile | 13 ± 1 | $(4 \pm 1) \times 10^{-5}$ | $(3 \pm 1) \times 10^5$ |
| isonicotinamide | 30 ± 15 | $(4 \pm 2) \times 10^{-6}$ | $(7 \pm 2) \times 10^6$ |
| pyridine | | | $(7 \pm 2) \times 10^6$ |
| pyrazine | | | $(1.7 \pm 0.4) \times 10^8$ |

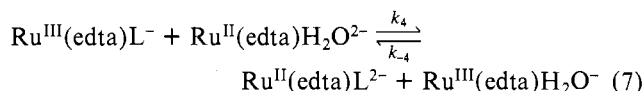
^a Acetate buffer, pH 5.1–5.5, $\mu = 0.2 \text{ M}$ (Ktfsms), $25.0 \text{ }^\circ\text{C}$.

^b Calculated from $k_{-3} = k_3/K_3$. ^c Calculated from $K_1 K_4$.

listed in Table VII. For L = pyrazine, zero-order behavior was observed even when extreme care was taken in the reduction of the Ru(III) solutions, and the rate constant for the substitution reaction could not be measured. Due to the difficulties in the kinetic study, reliable values for the reverse reaction rate constants (k_{-3}) could not be obtained by direct measurement. Instead, these values were calculated from the formal reduction potentials and the formation constants of the Ru(III) complexes. The equilibrium constants K_3 and the calculated reverse rate constants k_{-3} are given in Table VII.

The effect of the pH of the medium was studied only for L = acetonitrile. The second-order rate constant was independent of pH in acetate buffer between 3.5 and 5.5.

Reduction of $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$ by $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$. For L = isonicotinamide and acetonitrile, the electron-transfer reactions shown in eq 7 were studied in acetate buffer solutions at pH



5.5. When deaerated equilibrated solutions containing $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^+$, L, and $\text{Ru}^{\text{II}}(\text{edta})\text{L}^-$ were mixed with at least a tenfold excess of $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$, a rapid transmittance decrease was observed at 466 and 400 nm for isonicotinamide and acetonitrile, respectively. These initial rapid changes were succeeded by slower changes due to the redox reactions (eq 7), and the observed pseudo-first-order rate constants were proportional to the $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ concentration (Table VIII) with no apparent zero intercept. The calculated second-order rate constants k_4 are $(2.8 \pm 0.5) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $(3.3 \pm 0.4) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for L = isonicotinamide and acetonitrile, respectively.

Table VIII. Observed Pseudo-First-Order Rate Constants (k_{obsd}) for Electron-Transfer Reactions between $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$ and $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ ^a

| $[\text{Ru}(\text{III})\text{L}], \text{M}^{-1}$ | $[\text{Ru}(\text{II})], \text{M}^{-1}$ | $k_{\text{obsd}}, \text{s}^{-1}$ |
|--|---|----------------------------------|
| L = Acetonitrile | | |
| 5.9×10^{-5} | 1.0×10^{-3} | 330 ± 40 |
| 5.9×10^{-5} | 5.0×10^{-4} | 170 ± 20 |
| 5.9×10^{-5} | 3.0×10^{-4} | 100 ± 20 |
| L = Isonicotinamide | | |
| 6.5×10^{-6} | 1.0×10^{-4} | 300 ± 40 |
| 6.5×10^{-6} | 7.5×10^{-5} | 250 ± 20 |
| 6.5×10^{-6} | 5.0×10^{-5} | 100 ± 10 |

^a Rate constants were measured in pH 5.5 acetate buffer solutions, $\mu = 0.2 \text{ M}$ (Ktms), 25.0°C .

Discussion

Nature of edta Complexes of Ruthenium(III) and Ruthenium(II) in Aqueous Solution. The potentially hexadentate chelating agent edta forms complexes with most metal ions, with the nature of the complex formed depending strongly on the identity of the metal ion.²⁴ Among the known transition metal ion-edta complexes, terdentate ($\text{Cr}^{\text{III}}(\text{H}_3\text{edta})\text{Cl}_2 \cdot (\text{H}_2\text{O})^{25}$), tetradentate ($\text{Cr}^{\text{III}}(\text{edta})(\text{H}_2\text{O})_2^{26}$), pentadentate ($\text{Cr}^{\text{III}}(\text{Hedta})\text{H}_2\text{O}$,²⁷ $\text{Rh}(\text{edta})\text{H}_2\text{O}^{28}$), and hexadentate ($\text{NH}_4[\text{Co}^{\text{III}}(\text{edta})] \cdot 2\text{H}_2\text{O}$,²⁹ $\text{NH}_4[\text{Fe}(\text{edta})\text{H}_2\text{O}]^{30}$) coordination modes are encountered. Furthermore, in a few systems two or more such forms are known to be in equilibrium in aqueous solution.^{26,29} The complex of edta with Ru(III) has been shown to be pentadentate in aqueous solution at low pH by alkalimetric titration.^{1,4} The complex manifests a $\text{p}K_a$ of 2.37 corresponding to one titratable proton. This value is quite typical of that reported for free carboxylate groups in other pentadentate edta complexes.²² Furthermore, the single titratable proton with a $\text{p}K_a$ of 7.6 is consistent with the presence of one bound water molecule. Thus all of the available evidence indicates that the dominant form of the edta complex of Ru(III) in aqueous solution at 25°C is the pentadentate complex in which the sixth coordination site of the metal center is occupied by a water molecule (or, at high pH, by a hydroxide ion). Information bearing on the nature of the edta complex of Ru(II) is somewhat meager. As the Ru(III)/Ru(II) couple is electrochemically reversible in the range pH 3–5,⁴ it is presumed that Ru(II) has the same coordination environment as Ru(III)—that is, that it is present as a pentadentate complex containing one water molecule ($\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$) under these conditions. The pH dependence of the redox couple⁴ does, however, suggest that at lower pH two carboxylate groups may be protonated, indicating that $\text{Ru}^{\text{II}}(\text{H}_2\text{edta})(\text{H}_2\text{O})_2$ may be present in sufficiently acidic solutions. Finally, the high-pH behavior of the Ru(III)/Ru(II) couple indicates that the $\text{p}K_a$ for the water molecule bound to Ru(II) is greater than 10.

