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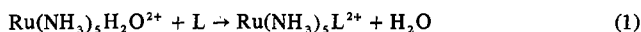
Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106

Kinetics of Ruthenium(II) Substitution Reactions. Reactions of *cis*- and *trans*-Diaquotetraammineruthenium(II)¹

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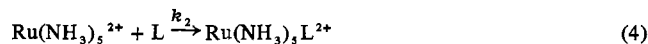
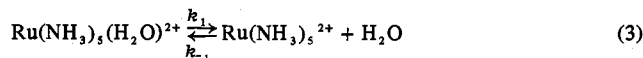
Recently, rate studies³⁻⁶ have been reported for substitution reactions of aquopentaammineruthenium(II), *i.e.*, the replacement of coordinated H₂O by a variety of organic ligands L in aqueous solution



These studies have led to the following general observations.³ Over all concentrations of ligand and Ru(NH₃)₅H₂O²⁺ studied, the reaction displayed a second-order rate law

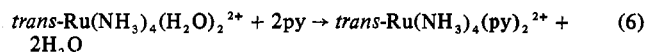
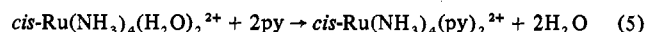
$$d[\text{P}]/dt = k_L [\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}] [\text{L}] \quad (2)$$

where P is the product Ru(NH₃)₅L²⁺ and k_L the second-order rate constant characteristic of the ligand L. However, the rate constants k_L and the appropriate activation parameters ΔH^\ddagger and ΔS^\ddagger are rather insensitive to the stability of Ru(NH₃)₅L²⁺, to whether L is uncharged or a unipositive cation, or to ligand substituent effects as reflected by a homologous series of substituted pyridines for L. Thus, it was concluded³ that the substitution mechanism is dissociative in character, perhaps approximating the limiting SN1 mechanism



Under experimentally attainable conditions where $k_2 [\text{L}] \ll k_{-1}$, this mechanism gives the rate law described in eq 2 with $k_L = k_1 k_2 / k_{-1}$.

An earlier report⁷ from this laboratory examined the stereochemistry of substitution reactions of the diaquotetraammine complex ions *cis*- and *trans*-Ru(NH₃)₄(H₂O)₂²⁺ (eq 5 and 6).



For L = pyridine, these reactions proved highly stereospecific giving retention of configuration. Here we report some rate studies of the successive substitution reactions which lead to Ru(NH₃)₄L₂²⁺ products.

Experimental Section

Reagents. Organic ligands were purchased as reagent chemicals and were further purified by distillation from barium oxide. The

isomers *cis*- and *trans*-dichlorotetraammineruthenium(III) chloride, [Ru(NH₃)₄Cl₂]Cl, were prepared from [Ru(NH₃)₅Cl]Cl₂ by the methods of Gleu and Breuel.⁸ Water for kinetics solutions was redistilled from alkaline permanganate. Recrystallized sodium *p*-toluenesulfonate was employed to maintain ionic strength. Argon used to entrain reaction solutions was deoxygenated by passage through Cr(II) solution in gas scrubbing bottles.

Isolation of the Complexes Ru(NH₃)₄(L)Cl²⁺. *trans*-[Ru(NH₃)₄(py)Cl]Cl₂. In deaerated aqueous solution, *trans*-[Ru(NH₃)₅Cl₂]Cl (0.1 g, 3.6 × 10⁻⁴ mol) was reduced with zinc amalgam to the Ru(II) analog and then allowed to react with pyridine (0.03 g, 3.8 × 10⁻⁴ mol) for a period of 8 hr. This resulted in approximately 80% formation of the monosubstituted product *trans*-Ru(NH₃)₄(py)H₂O²⁺ according to the visible spectrum. The reaction mixture was then decanted from the Zn(Hg), acidified by adding 3 N HCl, and O₂ was bubbled through the solution to oxidize Ru(II) species to Ru(III). The oxidation step in the presence of excess Cl⁻ gives the ion *trans*-Ru(NH₃)₄(py)Cl²⁺ as the principal Ru(III) species in solution. Cation exchange on a Dowex AG 50W-X4 resin column eluting with acidic sodium chloride led to separation of the desired complex from other ruthenium species. The combined eluent aliquots containing this complex were reduced in volume by rotary evaporation. During the evaporation, a white solid, presumably NaCl, precipitated and was removed by filtration. At the conclusion, a pale yellow solid was obtained and according to the uv-vis spectrum⁹ this was approximately 50% *trans*-[Ru(NH₃)₄Cl(py)]Cl₂. Extraction with 90% ethanol-water dissolved the Ru(III) salt leaving behind most of the NaCl impurity. The ethanol extract was evaporated to dryness to give a material about 90% the desired complex which was recrystallized from hot water. The overall yield was about 40%. Electronic spectral properties agreed with those previously reported.⁹

