

Synthesis and Properties of the Ru(tacn)₂^{3+/2+} Couple and NMR Study of the Electron Self-Exchange (tacn = 1,4,7-Triazacyclononane)

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The tridentate ligand tacn (1,4,7-triazacyclononane) reacted at room temperature with the Ru(DMF)₆²⁺ (DMF = *N,N'*-dimethylformamide) complex to form the complex Ru(tacn)₂²⁺, from which Ru(tacn)₂³⁺ was obtained by chemical or electrochemical oxidation. The couple exhibited a reversible formal potential of 0.37 V (vs NHE) and a large electron-self-exchange rate constant ($k_{\text{ex}} = 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $\mu = 0.1 \text{ M}$, $T = 23 \text{ }^\circ\text{C}$) as measured directly by the broadening, in the presence of Ru(tacn)₂³⁺, of (a) the single ¹³C NMR signal and (b) the ¹H multiplet of Ru(tacn)₂²⁺. The large rate constant fits well into the series of Ru amine complexes and, allowing for the effect of strain in the ligand on electron exchange reactions, also compares well with those for the corresponding cobalt and nickel couples, supportive of adiabatic behavior in all cases. Due to their high stability and inertness, both Ru(tacn)₂²⁺ and Ru(tacn)₂³⁺ are useful outer-sphere electron-transfer agents. Interestingly, Ru(tacn)₂³⁺ is rather unreactive toward dehydrogenation of the coordinated amine ligand, in contrast to other Ru(III) complexes. The UV-vis spectra of both complexes are dominated by charge-transfer bands. For the Ru(II) complex a weak band at 355 nm (60 M⁻¹ cm⁻¹) is assigned to the spin-allowed transition of ¹A_{1g}-¹T_{1g} parentage, confirming the observation made in other tacn complexes that the ligand exerts a substantially stronger ligand field on the metal than ammonia and ethylenediamine. Assignments for the absorption spectrum of Ru(tacn)₂³⁺, which exhibits a surprising low-energy band at 375 nm (300 M⁻¹ cm⁻¹), are discussed.

Introduction

Ruthenium(II) and -(III) complexes are among the most extensively studied redox couples owing to the pioneering work of Taube and collaborators.¹ Complexes with N-donor ligands exhibit substantial electron-self-exchange rate constants ranging from 10³ M⁻¹ s⁻¹ for the Ru(NH₃)₆^{3+/2+} to the nearly diffusion-controlled rate constant of 10⁹ M⁻¹ s⁻¹ for the Ru(2,2'-bipyridine)₃^{3+/2+} couple.³ Owing to their inertness these complexes are ideally suited for outer-sphere electron-transfer studies, and rates have been successfully interpreted in terms of the current electron-transfer theories.⁴ In spite of this, some aspects concerning basic thermodynamic properties of the complexes are less well understood. Examples are the stability of Ru(NH₃)₆³⁺ in acidic and neutral solution versus the instability of Ru(sar)₃³⁺ (sar = the encapsulating ligand 3,6,10,13,16,19-hexaazabicyclo[6.6.6]heptacosane) toward disproportionation to Ru(II) and Ru(IV) even in acidic solution⁵ and the evidence for protonation of the Ru(II) metal center at low pH.^{5b,6}

In the light of these disparate properties, the Ru(tacn)₂^{3+/2+} couple was of particular interest to us. The complexes possess (as do Ru(sar)₃^{3+/2+}) only secondary nitrogen atoms. It could be anticipated that the cyclic amine ligand would form inert complexes with ruthenium, as it does with many other transition and main-group elements,⁷ but the properties of the Ru(III) complex with respect to disproportionation could not be predicted.

In this paper we wish to report the syntheses and properties of this redox couple and the results of an NMR study on the electron-self-exchange rate and to discuss kinetic and thermodynamic implications of NMR, electrochemical, and spectral data. Some electron-transfer reactions of the couple have already been reported⁸ as well as a different synthetic route to Ru(tacn)₂²⁺⁹

Experimental Section

A. Materials and Physical Measurements. Deionized (for syntheses) and doubly distilled water (for electrochemical measurements) was used. Trifluoromethanesulfonic (triflic) acid was distilled at reduced pressure before use. AgCF₃SO₃¹⁰ and the ligand 1,4,7-triazacyclononane (tacn)¹¹ were synthesized as reported. Acetonitrile was distilled from CaH₂ before use. Tetrabutylammonium triflate (TBAT) was synthesized by neutralizing triflic acid with tetrabutylammonium hydroxide and was recrystallized from dichloromethane/ether (1:10). All other reagents were of analytical grade and were used without further purification. D₂O was obtained from the AAEC (Lucas Heights, Australia). UV-vis spectra were recorded on a HP 8450 rapid-scan spectrophotometer, and electrochemical measurements were performed on a BAS-100 or a PAR 173/174 system with the usual three-electrode configuration. Formal potentials were measured vs calomel or Ag/AgCl but are quoted vs NHE

with the couples (NH₃)₅RuL^{3+/2+} (L = NH₃, pyridine, isonicotinamide) as references.¹² Controlled-potential coulometry (CPC), using an AMEL 551 Coulostat and an AMEL 731 digital integrator, was performed in a small cell (3-10-mL capacity) at a Pt-gauze working electrode.