Solutions of both $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ and $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ are pale yellow, and strong absorption (presumably due to charge-transfer absorption) is found only in the ultraviolet region for both ions (Table I). Comparison of the spectrum of $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ (λ_{max} 350 and 280 nm) with that of $\text{Rh}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ (λ_{max} 352 nm, ϵ 713 $\text{M}^{-1} \text{cm}^{-1}$; λ_{max} 295 nm, ϵ 449 $\text{M}^{-1} \text{cm}^{-1}$) suggests that, for the Ru(III) complex, the lowest ligand field transition occurs at 350 nm and that another ligand field transition at ~ 280 – 290 nm may be masked by the intense 280-nm charge-transfer absorption. For $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ the lowest energy ligand field bands are observed at 392³¹ and 320 nm,³² respectively. Thus it might be tentatively concluded that the Ru(III) center in $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ experiences an average ligand field intermediate between that found in these two ions of higher symmetry. For $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$, a ligand field transition occurs at 427 nm. This may be compared with values for the

Table IX. Metal-to-Ligand Charge-Transfer Absorption Maxima (λ_{max} , nm) in Aqueous Solutions

| L | $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ | $\text{Fe}(\text{CN})_5\text{L}^{3-}$ | $\text{Ru}(\text{edta})\text{L}^{2-}$ |
|----------------------------|---|---------------------------------------|---------------------------------------|
| pyridine | 407 | 362 | 382 |
| isonicotinamide | 479 | 434 | 460 |
| pyrazine | 472 | 450 | 463 |
| <i>N</i> -methylpyrazinium | 538 ^b | 662 | 558 |

^a Reference 8. ^b Reference 35. ^c Reference 36.

hexaquo and hexaammine ions: $\text{Ru}(\text{H}_2\text{O})_6^{2+}$, λ_{max} 535 nm,³³ $\text{Ru}(\text{NH}_3)_6^{2+}$, λ_{max} 400 nm.⁸ Thus for Ru(II), as well, edta appears to create a ligand field intermediate between water and ammonia.

The potential for the $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-/\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ couple (-0.01 V , Table II) is not very different from the potentials of other Ru(III)/Ru(II) couples containing oxygen and nitrogen donor atoms ($\text{Ru}(\text{NH}_3)_6^{3+/2+}$, 0.05 V ;¹² $\text{Ru}(\text{H}_2\text{O})_6^{3+/2+}$, 0.22 V ³³). The behavior of the Ru(III)/Ru(II) couple thus differs greatly from that of first transition series M(III)/M(II) couples; for vanadium, chromium, and iron, complexation to EDTA stabilizes the M(III) center strongly over M(II), and the $\text{M}^{\text{II}}(\text{edta})$ complexes are very much stronger reducing agents (by 0.5–1 V) than their aquo-ion counterparts.

Properties of $\text{Ru}^{\text{III}}(\text{edta})\text{L}$ and $\text{Ru}^{\text{II}}(\text{edta})\text{L}$. As is evident from Tables I and II, a series of substituted $\text{Ru}(\text{edta})\text{L}$ complexes (comparable to $\text{M}^{\text{II}}(\text{edta})\text{L}$ with $\text{M} = \text{Co}, \text{Cu}, \text{Ni}$,³⁴ etc.) may be synthesized. These complexes exhibit spectral properties similar to those of the $\text{Ru}(\text{NH}_3)_5\text{L}$ series. Like $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{NCS}^{2+}$ (λ_{max} 495 nm, ϵ 3500 $\text{M}^{-1} \text{cm}^{-1}$; λ_{max} 327 nm, ϵ 520 $\text{M}^{-1} \text{cm}^{-1}$; $E^\circ = +0.13 \text{ V}$ ⁶), $\text{Ru}^{\text{III}}(\text{edta})\text{NCS}^{2-}$ manifests ligand-to-metal charge-transfer absorption in the visible region. (The complex $\text{Ru}^{\text{III}}(\text{edta})\text{NCS}^{2-}$ is presumably bonded to thiocyanate through nitrogen, as in the analogous pentaammine species.⁶) Although $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$ complexes are colorless or pale yellow when L is an aromatic N heterocycle, their Ru(II) counterparts are intensely orange, red, or purple. From the intensities and positions of the visible band maxima for the $\text{Ru}(\text{edta})\text{L}^{2-}$ complexes (Table I), the visible bands are undoubtedly due to metal-to-ligand charge-transfer absorption. Bands of similar energy and intensity have also been observed for the $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}^{2+}$ ⁸ and $\text{Fe}^{\text{II}}(\text{CN})_5\text{L}^{3-}$ ^{35,36} series. In Table IX, data for all three series are summarized. As anticipated for a metal-to-ligand charge-transfer transition, for all three series the band shifts to longer wavelength (lower energy) as the oxidizing ability of the ligand increases⁸ (down a column). On the other hand, it is difficult to interpret the shifts observed for a common ligand with different metal sites. On a qualitative level it is expected that the MLCT bands for $\text{Fe}(\text{CN})_5\text{L}^{3-}$ will lie at higher energy than those for the corresponding ruthenium complexes, since it is more difficult to remove an electron from the Fe(II) center (e.g., E° for $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{2-/3-}$ is $+0.39 \text{ V}$ ³⁷) than from the Ru(II) centers (e.g., E° for $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+/2+}$ is 0.07 V ³⁸ and for $\text{Ru}(\text{edta})\text{H}_2\text{O}^{-/2-}$ is -0.01 V). Such an argument does not, however, account for the relative ordering of the bands observed for $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ and $\text{Ru}(\text{edta})\text{L}^{2-}$ since those for the latter tend to occur at higher energy even though the metal center is more reducing. Other factors—perhaps a greater degree of excited-state distortion (Stokes shift) for the metal center in $\text{Ru}^{\text{II}}(\text{edta})\text{L}^{2-}$ —evidently determine the relative ordering. The latter explanation is not, however, sufficient when data for the strongly π -accepting *N*-methylpyrazinium ion ligand are considered. With this ligand as L, λ_{max} for $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}$ is at shorter wavelength than that for either $\text{Fe}^{\text{II}}(\text{CN})_5\text{L}$ or $\text{Ru}^{\text{II}}(\text{edta})\text{L}$. The spectral behavior of the

Table X. Comparison of Affinities of R-H₂O for Ligands^a

| L | Ru(NH ₃) ₅ H ₂ O | | Fe(CN) ₅ H ₂ O ^d | | Ru(edta)H ₂ O | |
|-----------------|--|------------------------------------|---|-----------------------------------|--|-----------------------|
| | K _{II} | K _{III} | K _{II} | K _{II} /K _{III} | K _{II} | K _{III} |
| hydroxide ion | 6 × 10 ² ^b | 4 × 10 ⁹ ^b | | | ≤ 10 ⁴ | 1.4 × 10 ⁶ |
| imidazole | 2.8 × 10 ⁶ ^b | 1.9 × 10 ⁶ ^b | 1.8 × 10 ⁵ | 8.3 × 10 ⁵ | K _{II} /K _{III} = 7.3 × 10 | |
| pyridine | 2.4 × 10 ⁷ ^b | 6 × 10 ³ ^b | 3.3 × 10 ⁵ | 9.4 × 10 ³ | 0.7 × 10 ⁷ | 1.0 × 10 ⁵ |
| isonicotinamide | K _{II} /K _{III} = 1.8 × 10 ⁵ ^c | | 4.0 × 10 ⁵ | 5.2 × 10 ³ | 0.7 × 10 ⁷ | 1.2 × 10 ⁴ |
| pyrazine | K _{II} /K _{III} = 4 × 10 ⁶ ^b | | 9.0 × 10 ⁵ | 1.7 × 10 ³ | 1.7 × 10 ⁸ | 1 × 10 ⁹ |
| acetonitrile | K _{II} /K _{III} = 1.9 × 10 ⁶ ^c | | | | 3 × 10 ⁵ | 1.0 × 10 |

