and HEtMeT (mp 371 K) were prepared in good yield by reacting ethylenediamine with isonitrosoethyl ethyl ketone and isonitrosopropyl methyl ketone in the same manner as that described for HMe_2T. These ligands are sparingly soluble in alcohol and are insoluble in ether.

(b) Nickel(II) Complexes. *Caution! Perchlorate salts of nickel complexes may explode.* $Ni(HMe_2T)_2(ClO_4)_2$ was prepared as follows. A 1.43-g sample of HMe_2T (0.01 mol) was added slowly to an ethanolic solution of 1.80 g of nickel(II) perchlorate hexahydrate (0.005 mol) which was being warmed and stirred continuously. Gradually the color of the solution changed to reddish brown. Upon concentration of this solution and scratching of the sides of the reaction vessel, reddish brown crystals deposited. The crystals were filtered off and were recrystallized from ethanol (~50% yield). These were dried over fused calcium chloride.

$Ni(HMe_2T)_2(NO_3)_2{\cdot}H_2O$ was prepared in an analogous manner from HMe_2T and nickel(II) nitrate hexahydrate. **$Ni(HEtMeT)_2(ClO_4)_2$** and **$Ni(HMeEtT)_2(ClO_4)_2$** were prepared in good yields by reacting nickel(II) perchlorate hexahydrate with HEtMeT and HMeEtT, respectively, in the same manner as that described for $Ni(HMe_2T)_2(ClO_4)_2$.

(c) Nickel(IV) Complexes. $Ni(Me_2T)_2(ClO_4)_2$ was prepared as follows. Five to six drops of concentrated nitric acid was added to 0.5 g of $Ni(HMe_2T)_2(ClO_4)_2$. Soon brown nitrous fumes evolved and the compound changed to a deep red mass. This was cooled to 273 K and was then diluted to twice its volume with cold water. Dark violet needles deposited (yield ~50%) out of this solution, when a few milliters of saturated sodium perchlorate solution was added to it. The crystals were filtered off and were washed successively with 95% ethanol and ether. These were then dried under vacuum over fused calcium chloride.

$Ni(EtMeT)_2(ClO_4)_2$ and **$Ni(MeEtT)_2(ClO_4)_2$** were prepared in the same manner (yield 50%) as above by treating $Ni(HEtMeT)_2(ClO_4)_2$ and $Ni(HMeEtT)_2(ClO_4)_2$, respectively, with concentrated HNO_3.

All ligands and complexes have been analyzed satisfactorily. (Analytical results are given as supplementary material.)

B. Titration of Nickel(IV) Species with Fe^{2+}. The nickel(IV) complexes $Ni(RR'T)_2{}^{2+}$ were titrated with Fe^{2+} in the same manner[12] as done with $Ni(RR'L)^{2+}$.

C. Physical Measurements. Magnetic moments, infrared spectra, electronic spectra and electrical conductivities were studied as before.[12,24] Potentiometric titrations were done on 40 mL of 0.01 M $Ni(HMe_2T)_2(NO_3)_2{\cdot}H_2O$ with carbonate-free sodium hydroxide solution (0.1 N) at 298 K. Details concerning treatment of data for obtaining K_1 and K_2 and formation curves are delineated elsewhere.[1] Cyclic voltammetry was performed in an instrument fabricated in this laboratory.[1] The i_{pa}/i_{pc} ratios were determined using procedures described in the literature.[25]

Registry No. $Ni(HMe_2T)_2(ClO_4)_2$, 63703-62-8; $Ni(HMe_2T)_2(NO_3)_2$, 63703-63-9; $Ni(HEtMeT)_2(ClO_4)_2$, 63703-65-1; $Ni(HMeEtT)_2(ClO_4)_2$, 63703-67-3; $Ni(Me_2T)_2(ClO_4)_2$, 63703-69-5; $Ni(EtMeT)_2(ClO_4)_2$, 63703-71-9; $Ni(MeEtT)_2(ClO_4)_2$, 63703-73-1; $Ni(Me_2T)_2{}^+$, 63703-74-2; $Ni(HMe_2T)(Me_2T)^+$, 63703-75-3; $Ni(EtMeT)_2{}^+$, 63703-76-4; $Ni(HEtMeT)(EtMeT)^+$, 63703-77-5; $Ni(MeEtT)_2{}^+$, 63703-78-6; $Ni(HMeEtT)(MeEtT)^+$, 63703-79-7; ethylenediamine, 107-15-3; biacetyl monoxime, 57-71-6; isonitrosoethyl ethyl ketone, 32818-79-4; isonitrosopropyl methyl ketone, 609-29-0; HMe_2T, 63702-99-8; HEtMeT, 63702-98-7; HMeEtT, 63703-00-4.