All the NMR measurements were performed with a Varian XL200E spectrometer operating at 200 MHz (¹H) and 50 MHz (¹³C); one spectrum of Ru(tacn)₂²⁺ was recorded with a Bruker 500-MHz instrument at the California Institute of Technology. All measurements were done at 23 °C, measured by the chemical shift difference of the signals of pure MeOH.¹³ Samples for the kinetic experiments were prepared as follows: Crystallized [Ru(tacn)₂](CF₃SO₃)₂ was added portionwise, under argon, to 0.4 mL of 0.01 M CF₃SO₃D until the solution was saturated (≈0.035 M). (This was achieved by bubbling the solution in the NMR tube with argon with the use of very fine PE tubing). Consecutive spectra of this solution allowed the measurement of the slow rate of the H/D exchange for the amine protons. Afterward, 0.05-mL aliquots of solutions (0.01 M CF₃SO₃D) of appropriate concentration in AgCF₃SO₃ were added successively, and the spectra were recorded after each addition. In one experiment a few large crystals of Ru(tacn)₂(CF₃SO₃)₂ were added in excess to keep the Ru(II) concentration constant. Concentrations of Ru(tacn)₂³⁺ and Ru(tacn)₂²⁺ are given in Table II. The ionic strength was thus $\mu \approx 0.1 \text{ M}$, largely determined by the Ru(II) concentration. The Ag metal formed was centrifuged to the bottom of the 5-mm NMR tube although no effect on the spectrum could be seen when the solutions were not centrifuged. This technique of generating Ru(tacn)₂³⁺ in the presence of an excess of Ru(tacn)₂²⁺ was used because the reactivity of Ru(tacn)₂³⁺ toward disproportionation was unknown at the time. No time dependence of the spectra was observed on the time scale of the

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experiments. Solutions of Ru(tacn)₂³⁺ slowly turned red-orange after 2–3 days (at pH 2).

Information about the electron self-exchange was obtained from the ¹³C spectra by determining the line width of the single signal of Ru(tacn)₂²⁺ at –10 ppm vs 1,4-dioxane and from the ¹H spectra by measuring the width of the multiplet at 2.8 ppm vs DSS. The widths of both signals were found to depend linearly on the concentration of Ru(tacn)₂³⁺

$$\Delta\nu_{1/2} = \Delta\nu_{1/2}^0 + k[\text{Ru}(\text{tacn})_2^{3+}] \quad (1)$$

but no change in chemical shift was observed, indicating that the system was in the slow-exchange domain.¹⁴ To assess this and thus the validity of eq 1, an excess of Ag⁺ was added to one of the solutions after the kinetic measurements in order to record the spectra of the paramagnetic Ru(tacn)₂³⁺ complex. Whereas no signal was detected in the ¹³C spectrum, a broad feature occurred at ≈5 ppm in the ¹H spectrum, overlapping with the solvent peak at 4.8 ppm. In a separate experiment, the concentrations of the two complexes were kept equal (0.012 M): the broad ¹H signal (≈250 Hz) was at the same chemical shift as the signal in the absence of Ru(tacn)₂³⁺. These observations indicate that the observed electron-exchange rate in the kinetic experiments is slow compared to the relaxation rates of the paramagnetic Ru(tacn)₂³⁺ complex and/or the differences in the chemical shifts between the two species and, therefore, that the system is in the slow-exchange domain.¹⁴

$$1/T_{2\text{obsd}} = 1/T_2^0 + k_{11}[\text{Ru}(\text{tacn})_2^{3+}] \quad (2)$$

where 1/T₂ and k₁₁ are the transverse relaxation rate (obsd: in the presence of Ru(tacn)₂³⁺) and the electron-self-exchange rate, respectively. Since¹⁴ 1/T₂ = π(Δν_{1/2}) and if comparison is made with eq 1

$$k_{11} = \pi k' \quad (3)$$

B. Syntheses. [Ru(tacn)₂](CF₃SO₃)₂. A 0.3-mmol amount of [Ru(DMF)₆](X)₂²⁺ was added under argon to 3 mL of dry ethanol (X = triflate) or propan-2-ol (X = tosylate) containing 0.8 mmol of 1,4,7-triazacyclononane.¹¹ The dark red solution was stirred at room temperature until all of the DMF salt had dissolved and was then kept at room temperature under argon for 2–3 days, during which time the color changed to yellow and a yellow crystalline material deposited. The solution was cooled to –10 °C to complete crystallization, and the precipitate was collected, washed with a small amount of ethanol or propan-2-ol and ether, and air-dried. The tosylate salt was recrystallized by dissolving it in oxygen-free water (≈0.1 M) and adding 4 M triflic acid (final [H⁺] ≈ 0.5 M). It was isolated as described above. Yield: 70%. Anal. Calcd (found) for [Ru(C₆H₁₅N₃)₂](CF₃SO₃)₂: C, 25.57 (25.8); H, 4.60 (4.6); N, 12.78 (12.7); S, 9.75 (9.1); F, 17.33 (16.7). The pale yellow compound was stable in air over weeks. Large crystals can be obtained by slowly cooling a saturated ethanolic solution under argon.

[Ru(tacn)₂](CF₃SO₃)₃. [Ru(tacn)₂](CF₃SO₃)₂ (0.2 mmol) was dissolved in 4 mL of 0.2 M TBAT in acetonitrile and oxidized by CPC at a constant potential of 0.8 V vs Ag/AgCl until the current had dropped to <0.5% of its initial value. Integration of the current indicated a clean one-electron oxidation. An equal amount of dichloromethane was added to the solution to precipitate the compound, which was collected, washed with a small amount of ether, air-dried, and then recrystallized from acetonitrile/ether. Yield: 80%. Anal. Calcd (found) for [Ru(C₆H₁₅N₃)₂](CF₃SO₃)₃: C, 22.33 (22.0); H, 3.75 (3.8); N, 10.42 (10.0); S, 11.92 (11.6); F, 21.19 (20.6). A faster method of preparing the (ClO₄)⁻ salt involved the oxidation of the Ru(II) complex in 0.1–1 M triflic acid by Fe³⁺ and precipitation by NaClO₄. *Caution!* The perchlorate salt is a potential hazard (explosive).

Results

Synthesis and Properties of the Complexes. Both Ru(tacn)₂^{3+/2+} ions have been synthesized from the remarkably labile Ru(DMF)₆²⁺ ion and the pure ligand in alcohol solution. This method has now been employed successfully with various strongly basic ligands^{5,15,48} and is clearly a general synthetic route. The DMF complex should be freshly prepared: "Aged" material (brown color) gives drastically reduced yields.