cis-[Ru(NH₃)₄(C₆H₅CN)Cl]Cl₂. The isolation procedure was analogous. Benzonitrile (4.5 × 10⁻³ mol) was allowed to react in deaerated solution with *cis*-Ru(NH₃)₄(H₂O)₂²⁺ (3.7 × 10⁻³ mol, prepared by Zn(Hg) reduction of aqueous *cis*-Ru(NH₃)₄Cl₂²⁺) for 5 hr. The reaction was quenched by acidifying with HCl and then oxidizing with O₂. Elution with acidic NaCl from a cation-exchange column gave a volume of eluent containing *cis*-[Ru(NH₃)₄(C₆H₅CN)Cl]Cl₂, which was recovered by rotary evaporation, extraction with aqueous ethanol, and recrystallization in a manner analogous to the above preparation. The spectrum of the Ru(II) complex *cis*-Ru(NH₃)₄(C₆H₅CN)H₂O²⁺ was obtained by Zn(Hg) reduction of *cis*-[Ru(NH₃)₄(C₆H₅CN)Cl]Cl₂ in gravimetrically prepared, deaerated aqueous solution. The validity of the spectral data obtained was checked by adding excess benzonitrile and (after allowing a few minutes for reaction) comparing the spectrum of the resulting solution to that of the known¹⁰ complex ion *cis*-Ru(NH₃)₄(C₆H₅CN)₂²⁺. The agreement was very good. The charge-transfer band of *cis*-Ru(NH₃)₄(C₆H₅CN)(H₂O)²⁺ has a maximum at 358 nm (ϵ 6.8 × 10³ M⁻¹ cm⁻¹).

Rate Studies and Analysis of Data. Rates were studied by observing optical density changes in reaction solution with a Cary 14 recording spectrophotometer equipped with a thermostated cell compartment. The aqueous *cis*- and *trans*-diaquo ions Ru(NH₃)₄(H₂O)₂²⁺ were prepared from the respective dichlororuthenium(III) ions Ru(NH₃)₄Cl₂⁺ by reduction over Zn(Hg) in deaerated solutions. Solutions were transferred by syringe techniques, and other procedures were analogous to those reported for previous rate studies.³

Data analysis showed that simple first-order plots of $-\ln(A_\infty - A)$ vs. time for reactions of Ru(NH₃)₄(H₂O)₂²⁺ with excess L were not linear. This result was expected since the system very likely involves consecutive replacement of coordinated H₂O to form the species Ru(NH₃)₄(H₂O)L²⁺ and Ru(NH₃)₄L₂²⁺, both of which absorb at the wavelengths used for observation but with different extinction coefficients. Thus, the optical density increases related to the formation of these species were analyzed by iterative computation on an IBM 360/65 assuming an A → B → C system of consecutive first-order reactions. The computer program was a modification of one by Wiberg¹¹ and required an estimate of the two rate constants of the

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Table I. Second-Order Rate Constants and Activation Parameters for the Reactions^a

$$\text{M}(\text{H}_2\text{O})_2^{2+} + \text{L} \xrightarrow{k_1\text{L}} \text{M}(\text{H}_2\text{O})\text{L}^{2+} + \text{H}_2\text{O}$$

$$\text{M}(\text{H}_2\text{O})\text{L}^{2+} + \text{L} \xrightarrow{k_2\text{L}} \text{ML}_2^{2+} + \text{H}_2\text{O}$$

