resulting in a higher wave number value than in $[Ru(NAz)_2Cl_2]$, exactly as observed for $[Ru(Azpy)_3](ClO_4)_2$.[3]

Further support for our structural assignments for the isomers of $[Ru(NAz)_2Cl_2]$ is obtained from the metal-ligand vibrational region. While spectra are of poorer quality than those of the $[Ru(Azpy)_2Cl_2]$ isomers, there is a marked similarity between the two series of compounds. As with the Azpy series, $\gamma$-$[Ru(NAz)_2Cl_2]$ has fewer bands than the $\alpha$- and $\beta$-isomers, suggesting the presence of the $C_{2h}$ symmetry required of the trans-trans isomer.[2] Assignments in this region are difficult, but we tentatively assign the Ru-Cl mode at 316 $cm^{-1}$ in $\gamma$-$[Ru(NAz)_2Cl_2]$, at 308 and 336 $cm^{-1}$ in the $\alpha$-form, and at 306 and 328 $cm^{-1}$ in the $\beta$-isomer, consistent with our earlier observations[2] and those of others.[15]

**Electrochemical Measurements.** NAz complexes were of too low solubility to obtain cyclic voltammetry measurements; however, acetonitrile solutions were sufficiently concentrated for differential-pulse voltammetry (DPV). This technique gives a peak potential slightly displaced from the formal potentials of CV measurements;[16] unfortunately no straightforward calculation of $E^{\circ\prime}$ is readily made by using finite pulse heights. Reversibility can be established from peak widths at half-height; for small pulse amplitudes a one-electron transfer should show $W_{1/2}$ of 90.4 mV.[16] The data of Table I show the known reversible ferrocene system to have $W_{1/2}$, under our conditions, of 135 mV, and this serves as our criterion of reversibility.

All isomers of $[Ru(NAz)_2Cl_2]$ showed greater stabilization of ruthenium(II) than the corresponding Azpy complexes, as anticipated. The peak potentials indicate NAz to be one of the most effective ligands for stabilizing ruthenium(II) yet reported. This most certainly is a consequence of the strong $\pi$-acceptor properties of NAz caused by the inductive effect of the nitro group. A comparable situation occurs in $[Ru((NO_2)_2bpy)_2Cl_2]$ where the potential is increased to 0.85 V, compared with 0.35 V for $[Ru(bpy)_2Cl_2]$.[7]

The observed trend in potentials of the three isomers of $[Ru(NAz)_2Cl_2]$ parallels that in the corresponding Azpy complexes, lending further support to our configuration assignments based on the optical spectra.

Strong metal-ligand $\pi$-bonding is further exemplified in $[Ru(NAz)_3]^{2+}$. Neither $[Ru(NAz)_3]^{2+}$ nor $[Ru(Azpy)_3[^{2+}$ shows electrochemical oxidation up to the solvent cutoff (ca. 2 V). Reduction of both compounds, however, is favorable, with $[Ru(NAz)_3]^{2+}$ going to its first reduced form at a peak potential of 0.015 V (ca. 0.1 V vs. NHE). Such a high reduction potential for $[Ru(NAz)_3]^{2+}$ may explain the instability of this compound in both solution and solid state. We presume $[Ru(NAz)_3]^+$ to contain a ligand-localized radical; $[Ru(Azpy)_3]^+$ shows an ESR signal characteristic of such a species ($g \approx 2.00$). Other workers have observed ligand-localized radicals in the transient $[Ru(bpy)_3]^+$.[17]

Reduction of $[Ru(NAz)_3]^{2+}$ is more complex than that of $[Ru(Azpy)_3]^{2+}$, with more peaks occurring as the sweep becomes more cathodic. This most likely is due to electrochemistry on the ligand nitro groups and has been considered no further.

Reduction of other ruthenium(II) complexes of strong $\pi$-acceptor ligands is well documented. The $[Ru(bpy)_3]^{2+/+}$ potential is $-1.33$ V[18] while with the stronger $\pi$-acid ligand 2,2′-bipyrazyl the $[Ru(bpz)]^{2+/+}$ potential is $-0.86$ V.[19] Vlček[20] has considered the stabilization of reduced ligands by coordination and points out that this is caused for the most part by the central field (positively charged) of the metal. Thus, metal-ligand back-$\pi$-bonding, which increases the metal ion effective charge, should lead to stabilization of reduced forms. It should be possible, then, to design complexes having stabilized ligand radical anions by adjusting the extent of back-$\pi$-interaction.