The absorption spectra of the two complexes are shown in Figure 1, and for comparative purposes, spectral and electrochemical properties of various Ru(II) and Ru(III) amine complexes are summarized in Table I. The spectrum of the Ru-

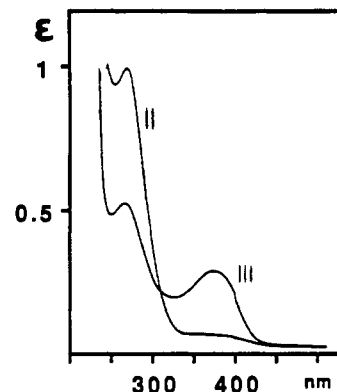


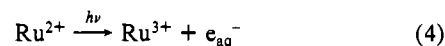
Figure 1. Optical spectra of Ru(tacn)₂²⁺ (II) and Ru(tacn)₂³⁺ (III) in 0.1 M CF₃SO₃H (ε in 10³ M⁻¹ cm⁻¹).

Table I. Spectral and Electrochemical Properties of Ruthenium Amine Complexes

	10 ⁻³ ν _{max} , cm ⁻¹ (ε _{max} , M ⁻¹ cm ⁻¹)		E', V ^a
	z = 2	z = 3	
Ru(NH ₃) ₆ ²⁺ ^b	25.64 (35)	31.25 (100)	0.07
	36.36 (640)	36.36 (480)	
Ru(en) ₃ ²⁺ ^c	27.03 (120)	32.25 (360)	0.15
	33.11 (1020)		
Ru(sar) ²⁺ ^d	25.97 (40)		0.29
	25.46 (2000)		
Ru(tacn) ₂ ²⁺ ^e	28.17 (60)	26.59 (330)	0.37 ^f
	37.45 (980)	37.45 (550)	

^a Versus NHE. ^b 0.1 M NaClO₄; ref 2a. ^c 0.01 M CF₃COOH; ref 2a. ^d 0.1 M CF₃SO₃H; ref 5a. ^e 0.1 M CF₃SO₃H; this work. ^f In agreement with ref 9.

(tacn)₂²⁺ complex (II) exhibits a shoulder at 355 nm (28.17 × 10³ cm⁻¹), which is assigned to the lowest spin-allowed transition of ¹A_{1g}–¹T_{1g} parentage. This assignment implies a significantly stronger ligand field for tacn than for the other amines (Δ (in 10³ cm⁻¹): tacn, 29.2; en, 28.1;¹⁶ NH₃, 26.8¹⁷). A similar observation has been made for Fe,¹⁸ Co,¹⁹ and Ni²⁰ complexes as well. The intensity of the band at 267 nm implies charge-transfer character. Good evidence has been presented in the case of Ru(NH₃)₆²⁺ and Ru(en)₃²⁺²¹ that this is a charge transfer to the solvent (CTTS) according to



As can be seen from Table I, this band is particularly strong in the cage complex Ru(sar)²⁺ and is responsible for the great UV light sensitivity of this complex, since the photooxidized product, Ru(sar)³⁺, disproportionates rapidly forming a Ru(II)–imine species.⁵ Further support for this spectral assignment was obtained from the spectrum of the Ru(tacn)₂²⁺ complex in acetonitrile. The intense band shifted to ≈250 nm (shoulder), consistent with the decreased stability of the charge-separated state in the less polar solvent,²¹ whereas the ligand field transition, now well separated from the CTTS band, was practically unchanged in position.

In view of the stronger ligand field of the tacn ligands, the spectrum of Ru(tacn)₂²⁺ (III in Figure 1) exhibits a surprising feature. Besides a band at 267 nm (37.45 × 10³ cm⁻¹), which is seen at roughly the same spectral position for Ru(NH₃)₆³⁺, a relatively strong band is also seen at 375 nm (26.59 × 10³ cm⁻¹).

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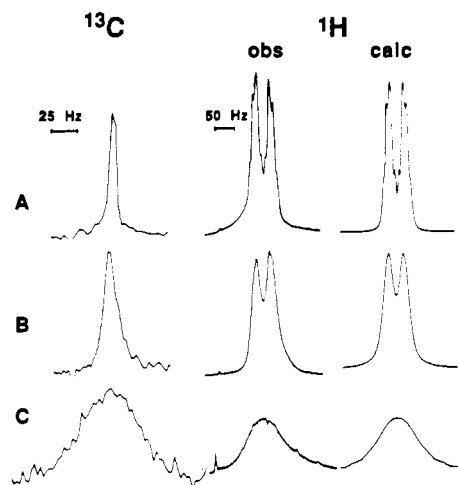


Figure 2. 200-MHz ^1H and 50-MHz ^{13}C NMR spectra of $\text{Ru}(\text{tacn})_2^{2+}$ in 0.01 M $\text{CF}_3\text{SO}_3\text{D}$ in the presence of $\text{Ru}(\text{tacn})_2^{3+}$. $10^4[\text{Ru}(\text{III})]$, M: (A) 1.3; (B) 3.9; (C) 35.

$\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Ru}(\text{en})_3^{3+}$ do not exhibit such bands; those at 310 and 322 nm in these complexes, respectively, are commonly assigned to the lowest spin-allowed ligand field transitions ($^2\text{T}_{2g} \rightarrow ^2\text{T}_{1g}, ^2\text{A}_{2g}$).²² The origin of the band at 375 nm, therefore, has to be a charge transfer. In order to make sure that this band was not due to a Ru(II) imine impurity, which could exhibit a band in this region, the complex was prepared by various methods. The spectrum was reproducible in all cases. For instance, the complex was generated in strong acid (1 M $\text{CF}_3\text{SO}_3\text{H}$) from the Ru(II) complex by oxidation with $\text{Fe}_{\text{aq}}^{3+}$, the Ru(II) complex being kept in excess at first. The intensity of the band increased proportionally to the amount of $\text{Fe}_{\text{aq}}^{3+}$ added. After 1 equiv (of $\text{Fe}_{\text{aq}}^{3+}$) had been added, the intensity of the band stayed constant upon further addition of $\text{Fe}_{\text{aq}}^{3+}$, which is inconsistent with formation of a Ru(II) imine complex (2-e oxidation). Furthermore, the stability of the $\text{Ru}(\text{tacn})_2^{3+}$ complex (in acidic media) had already been demonstrated by electrochemical techniques, and solutions of the complex had been used in electron-transfer studies.⁸ The band at 375 nm is thus clearly a feature of the $\text{Ru}(\text{tacn})_2^{3+}$ complex, and possible assignments in the spectrum will be discussed later.