Supplementary Material Available: Table V, analytical data for ligands and complexes (1 page). Ordering information is given on any current masthead page.

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Kinetic and Equilibrium Parameters for the Reaction of Neptunium(III) with Tris(ethylenediamine)ruthenium(III)

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The kinetic and equilibrium parameters for the reaction $Np^{3+} + Ru(en)_3{}^{3+} \rightleftarrows Np^{4+} + Ru(en)_3{}^{2+}$ have been determined in aqueous trifluoromethanesulfonate media. The observed forward rate constants (in $M^{-1}\ s^{-1}$, $\mu = 1.00$ M) are: 6.40 ± 0.23 (4.3 °C), 8.96 ± 0.38 (25 °C), and 9.78 ± 0.60 (40.3 °C). The enthalpy and entropy of the reaction are −12.6 ± 1.0 kcal/mol and −41.5 ± 3.3 eu, respectively. From these values, the E_f for $Ru(en)_3{}^{3+/2+}$ in 1.0 M HCF_3SO_3 at 25 °C is calculated to be 0.167 V, in close agreement with the value of 0.172 V ($\mu = 0.013$ M) previously determined electrochemically. Activation parameters and the temperature dependence of the equilibrium quotients are similar to those determined for reactions of Np^{3+} with $Ru(NH_3)_6{}^{3+}$ and $Ru(NH_3)_5H_2O^{3+}$. From the Marcus cross relation, the self-exchange rate for $Ru(en)_3{}^{2+/3+}$ is calculated to be 5 times the corresponding rate for $Ru(NH_3)_6{}^{2+/3+}$ in contrast to the value of 0.25 times this rate reported earlier. The relative exchange rate for these two species, as calculated from expected outer-sphere reorganization energy differences, is of the same order of magnitude and direction as we report.

Introduction

A previous study[1] demonstrated that the reactions of neptunium(III) with hexaammineruthenium(III) and aquopentaammineruthenium(III) in acidic aqueous media proceed to an equilibrium position that is readily measurable. We have investigated the reaction of Np(III) with tris(ethylenediamine)ruthenium(III) and the reverse reaction of Np(IV) with tris(ethylenediamine)ruthenium(II). The resulting equilibrium data provide a basis for comparison of electrochemically derived values for the Ru(II)–Ru(III) couple.[2] Since the ligands associated with the Ru(III) complex do not allow reaction via a classical bridged mechanism, the kinetic data may be treated by means of the Marcus cross relation[3] to give an estimate of the homonuclear electron transfer rate for the Ru(II)–Ru(III) complexes.

Experimental Section

Standard Reagents. Unless otherwise specified, all chemicals were Fisher Certified or Baker Analyzed Reagent Grade. Water was distilled a second time from alkaline permanganate. Anhydrous trifluoromethanesulfonic acid (3M Co.) was slowly added to an equimolar amount of water (exercise caution! CF_3SO_3H causes severe burns) and vacuum distilled twice from an all glass apparatus. The resulting monohydrate contained 5.85 mmol of H^+/g and had a density of 1.68 g/mL at 25 °C (9.83 M). Standard lithium trifluoromethanesulfonate was prepared from weighed lithium carbonate (Baker Ultrex grade) and standardized trifluoromethanesulfonic acid. Amalgamated zinc was prepared from fine zinc powder (Alfa Ventron 99.999%) added to doubly distilled mercury, using a method adapted from Kolthoff and Belcher.[4] The mixture (4% zinc by weight) was stirred while acid was added to initiate amalgamation. The amalgam was rinsed several times with dilute acid and water. Amalgams were stirred with a magnetic stirrer during reductions of neptunium solutions.

Neptunium. Neptunium was provided by Los Alamos Scientific Laboratory on a loan basis[5] in the form of neptunium(V) hydroxide. The hydroxide was dissolved in 4 M $HClO_4$ to give a stock solution 0.08 M in neptunium and 2 M in $HClO_4$.

When Np(III) was the neptunium reactant, it was usually prepared by reduction of the Np(V) stock, diluted with appropriate amounts of acid and water, over a stirred zinc amalgam. The solution gradually changed color from green Np(V) to yellow-green Np(IV) and finally to purple Np(III), which appeared within 15 min. Since the peroxide formed from α decay[6] of ^{237}Np is reduced over zinc amalgam,[7] an additional 60 min of reducing time was allowed to ensure peroxide removal. Kinetic results obtained using Np(III) prepared by the method involving fuming perchloric acid (see below) were indistinguishable from those obtained using Np(III) prepared by reduction of Np(V).