**Acknowledgment.** We thank Douglas Burbach, Jr., for experimental help during the synthesis of the ligand and Professor F. W. Wassmundt for helpful discussions. Portions of this work were conducted at Kemisk Laboratorium IV, H. C. Ørsted Institute, Copenhagen, Denmark, and we wish to extend our thanks for Professor C. J. Ballhausen's hospitality.

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## Photochemistry of the *cis*- and *trans*-Dibromobis(ethylenediamine)ruthenium(III) Cations

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*Received August 24, 1983*

Irradiation of the ligand field bands of many transition-metal complexes causes ligand labilization and solvolysis, often with geometric (or optical) isomerization. The development of models to predict which of the six ligands in a given complex is photolabile has been a spirited research area,[2-6] but until recently, the stereochemical consequences of photoinduced substitutions have received less attention. Theoretical approaches to photoinduced stereochemical changes (or the lack of change) have recently been presented,[7-9] and experimental studies are exploring their validity.[10-13]

One assumption of these models[7,8] is that photoinduced substitutions can be considered to result from three consecutive events: (1) ligand loss, with a 5-coordinate complex of square-pyramid (SPY) geometry remaining, (2) intramolecular rearrangement of the 5-coordinate species to the lowest energy configuration, and (3) nucleophilic attack by water. The most stable geometry for the 5-coordinate excited state is calculated and depends on the electronic structure of the metal and the $\sigma$- and $\pi$-donor properties of the five ligands. The possibility that the three steps may be concerted is recognized,[7] but the

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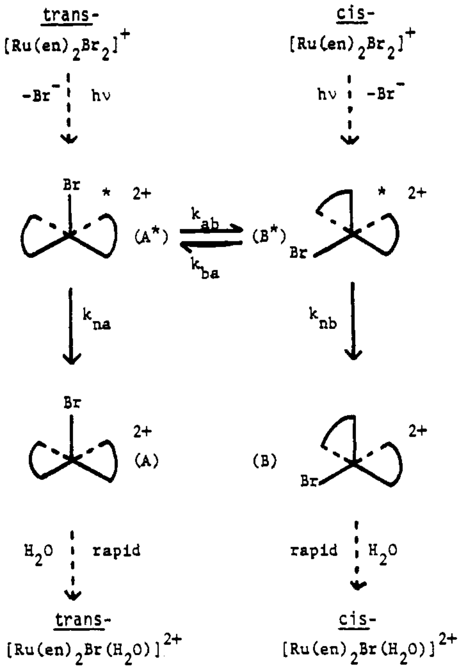

**Figure 1.** Dynamic excited-state model[15] applied to *cis-* and *trans-*[Ru(en)$_2$Br$_2$]$^+$. The reaction rate constants represented by the solid arrows are incorporated into the Runge–Kutta analysis.

assumption of a coordinatively unsaturated excited state, existing long enough to attain the most stable geometry (the thexi state) is inherent to these models.

This assumption was questioned for the d$^5$ case in the report of the photolysis of *cis-* and *trans-*[Ru(en)$_2$Cl$_2$]$^+$(aq).[14] The geometry of a thermally equilibrated {[Ru(en)$_2$Cl]$^{2+}$} excited state would not depend on the geometry of the dichloro precursor, so the observed difference in the photoproduct mixtures upon photolysis of the two dichloro isomers suggested that models involving an equilibrated 5-coordinate intermediate did not apply.