The reversible reduction potential of 0.37 V (vs NHE) is the highest so far encountered for a saturated Ru hexaamine couple. The potential, as measured by cyclic and rotating-disk voltammetry is independent of pH up to $\approx\text{pH}$ 7.5; thereafter, the potential starts to shift toward more negative values. As a consequence of the high potential in acidic media, $\text{Ru}(\text{tacn})_2^{2+}$ reacts only very slowly with oxygen ($k = 0.14 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}$, $T = 25^\circ\text{C}$, 0.1 M $\text{CF}_3\text{SO}_3\text{H}$), the rate constant being practically identical with those for $\text{Ru}(\text{NH}_3)_5(\text{isn})^{2+}$ and *cis*- $\text{Ru}(\text{NH}_3)_5(\text{isn})(\text{H}_2\text{O})^{2+}$,²³ which have also very similar reduction potentials (0.38 V and 0.36 V vs NHE, respectively).²³

Electron Self-Exchange of $\text{Ru}(\text{tacn})_2^{3+/2+}$: ^1H NMR Spectrum of $\text{Ru}(\text{tacn})_2^{2+}$. The ^1H spectrum in D_2O was of higher order and resembled strongly that for the cobalt complex, which has been published²⁴ but not analyzed. Also seen was some similarity to the well-resolved spectrum of $\text{Ru}(\text{en})_3^{2+}$, which has been analyzed as an AA'BB' pattern.²⁵ A rigorous analysis of the ^1H spectra was beyond the scope of this study, but a series of spectra were simulated²⁶ by using the experimental chemical shift difference (0.21 ppm) and a similar geminal coupling constant as in the $\text{Ru}(\text{en})_3^{2+}$ analysis.²⁵ The parameters that best reproduced the spectra were $J_{12} = 8 \text{ Hz}$, $J_{13} = J_{24} = -13.5 \text{ Hz}$, $J_{14} = J_{23} = 6 \text{ Hz}$, $J_{34} = 6 \text{ Hz}$ (with 1,4 and 2,3 identical in chemical shift and with

Table II. Line Widths of the $\text{Ru}(\text{tacn})_2^{2+}$ ^1H and ^{13}C NMR Signals in the Presence of $\text{Ru}(\text{tacn})_2^{3+}$ (0.01 M $\text{CF}_3\text{SO}_3\text{D}$, 23 $^\circ\text{C}$)

$10^2[\text{Ru}(\text{tacn})_2^{2+}]$, M	$10^4[\text{Ru}(\text{tacn})_2^{3+}]$, M	$\Delta\nu_{1/2}^{(13\text{C})}$, Hz	$\Delta\nu_{1/2}^{(1\text{H})}$, ^a Hz
Experiment 1 ^b			
3.4		6	57
3.0	1.1		65
2.7	3.5		68
2.4	12.0		82
2.0	35.0	59	105
Experiment 2 ^c			
3.4	1.3	8	59
3.4	3.9	15	67
3.4	14.0	28	84
3.4	30.0	56	100
(1.2)	120.0		≈ 250) ^d

^aTotal width of multiplet. ^b $\mu = 0.09\text{--}0.1 \text{ M}$. ^c $\mu = 0.1\text{--}0.13 \text{ M}$. ^dNot used in analysis.

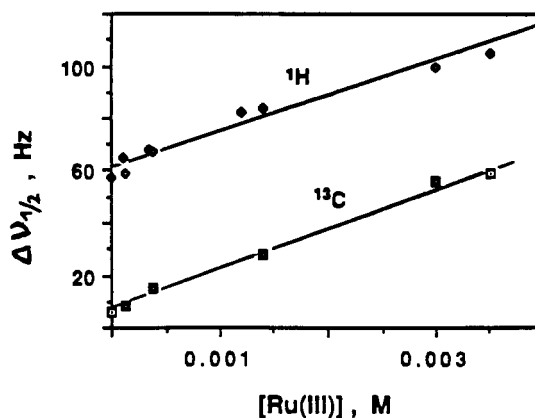


Figure 3. Widths of 200-MHz ^1H and 50-MHz ^{13}C signals of $\text{Ru}(\text{tacn})_2^{2+}$ as a function of $[\text{Ru}(\text{tacn})_2^{3+}]$ (values in Table II).

a natural line width of 3 Hz). However the possibility that there is another set of coupling constants that reproduce the spectra equally well, given the low resolution, is not excluded.

Electron Self-Exchange of $\text{Ru}(\text{tacn})_2^{3+/2+}$. The single ^{13}C signal offered easy access to the measurement of the rate of the electron self-exchange although the total width of the ^1H multiplet was used as well for this purpose (see Experimental Section). The natural line width of the ^{13}C signal of $\text{Ru}(\text{tacn})_2^{2+}$ in 0.01 M $\text{CF}_3\text{SO}_3\text{D}$ was 6 Hz. Examples of ^1H and ^{13}C spectra in the presence of $\text{Ru}(\text{tacn})_2^{3+}$ are shown in Figure 2. Plots of the experimental line widths (Table II; for ^1H : total width of multiplet) versus $[\text{Ru}(\text{tacn})_2^{3+}]$ are shown in Figure 3, and from the regression analyses (eq 1–3) we obtain

$$^{13}\text{C}: \Delta\nu_{1/2}^0 = 6.9 \pm 1.2 \text{ Hz}$$

$$k_{11} = (4.8 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$$

$$^1\text{H}: \Delta\nu_{1/2}^0 = 61 \pm 2 \text{ Hz}$$

$$k_{11} = (4.3 \pm 0.5) \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \quad (5)$$

The broadened ^1H spectra were simulated²⁶ by using the parameters for the multiplet mentioned above and the corresponding values for the exchange rate obtained from the ^{13}C spectra and were visually compared to the experimental spectra. Examples are shown in Figure 2. The visual agreement between the spectra and between the two methods (^{13}C and ^1H) gives us confidence in the extracted rate constant. As a representative value for the electron-self-exchange rate constant, k_{ex} , for the $\text{Ru}(\text{tacn})_2^{3+/2+}$ couple we adopt

$$k_{\text{ex}} = 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \quad (T = 23^\circ\text{C}, \mu = 0.1 \text{ M}) \quad (6)$$