When the reaction of Np(IV) with Ru(II) was to be monitored, the Np(IV) was prepared in the following manner: 1 or 2 mL of the stock Np(V) solution and 1 mL of concentrated $HClO_4$ were fumed to dryness, during which the neptunium is oxidized to the 6+ state and the peroxides and radicals resulting from the α decay of ^{237}Np in aqueous solution[6] are removed. The Np(VI) precipitate was then dissolved in 10 mL of 1.0 M trifluoromethanesulfonic acid, yielding a pink solution. A syringe was used to transfer 7.0 mL of the Np(VI) to a stirred zinc amalgam, where it was then reduced to the 3+ state. After deaeration of the 3 mL of Np(VI) solution remaining, 6.1 mL of Np(III) was transferred back into it. Np(V) was formed within the time of mixing and Np(IV) was formed within 30 min. The slight excess of Np(III) was gradually oxidized by trace oxygen to Np(IV), as determined spectrophotometrically.

Ruthenium(III) Complex. Tris(ethylenediamine)ruthenium(II) tetrachlorozincate was prepared by the method of Beattie[8] from acid activated $RuCl_3 \cdot nH_2O$ (Alfa Ventron), ethylenediamine, and zinc powder. Brownish-gold crystals of the tetrachlorozincate salt were obtained by cooling the acidified reaction mixture. The crystals were twice dissolved and precipitated by the addition of zinc chloride solution, giving light golden crystals.

Tris(ethylenediamine)ruthenium(III) trifluoromethanesulfonate was prepared by addition of a deaerated solution of Br_2 (1.5 g) in lithium trifluoromethanesulfonate (35 mL, 4 M) to a deaerated solution of the ruthenium(II) tetrachlorozincate salt (2 g) dissolved in trifluoromethanesulfonic acid (60 mL, 0.2 M). Bubbling with argon removed excess bromine. A cream colored or very pale green precipitate appeared when the solution was cooled in an ice bath. The precipitate (3 g) was dissolved in 5 M HCF_3SO_3 (25 mL) and 5 M $LiCF_3SO_3$ (3 mL) and cooled in an ice bath. The resulting precipitate was filtered and dried in a vacuum oven at 58 °C for 4 h (68% yield). The dried precipitate was always cream colored. The magnetic susceptibility (Faraday method, Cahn system) was 1.95 μ_B at 298 °C (no diamagnetic correction) as expected for low-spin Ru(III). Anal. Calcd for $Ru(en)_3(CF_3SO_3)_3$: C, 14.84; H, 3.32; N, 11.53; Br, 0.0. Found: C, 14.83; H, 3.33; N, 11.36; Br, 0.32. Purification on Dowex 50W-X2 cation exchange resin to remove Br^-, followed by crystallization, produced material which gave kinetic results that were indistinguishable from the analyzed material. Although the crystalline material is stable, solutions of $[Ru(en)_3](CF_3SO_3)_3$ decompose over a period of days to give dark yellow solutions of undetermined composition. When Ru(II) was the reactant form, it was prepared immediately before use by reacting a slight excess of the Ru(III) complex with Eu(II).

Apparatus. An all glass and Teflon inert gas train was utilized. Argon was passed through two chromous scrubbing towers. Solutions requiring deaeration were contained in Erlenmeyer flasks adapted for this purpose by attachment of an L-shaped gas inlet tube near the base of the flask. The other end of the inlet tube terminated in a ball joint which was clamped to the gas train. The top of the flask was protected by a loose fitting thimble-shaped insert with a 1–2-mm hole at its lowest point to allow withdrawal of solution by syringe. Gas-tight syringes and Teflon needles (Hamilton G) were used.

The Cary 14 cell compartment was modified as described by Newton and Baker[9] to accommodate the use of stirred cells. The stirred cells used were Pyrex test tubes (15 × 125 mm), with an effective path length of 14.0 ± 0.1 mm. Cell contents were homogenized within 5 s by a 0.5-in. Teflon stir bar. The level of the reactant solution in the test tube was lower than the level of liquid in the bath surrounding the tube. Temperature control was achieved to 0.1 °C with a Haake Model FK-2 circulating bath.