This work has been reinterpreted[15] in terms of a dynamic excited-state model, in which photolysis of either isomer would lead to a square-pyramidal excited state (A* with the halide in the apical site and B* for the species with the halide in a basal site) (Figure 1). Rapid interconversion between these excited states (via $k_{ab}$ and $k_{ba}$) allows the lower energy structure to dominate, but nonradiative deactivation to the electronic ground states (via $k_{na}$ and $k_{nb}$ in Figure 1) prevents true equilibration between A* and B*. Ajustment of the four rate constants ($k_{ab}$, $k_{ba}$, $k_{na}$, and $k_{nb}$) can then be used to account for the differing cis/trans photoproduct ratios upon photolysis of different isomers. With four independent parameters, this dynamic excited-state model is very flexible; its utility is limited, however, as there are an infinite number of sets of values for the four rate constants that can be used to account for a given experimental result. Perhaps surprisingly, not all experimental results can be interpreted by this model.

Vanquickenborne et al.[16] have extended their angular-overlap model to these d$^5$ complexes and note several differences between the well-studied d$^3$ and d$^6$ systems and the relatively unexplored d$^5$ configuration.

This note presents new experimental results on the photochemistry of *cis-* and *trans-*[Ru(en)$_2$Br$_2$]$^+$ and discusses the results in terms of the dynamic excited-state[15] and angular-overlap[16] models.

Table I. Electronic Spectra[a] and Quantum Yields[b]

| | [Ru(en)$_2$Br$_2$]$^+$ | | [Ru(en)$_2$Br(H$_2$O)]$^{2+}$ | |
|---|---|---|---|---|
| | cis | trans | cis | trans |
| $\lambda_{max}$ ($\epsilon$), nm (cm$^{-1}$ M$^{-1}$) | 445 (1320)<br>380 (1280)<br>298 (430) | 409 (4220)<br>342 (680) | 400 (1440) | 392 (1820)<br>305 (210) |
| $\phi_{total}$ | 0.0012 | 0.0088 | 0.020 | 0.015 |
| $\phi_{isom}$ | 0.00065 | 0.0066 | 0.020 | 0.015 |
| $\phi_{ret}$ | 0.00060 | 0.0022 | | |

[a] 0.2 M CH$_3$SO$_2$H as solvent. [b] Quantum yields are the average of three independent experiments and are accurate to ±10%.

## Experimental Section

**Preparation of Compounds.** ***cis-* and *trans-*Dibromobis(ethylenediamine)ruthenium(III) Bromide Hydrate.** The methods of Broomhead and Kane-Maguire[17,18] were used to synthesize the dibromo ions, which were recrystallized from 1 M HBr before use. With one exception (vide infra) the electronic spectra and molar absorptivity coefficients agreed with the reported values.

***cis-* and *trans-*Aquobromobis(ethylenediamine)ruthenium(III) Cations.** An aqueous methanesulfonic acid solution (1 × 10$^{-3}$ M) of the [Ru(en)$_2$Br$_2$]$^+$ ion of the appropriate geometry was heated at 65 °C for 60 min. After cooling to room temperature, the solution was placed on a Sephahex SP-C-25 cation-exchange column in the H$^+$ form. The unreacted dibromo ion was eluted with 0.02 M CH$_3$SO$_3$H, and the desired aquobromo ion was eluted with 0.2 M CH$_3$SO$_3$H. Bromide anation of the aquobromo ion regenerated the dibromo ion of the appropriate geometry. Aquobromo ion solutions were used as soon as they eluted from the column.

**Photolyses.** A 200-W high-pressure Hg short-arc lamp (Illumination Industries Inc.) was used as a radiation source. Wavelength selection was done with an interference filter (Baird Atomic) with a transmittance maximum at 405 nm (fwhh of 20 nm), which corresponded to the lowest energy band in the electronic spectra. Incident light intensities were measured with ferrioxalate actinometry[19] and averaged 1.8 × 10$^{-8}$ einstein/s over a rectangular (0.8 × 2.0 cm) cell face. Samples were held at 4 (±1) °C to minimize any thermal reactions. Electronic spectra were recorded on a Beckman Acta MIV spectrophotometer in the absorbance mode.

**Product Analyses.** Due to similarities in their spectra, aqueous solutions of *cis-* and *trans-*[Ru(en)$_2$Br(H$_2$O)]$^{2+}$ were analyzed after bromide anation to the dibromo ions (as described previously[14]). Isosbestic points between *cis-* and *trans-*[Ru(en)$_2$Br$_2$]$^+$ occurred at 439, 384, and 296.2 nm. The concentration of small amounts of aquobromo ion in the presence of large excesses of the dibromo ion was determined as described for the dichloro system;[14] the two aquobromo ions had isosbestics at 412.5 and 350 nm.