H/D Exchange Rate for $\text{Ru}(\text{tacn})_2^{2+}$. A signal for the amine protons was observed at 5.35 ppm vs DSS after dissolution of the compound in 0.01 M $\text{CF}_3\text{SO}_3\text{D}$, which disappeared with a rate

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Table III. NH Proton Resonances and H/D Exchange Rates for Ruthenium Amine Complexes

	δ^a	$\Delta\nu_{1/2}^b$, Hz	$k_{\text{H/D}}^c$, s ⁻¹
Ru(NH ₃) ₆ ²⁺	2.1 ^b	23 ^b	$5 \times 10^{-3}^c$
Ru(NH ₃) ₆ ³⁺			1.0 ^c
Ru(en) ₃ ²⁺	3.1, 3.8 ^d	23 ^d	$3 \times 10^{-3}^c$
Ru(en) ₃ ³⁺			2.2 ^c
Ru(sar) ²⁺	4.45	25	3×10^{-3}
Ru(sar) ³⁺			$> 10^3$
Ru(tacn) ₂ ²⁺	5.35	16	4×10^{-4}

^a Versus TMS or DSS. ^b Reference 2c. ^c $T = 25^\circ\text{C}$, $\mu \approx 0.1\text{ M}$; ref 2a. ^d Reference 2d. ^e $T = 23^\circ\text{C}$, $[\text{CF}_3\text{SO}_3\text{D}] = 0$ and 0.1 M ; ref 5b. ^f Reference 50. ^g $T = 23^\circ\text{C}$, $[\text{CF}_3\text{SO}_3\text{D}] = 0.01\text{ M}$; this work.

constant of $4 \times 10^{-4}\text{ s}^{-1}$, as obtained from a first-order fit of the intensities versus time. Table III summarizes available data for Ru amine complexes. The rate for Ru(tacn)₂²⁺ is 1 order of magnitude slower than for the other Ru(II) amine complexes, which may be taken as an indication of the rigidity of the ligand tacn.²⁰ Another remarkable feature is the large differences in the chemical shift of the NH proton(s) in the Ru(II) complexes. The shift toward high frequency seems to correlate roughly with the energy separation between the electronic ground and the excited states (Table II). However, a similar correlation is also observed with the energies of the CTTS transition (after correction for the different sizes of the complexes²¹), which is probably more reflective of pure ground-state properties being responsible for the large shift differences. The ¹H NMR shift may respond quite sensitively to changes in the electron distribution in the ground state due to the substantial radial extension of the 4d orbitals. These shifts could thus illustrate independently what has been suggested as an explanation for the protonation of the Ru(II) metal center at low pH.^{5b,6}

Discussion

The value of the self-exchange rate constant hardly needs any comment in view of the large number of papers^{1,2,8,27,28} that have dealt with the electron-transfer properties of Ru amine complexes. We expected that the value would be close to those for the Ru(en)₃^{3+/2+} ($2 \times 10^4\text{ M}^{-1}\text{ s}^{-1}$, $\mu = 0.75\text{ M}$)²⁸ and the Ru(sar)^{3+/2+} ($1.2 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$, $\mu = 0.1\text{ M}$) couples.⁸ When one considers that the rate is probably even faster in H₂O, it can be assumed close to that for the encapsulated couple. The latter has not been measured directly due to the instability of the Ru(sar)³⁺ ion in aqueous solution, but it has been derived from six rates of oxidation by applying the Marcus cross relation.²⁹ The value of $5 \times 10^4\text{ M}^{-1}\text{ s}^{-1}$ for Ru(tacn)₂^{3+/2+} thus fits into the series of Ru amine systems (both aliphatic and aromatic) of different size as illustrated in Figure 4.³⁰ The correlation of the rate with the size of the complexes implies that the solvent reorganization is a dominant contribution to the differences in the energy of activation, which overall are rather small. Another implication is that all other factors influencing the self-exchange rates are similar for all of the complexes. In particular, we conclude that the reactions are adiabatic since identical degrees of nonadiabaticity for the saturated and aromatic complexes (which could lead to the same correlation) would be unlikely.

Another comparison can be made to the Co(tacn)₂^{3+/2+} ($0.18\text{ M}^{-1}\text{ s}^{-1}$, $\mu = 0.1\text{ M}$)²⁴ and the Ni(tacn)₂^{3+/2+} ($1.6 \times 10^3\text{ M}^{-1}\text{ s}^{-1}$, corrected to $\mu = 0.1\text{ M}$)³¹ couples which are different from Ru(tacn)₂^{3+/2+} in both structure and spin state. In this comparison we assume that the differences in the self-exchange rates largely

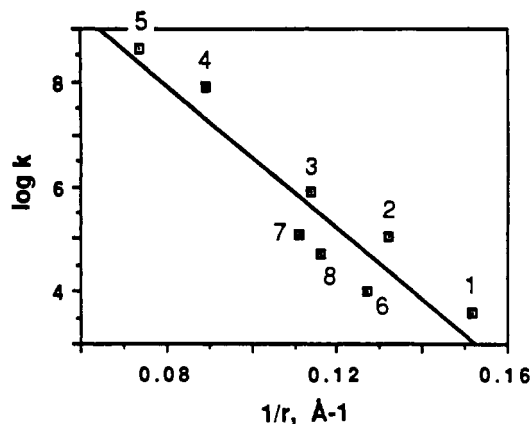


Figure 4. Plot of the logarithm of the observed exchange rate constant vs the reciprocal of the mean distance of closest approach of the ruthenium centers: 1, Ru(NH₃)₆^{3+/2+}; 2, (NH₃)₅Ru(py)^{3+/2+}; 3, (NH₃)₄Ru(bpy)^{3+/2+}; 4, (NH₃)₂Ru(bpy)₂^{3+/2+}; 5, Ru(bpy)₃^{3+/2+}; 6, Ru(en)₃^{3+/2+}; 7, Ru(sar)^{3+/2+}; 8, Ru(tacn)₂^{3+/2+} (see also ref 27, 30).