Procedures. Reactant solutions were used the same day as prepared. Deaeration of solutions in the stirred cells was accomplished by 15 min of argon flow. The rate of oxygen leakage was $<4 \times 10^{-4}$ mequiv/min, as determined by the rate of formation of Np(IV) from Np(III) before addition of Ru(III). This is insignificant on the time scale of the reactions reported herein.

Analysis of trifluoromethanesulfonate anion was conducted by gravimetric determination of the tetraphenylarsonium salt.[10] As an example of the reliability of this method, the following comparative results were obtained: treatment of lithium trifluoromethanesulfonate aliquots gave calculated molarities of the original solution of 5.55 ± 0.02 M (three determinations), while standardization by cation exchange gave 5.55 ± 0.07 M (three determinations).

Concentrations of Np(III) and Np(IV) solutions were determined spectrophotometrically from absorption maxima in the visible or near-infrared region of the spectrum. Extinction coefficients at 40, 25, and 5 °C were determined by spectrophotometric titration of Np(III) at each temperature. The titrant was Ce(IV) in 1.0 M $HClO_4$, which was itself standardized vs. Fe(II) after each neptunium titration. Although Ce(IV) is capable of oxidizing Np(III) to Np(V) and Np(VI) as well as Np(IV), these species react to form Np(IV) as long as some Np(III) is present. The solutions were allowed to come to equilibrium after each Ce(IV) addition. The slope of the plot of absorbance vs. Ce(IV) concentration was used to obtain extinction coefficients. These were in excellent agreement with those determined from the Ce(IV) titre. Average values of the extinction coefficients (in M^{-1} cm^{-1}) in 1.0 M $HClO_4$ are: from the slope, Np(III) at 552 nm, 46.2 ± 0.4 (5 °C), 43.6 ± 0.01 (25 °C), 41.6 ± 0.5 (44 °C), and from the titre, 42.5 ± 1.5 (25 °C); from the slope, Np(III) at 723.5 nm, 1.3 ± 0.4 (5 °C), 0.9 ± 0.01 (25 °C), 0.5 (1 determination, 44 °C); Np(IV) at 723.5 nm, 167 ± 1 (5 °C), 154 ± 1 (25 °C), 139 ± 1 (44 °C), and from the titre, 155 ± 1 (25 °C); and Np(IV) at 552 nm, 0.0 ± 0.5 at all three temperatures. The value for the extinction coefficient of Np(IV) agrees with that reported previously[1] of 158 ± 5 at 723.5 nm at 25 °C.

For experiments in which Np(IV) was reduced by Ru(II), the initial Ru(II) concentration was set equal to the total concentration of the europium that was used to reduce the corresponding Ru(III) species. The initial Ru(III) concentration was set equal to the difference between the total ruthenium and the ruthenium(II) concentration. The initial Np(IV) concentration was obtained by extrapolating the absorbance vs. time curve to the time of mixing.

Data Treatment. The Los Alamos Non-Linear Least Squares Program,[13] with subroutines related specifically to the data reported herein, was used to fit all data. Absorbance vs. time data were in accordance with the rate law

$$R = k_f[\mathrm{Np(III)}][\mathrm{Ru(III)}] - k_r[\mathrm{Np(IV)}][\mathrm{Ru(II)}]$$

Table I. Typical Rate Run for the Reaction[a] $Np^{3+} + Ru(en)_3{}^{3+} \rightleftarrows Np^{4+} + Ru(en)_3{}^{2+}$

	OD			OD	
Time,[c] s	Obsd	Calcd[b]	Time, s	Obsd	Calcd
0.0	0.087[d]				
3.75	0.247	0.249	17.5	0.517	0.517
5.0	0.289	0.288	20.0	0.541	0.540
6.25	0.323	0.323	22.5	0.558	0.560
7.50	0.358	0.355	25.0	0.577	0.576
8.75	0.382	0.383	27.5	0.588	0.589
10.0	0.409	0.409	30.0	0.599	0.599
11.25	0.431	0.432	35.0	0.614	0.615
12.5	0.451	0.453	40.0	0.623	0.626
13.75	0.472	0.471	50.0	0.638	0.638
15.0	0.489	0.488	70.0	0.650	0.647
16.25	0.505	0.503	∞	0.656	0.649

[a] Starting conditions: $[Np(III)]_i = 4.02 \times 10^{-3}$M, $[Ru(III)]_i = 6.01 \times 10^{-3}$M, $[Np(IV)]_i = 1.0 \times 10^{-5}$M, $[Ru(II)]_i = 0$, $T = 25$ °C. [b] Calculated using the integrated form of the rate law for second-order approach to equilibrium, $k_f = 9.51 \pm 0.078$ M^{-1} s^{-1}. [c] Effective starting time of reaction was −0.25 s. [d] Fixed.