^a At ~25 °C; media as stated in the original references. K values refer to the reaction RH₂O + L ⇌ RL + H₂O; the subscripts refer to the oxidation state of the metal. ^b Data taken from ref 11. ^c Reference 12. ^d Reference 37.

pentaammineruthenium(II) complex of *N*-methylpyrazinium ion has previously been ascribed to very strong resonance interaction.³⁸ This appears likely to be the case for the edta complex as well.

In Table X equilibrium data for the replacement of water by other ligands on low-spin d⁶ Ru(II) and Fe(II) and low-spin d⁵ Ru(III) and Fe(III) metal centers are summarized. The data for the Ru(NH₃)₅- and Fe(CN)₅- series are discussed and compared elsewhere.^{11,37} The data for the Ru(edta)L systems qualitatively follow the trends observed in the other series. The affinity of the M(II) oxidation state for the π-acceptor ligands isonicotinamide, pyrazine, and acetonitrile is quite large. The affinity of Ru^{III}(edta) for pyridine, isonicotinamide, and pyrazine is quite substantial as well. In fact, in the Ru(edta)L series the differences in the affinities of Ru(II) and Ru(III) for such ligands is smaller than those in the Ru(NH₃)₅L series so that the range of reduction potentials spanned in the Ru(edta)L series is smaller.

Substitution Reactions of the edta Complex of Ru(III).

From the pH dependence of the rate constants, it is established that substitution on the edta complex of Ru(III) proceeds through the pentadentate aquo complex Ru^{III}(edta)H₂O⁻. The rate constants observed for complexation of this species range from 10 to 10⁴ M⁻¹ s⁻¹ at 25 °C (Table IV). Literature data for substitution in other Ru(III) complexes are somewhat sparse but are sufficient to establish a pattern: Kallen and Earley have estimated a rate constant of 5 × 10⁻⁵ M⁻¹ s⁻¹ for formation of Ru(H₂O)₅Cl²⁺ from Ru(H₂O)₆³⁺ and chloride at 25 °C.³² A rate constant of 4.7 × 10⁻⁴ M⁻¹ s⁻¹ at 35 °C has been reported for chloride anation of Ru(NH₃)₅H₂O³⁺³⁹ while that for reaction with pyrazine is <4 × 10⁻⁶ M⁻¹ s⁻¹ at 25 °C.⁴⁰ Similar or even smaller rate constants have been recorded for other ruthenium(III) amine-aquo complexes^{14,16,18} at 25 °C. Thus the substitution reactions of Ru^{III}(edta)H₂O⁻ are as much as 10 orders of magnitude more rapid than those of other Ru(III) complexes containing oxygen and nitrogen donor atoms.⁴¹

This extraordinary alteration of the reactivity of the Ru(III) metal center is not well understood at this time, but some of the factors associated with it can be surmised. Despite the mass of evidence for dissociative substitution pathways for octahedral metal ions,⁴² substitution reactions of Ru^{III}(edta)H₂O⁻ clearly proceed by an associative route. The rate constant (k₁) for substitution is a sensitive function of the equilibrium constant (K₁) for ligand binding⁷ (see also Table IV). The identity of the entering ligand is crucial in determining the substitution rate, and the degree of bond making in the transition state is substantial.⁴³

The activation parameters (Table V), feature values of ΔH[‡] ranging from 5.7 to 8.3 kcal mol⁻¹ and ΔS[‡] values in the range -18 to -24 cal mol⁻¹ deg⁻¹. Since the values of the entropy of activation are relatively constant and the TΔS[‡] terms make about a 50% contribution to the free energy of activation at 25 °C, the observed rate variation with ligand is essentially determined by the enthalpy terms. By contrast, enthalpies of activation are typically 20–24 kcal mol⁻¹^{17,39} for other reactions

involving the substitution of a Ru^{III}-OH₂ species. The latter data most likely reflect the barriers for a dissociative process, and ~20 kcal mol⁻¹ may provide a reasonable estimate of the Ru^{III}-OH₂ bond energy. If the strength of the Ru^{III}-H₂O bond is not altered markedly in the edta complex, the enthalpic activation barrier must be lowered by ~10–15 kcal mol⁻¹, reflecting a large amount of bond making in the transition state. Furthermore, the variation of ΔH[‡] with the identity of L indicates that the degree of bond making varies with L, as is also expected on the basis of an associative pathway. The large negative entropies of activation observed could reflect steric crowding and distortion in the edta ligand around the seven-coordinate metal center in the transition state.

What are the factors which activate the edta complex for associative, rapid substitution? Several kinds of experimental results will now be examined in an effort to determine these factors. We begin with the general reaction (eq 8) and assess



for which L and L' high reactivity is observed. The complexation of the aquo species (eq 4) is a special case with L = H₂O. In order to compare the case where L' = H₂O (the reverse of eq 4) with the substitution process for other L', the first-order rate constants k₋₁ are converted to second-order rate constants k₋₁' (k₋₁' = k₋₁/55.5 M⁻¹ s⁻¹), and the equilibrium constants K₁ and 1/K₁ are corrected for the concentration of water to give K₁' = 55.5K₁ and 1/K₁' = 1/55.5K₁ for the reaction involving water as leaving and entering ligand, respectively. In this way the parameters for substitution on Ru(edta)H₂O⁻ and aquation of Ru(edta)L⁻ are placed on a consistent free-energy scale and may be compared on the same free-energy plot. In Figure 4, log k for replacement of L by L' (eq 8) is plotted as a function of log K for this process. The open circles on the right-hand side of the plot are for replacement of water in Ru(edta)H₂O⁻ (L = H₂O), while those on the left-hand side are for the aquation of Ru(edta)L⁻ (L' = H₂O). The data for thiocyanate, acetonitrile, and pyridine fall on a line of slope 0.5 while the points for pyrazine and isonicotinamide fall above this line.