arise from differences in the reorganization energy for the metal-ligand framework (ΔG_{in}^*)⁴

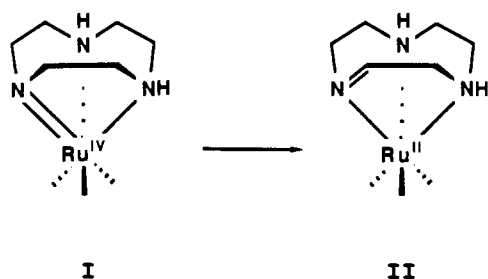
$$\Delta G_{\text{in}}^* = 3f_{\text{II}}f_{\text{III}}(\Delta d)^2 / (f_{\text{II}} + f_{\text{III}}) \quad (7)$$

where f_{II} , f_{III} , and Δd are the force constants for the symmetric (A_{1g}) metal-ligand atom stretching vibration and the difference in the metal-ligand bond length between the two oxidation states, respectively. Because force constants for the tacn complexes from a normal-coordinate analysis are not yet available, we use the corresponding values for the hexamine complexes as the best approximation. ΔG_{in}^* for cobalt has recently been calculated²⁴ as 51.5 kJ mol^{-1} . For the nickel complexes we calculate $\Delta G_{\text{in}}^* = 11\text{ kJ mol}^{-1}$ using force constants f_{II} and f_{III} of 139 and 220 N m^{-1} ³² and $\Delta d = 0.09\text{ \AA}$.³³ No structural information is available for the ruthenium complexes at present, but we adopt the calculated value for the Ru(en)₃^{3+/2+} couple (3 kJ mol^{-1}).^{27,28} Calculated (experimental) ratios of the rates are thus $k_{\text{Ru}}/k_{\text{Co}} \approx 3 \times 10^8$ (3×10^5) and $k_{\text{Ru}}/k_{\text{Ni}} \approx 25$ (30). Inclusion of a nuclear tunneling factor,^{4,24} which is only significant for Co, reduces the corresponding ratio by less than 1 order of magnitude. The principal reason for the discrepancy between the calculated and observed rates for $k_{\text{Ru}}/k_{\text{Co}}$ and thus $k_{\text{Ni}}/k_{\text{Co}}$ is most likely the strain in the cyclic ligand. The presence of strain will affect complexes with large inner-sphere activation energies the most (Co), i.e. increase the self-exchange rate. In this situation eq 7 is no longer appropriate. This effect has been addressed elsewhere for encapsulated cobalt complexes.³⁴ It is also worth noting in this context that the self-exchange rates for the tacn and the sar complexes are virtually identical in the case of Ni and of Ru but that in the case of cobalt the rates differ by 1 order of magnitude (the self-exchange rate constant for Co(sar)^{3+/2+} is $2.1\text{ M}^{-1}\text{ s}^{-1}$),³⁵ which indicates that the strain argument is more important for cobalt than it is for nickel and ruthenium, which exhibit small inner-sphere activation energies. In any case, these comparisons would not support any suggestions of nonadiabatic behavior: The data in Figure 4 support adiabatic behavior for the ruthenium complexes, and the good agreement between calculated and ob-

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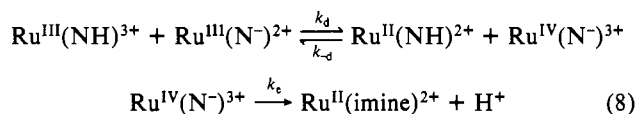
- (32) f_{III} for Ni(tacn)₂³⁺ was estimated as follows: from the ratios $f_{\text{III}}/f_{\text{II}}$ for Ru (1.4);³⁸ no difference in e_g -orbital population between the oxidation states) and for Co (1.8;³⁹ difference of two e_g electrons), we adopt a corresponding value of 1.6 for Ni (difference of one e_g electron between the two oxidation states); hence, $f_{\text{III}} = 1.6 \times 139\text{ N m}^{-1} = 220\text{ N m}^{-1}$.
 (33) Ni(tacn)₂³⁺ exhibited a strong tetragonal distortion with (d_{ax}) = 2.11 Å and (d_{eq}) = 1.97 Å.⁴⁰ The average bond length was calculated as in ref 47 for Ni(bpy)₃³⁺: $\langle d_{\text{av}} \rangle = \{[2(d_{\text{ax}})^2 + 4(d_{\text{eq}})^2]/6\}^{1/2} = 2.018\text{ \AA}$. For Ni(tacn)₂²⁺ an average bond length of 2.105 Å has been reported.⁴¹
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Scheme I

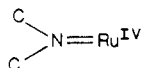


served relative rates for Ru and Ni supports adiabatic behavior of the latter complex, but for Co a rate that, in terms of the classical model, is 100 fast has to be accounted for.

As mentioned in the Introduction, one of the factors that led us to investigate this system was the question of the stability of the Ru(tacn)₂³⁺ complex toward disproportionation into Ru(II) and Ru(IV). The rapidity of the ligand oxidation for Ru(sar)³⁺ in aqueous solution is unique, so far, among saturated amine systems. Key reactions in the oxidative dehydrogenation of Ru(III) amine complexes have been shown to be^{5b,36}



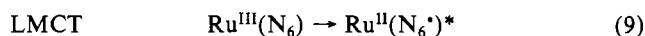
where Ru(N⁻) represents the complex that is deprotonated at a nitrogen atom. The observed rate at a given pH is dependent upon the forward (*k_d*) and the backward (*k_{-d}*) disproportionations, the intramolecular-electron-transfer rate (*k_e*) constants, and the *pK_a* of the Ru³⁺ complex. For comparison, the half-life of Ru(sar)³⁺ (10⁻⁴ M) at pH 2.3 in the presence of 5 × 10⁻⁴ M Ru(sar)²⁺ is 2 s.^{5b} Under analogous conditions the half-life of Ru(tacn)₂³⁺ is >1 day, in spite of the fact that the higher reduction potential for the Ru(tacn)₂^{3+/2+} couple is favorable. This enormous difference in reactivity can arise either from higher *pK_a* for the Ru(tacn)₂³⁺ complex or from an unfavorable disproportionation reaction induced by the instability of the Ru(IV) intermediate. Given the requirement that the deprotonated Ru(IV) ion donate the lone pair from the N site to the Ru(IV) center (I), the stereochemistry for the