## Results

**Thermal Chemistry and Electronic Spectra.** The solution chemistry of the two [Ru(en)$_2$Br$_2$]$^+$ ions is similar to that of the analogous [Ru(en)$_2$Cl$_2$]$^+$ ions, with stereoretentive aquation of the non-amine ligands the only detected thermal reaction in acidic aqueous solution. The electronic spectra of *cis-* and *trans-*[Ru(en)$_2$Br$_2$]$^+$ in methanesulfonic acid (0.2 M) are similar to those reported in dilute hydrobromic acid, except that the *trans-*[Ru(en)$_2$Br$_2$]$^+$ ion had peaks at 409 and 342 nm, rather than at 409 and 382 nm.[17,20] The two aquobromo cations have not been previously reported, and their spectral

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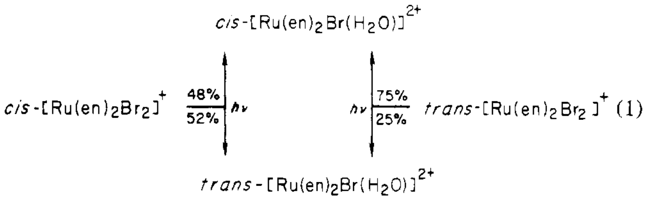
features are given in Table I. The addition of HBr (1 mL, 48%) to a solution of the aquobromo ion (3 mL, $4 \times 10^{-4}$ M) led to the complete (>99%) regeneration of the dibromo starting material, confirming that both aquation and bromide anation occur with retention of geometry.

**Photolyses.** Excitation at 405 nm (corresponding to the lowest energy band of *trans*-$[Ru(en)_2Br_2]^+$ and the first two low-energy bands of the cis isomer) produces spectral changes similar to those observed upon photolysis of the analogous dichloro complexes.[14] Direct irradiation of the higher energy ligand-to-metal charge-transfer bands led to the same spectral changes observed upon excitation of the lower energy, presumably ligand field, bands. The same spectral changes were observed when photolyses were done in an atmosphere of pure Ar, pure $O_2$, pure $N_2$, or air. Even in a pure $N_2$ atmosphere, no evidence for the formation of a Ru(II)–dinitrogen complex could be found; this implies that photoreduction to the Ru(II) state is not significant, even upon direct population of the LMCT bands.

Bromide anation of the photolyzed solutions led to mixtures of *cis*- and *trans*-$[Ru(en)_2Br_2]^+$, showing that geometric isomerization occurred upon photoinduced bromide aquation. Quantitative product analysis, using halide anation/spectral analysis,[14] led to the quantum yields given in Table I and to the isomeric composition given in eq 1.



$$\begin{tikzcd} & cis\text{-}[Ru(en)_2Br(H_2O)]^{2+} & \\ cis\text{-}[Ru(en)_2Br_2]^+ \arrow[ur, "48\%"] \arrow[dr, "52\%"', "h\nu"] & & trans\text{-}[Ru(en)_2Br_2]^+ \arrow[ul, "75\%"'] \arrow[dl, "25\%", "h\nu"'] \\ & trans\text{-}[Ru(en)_2Br(H_2O)]^{2+} & \end{tikzcd} \qquad (1)$$

Interference from secondary photolysis was reduced by limiting the photochemical aquations to the first 15%. The ratio of *cis*- to *trans*-aquobromo ions was not dependent upon photolysis time, as long as the total conversion to the aquobromo ions was less than about 15%. Thus, secondary photoisomerization of the aquobromo ions does not significantly affect the product ratios shown in eq 1.

Ligand field irradiation of either *cis*- or *trans*-$[Ru(en)_2Br(H_2O)]^{2+}$ resulted in minor spectral changes, but bromide anation of the photoproducts showed that photolysis caused each isomer to isomerize to the other. The quantum yields for the isomerizations are given in Table I.