A description of the integrated form of the rate law for second-order approach to equilibrium has been presented previously.[1] Rate data used in calculating activation parameters were weighed as $1/\sigma^2$ where σ is the least-squares estimate of the uncertainty in each rate constant.

The equilibrium quotients can be expressed as:

$$Q = \frac{([Np(IV)]_i + \Delta)([Ru(II)]_i + \Delta)}{([Np(III)]_i - \Delta)([Ru(III)_i - \Delta)} \tag{1}$$

where Δ, the change in concentration of neptunium(IV), is given by

$$\Delta = \frac{OD_\infty - OD_i}{l\Delta\epsilon} \tag{2}$$

and $\Delta\epsilon = \epsilon(Np(IV)) - \epsilon(Np(III))$. The magnitude of Δ was usually determined at 723.5, and occasionally at 552 nm. The values of $\Delta H°$ and $\Delta S°$ are obtained from the least-squares fit of the equation

$$\Delta = \frac{-B + [B^2 - 4AC]^{1/2}}{2A} \tag{3}$$

where

$$\begin{aligned} A &= Q - 1 \\ B &= -Q([Np(III)]_i + [Ru(III)]_i) + [Np(IV)]_i + [Ru(II)]_i \\ C &= Q[Np(III)]_i[Ru(III)]_i - [Np(IV)]_i[Ru(II)]_i \end{aligned} \tag{4}$$

and Q is given by

$$Q = e^{-\Delta H°/RT} e^{\Delta S°/R} \tag{5}$$

The adjustable parameters are $\Delta H°$ and $\Delta S°$ and the independent variables are the initial concentrations of reactants and products and the temperature. Q is obtained from the least-squares values of $\Delta H°$ and $\Delta S°$.[11]

Results and Discussion

Equilibrium Quotients. Using data obtained from monitoring the forward reaction, the values obtained for $\Delta H°$ and $\Delta S°$ are −12.6 ± 1.0 kcal/mol and −41.5 ± 3.3 eu. Including the data obtained from monitoring the reverse reaction the values obtained for $\Delta H°$ and $\Delta S°$ are −13.2 ± 1.5 kcal/mol and 43.0 ± 5.1 eu. The root mean square of the deviation between the experimentally determined and calculated values of $\Delta OD/l\Delta\epsilon$ are 6 and 11% for the small and large data sets, respectively. The larger deviation reflects the uncertainty added when OD_0 (and $[Np(IV)]_i$) are obtained by extrapolation. The thermodynamic parameters obtained by considering only data derived from the forward reaction are therefore used to determine the values of Q used in further calculations. These values are: 7.81 (4.3 °C), 1.59 (25 °C), and 0.560 (40.3 °C).[12] The highly negative entropy is consistent with the change in charge distribution.

Calculations from Thermodynamic Data. The formal potential can be calculated for the $Ru(en)_3{}^{3+/2+}$ couple using the known value[14] of the $Np^{4+/3+}$ formal potential of +0.1551 V at 25 °C in 1 M $HClO_4$. The calculated potential for the reduction of tris(ethylenediamine)ruthenium(III) is 0.167 V in 1 M HCF_3SO_3. Meyer and Taube[2] report a value of 0.172 V at 25 °C at an ionic strength of 0.013 M. The agreement of these two figures indicates that the potential is insensitive to ionic strength.

A summary of thermodynamic quantities for the reactions of Np^{3+} with three ruthenium(III) ammine complexes is given in Table II. The quantity $S°_{2+} - S°_{3+}$ has been calculated using two other quantities:

$Np^{3+} + H^+ \rightarrow Np^{4+} + {}^1/_2H_2$ $\Delta S° = -31.2 \pm 0.8$ eu

$e^- + H^+ \rightarrow {}^1/_2H_2$ $\Delta S° = 21.1$ eu

The second half-reaction assumes $S°(H^+) = -5.5$ eu[15] and $S°(H_2) = 31.2$ eu.[16] For the case of the hexaammineruthenium complex the quantity $S°_{red} - S°_{ox}$ has been corrected from that reported earlier. The similarity in the $\Delta S°$ values for the hexaammineruthenium(III) and tris(ethylenediamine)ruthenium(III) reactants indicates the great degree of similarity of the two complexes. The addition of the ethylene bridges in the latter complex apparently does not significantly alter the change in entropy of the ruthenium couple, indicating that approximately the same changes in the outer hydration shell occur during reduction of both ruthenium complexes.