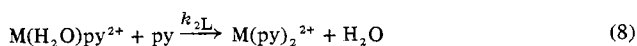
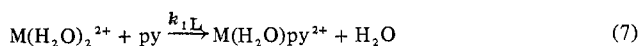
M(H ₂ O) ₂ ²⁺ or M(H ₂ O)L ²⁺	L	Temp, °C	$k_1\text{L}$ or $k_2\text{L}$, $M^{-1} \text{sec}^{-1} \times 10^2$	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
<i>cis</i> -Ru(NH ₃) ₄ (H ₂ O) ₂ ²⁺	py	18.0	9 ± 1	16.7 ± 1	-6 ± 3
		25.0	20.7 ± 1.0		
		33.9	49 ± 2		
		43.6	101 ± 2		
	bz	18.0	23.8 ± 0.5	16.3 ± 1.2	-5 ± 4
		25.0	44.5 ± 3.0		
		33.9	122 ± 7		
		43.6	233 ± 20		
	AMP ^b	18.0	6.8 ± 0.3	15.9 ± 0.4	-9 ± 2
		25.0	13.5 ± 0.8		
		33.9	30.3 ± 1.5		
		43.6	67 ± 3		
<i>cis</i> -Ru(NH ₃) ₄ (H ₂ O)py ²⁺	py	18.0	1.2 ± 0.5	16.0 ± 2	-13 ± 7
		25.0	2.0 ± 0.5		
		33.9	6 ± 1		
		43.6	11 ± 2		
<i>cis</i> -Ru(NH ₃) ₄ (H ₂ O)bz ²⁺	bz	18.0	1.7 ± 0.1	14.4 ± 1.1	-17 ± 4
		25.0	3.9 ± 0.2		
		33.9	7.3 ± 0.2		
		43.6	14.3 ± 0.4		
<i>trans</i> -Ru(NH ₃) ₄ (H ₂ O) ₂ ²⁺	py	18.5	0.74 ± 0.08	15.3 ± 1.2	-15 ± 4
		25.0	1.65 ± 0.1		
		33.9	2.9 ± 0.2		
		43.6	7.0 ± 0.5		
<i>trans</i> -Ru(NH ₃) ₄ (H ₂ O)py ²⁺	py	18.5	0.50 ± 0.05	15.5 ± 1	-15 ± 3
		25.0	1.07 ± 0.08		
		33.9	2.02 ± 0.12		
		43.6	4.7 ± 0.2		

^a In aqueous solution; ionic strength maintained at 0.2 *M* with sodium *p*-toluenesulfonate; pH 7.7 ± 0.3 except where noted; py = pyridine, bz = benzonitrile, AMP = 2-aminomethylpyridine. ^b pH 10.0.

consecutive steps and the extinction coefficient of the intermediate B. Since accurate values for the presumed monosubstituted intermediate (Ru(NH₃)₄L(H₂O)²⁺) are known (this work and ref 9), these were used as estimates of ϵ_B and this value was normally not allowed to vary in the iterative calculation. Stepwise iterations of the rate constants were carried out until convergence on values which gave best fits of calculated optical densities to those observed experimentally. Convergence to the same values from significantly different estimates of the rate constants and agreement of all calculated and observed optical densities to within ±2% or ±0.01 OD unit (whichever was larger) were the criteria for acceptance of the computed rate constants. For the reaction of *trans*-Ru(NH₃)₄(H₂O)₂²⁺ with pyridine, the validities of the computed rate constants were confirmed at 25° by independently examining the second step. Reported activation parameters were obtained from Arrhenius plots ($\Delta H^\ddagger = E_a - RT$) using a least-squares method to determine the slope of the best straight line with uncertainties based on a 95% confidence limit.