We turn now to cases of reaction 8 in which neither L nor L' is H₂O. We have attempted to study this process with Ru^{III}(edta)NCCCH₃⁻ and Ru^{III}(edta)NCS²⁻ as Ru^{III}(edta)L⁻ and pyrazine as L'. In both cases the rate constant for reaction to form Ru^{III}(edta)pz⁻ was independent of the pyrazine concentration and within experimental error of k₋₁ for eq 4. Thus only upper limits of 0.025 and 0.2 M⁻¹ s⁻¹ for L = CH₃CN and SCN⁻, respectively, could be determined for direct replacement of L by L'. In fact we find no evidence for the direct displacement; reaction proceeds through Ru^{III}(edta)H₂O⁻ formed by dissociation of Ru^{III}(edta)L⁻ (reverse of eq 4). From the equilibrium constants in Table IV, K for the displacements by pyrazine are 1.3 × 10³ and 1.9 × 10¹ for CH₃CN and SCN⁻, respectively. These data are included in Figure 4 as the arrows 11 and 12, and for the reverse reactions as 14 and 13. As is apparent from the figure, displacement of thiocyanate and acetonitrile by pyrazine is

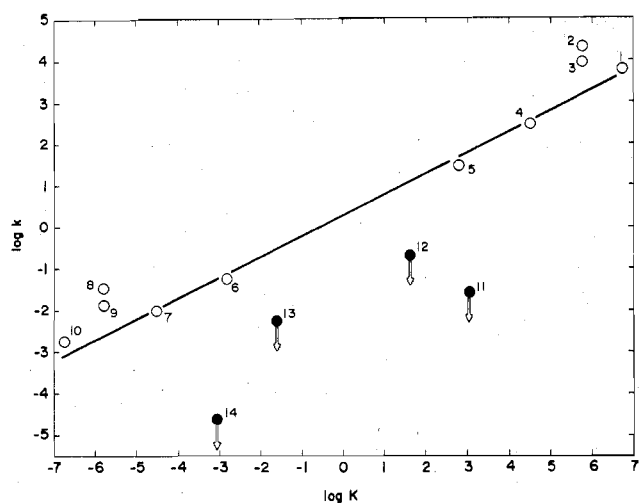
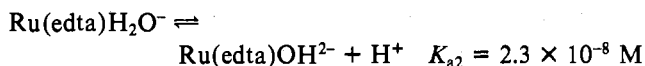


Figure 4. Plot of the logarithm of the second-order rate constant (k) for the substitution reaction of $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$ with L' (see eq 8) vs. the logarithm of the equilibrium constant (K) (pH 5.1 to ~ 5.5 , $\mu = 0.2$ M (Ktfsms), 25.0°C ; pz = pyrazine, isn = isonicotinamide, py = pyridine): 1, $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^- + \text{py} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{py}^- + \text{H}_2\text{O}$; 2, $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^- + \text{pz} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{pz}^- + \text{H}_2\text{O}$; 3, $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^- + \text{isn} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{isn}^- + \text{H}_2\text{O}$; 4, $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^- + \text{SCN}^- \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{NCS}^{2-} + \text{H}_2\text{O}$; 5, $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^- + \text{CH}_3\text{CN} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{NCCH}_3^- + \text{H}_2\text{O}$; 6, $\text{Ru}^{\text{III}}(\text{edta})\text{NCCH}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^- + \text{CH}_3\text{CN}$; 7, $\text{Ru}^{\text{III}}(\text{edta})\text{NCS}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^- + \text{SCN}^-$; 8, $\text{Ru}^{\text{III}}(\text{edta})\text{pz}^- + \text{H}_2\text{O} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^- + \text{pz}$; 9, $\text{Ru}^{\text{III}}(\text{edta})\text{isn}^- + \text{H}_2\text{O} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^- + \text{isn}$; 10, $\text{Ru}^{\text{III}}(\text{edta})\text{py}^- + \text{H}_2\text{O} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^- + \text{py}$; 11, $\text{Ru}^{\text{III}}(\text{edta})\text{NCCH}_3^- + \text{pz} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{pz}^- + \text{CH}_3\text{CN}$; 12, $\text{Ru}^{\text{III}}(\text{edta})\text{NCS}^{2-} + \text{pz} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{pz}^- + \text{SCN}^-$; 13, $\text{Ru}^{\text{III}}(\text{edta})\text{pz}^- + \text{SCN}^- \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{NCS}^{2-} + \text{pz}$; 14, $\text{Ru}^{\text{III}}(\text{edta})\text{pz}^- + \text{CH}_3\text{CN} \rightleftharpoons \text{Ru}^{\text{III}}(\text{edta})\text{NCCH}_3^- + \text{pz}$.

much slower than would be predicted from the trend for the other substitution reactions. This result seems to suggest that H_2O (the one component common to the other reactions presented in Figure 4) is a special entering and leaving ligand.

For further information concerning the generality of the high substitution reactivity of complexes containing the $\text{Ru}^{\text{III}}(\text{edta})$ moiety, we return to the pH dependence of the substitution reactions. It will be recalled that only upper limits could be obtained for the rate constants for the reactions of SCN^- and pyrazine with $\text{Ru}(\text{edta})\text{OH}^{2-}$ and $\text{Ru}(\text{Hedta})\text{H}_2\text{O}$; both are at least 10^2 times less reactive than $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$. The lower reactivity of $\text{Ru}(\text{edta})\text{OH}^{2-}$ compared to $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ is not surprising: replacement of H_2O by L is thermodynamically more favorable than replacement of OH^- by L . This can be seen by considering the following equilibria



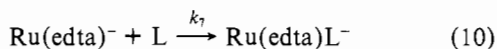
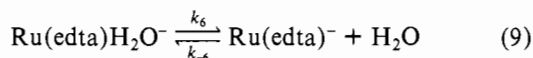
to obtain $K_{\text{OH}} = K_{a2}/K_w = 1.4 \times 10^6 \text{ M}^{-1}$. Thus the replacement of OH^- by CH_3CN , SCN^- , etc., is 6 orders of magnitude less favorable than when H_2O is the leaving ligand. Rate constants for complexation of $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ (eq 4) are very sensitive to the stability of the product vs. the reactant. Should substitution on $\text{Ru}(\text{edta})\text{OH}^{2-}$ be determined by the same factors, very small rate constants would be anticipated simply on the basis of the relatively high stability of the reactant hydroxo complex. By contrast, the state of protonation of the pendant carboxylate group in a pentadentate complex ($\text{Ru}(\text{edta})\text{L}^-$ or $\text{Ru}(\text{Hedta})\text{L}$) is not likely to markedly affect the affinity of the metal center for L . In fact we have found that with $\text{L} = \text{SCN}^-$, the equilibrium constant for