Activation Parameters. Tables III and IV include rate data at 4.3, 25, and 40.3 °C. The average values at these three temperatures are: 6.40 ± 0.25 M^{-1} s^{-1} (k_f), 8.96 ± 0.51 M^{-1} s^{-1} (k_f) and 5.65 ± 0.66 M^{-1} s^{-1} (k_r), and 9.78 ± 0.60 M^{-1} s^{-1} (k_f), respectively. The activation parameters for the forward reaction calculated from these data are $\Delta H^\ddagger = 1.50 \pm 0.21$ kcal/mol and $\Delta S^\ddagger = -49.2 \pm 0.7$ eu. Using the thermodynamic data and these activation parameters, the calculated values of the activation parameters for the reverse reaction are $\Delta H^\ddagger = 14.1 \pm 1.2$ and $\Delta S^\ddagger = -90.7 \pm 4.0$.

Magnitude of Activation Parameters. A comparison of the activation parameters demonstrates that the behavior of the tris(ethylenediamine)ruthenium complex toward Np^{3+} is very similar to that of the other two ruthenium complexes. The enthalpy terms are all small, making the entropic barrier the most significant factor in determining the reaction rate. The striking feature of all these reactions is the large magnitude of the activation entropy. The most negative of all is that observed for the $Ru(en)_3{}^{3+}$ complex. It was previously suggested[1] that the magnitudes of $\Delta S^\ddagger$ for the other two ruthenium complexes may indicate an unorthodox transition state, possibly involving electron transfer at an octahedral face of the ruthenium complex. The ethylene bridges in the

Table II. Thermodynamic Parameters for Reactions of the Type Np(III) + Ru(III) ⇄ Np(IV) + Ru(II)

Reaction	$\Delta H°$, kcal/mol	$\Delta S°$, eu	$S°_{2+} - S°_{3+}$,[a] eu
$Np^{3+} + Ru(NH_3)_5H_2O^{3+} \rightarrow Np^{4+} + Ru(NH_3)_5H_2O^{2+}$	−8.7 ± 0.2	−34.8 ± 0.8	17.5 ± 1.1
$Np^{3+} + Ru(NH_3)_6{}^{3+} \rightarrow Np^{4+} + Ru(NH_3)_6{}^{2+}$	−11.5 ± 0.7	−45.4 ± 1.7	6.9 ± 1
$Np^{3+} + Ru(en)_3{}^{3+} \rightarrow Np^{4+} + Ru(en)_3{}^{2+}$	−12.6 ± 1.0	−41.5 ± 3.3	10.9 ± 3.7

[a] Assuming $S°(H^+) = -5.5$ eu and $S°(H_2) = 31.2$ eu (ref 15 and 16).

Table III. Values of the Rate Constant Determined at 25 °C in 1.0 M HCF_3SO_3

$Np^{3+} + Ru(en)_3{}^{3+} \xrightarrow{k_f} Np^{4+} + Ru(en)_3{}^{2+}$				$Np^{4+} + Ru(en)_3{}^{2+} \xrightarrow{k_r} Np^{3+} + Ru(en)_3{}^{3+}$			
$[Ru(III)]_0 \times 10^{+3}$, M	$[Np(III)]_0 \times 10^{+3}$, M	$[Np(IV)]_0 \times 10^{+3}$, M	k_f, M^{-1} s^{-1}	$[Ru(II)]_0 \times 10^{+3}$, M	$[Np(IV)]_0 \times 10^{+3}$, M	$[Ru(III)]_0 \times 10^{+3}$, M	k_r, M^{-1} s^{-1}
3.60	8.37	0.15	8.71 ± 0.11	4.99	3.27	0.51	5.39 ± 0.12
3.60	7.52	0.14	9.20 ± 0.07	5.13	5.89	0.43	6.65 ± 0.12
4.82	9.75	0.00	8.86 ± 0.04	5.24	4.88	0.44	5.89 ± 0.12
3.60	6.81	0.16	9.19 ± 0.15[a]	5.86	3.13	0.92	4.54 ± 0.13
4.02	6.08	0.034	8.83 ± 0.09	7.11	4.54	0.59	6.23 ± 0.19
4.02	5.96	0.003	9.14 ± 0.11[a]	7.82	4.64	0.82	5.34 ± 0.11
4.02	6.01	0.010	9.51 ± 0.08[a]	3.59	5.05	0.85	6.04 ± 0.26
4.02	5.92	0.68	8.74 ± 0.15	5.98	2.11	0.94	5.43 ± 0.21
4.57	5.34	0.064	8.10 ± 0.06	5.98	1.94	0.94	4.82 ± 0.20
6.54	6.90	0.28	8.45 ± 0.10	7.97	4.59	0.84	6.16 ± 0.07
5.36	5.34	0.076	8.47 ± 0.05				
7.23	5.39	0.010	8.54 ± 0.07				
7.23	5.41	0.020	8.79 ± 0.06				
7.20	3.89	0.079	8.39 ± 0.09[a]				
7.20	3.73	0.11	9.16 ± 0.14				
9.65	4.05	0.00	9.37 ± 0.06				
2.99	3.99	0.00	9.71 ± 0.11				
2.90	4.73	0.00	8.40 ± 0.11				
2.70	4.21	0.00	9.94 ± 0.09				
2.99	4.27	0.036	9.66 ± 0.06				
			Av 8.96 ± 0.51				Av 5.65 ± 0.66