## Discussion

Apart from numerical values for quantum yields and photoproduct composition, the photochemical behavior of these $[Ru(en)_2Br(X)]^{n+}$ (X = Br, $H_2O$) ions is similar to that of the analogous chloro complexes. Despite ambiguity in assigining the lowest electronic transitions as "ligand field bands",[14] the observed photosubstitutions are characteristic of ligand field excited states; as has been observed earlier for Ru(III),[21] the LMCT states appear photoinert.

Separate photolyses of *cis*- and *trans*$[Ru(en)_2Br_2]^+$ yield different mixtures of *cis*- and *trans*$[Ru(en)_2Br(H_2O)]^{2+}$, ruling out the intermediacy of a thermally equilibrated, five-coordinate species. The stereochemistry of the aquation of an equilibrated $\{[Ru(en)_2Br]^{2+}\}$ intermediate would not depend on the structure of the dibromo starting material. Despite the flexibility of four adjustable rate constants, Runge–Kutta calculations cannot be made to mimic the observed photoproduct composition.

Photolysis of *trans*-$[Ru(en)_2Br_2]^+$ would initially lead to A* (Figure 1), but since the dominant photoproduct is the *cis*-aquobromo ion (75%), formation of B* (via $k_{ab}$) must be important. Photolysis of *cis*-$[Ru(en)_2Br_2]^+$ would initially generate the same B*, but facile isomerization to A* must now be invoked, for in this case the predominant photoproduct has the trans geometry. Dominance of the trans photoproduct is not large (52%), but in all three photolyses of *cis*-$[Ru(en)_2Br_2]^+$ analyzed, *trans*-$[Ru(en)_2Br(H_2O)]^{2+}$ was the major product. An error limit of 10% in the absolute quantum yield values is typical for such a study (Table I), but the relative error in the analysis of the cis/trans photoproduct ratio is generously set at 2%. Even though the absolute $\phi_{isom}$ and $\phi_{ret}$ values for *cis*-$[Ru(en)_2Br_2]^+$ are similar, there is no doubt that photoisomerization to the *trans*-aquobromo ion is the dominant photoreaction.

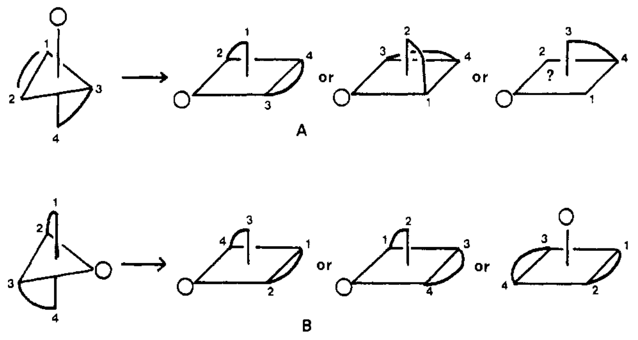


**Figure 2.** Possible TBP → SPY distortions for the two $\{[Ru(en)_2X]^{2+}\}$ species.

In short it is not possible to have B dominate over A when A* is the initial excited state and then have A dominate over B when B* is the initial excited species. This can be treated more rigorously by applying the steady-state approximation to the excited states A* and B*, for it can be shown that upon the initial formation of A* (photolysis of the trans isomer)

$$\frac{d[A]/dt}{d[B]/dt} = \frac{k_{na}(k_{ba} + k_{nb})}{k_{ab}k_{nb}} < 1 \qquad (2)$$

The experimentally observed photoproduct ratio (75% cis product) implies that this ratio would have a value less than 1. Upon photolysis of *cis*-$[Ru(en)_2Br_2]^+$, the trans photoproduct dominates, and

$$\frac{d[A]/dt}{d[B]/dt} = \frac{k_{ba}k_{na}}{k_{nb}(k_{ab} + k_{na})} > 1 \qquad (3)$$

Combination of inequalities 2 and 3 leads to the impossible statement that $k_{na}k_{nb} < 0$. In light of such a contradiction, one is forced to conclude that the four-parameter kinetic scheme cannot describe the photochemical behavior of the $[Ru(en)_2Br_2]^+$ isomers.