Results and Discussion

Rate data for the reaction of either *cis*-Ru(NH₃)₄(H₂O)₂²⁺ or *trans*-Ru(NH₃)₄(H₂O)₂²⁺ with excess pyridine in aqueous solution did not give straight lines when plotted in a simple first-order manner (ln(A_∞ - A) vs. t) thus suggesting that if replacement of the coordinated water occurred stepwise (eq 7 and 8), neither step is clearly rate determining, where M =



cis-Ru(NH₃)₄ or *trans*-Ru(NH₃)₄. Computational analysis of rate data demonstrated that, in the presence of excess ligand, the rate behavior was consistent with the operation of consecutive first-order reactions (A → B → C). The pseudo-

first-order rate constants thus derived displayed first-order dependence on the free ligand concentration [py], and for each reaction, an overall second-order rate law is observed, e.g.

$$\text{rate for eq 7} = k_1\text{L} [\text{M}(\text{H}_2\text{O})_2^{2+}] [\text{py}] \quad (9)$$

In the pH region ~7.7 where these studies were carried out, the computed rate constants were apparently insensitive to small changes in solution pH, and with other variables held constant pH differences of ±0.3 pH unit led to no discernible changes in rates. This supports the contention that the di-aquo complexes are the dominant contributors to the substitution reaction. Similar rate behavior was observed for the successive reactions of benzonitrile with *cis*-Ru(NH₃)₄(H₂O)₂²⁺; however, attempts to evaluate rates of the reactions of benzonitrile with *trans*-Ru(NH₃)₄(H₂O)₂²⁺ were complicated by apparent instability of the *trans*-Ru(NH₃)₄(C₆H₅CN)₂²⁺ product.¹⁰ Rate constants and activation parameters for those reactions studied are summarized in Table I.

The comparative reactivities of benzonitrile and pyridine toward *cis*-Ru(NH₃)₄(H₂O)₂²⁺ are analogous to those seen when Ru(NH₃)₅(H₂O)²⁺ was used as a substrate. At 25° benzonitrile is about twice as reactive as pyridine, an observation which previously was attributed in part to steric differences between the two ligands. The same reactivity order holds for the second step. For the reaction of L with *cis*-Ru(NH₃)₄L(H₂O)₂²⁺, the rate is about twice as fast for L = benzonitrile than for L = pyridine. However, in both cases the second step is about one-tenth as rapid as the first step. One interpretation of the decreased reactivity of the second step is that the bulk of the first ligand already occupying a *cis* co-

ordination site may inhibit approach of the second ligand. Electronic considerations might also be applicable if one argues that π back-bonding to the cis ligands increases the effective positive charge of the Ru(II) center thus making less favorable a dissociative path for departure of the water molecule. The π -acceptor character of benzonitrile in its interactions with Ru(II) has been reasonably well established,^{10,12} while that of pyridine remains somewhat controversial.^{6,13}

Perhaps the most important conclusion that can be drawn from the data in Table I is that the activation parameters ΔH^\ddagger and ΔS^\ddagger are essentially identical (within experimental uncertainty) for all reactions listed. Furthermore these values are close to those for the substitution reactions of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ ($k_L = 0.091 \text{ M}^{-1} \text{ sec}^{-1}$, $\Delta H^\ddagger = 15.3 \pm 0.2$ and $\Delta S^\ddagger = -13 \pm 1$ for the reaction of pyridine with $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ at 25°).^{3,14} This implies that the substitution mechanisms for the various systems are similar.

The rates for the reaction of pyridine with *trans*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{2+}$ and *trans*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})\text{py}^{2+}$ are both slower than the analogous reactions with $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ or *cis*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{2+}$ as substrates. The differences between the *trans* aquo and the *trans* pyridyl complexes are relatively small and the activation parameters are comparable, and these differences could be due to minor steric or solvation effects. The activation parameters are comparable to the reactions of the *cis* isomer and of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$; thus mechanistic similarity is inferred. Nonetheless, the reactivity difference between a *trans*-substituted aquotetraammine and the aquopentaammine ion may also reflect electronic factors. For ruthenium(II)-ammine complexes, it has been observed that a very strong π -acceptor ligand such as SO_2 or NO^+ leads to labilization of the ligand *trans* to it.¹⁵ This effect is apparently in large part due to weakening of the σ bond between the *trans* ligand and the Ru(II), as demonstrated by the abnormally long bond (and lability) of the *trans* NH_3 of $\text{Ru}(\text{NH}_3)_5\text{NO}^{3+}$. Back-bonding alone should strengthen not weaken the metal's σ -bonding ability to the *trans* ligand. Thus, the σ -bond weakening is likely to be in large part due to the substantial σ overlap between the π -acceptor ligand and the metal owing to the very short bond length. However, in the present case, *trans*- $\text{Ru}(\text{NH}_3)_4\text{py}(\text{H}_2\text{O})^{2+}$ is less substitution labile than $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$. Despite the apparent π -acceptor character of pyridine,⁶ this result suggests that the interaction is sufficiently weak that other factors are more important in establishing the relative lability of the *trans* position.