[a] In 0.3 M HCF_3SO_3 and 0.7 M $LiCF_3SO_3$.

Table IV. Values of the Rate Constant Determined at 4.3 and 40.3 °C in 1.0 M HCF_3SO_3

4.3 °C				40.3 °C			
$[Ru(III)]_0 \times 10^3$, M	$[Np(III)]_0 \times 10^3$, M	$[Np(IV)]_0 \times 10^3$, M	k_f, M^{-1} s^{-1}	$[Ru(III)]_0 \times 10^3$, M	$[Np(III)]_0 \times 10^3$, M	$[Np(IV)]_0 \times 10^3$, M	k_f, M^{-1} s^{-1}
2.88	5.13	0.00	6.62 ± 0.07	5.64	6.98	0.016	8.94 ± 0.09
4.57	4.96	0.018	6.37 ± 0.05	4.49	5.43	0.035	10.38 ± 0.18
4.57	4.85	0.00	6.63 ± 0.07	4.57	5.08	0.164	10.25 ± 0.14
5.36	4.87	0.00	6.03 ± 0.05	7.89	6.08	0.00	10.08 ± 0.13
5.36	4.67	0.023	6.36 ± 0.05	8.05	5.43	0.037	9.15 ± 0.06
				8.20	4.91	0.092	9.90 ± 0.08
			Av 6.40 ± 0.25				Av 9.78 ± 0.60

tris(ethylenediamine)ruthenium complex would not be expected (from space filling models) to block these faces significantly; hence, the highly negative $\Delta S^{\ddagger}$ obtained for this reaction is not inconsistent with this hypothesis. The evidence concerning the possibility of such an activated complex has been reviewed by Taube.[17]

Calculations of Exchange Rates. According to the Marcus cross relation

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$$

where k_{11} and k_{22} are the self-exchange rates of the reactants, k_{12} is the rate of the cross reaction, and K_{12} is the equilibrium constant for the cross reaction, and f, for the case of K_{12} close to unity, is also near unity. In terms of k_{RuA_6}, the self-exchange rate for hexaammineruthenium(III), $k_{Ru(en)_3}$, the self-exchange rate for the tris(ethylenediamine)ruthenium complex, can be calculated using the expression

$$k_{Ru(en)_3} = \frac{k_{Ru(en)_3\text{-}Np}{}^2}{K_{Ru(en)_3\text{-}Np}} \frac{K_{RuA_6\text{-}Np}}{k_{RuA_6\text{-}Np}{}^2} k_{RuA_6}$$

The rate of reaction of $RuA_6{}^{3+}$ with Np^{3+} has been determined at an ionic strength of 0.5 ($k_{RuA_6\text{-}Np} = 0.305$ M^{-1} s^{-1}, 25 °C). Because of the squared dependence on this quantity, an estimate of its value at 1.0 M should be made. As pointed out by Newton,[18] the values of the ionic strength parameters for a large number of redox reactions are approximately constant. In other work in this laboratory,[19] the ratio of rate constants for the reaction of U(III) with $Ru(NH_3)_6{}^{3+}$ at $\mu = 1.0$ and 0.5 M had been obtained. Assuming that the ratios of rate constants obtained at 1.0 and 0.5 M are the same for the reactions of hexaammineruthenium(III) with both U(III) and Np(III),[18] the value of k_f for the reaction with Np(III) is 1.8 times faster at 1.0 M than at 0.5 M.