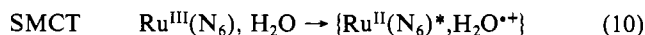
fragment is clearly unfavorable (Scheme I). Considerable distortion from a planar configuration (for N) is required, and this must necessarily destabilize such an intermediate and thereby raise the Ru(IV)/Ru(III) potential. In short, the concentration of the Ru(IV) ion would be low and the oxidation rate therefore slow. An additional factor in this process is a strained nonplanar imine fragment in the Ru(II) imine product (II), which would also inhibit the process. A combination of these effects, despite the more favorable Ru^{3+/2+} reduction potential, could readily account for the slow rate, and this is reflected in the electrochemical behavior. Whereas the potential for the Ru(sar)^{3+/2+} couple becomes pH dependent at pH >2.3, the potential of the Ru(tacn)₂^{3+/2+} couple alters only at pH >7.5. The difference in reactivity of at least 5 orders of magnitude is, as mentioned above, not straightforwardly related to the *pK_a* of the Ru³⁺ complexes because of the interference of the second electron-transfer step (Ru(III) → Ru(IV)) at the electrode (ECE mechanism)³⁷ and/or disproportionation

in solution (DISP).³⁷ In spite of this complication, we suspect that a much higher *pK_a* for Ru(tacn)₂³⁺ compared to that for Ru(sar)³⁺ (*pK_a* ≈ 5–7)^{5b} is mainly responsible for its lower reactivity. It is evident that the tridentate tacn ligand has a constrained stereochemistry;²⁰ a deprotonated nitrogen atom is apparently not as easily accommodated as in the encapsulating ligand sar. The substantial difference in the H/D exchange rate (Table III) in the Ru(II) complexes is in agreement with this interpretation, but the effect is expected to be much larger in the Ru(III) complexes due to the stabilizing interaction between the nitrogen lone pair and the t_{2g} orbital of the metal, given the right geometry.

In the remaining text, a possible assignment of the absorption bands in the optical spectrum of Ru(tacn)₂³⁺, particularly for the surprising band at 26.67 × 10³ cm⁻¹ (375 nm), is discussed. As mentioned earlier, a spin-allowed ligand field transition is not expected in this spectral region, since that would imply a weaker ligand field for Ru(III) than for Ru(II). Assuming a similar increase in ligand field strength for Ru(III) as for Ru(II) complexes and using *B* = 460 cm⁻¹ (*C/B* = 4),⁴² we calculate an energy of ≈34 000 cm⁻¹ (295 nm) for the lowest spin-allowed (²T_{2g} → ²T_{1g}, ²E_g) ligand field transitions; no indication of a band is seen at this position, but the relatively strong band at 267 nm may obscure the transitions. The conclusion from this calculation is that the bands at both 267 and 375 nm are due to charge-transfer transitions, and since no empty ligand orbitals are accessible at this energy, it has to be either a charge transfer from the ligand to the metal (LMCT) producing a ligand radical



or a solvent to metal charge transfer (SMCT)



The latter process has not been proposed often in the literature although it is conceptually not different from a charge transfer within an ion pair (e.g. with halides), which is well-known and has been ascribed to weak low-energy bands in solutions of Ru(NH₃)₆³⁺ containing I⁻ or Br⁻.⁴³ Since the only counterion present is triflate (or ClO₄⁻), which did not even interfere in the study of the photoreduction of Ru(NH₃)₆³⁺ at 185 nm,⁴⁴ neither the band at 267 nm nor that at 375 nm can be due to an ion-pair charge transfer. A comparison with this study⁴⁴ would also lead to the conclusion that a SMCT is unlikely to be responsible for either of the bands. Such transitions have been discussed^{43,45} for cobalt complexes and Ru(NH₃)₆³⁺; generally, a lower limit (in energy) of ≈40 × 10³ cm⁻¹ (250 nm) was given, but because the nature of the generated species is unknown, energy calculations are subject to substantial errors. Overall, a low-energy shift for Ru(tacn)₂³⁺ compared to Ru(NH₃)₆³⁺ for both the LMCT and the SMCT can be expected due to the lowering of the acceptor orbital (t_{2g}) and the larger size of Ru(tacn)₂³⁺. Because of this and due to the lack of any other explanation, we assign the low-energy transition at 375 nm to a LMCT and the band at 267 nm to a SMCT. Further insight into the problem could be gained from the medium dependence of the band positions and intensities.

Conclusions

Due to their great thermodynamic and kinetic stabilities, the Ru(tacn)₂²⁺ (*z* = 2, 3) complexes, prepared by a convenient route from Ru(DMF)₆²⁺, are useful outer-sphere electron-transfer agents. The electron self-exchange rate constant of 5 × 10⁴ M⁻¹ s⁻¹, directly measured by ¹H and ¹³C NMR spectroscopy in dilute solutions of known ionic strength, fits well into the series of rate constants for other saturated Ru amine redox couples. In spite

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of the orderly electron-transfer properties, the conclusion can be drawn that intrinsic properties of the complexes, such as the pK_a of the amine protons or the formal potential, are much more sensitive to changes in the ligand, leading to differences in reactivity of several orders of magnitude. In this respect, the comparison between the closely related $Ru(sar)^{3+/2+}$ and $Ru(tacn)_2^{3+/2+}$ couples provides an excellent example.⁴⁶ Work on

these questions is continuing.⁴⁸

Acknowledgment. The authors are grateful to the Microanalytical Service Unit of ANU for analyses and to R. Wijeksera for a sample of the ligand $tacn\cdot 3HCl$.