Reaction of *cis*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{2+}$ with excess 2-amino-methylpyridine followed simple first-order kinetics indicating that substitution of the first coordination site is rate determining, regardless of whether the pyridine or amine nitrogen coordinates initially. When the product solutions of the rate studies were exposed to air, the originally yellow solution (λ_{max} 414 nm) turned a deep red owing to oxidation of the coordinated ligand to give the complex tetraammine (2-iminomethylpyridine)ruthenium(II). Characterization of this oxidation product was accomplished by spectral and chemical analysis.¹⁶

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(14) Reference 6 reports the values $k_L = 0.093 \text{ M}^{-1} \text{ sec}^{-1}$, $\Delta H^\ddagger = 16.9 \text{ kcal/mol}$, and $\Delta S^\ddagger = -7 \text{ eu}$ for the same reaction. The values for reaction of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ with benzonitrile are $k_L = 0.27 \text{ M}^{-1} \text{ sec}^{-1}$, $\Delta H^\ddagger = 15.8 \text{ kcal/mol}$, and $\Delta S^\ddagger = -8$.³

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Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (GP-26199) for support of this research.

Registry No. *cis*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{2+}$, 29946-00-8; *cis*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})\text{py}^{2+}$, 26540-33-0; *cis*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})\text{bz}^{2+}$, 42230-43-3; *trans*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{2+}$, 42230-44-4; *trans*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})\text{py}^{2+}$, 26518-89-8; *py*, 110-86-1; *bz*, 100-47-0; *AMP*, 3731-51-9.

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Magnetically Perturbed Mossbauer Study of a Distorted Five-Coordinate Iron(II) Complex

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Recent Mossbauer studies of five-coordinate high-spin iron(II) complexes indicate that this coordination environment is often associated with relatively large quadrupole effects. For instance, the monoterpyridyl¹ ferrous halides and pseudohalides whose geometries are believed intermediate² between square pyramidal and trigonal bipyramidal show quadrupole splittings (ΔE) ranging from 2.7 to 3.2 mm/sec. Even larger values are found for five-coordinate complexes of Curtis macrocyclic ligands.³ In this note, we discuss the magnetically perturbed Mossbauer spectra of one such system, $\text{Fe}(1,7\text{-CTCl})\text{ClO}_4$ (1,7-CT = 5,5,7,1,2,1,2,1,4-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-diene), in an attempt to assess bonding and nonbonding electron contributions to the very large electric field gradient in these and similar systems and to ascertain also the nature of the orbital ground state. A schematic of the structure of the cation $\text{Fe}(1,7\text{-CTCl})^+$ as well as the ligand is shown in Figure 1. A crystallographic study⁴ of $[\text{Fe}(1,7\text{-CTCl})\text{I}]$ indicates that it possesses at most C_2 symmetry with the C_2 axis corresponding to the Fe-Cl bond and that the coordination environment may be approximated as distorted trigonal bipyramidal. However, for distorted five-coordinate stereochemistry, the question of whether a system is closer to trigonal bipyramidal or square pyramidal is often difficult to decide, if in fact it has any meaning. Previous electronic spectral results as well as those of this investigation favor square-pyramidal symmetry for the ligand field of the $[\text{Fe}(1,7\text{-CTCl})]^+$ cation.

Results and Discussion

Figures 2 and 3 show the unperturbed and corresponding magnetically perturbed Mossbauer spectra of $\text{Fe}(1,7\text{-CTCl})\text{ClO}_4$ at 300°K. It is evident from the lower energy triplet of the room-temperature spectrum that the principal component of the electric field gradient tensor (V_{zz}) is positive⁵ and the asymmetry parameter η is small suggesting nearly

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