The ligand-field model of Vanquickenborne et al.[16] qualitatively accounts for the stereophotochemistry of the $[Ru(en)_2Cl_2]^+$ system by noting that any trigonal bipyramid (TBP) has three equally probable distortion modes that lead to a square pyramid (SPY). For the TBP with the apical halide, all three modes lead to a SPY with a basal chloride and hence a *cis*-aquohalo photoproduct (Figure 2A). Distortion of the TBP with the equatorial halide leads to a SPY with a basal halide in two cases and an apical chloride in one case (Figure 2B). Assuming photolysis of *trans*-$[Ru(en)_2X_2]^+$ leads to only the TBP with the equatorial halide, a cis/trans photoproduct ratio of 2/1 would be expected (Figure 2B), and if photolysis of *cis*-$[Ru(en)_2X_2]^+$ led to the equal formation of both TBP structures, a cis/trans photoproduct ratio of about 5/1 would be anticipated. The predictions are remarkably close to the observed cis/trans photoproduct ratios observed in the $[Ru(en)_2Cl_2]^+$ system.

However successful, this analysis of the chloro system can be questioned on several points and is not readily extended to

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the bromo complexes reported here. The non-halide ligands are treated as monodentate ammines, while the complexes involved have two bidentate amines; not all geometries are possible for $\{[Ru(en)_2X]^{2+}\}$. For example, a TBP with an apical halide (Figure 2A) forces one ethylenediamine to span the 120° angle between equatorial sites, a highly strained, if not impossible, configuration for ethylenediamine. (One of the distortions from that TBP would force the ethylenediamine to span trans sites in the resulting SPY.) This has the effect of raising the energy of the $^4E$ state (Figure 1 of ref 16) and makes isomerization through the $C_{3v}$ form of the TBP impossible. (This is analogous to the restriction in the $d^6$ case, brought on by electronic considerations.) In addition, the three TBP → SPY distortions of the TBP with the equatorial halide (Figure 2B) need not be equally probable, as all three equatorial ligands are not identical.

Photolysis of *cis*-$[Ru(en)_2Cl_2]^+$ is fundamentally stereoretentive, with a cis/trans photoproduct ratio near 5/1; the analogous *cis*-$[Ru(en)_2Br_2]^+$ ion is much less stereoretentive upon photolysis, with a slight preponderance of the isomerized trans product (the cis/trans ratio is about 0.9/1). Both *trans*-$[Ru(en)_2X_2]^+$ ions photoisomerize, with a cis/trans ratio of 2/1 for X = Cl and 3/1 when X = Br. Lowering the average ligand field, by replacing chloride with bromide, leads to increased photoisomerization, rather than the increased stereoretention predicted.[16]

At this early stage in the study of Ru(III) photochemistry, we do not understand the seemingly chaotic stereophotochemistry observed. Available models, based on rearrangements of coordinately unsaturated species, seem inadequate, which again raises the question of whether these photoaquations should be considered to be dissociative processes, with no place for the incoming water until the stereochemistry of the 5-coordinate species has been established. More experimental work is necessary to determine whether a pattern in the stereophotochemistry of Ru(III) complexes will emerge.

**Acknowledgment.** We thank Professor Michael Starzak (SUNY—Binghamton) for assistance in the fundamentals of Runge–Kutta analysis and Michael Siegel for computer work. Support from the Cottrell Grants Program of the Research Corp. is gratefully acknowledged.

**Registry No.** *cis*-$[Ru(en)_2Br_2]^+$, 55822-57-6; *trans*-$[Ru(en)_2Br_2]^+$, 73238-27-4; *cis*-$[Ru(en)_2Br(H_2O)]^{2+}$, 53368-48-2; *trans*-$[Ru(en)_2Br(H_2O)]^{2+}$, 15337-42-5.