Substituting in all values

$$k_{Ru(en)_3} = \frac{8.96^2}{1.57} \frac{0.031}{(0.305 \times 1.8)^2} k_{RuA_6}$$

or

$$k_{Ru(en)_3} = 5k_{RuA_6}$$

Data obtained by Taube and Meyer[2] from an attempt to measure the self-exchange rate directly (at 0.013 M) indicate that the relation between the two is $k_{Ru(en)_3} = 0.25k_{RuA_6}$. In general, the direct experiment would be expected to give the better estimate of the self-exchange rate; however, in this case the experimental difficulties encountered in the direct experiment discourage this choice. In the previous work, much of the data does suggest a higher value for the self-exchange rate and the reasonable assumption was made that the high values were caused by catalytic impurities. In this work, no evidence of catalytic impurities has been found. No variation in the rate of reaction is observed as preparations of the ruthenium compound were varied, including the preparation separated by ion exchange. The reaction also gives no erratic results and the equilibrium constants calculated from the rates of forward and reverse reactions agree with the equilibrium constants calculated from the concentrations of the species observed at equilibrium. The observed OD_∞ values also agree

Table V. Summary of Exchange Rates Relative to the Exchange Rate of Hexaammineruthenium

$k_{Ru(en)_3}$	$k_{RuA_5H_2O}$	μ, M	Method of calcn
$0.25k_{RuA_6}$		0.013	Direct self-exchange[a]
$5k_{RuA_6}$	$0.12k_{RuA_6}$	1.0	Rate of Ru–Np series; application of Marcus cross relation

[a] Reference 2.

with calculated OD_∞ values, indicating no lag in the establishment of the equilibrium observed at the kinetic t_∞. The lack of any spurious behavior suggests that the present results can be considered as a true representation of the Np^{3+}–$Ru(en)_3{}^{3+}$ reaction, unperturbed by the presence of catalysts or inhibitors. Hence, in this case the estimate of the self-exchange rate from the Marcus cross relation may be the more accurate value. Table V presents the results of the various estimates for the self-exchange rates of these ruthenium–ammine complexes. The value for the exchange rate of aquopentaammineruthenium(III) has been recalculated from that reported earlier using the estimate of the rate constant at 1.0 M for the reaction of Np^{3+} with $Ru(NH_3)_6{}^{3+}$.

The factor of 5 in rate for the case of the tris(ethylenediamine)ruthenium complex indicates a difference of 0.5 kcal in the energy of activation. A difference of this magnitude can be explained on the basis of differences in outer-sphere reorganizational energy; for an exchange reaction in aqueous solution at 25 °C, the equation for describing $\Delta G_0{}^\ddagger$ (the outer-sphere reorganizational barrier contribution) for a one-electron transfer reduces to the form[20]

$$\Delta G_0{}^\ddagger = 22.7/r_\ddagger \text{ kcal/mol}$$

where $r_\ddagger$ is the radius of either complex in the activated complex. Clearly, the contribution of this term to the exchange rate decreases as $r_\ddagger$ increases. The difference in this term for two different exchanges will be

$$\Delta\Delta G_0{}^\ddagger = \frac{-22.7\Delta r}{r_\ddagger(r_\ddagger + \Delta r)} \text{ kcal/mol}$$

where the difference has been taken for $\Delta G_0{}^\ddagger$ of the larger ($r = r_\ddagger + \Delta r$) minus $\Delta G_0{}^\ddagger$ of the smaller ($r = r_\ddagger$). The magnitude of $\Delta\Delta G_0{}^\ddagger$ will be quite sensitive to the evaluation of the radii. If the radius of the hexaammineruthenium complexes is taken to be 5 Å[21] and the presence of the ethyl groups in the chelated complex is assumed to add 20% to the radius,[22] then the estimate of $\Delta\Delta G_0{}^\ddagger$ in this case will be −0.76 kcal/mol. This value is of the same order of magnitude and in the correct direction as the difference in exchange rate that has been predicted from the Np^{3+}–$Ru(en)_3{}^{3+}$ reaction.

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Registry No. $Ru(en)_3(CF_3SO_3)_3$, 63703-89-9; $Ru(NH_3)_5H_2O^{3+}$, 25590-52-7; $Ru(NH_3)_6{}^{3+}$, 18943-33-4; $Ru(en)_3{}^{2+}$, 21393-86-2; $Ru(NH_3)_6{}^{2+}$, 19052-44-9; $Ru(NH_3)_5H_2O^{2+}$, 21393-88-4; Np^{3+}, 21377-65-1; Np^{4+}, 22578-82-1.

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