binding to the $\text{Ru}(\text{III})$ -aquo complex ($\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ or $\text{Ru}(\text{Hedta})\text{H}_2\text{O}$) varies less than a factor of 2 between pH 5 ($\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ dominant form) and pH 0.8 ($\text{Ru}(\text{Hedta})\text{H}_2\text{O}$ dominant form). Consequently, there is no thermodynamic rationalization for the low reactivity of $\text{Ru}(\text{Hedta})\text{H}_2\text{O}$ compared to that of $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$. Indeed, these considerations indicate that the pendant free carboxylate group is an important ingredient in the high reactivity of $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$. This conclusion is supported by the observations of Oyama and Anson who have "blocked" the pendant carboxylate of $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ by binding it to a graphite electrode.⁶ The electrode-attached $\text{Ru}(\text{III})$ does not equilibrate with an aqueous solution of isonicotinamide, etc.; only when the attached complex is reduced to $\text{Ru}(\text{II})$ is binding of isonicotinamide observed. Finally, the importance of the free carboxylate group is also suggested by some results obtained with a related $\text{Ru}(\text{III})$ complex, $\text{Ru}(\text{hedtra})\text{H}_2\text{O}$ (hedtra = *N*-(hydroxyethyl)ethylenediaminetriacetate), in which the free carboxylate is replaced by a $-\text{CH}_2\text{OH}$ group. The rate constant for reaction of $\text{Ru}(\text{hedtra})\text{H}_2\text{O}$ with pyrazine is $50 \text{ M}^{-1} \text{ s}^{-1}$ (25°C , $\mu = 0.2 \text{ M}$, pH 5);⁴⁰ this is 400 times slower than for $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$.

The review of the data suggests that both H_2O and a pendant free carboxylate group are required for maximal reactivity in an edta complex of $\text{Ru}(\text{III})$. Furthermore, when both are present, the high reactivity is manifested via an *associative* substitution pathway. We focus on the evidently critical components, bound water and a pendant free $-\text{CO}_2^-$ group, and note that inspection of a space-filling model of $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ indicates that hydrogen bonding between the hydrogen of the coordinated water and the oxygen of the free carboxylate appears favorable. This hydrogen bonding has the net effect (at least in the model) of distorting slightly all of the metal-ligand bonds so that a very open area is created adjacent to the hydrogen bond. In this way the hydrogen bonding may sterically activate $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ toward associative substitution by creating an accessible site for attack by the incoming ligand. For the reverse reaction, aquation of $\text{Ru}(\text{edta})\text{L}^-$, the pendant $-\text{CO}_2^-$ group would fulfill the special role of hydrogen bonding to the incoming ligand, water. Thus the activation of the $\text{Ru}(\text{III})$ center is tentatively ascribed to steric activation resulting from hydrogen bonding. This hypothesis accounts for the reduction in substitution rate encountered when one oxygen of the pendant carboxylate group is blocked by protonation or binding to the graphite electrode. In the hedtra complex the analogous oxygen of the $-\text{CH}_2\text{OH}$ group is much less basic than $-\text{CO}_2^-$, so that hydrogen bonding is not as feasible. Further, when water is neither the entering nor leaving ligand (eq 8, L and $\text{L}' \neq \text{H}_2\text{O}$), hydrogen bonding of L or L' to the pendant carboxylate cannot occur because the ligands studied do not possess acidic hydrogens.

Several explanations have been invoked elsewhere in accounting for heightened substitution reactivity in edta complexes. First, it seems that the $\text{M}^{\text{III}}-\text{OH}_2$ bond may be very weak in some edta complexes. That in seven-coordinate $\text{Fe}(\text{edta})\text{H}_2\text{O}^-$ is remarkably long.³⁰ A weak $\text{Cr}^{\text{III}}-\text{H}_2\text{O}$ bond has been postulated in explaining rapid substitution rates for $\text{Cr}(\text{edta})\text{H}_2\text{O}^-$.⁴⁴ In the present $\text{Ru}(\text{III})$ system it would be attractive to postulate that hydrogen bonding between the bound water and the pendant carboxylate group weakens a ruthenium(III)-oxygen bond ($\text{Ru}^{\text{III}}-\text{H}_2\text{O}$ or, more likely, one of the three $\text{Ru}^{\text{III}}-\text{O}_2\text{C}^-$ bonds). Such arguments about bond weakening in $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$, though attractive in accounting for enhanced lability of the metal center, do not in any way shed light on activation toward *associative* pathways. On the contrary, the labilization conferred by metal-ligand bond weakening should occur via dissociative pathways. Sulfab et

al. have proposed (again in accounting for the rapidity and pH dependence of $\text{Cr}(\text{edta})\text{H}_2\text{O}^-$ substitutions) that the aquo pentadentate complex is in rapid equilibrium with a small amount of the hexadentate complex $\text{Cr}(\text{edta})^-$, through which the substitution proceeds.⁴⁵ Although it is not evident why the hexadentate species should exhibit any greater facility in undergoing associative substitution processes than the pentadentate complex, such a mechanism (eq 9 and 10) can be



seen to be unlikely for Ru(III) on the basis of the experimental observations: consider eq 9 and 10. As no hexadentate species is detected in solutions of $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$, $K_6 = k_6/k_{-6} < 10^{-1}$. At sufficiently high concentration of L, the above scheme gives rise to rate saturation when $k_7[\text{L}] > k_{-6}$. As no evidence for saturation has been observed for k_{obsd} values up to 600 s^{-1} , $k_6 > 3000 \text{ s}^{-1}$; thus $k_{-6} > 3 \times 10^4 \text{ s}^{-1}$. Such rates seem implausibly high for the Ru(III) center. Neither of the above explanations accounts satisfactorily the observations, and the model based on steric activation via hydrogen bonding is unique in accounting for the associative pathway.

Substitution Reactions of the edta Complex of Ru(II). Our studies of the Ru(II) system were less ambitious than those for Ru(III): the Ru(III)-catalyzed pathway⁷ is difficult to suppress, so that the data are more difficult to obtain and generally of poorer quality than those for Ru(III). Furthermore, as will be seen, the behavior of Ru(II) complexed to edta does not differ markedly from that of other six-coordinate Ru(II) complexes, so that there was less motivation for an extensive study. The reactions of $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ with thiocyanate, acetonitrile, and isonicotinamide at pH ~ 5 (Table VII) were first order in both Ru(II) and entering ligand, with the reverse rate constants being so small that it was not practical to determine them kinetically. The forward rate constants range from $2.7 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$ to $30 \pm 15 \text{ M}^{-1} \text{ s}^{-1}$ while the equilibrium constants range from $(1.3 \pm 0.3) \times 10^4 \text{ M}^{-1}$ to $(7 \pm 2) \times 10^6 \text{ M}^{-1}$. Thus the driving-force dependence of the rate constants seen for Ru(III) is largely (or totally) absent for the Ru(II) system. The rate constant for SCN^- is the smallest, and this is reasonably ascribed to the electrostatic repulsion experienced between the negatively charged reactants SCN^- and $\text{Ru}(\text{edta})\text{H}_2\text{O}^{2-}$. Finally, the lack of pH dependence for the CH_3CN reaction over the range pH 5.5 to 3.5 indicates that the reactivities of $\text{Ru}(\text{edta})\text{H}_2\text{O}^{2-}$ and $\text{Ru}(\text{Hedta})\text{H}_2\text{O}^-$ are comparable. Unlike the case of Ru(III), the Ru(II) substitutions do not proceed via a pathway requiring a free, unprotonated carboxylate group. For the most part the experimental evidence indicates that substitution reactions of six-coordinate Ru(II) complexes proceed by a dissociative route.⁴⁶ The limited data obtained in the present study indicate that $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ is probably not exceptional in this respect.