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# (Trifluoromethanesulfonato)pentaammineruthenium(III): A Relatively Labile Synthetic Intermediate[1]

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*Received September 22, 1983*

Typical syntheses of ruthenium(III) complexes involve the use of relatively labile ruthenium(II) intermediates (for example, $[Ru(NH_3)_5(H_2O)]^{2+}$ or $[Ru(NH_3)_4(SO_3)(H_2O)]$).[2,3] After a ligand on the Ru(II) complex ($H_2O$ in the two examples above) has been replaced by the desired ligand, a Ru(III) complex is obtained by oxidation with reagents such as Ag(I),[4] Ce(IV),[4] $Br_2$,[5] and $H_2O_2$.[5] Unfortunately, in some instances, these convenient methods are inappropriate: in the synthesis of bimetallic complexes in which a second atom, for example Co(III), is reducible by Ru(II); in situations when the ligands themselves are oxidizable; in cases where these methods require that the ligand compete successfully against the solvent, water, in binding to Ru(II). Recently, Sargeson and co-workers described a facile general method for the preparation of Co(III) complexes using the trifluoromethanesulfonate anion as a noncompeting leaving group.[6] We have adapted this method for the syntheses of Ru(III) complexes. The reaction involves substitution of Ru(III), which is normally highly inert,[7] without the necessity for Ru(II) intermediates or oxidizing agents.

In this report we describe the synthesis and some kinetics of formation of several classes of pentaammine complexes of Ru(III) that have received considerable attention in recent years: nitrile complexes, halide complexes, and complexes of aromatic nitrogen heterocycles.

## Experimental Section

**Reagents.** Commercially available ACS grade reagents (Fisher) or redistilled solvents were used unless otherwise specified. Anhydrous trifluoromethanolsulfonic acid hydrate and tetramethylene sulfone (Alfa) were distilled under reduced pressure twice.

**Instrumentation.** Visible absorption spectra were recorded with thermostated Cary 14 or Beckman DU-8 spectrophotometers. Infrared spectra (KBr disk) were recorded with a Beckman Model 4240 spectrometer. Cyclic voltammograms were obtained with a Bioanalytical Systems CV-1 three-electrode system (Ag/AgCl reference electrode).

**(Trifluoromethanesulfonato)pentaammineruthenium(III) Trifluoromethanesulfonate, $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$.** This synthesis proceeds as described by A. M. Sargeson et al.[6] for the analogous cobalt complex, $[Co(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$, with the following exceptions: (1) the ruthenium precursor, $[Ru(NH_3)_5Cl]Cl_2\cdot{}^2/_3H_2O$,[8] was allowed to react for 2 h at 95 °C instead of 1 h and (2) the product was filtered by equally dividing the reaction mixture into three medium-porosity fritted filter funnels of 2.5-cm diameter and 10.5-cm height fitted with a septum cap and kept under positive pressure of dry nitrogen gas. The most convenient scale for this preparation is 5–10 g of product. Anal. Calcd for $RuC_3H_{15}N_5F_9O_9S_3$: C, 5.68; H, 2.38; N, 11.05; F, 26.97; S, 15.16; O, 22.70. Found (Galbraith Laboratories, Knoxville, TN): C, 5.56; H, 2.73; N, 10.72; F, 26.79; S, 14.96; O, 22.91. Visible spectrum: 285 nm, $\epsilon = 890$ (in anhydrous $HCF_3SO_3$); 284 nm, $\epsilon = 870$ (in sulfolane).

**Halopentaammineruthenium(III), Pyridylpentaammineruthenium(III), and (Organonitrile)pentaammineruthenium(III) Complexes.** In a typical preparation of these complexes, a solution containing $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ (0.01–0.10 M) was prepared in doubly distilled sulfolane and an excess of the ligand was added. For reactions involving relatively neutral ligands such as the halides and organonitriles, a stoichiometric amount of trifluoromethanesulfonic anhydride was added. The vessel was stoppered to eliminate moisture. After the reaction was complete and the reaction mixture allowed to cool, the product was isolated by extraction. An equal volume of water was added, and excess ligand and sulfolane were extracted with several portions of dichloromethane, each of which was 10 times the volume of the original reaction mixture. The volume of the water layer was then reduced with use of a rotary evaporator until the product had precipitated. The solid was washed with methanol or acetone, rinsed with diethyl ether, and air-dried.

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(1) Presented in part at the 183rd National Meeting of the American Chemical Society, Kansas City, MO, Sept 1982; Abstract INOR 15.
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