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Contribution from the Chemistry Department,
 University of Canterbury, Christchurch, New Zealand

Kinetics of the Base Hydrolysis of Chloro(diamine)(triamine)chromium(III) Complexes: Evidence for the SN_1CB Mechanism in Chromium(III) Polyamine Complexes

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Spectrophotometrically determined kinetic parameters for the rate of base hydrolysis ($\mu = 0.1$ M, NaCl) of *sfac*-CrCl(AA)(dien)²⁺ [AA = en (I), tn (II)], *ufac*-CrCl(NMetn)(dien)²⁺ (III), *mer*-CrCl(AA)(dpt)²⁺ [AA = en (IV), pn (V), tn (VI), Me₂tn (VII)], *mer*-CrCl(tn)(2,3-tri)²⁺ (VIII), *sfac*-CrCl(dien)(DMSO)₂²⁺ (IX), and *cis*-CrCl(AA)₂(DMSO)²⁺ [AA = en (X), tn (XI)] are (in order I–XI) as follows: $10^2k_{OH}(298.2)$ (M⁻¹ s⁻¹) = 1.56, 1.85, 22.1, 10.5, 9.64, 60.6, 58.6, 73.5, 2.06, 0.500, 7.53; E_a (kJ mol⁻¹) = 104, 108, 109, 95.5, 98.1, 108, 84.7, 110, 102, 125, 105; ΔS_{298}^\ddagger (J K⁻¹ mol⁻¹) = 61, 75, 101, 48, 56, 105, 26, 113, 58, 121, 84. Titrimetrically determined kinetic parameters for the rate of loss of chloride in acid (0.1 M HClO₄) for IX–XI are as follows: $10^6k_H(298.2)$ (s⁻¹) = 110, 24.4, 5.50; E_a (kJ mol⁻¹) = 68.0, 82.6, 96.2; ΔS_{298}^\ddagger (J K⁻¹ mol⁻¹) = -100, -64, -31. Similar data for the rate of Hg²⁺-assisted chloride release ($\mu = 1.0$ M, HClO₄, determined spectrophotometrically): $10^3k_{Hg}(298.2)$ (M⁻¹ s⁻¹) = 428, 43.0, 43.5; E_a (kJ mol⁻¹) = 74.4, 67.3, 73.3; ΔS_{298}^\ddagger (J K⁻¹ mol⁻¹) = -7, -53, -33. Several of these complexes contain a meridional or "flat" *sec*-NH proton, but this gives only a small (<50 times) base hydrolysis rate increase with respect to related Cr(III) systems where this feature is absent. The observation that there is an inverse relationship between k_{OH} and k_H (aquation rate constant) is used to propose that a dissociative conjugate base mechanism is applicable to Cr(III) complexes of this type.

Introduction

Base hydrolysis (or base-catalyzed solvolysis^{1,2}) of octahedral Co(III) polyamine complexes is a well-studied reaction, and considerable evidence for the conventionally accepted SN_1CB mechanism^{1,2} has been accumulated.

A fairly general observation is that the presence of a meridional or "flat" *sec*-NH proton, *cis* to the leaving group, leads to high sensitivity toward base hydrolysis in Co(III) complexes.^{2,3}

In a consideration of base hydrolysis studies of complexes with other inert transition-metal centers, the SN_1CB mechanism is generally assumed, although by no means as well established as for Co(III).² For Cr(III), in particular, the lower reactivity requires either less acidic NH protons or a less reactive conjugate base.^{4,5}

In a recent review of base hydrolysis,² the significance of investigating the "flat *sec*-NH proton effect" for Cr(III) is commented on, as "the results should provide guidance about the importance of any trigonal-bipyramidal intermediates."

We are now in a position to discuss these effects as we have recently synthesized⁶ a series of *mer*-CrCl(AA)(3,3-tri)²⁺ complexes⁷ (AA = diamine) that incorporate this structural feature,

and we report the results for their base hydrolysis kinetics, as well as base hydrolysis data for several other CrCl(L₅)²⁺ complexes (Figure 1).

Experimental Section

Analytically pure^{6,8-9b} tetrachlorozincate(II) salts of *sfac*-CrCl(en)-(dien)²⁺ (I),⁸ *sfac*-CrCl(tn)(dien)²⁺ (II),⁸ *ufac*-CrCl(NMetn)(dien)²⁺ (III),^{9a} *mer*-CrCl(AA)(3,3-tri)²⁺,⁶ [AA = en (IV), pn (V), tn (VI), Me₂tn (VII)], *mer*-CrCl(en)(2,3-tri)²⁺ (VIII),⁶ *sfac*-CrCl(dien)(DMSO)₂²⁺ (IX),^{9b} and *cis*-CrCl(AA)₂(DMSO)²⁺ [AA = en (X), tn (XI)]^{9b} were prepared according to the literature methods. These were converted to zinc(II)-free salts [either Cl⁻·ClO₄⁻ (I, II), NO₃⁻·ClO₄⁻ (VII, VIII, X, XI), (I₂)₂ (III), or (ClO₄)₂ (IX)] or else the directly prepared chloride salts⁶ (IV–VI) were used without further purification. (Caution! ClO₄⁻ salts are potentially explosive.)

Base hydrolysis kinetic data were obtained spectrophotometrically by using repeated continuous- (700–300 nm) or repeated fixed-wavelength scans (Table I) with a Varian DMS-100 recording spectrophotometer.

NaOH solutions ($\mu = 0.1$ M, NaCl) were standardized by HCl titration and adjusted to the appropriate temperature. Small samples of the complex were added, and after dissolution (usually rapid), the solution was transferred by syringe into a temperature-controlled 5.00-cm cell (approximately 6-mL capacity). The complex:NaOH ratio was always less than 1:8, even at the most dilute NaOH concentration (0.01 M). Pseudo-first-order rate constants (k_{obsd} , s⁻¹) were calculated from the fixed-wavelength data over 3–4 half-lives by using 12–15 data points, and the average results are reported in Table I. These have been converted to k_{OH} (M⁻¹ s⁻¹) (Table I) by using the expression $k_{obsd} = k_{OH}[\text{OH}^-]^{-1}$. Satisfactory linear Arrhenius plots of $\ln [k_{OH}]$ vs T^{-1} over a 10-fold $[\text{OH}^-]$ range confirm the relationship between k_{obsd} and k_{OH} . Activation

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