The rate constants reported here may be compared with those recorded for other six-coordinate ruthenium(II) complexes containing O or N donors. A rate constant of $2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ has been found for reaction of $\text{Ru}(\text{H}_2\text{O})_6^{2+}$ with dinitrogen⁴⁷ while $8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ has been noted for reaction of the same ion with chloride.³² The rate of replacement of water by isonicotinamide has been studied for $\text{Ru}^{\text{II}}(\text{NH}_3)_4\text{LH}_2\text{O}^{2+}$. Shepherd and Taube report a rate constant of $0.11 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C, $\mu = 0.10 \text{ M}$) when $\text{L} = \text{NH}_3$.⁴⁸ The extensive studies of Isied and Taube reveal rate constants ranging from $< 10^{-5}$ (cis or trans $\text{L} = \text{CO}$) to $25 \text{ M}^{-1} \text{ s}^{-1}$ for trans $-\text{SO}_3^{2-}$.⁴⁹ The rate constants for reaction of $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ with the neutral ligands acetonitrile and isonicotinamide are about 4 orders of magnitude larger than those

typical of $\text{Ru}(\text{H}_2\text{O})_6^{2+}$ and 2 orders of magnitude greater than those for $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$; $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ is labilized by at least 2 orders of magnitude compared to those six-coordinate complexes of charge 2+. This labilization of the $\text{Ru}^{\text{II}}-\text{H}_2\text{O}$ bond is reasonably ascribed to the lowering of the effective positive charge on the metal center. The total net difference in charges between the complexes $\text{Ru}(\text{edta})\text{H}_2\text{O}^{2-}$ and $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ or $\text{Ru}(\text{H}_2\text{O})_6^{2+}$ is four units, so that the effective charge at the metal center in $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ is certainly less than in the cationic complexes. To the extent that the metal-center charge is diminished, the interaction between the metal and the negative end of the dipole of the departing water ligand is lowered, and the barrier for a dissociative process should be smaller for $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ than for the cations. Specific electronic effects may also be operative: it has been proposed that ligand field stabilization energy (LFSE) is a major rate-determining factor in the substitution process of the transition-metal ions. For octahedral low-spin d^6 ions the magnitude of the LFSE activation energy is proportional to the magnitude of $10Dq$. As was mentioned earlier, the average values of $10Dq$ for these Ru(II) complexes are in the order $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+} > \text{Ru}(\text{edta})\text{H}_2\text{O}^{2-} > \text{Ru}(\text{H}_2\text{O})_6^{2+}$. The order of labilities is $\text{Ru}(\text{edta})\text{H}_2\text{O}^{2-} > \text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+} > \text{Ru}(\text{H}_2\text{O})_6^{2+}$. It is likely this analysis fails because the lowered symmetry of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ and $\text{Ru}(\text{edta})\text{H}_2\text{O}^{2-}$ is not taken into account in comparing average ligand fields and because cations cannot be directly compared with anions.

Substitution Reactivities of edta Complexes. Complexation of both Ru(III) and Ru(II) to edta brings about enhanced rates of substitution. However, the magnitude of the enhancement is so much greater for Ru(III) than for Ru(II) that the normal order of reactivities of these two is inverted; substitution on Ru(III) becomes more rapid than on Ru(II). The labilization of Ru(III) is accompanied by a sharp pH dependence, and the rates of substitution are extremely responsive to the stability of the product. By contrast, the smaller effect found for Ru(II) shows no pH dependence (in acid solution) and no large sensitivity to the nature of the incoming ligand. It appears then that two labilization mechanisms are operative. For $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ it seems that the lowered effective charge on Ru(II) results in a lowered activation barrier for a dissociative path. For Ru(III), activation toward an associative route is observed.

In an effort to understand why the metal centers Ru(II) and Ru(III) are not activated in the same way, we review data for these and other metal centers. In Table XI complexation rate constants (25 °C) for aquopentaammine complexes (k_p) of divalent and trivalent metals are compared with those for the corresponding pentadentate edta complexes (k_e). In both reaction series a bound water is replaced by the ligand L to give $\text{M}(\text{NH}_3)_5\text{L}$ or $\text{M}(\text{edta})\text{L}$ as product. The metal ion electronic configuration and the $\text{p}K_a$ of the bound water in $\text{M}(\text{edta})\text{H}_2\text{O}$ are tabulated at the left. At the far right the rate ratio k_e/k_p is given for each metal center. All of the 3+ metal ions included are normally quite inert to substitution as is illustrated by the small magnitudes (10^{-6} – $10^{-4} \text{ M}^{-1} \text{ s}^{-1}$) of the rate constants for the pentaammine reactions. In fact, substitution on d^3 , low-spin d^5 , and low-spin d^6 centers is generally very slow. Thus (with the exception of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$) the centers Cr(III), Ru(III), Os(III), and Rh(III) fall into a single class when only the ammine reactions are considered. The same metal centers are, however, seen to fall into two classes when the edta reactions are compared. The first three entries, Cr(III), Ru(III), and Os(III), are markedly labilized on complexation to edta and undergo substitution 10^5 – 10^{10} times more rapidly than the corresponding pentaammines. By contrast, the last three entries, Co(III), Rh(III), and Ru(II), are labilized at most by 2 orders

Table XI. Comparison of Rate Constants for Replacement of Water in d^3 , Low-Spin d^5 , and d^6 $M(\text{NH}_3)_5\text{H}_2\text{O}$ and $M(\text{edta})\text{H}_2\text{O}$ Complexes^a

| electronic config | $pK_a(\text{H}_2\text{O})$ in $M(\text{edta})\text{H}_2\text{O}$ | reactants and rate constants | | k_e/k_p |
|-------------------|--|---|--|-------------------|
| $3d^3$ | 7.4 | $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} + \text{Cl}^-$ $k_p \leq 2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ ^b | $\text{Cr}(\text{edta})\text{H}_2\text{O}^- + \text{CH}_3\text{CO}_2^-$ $k_e = 3.3 \text{ M}^{-1} \text{ s}^{-1}$ ^c | $\geq 10^5$ |
| $4d^5$ | 7.6 | $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} + \text{pz}$ $k_p \leq 2 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ ^d | $\text{Ru}(\text{edta})\text{H}_2\text{O}^- + \text{pz}$ $k_e = 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ | $\geq 10^{10}$ |
| $5d^5$ | | $\text{Os}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} + \text{Br}^-$ $k_p \approx 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ ^f | $\text{Os}(\text{edta})^- + 1,4\text{-pz}$ $k_e \approx 10^2 \text{ M}^{-1} \text{ s}^{-1}$ ^g | $\sim 10^6$ |
| $3d^6$ | 8.1 | $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} + \text{Cl}^-$ $k_p = 2 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ ^h | $\text{Co}(\text{edta})\text{H}_2\text{O}^- + \text{Cl}^-$ $k_e \leq 2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ ⁱ | ≤ 10 |
| $4d^6$ | 9.1 | $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} + \text{Cl}^-$ $k_p = 1.3 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ ^j | $\text{Rh}(\text{edta})\text{H}_2\text{O}^- + \text{Cl}^-$ $k_e \approx 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ ^k | ~ 1 |
| $4d^6$ | ≥ 10 | $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+} + \text{isn}$ $k_p = 1.1 \times 10^{-1} \text{ s}^{-1}$ ^l | $\text{Ru}(\text{edta})\text{H}_2\text{O}^{2-} + \text{isn}$ $k_e = 2.5 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$ ^e | 2.5×10^2 |

^a For the reactions $M(\text{NH}_3)_5\text{H}_2\text{O} + \text{L} \rightarrow M(\text{NH}_3)_5\text{L}$ and $M(\text{edta})\text{H}_2\text{O} + \text{L} \rightarrow M(\text{edta})\text{L} + \text{H}_2\text{O}$, respectively (25 °C, H_2O). ^b A. E. Ogard and H. Taube, *J. Am. Chem. Soc.*, **80**, 1084 (1958). ^c Reference 44. ^d Reference 40. ^e This work; 0.2 M ionic strength. ^f Estimated from assumed $K = 10^2$ M and an observed aquation rate in 1 M HTFMS of $< 10^{-6} \text{ s}^{-1}$. C. Lawrence and C. Creutz, unpublished observations. ^g At 0.2 M ionic strength; the dominant form of the starting species is a hexadentate complex, but the reaction appears to proceed through the pentadentate form: T. X. Aufiero and C. Creutz, work in progress. ^h Reference 42, pp 164-165. ⁱ No data bearing directly on the value of this rate constant are available. Indirect information may, however, be derived from the results of R. Dyke and W. C. E. Higginson, *J. Chem. Soc. A*, 2788 (1963), who report a value of $1.7 \times 10^{-5} \text{ s}^{-1}$ (25 °C, $\mu = 1.0$ M) for the net reaction $\text{Co}(\text{edta})\text{Cl}^{2-} \rightarrow \text{Co}(\text{edta})^- + \text{Cl}^-$. In this system the initial reaction $\text{Co}(\text{edta})\text{Cl}^{2-} + \text{H}_2\text{O} \rightarrow \text{Co}(\text{edta})\text{H}_2\text{O}^- + \text{Cl}^-$ cannot be ruled out since the pentadentate product is unstable with respect to the hexadentate complex, and this interconversion, $\text{Co}(\text{edta})\text{H}_2\text{O}^- \rightarrow \text{Co}(\text{edta})^- + \text{H}_2\text{O}$, occurs more rapidly ($k = 1.2 \times 10^{-3} \text{ s}^{-1}$, 15 °C, $\mu = 0.1$ M: R. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc. A*, 260 (1958)) than chloride loss under the conditions of the experiment. If $\text{Co}(\text{edta})\text{H}_2\text{O}^-$ is the first reaction product, the rate constant for chloride anation is estimated to be $\sim 2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ by assuming that the equilibrium constant for the binding of chloride ion is $\sim 1 \text{ M}^{-1}$. If $\text{Co}(\text{edta})\text{H}_2\text{O}^-$ is not formed as an intermediate, the rate of chloride loss to form $\text{Co}(\text{edta})\text{H}_2\text{O}^-$ must be even smaller than $1.7 \times 10^{-5} \text{ s}^{-1}$. Then on the assumption again of an equilibrium constant of 1 for chloride binding, the rate constant for chloride anation of $\text{Co}(\text{edta})\text{OH}_2^-$ must be even smaller than $1.7 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. ^j 35 °C, $\mu = 1.5$ M: H. L. Bott, A. Poè, and K. Shaw, *J. Chem. Soc. A*, 1745 (1970). ^k Rough estimate based on the qualitative observations of Dwyer and Garvan.²⁸ ^l Reference 48, 0.1 M ionic strength.

of magnitude by binding to edta.

The $M(\text{edta})\text{H}_2\text{O}$ complexes of the latter three ions have in common the low-spin d^6 electronic configuration and somewhat higher pK_a 's (second column in Table XI) than the first three entries. Furthermore, there is no evidence for associative character in the complexation reactions. On the other hand, the associative character of both $\text{Cr}(\text{edta})\text{H}_2\text{O}^{4-}$ and $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ substitutions is established. Chromium(III) and ruthenium(III), while they do not have the same valence d-orbital occupancy, do have in common partially vacant nonbonding d orbitals to which the incoming ligand may bond in the transition state for substitution. It seems reasonable that this is the crucial feature which enables edta activation of Cr(III) and Ru(III) but not of Co(III), Rh(III), and Ru(II). In addition, the fact that the bound water molecules in $\text{Cr}(\text{edta})\text{H}_2\text{O}^-$ and $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ are more acidic than in the other edta complexes may be significant. Earlier, steric activation toward associative substitution was proposed for $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$. The hydrogen bonding responsible for this phenomenon requires a relatively acidic proton source. Thus both the electron "hole" on the metal center and an acidic water molecule may be critical. It might be possible to test this possibility by studies of d^3 or low-spin d^5 pentadentate edta complexes in which the metal oxidation state is II.

Summary

Two series of pentadentate edta complexes of ruthenium, $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$ and $\text{Ru}^{\text{II}}(\text{edta})\text{L}^{2-}$, have been synthesized. The spectra of the $\text{Ru}^{\text{II}}(\text{edta})\text{L}^{2-}$ complexes strongly resemble those of $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}^{2+}$, in that, when L is a π -acceptor ligand, intense metal-to-ligand charge-transfer absorption is found in the visible region of the spectrum. Furthermore the ligand field spectra of $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ and $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ are shifted only slightly to lower energy and enhanced somewhat in intensity compared to $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ (or $\text{Ru}(\text{NH}_3)_6^{2+}$) and $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ (or $\text{Ru}(\text{NH}_3)_6^{3+}$), respectively. Both $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ and $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$ exhibit high affinities for N heterocycles (pyridine, pyrazine, etc). Since the Ru(II) affinities are 10^2 to 10^4 times greater than those for Ru(III), $\text{Ru}^{\text{III}}(\text{edta})\text{L}^-$ (L = N heterocycle) is a somewhat stronger

oxidant than $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$. Binding to edta labilizes both the Ru(III) and Ru(II) metal centers, with the magnitude of the activation being much greater for Ru(III). For Ru(II) the labilization is ascribed to an electrostatic reduction of the barrier to a dissociative substitution process. For Ru(III) the maximum reactivity observed for $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ is ascribed to steric activation of an associative process.

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Registry No. $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$, 68122-22-5; $\text{Ru}^{\text{III}}(\text{edta})\text{NCS}^{2-}$, 70208-94-5; $\text{Ru}^{\text{II}}(\text{edta})\text{H}_2\text{O}^{2-}$, 70208-95-6; $\text{Ru}^{\text{II}}(\text{edta})\text{py}^{2-}$, 70208-96-7; $\text{Ru}^{\text{II}}(\text{edta})\text{isn}^{2-}$, 70208-97-8; $\text{Ru}^{\text{II}}(\text{edta})\text{pz}^{2-}$, 70208-98-9; $\text{Ru}^{\text{II}}(\text{edta})\text{CH}_3\text{pz}^-$, 70208-99-0; $\text{Ru}^{\text{II}}(\text{edta})\text{NCS}^{3-}$, 70209-00-6; $\text{Ru}^{\text{III}}(\text{edta})\text{py}^-$, 70209-01-7; $\text{Ru}^{\text{III}}(\text{edta})\text{isn}^-$, 70209-02-8; $\text{Ru}^{\text{III}}(\text{edta})\text{pz}^-$, 68079-91-4; $\text{Ru}^{\text{III}}(\text{edta})\text{CH}_3\text{CN}^-$, 70209-03-9; $\text{Ru}^{\text{II}}(\text{edta})\text{CH}_3\text{CN}^{2-}$, 70209-04-0; $\text{Ru}^{\text{III}}(\text{edta})\text{im}$, 70235-78-8; $\text{Ru}^{\text{II}}(\text{edta})\text{im}$, 70235-79-9; imidazole, 288-32-4; pyridine, 110-86-1; isonicotinamide, 1453-82-3; pyrazine, 290-37-9; acetonitrile, 75-05-8; thiocyanate, 302-04-5.

Supplementary Material Available: Table SI, showing observed pseudo-first-order rate constants for $\text{Ru}^{\text{III}}(\text{edta})\text{H}_2\text{O}^-$ reactions with acetonitrile, isonicotinamide, pyrazine, and pyridine (4 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of ((Trimethylsilyl)methyl)indium(III) Compounds

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A series of organoindium compounds which incorporate the (trimethylsilyl)methyl ligand, $\text{In}(\text{CH}_2\text{SiMe}_3)_x\text{Cl}_{3-x}$ ($x = 1, 2, 3$), have been prepared and fully characterized by elemental analyses, NMR and IR spectroscopy, molecular weight data, solubility properties, Lewis acid-base studies, and hydrolysis experiments. The parent compound $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ was prepared from InCl_3 by a standard Grignard reaction in diethyl ether solution. All data confirm that $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, a liquid at room temperature, exists as a monomeric three-coordinate species. The ((trimethylsilyl)methyl)indium-chlorine compounds were prepared from $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ by means of an exchange reaction with InCl_3 or an elimination reaction with HCl. All properties of $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2]_2$, crystalline solids at room temperature, are consistent with chlorine-bridged dimeric structures. The available data suggest that the chlorine-bridged dimer of $[\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2]_2$ probably has extensive association in the solid state. The Lewis acid-base and hydrolysis studies suggest that the bulky (trimethylsilyl)methyl ligand does not substantially alter the behavior of the indium derivatives when compared to other analogous organoindium compounds.

Introduction

Organometallic compounds which incorporate the (trimethylsilyl)methyl ligand are of interest because of their unusual chemical properties.¹ A characteristic property of this class of compounds is their enhanced thermal stability when compared with methyl or ethyl analogues. Even though this bulky ligand has produced some transition-metal derivatives with unusual coordination numbers, many compounds are normal. Tris((trimethylsilyl)methyl)aluminum,² $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$, exists as the expected mixture of monomeric and dimeric species in benzene solution. All attempts to prepare the corresponding gallium compound² were surprisingly unsuccessful. Some compounds of the group 4 elements, germanium, tin, and lead, with the bis(trimethylsilyl)methylene ligand, $-\text{CH}(\text{SiMe}_3)_2$, have been investigated.^{3,4} The tin(II) compound exists as a dimer in the crystalline state³ and has an extensive chemistry,⁴ (i) behaving as a Lewis base, (ii) behaving as a Lewis acid, and (iii) undergoing oxidative addition reactions. Unusual radicals of the general formula, $\cdot\text{M}[\text{CH}(\text{SiMe}_3)_2]_2$ ($\text{M} = \text{Si, Ge, Sn}$), have also been prepared and characterized.⁵

In this paper we report the syntheses and complete characterization of some (trimethylsilyl)methyl derivatives of indium(III) including $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$, and

$\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$. The goal of this research was to determine whether the CH_2SiMe_3 ligand introduced any unusual or unexpected chemical properties in indium(III) chemistry.

Experimental Section

All compounds described in this investigation were manipulated in a vacuum line or a purified nitrogen or argon atmosphere. The solvents and reagents were purified by conventional means. New compounds were analyzed for indium by EDTA titration.⁶ Chlorine was determined by standard gravimetric procedures.

Preparation of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$. The compound $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ was prepared from InCl_3 and the Grignard reagent $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in diethyl ether solution.⁷ An argon-purged flask, charged with 5.62 g (25.4 mmol) of InCl_3 and 50 mL of ether, was equipped with a mechanical stirrer, condenser, dropping funnel, and inert-gas bubbler. Then, the previously prepared and standardized Grignard reagent (65 mL, 1.24 M) in ether solution was slowly added to the InCl_3 over a period of 1 h. After addition was complete, the white pasty mixture was refluxed for 3 h. Diethyl ether was removed by vacuum distillation. The product, $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, a liquid at room temperature, was then distilled from the reaction flask at 110 °C under high vacuum. The yield of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ was 7.78 g (81.5%) based on InCl_3 . Anal. Calcd for $\text{In}(\text{CH}_2\text{SiMe}_3)_3$: In, 30.5. Found: In, 30.4.

Preparative reactions for $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ with InBr_3 in diethyl ether or tetrahydrofuran lead to impure products or an adduct, $\text{In}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{THF}$. It was not possible to remove the THF from $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ quantitatively. Typical solvents for $\text{In}(\text{CH}_2\text{SiMe}_3)_3$