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Syntheses and Properties of the Ruthenium(III) Complexes *cis*- and *trans*-$Ru(NH_3)_4(L)X^{2+}$. Application of Cyclic Voltammetry to Study Cis and Trans Effects on Substitution Reactions of the Ruthenium(II) Analogues

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Reported are the syntheses, spectral properties, and formal reduction potentials (E_f) of the mixed ligand complexes *cis*- and *trans*-$Ru(NH_3)_4(L)X^{2+}$ (L = pyridine or isonicotinamide, $X^- = Cl^-, Br^-$, or I^-; L = acetonitrile, $X^- = Cl^-$). Each of the haloruthenium(III) complexes in aqueous solution displays a ligand to metal charge-transfer electronic spectral absorption band which is markedly dependent on the nature of X^- and modestly dependent on the nature of L. In contrast, whether X^- is Cl^-, Br^-, or I^- has little influence on E_f while L is much more influential following the order $NH_3 <$ pyridine $<$ isonicotinamide $<$ acetonitrile. In addition cyclic voltammetry methods were used to examine the kinetics of halide aquation from the ruthenium(II) analogues $Ru(NH_3)_4(L)X^+$. The rates for this reaction are relatively independent of the identity of X^- but are strongly dependent on the character and stereochemistry of L. π-Acceptor ligands such as pyridine slow the reaction in comparison to the pentaammine complex, an effect attributed to the increased effective charge on the Ru(II) site. The patterns of ruthenium(II) substitution labilities measured in this laboratory and others are summarized to give separate series for the cis effect and the trans effect of L in $Ru(NH_3)_4(L)X^+$. The trans effect series is argued to be dominated by the σ-donor ability of the trans ligand with strong σ donors having a labilizing effect on the trans position. π-Acceptor ligands which are not strong σ donors deactivate both the cis and trans sites. For the more limited cis series the only L's known to be labilizing are of π donor character and this is rationalized in terms of the bonding factors in the transition state of a dissociative mechanism.

The chemistry of ruthenium(II) and ruthenium(III) ammine complexes has been an area of considerable activity in recent years.[3-7] A variety of observations have demonstrated that the Ru(II) and Ru(III) centers show contrasting characters with regard to π-symmetry interactions with coordinated ligands; i.e., Ru(II) is a good π donor[4] while the $4d^5$ Ru(III) is a good π acceptor.[8] The contrasting π-bonding properties lend particular interest to those complexes where both a π-donor and a π-acceptor ligand are in the same coordination sphere. The syntheses and properties of several such ruthenium(III) species, *cis*- and *trans*-$Ru(NH_3)_4(L)X^{2+}$, are described here.

The reported data include the results of cyclic voltammetry (CV) studies on these mixed-ligand complexes. The CV experiment can provide formal reduction potentials for Ru(III)/Ru(II) complexes from the reversible waves of the cyclic scan[3,9] and kinetics information for reactions of the analogous ruthenium(II) complexes produced at the electrode, if the reaction rates fall within the time scale of the cyclic scan.[3,10] The reaction of interest in this context is the loss of halide ion (X^-) from the Ru(II) coordination sphere (eq 1). Although

$$Ru(NH_3)_4(L)X^+ + H_2O \xrightarrow{k_1} Ru(NH_3)_4(L)H_2O^{2+} + X^- \qquad (1)$$

the halide is relatively substitution inert in the coordination sphere of Ru(III), it is quite labile in the Ru(II) sphere. This has been demonstrated by Kuempel and co-workers[10a] who used the CV technique to examine the aquation kinetics for $Ru(NH_3)_5Cl^+$ and $Ru(NH_3)_5Br^+$. The present studies have particular interest in the context of several investigations[6,7a] of rate effects induced by variations of the ligand L for the substitution reactions of $Ru(NH_3)_4(L)H_2O^{2+}$ (eq 2).

$$Ru(NH_3)_4(L)H_2O^{2+} + N \xrightarrow{k_2} Ru(NH_3)_4(L)(N)^{2+} + H_2O \qquad (2)$$

Analogous reactions for the pentaammine complex $Ru(NH_3)_5H_2O^{2+}$ have been argued to proceed via a dissociative mechanism.[11,12] Thus, the question is raised whether the effects by various L predominantly reflect perturbations on the rates of H_2O dissociation or on the competition between solvent H_2O and the incoming nucleophile N for the coordinatively unsaturated intermediate. Insight into this question is provided by the CV technique which allows a more direct observation of the loss of X^- from the Ru(II).

Experimental Section

Materials. [*cis*-$Ru(NH_3)_4Cl_2$]Cl, [*trans*-$Ru(NH_3)_4(SO_2)Cl$]Cl, and [*trans*-$Ru(NH_3)_4Cl_2$]Cl were prepared by the literature procedures.[13] Ligands used in syntheses were reagent grade and were used without further purification. Potassium *p*-toluenesulfonate (KpTS) employed in electrochemical measurements was prepared as described.[3] Redistilled water was used in all solution preparation.

Analysis. Carbon/hydrogen/nitrogen microanalyses were performed by Galbraith Laboratories of Knoxville, Tenn. Ruthenium analyses were carried out using Malouf's modification of several earlier procedures.[14] In a typical determination, 8 mg of the ruthenium complex was first dissolved in 5 mL of 2 M KOH solution. To this were added 5 mg of solid potassium persulfate and 1 ml of 5% sodium hypochlorite solution. The resulting golden solution was heated just below boiling for 10 min, then allowed to cool to room temperature. The solution was then diluted with water to 25 mL in a volumetric flask. Ruthenium concentration was determined by measuring the solution optical density at 415 nm and by using the extinction coefficient of 1047 M^{-1} cm^{-1} for the isosbestic point for RuO_4^- and RuO_4^{2-} at this wavelength.

Apparatus. The cyclic voltammetry apparatus used to measure Ru(III)/Ru(II) reduction potential is identical with that described previously.[3] Electronic spectra were obtained on a Cary 14 or a Cary 15 recording spectrophotometer. All spectra were recorded at room temperature (23 ± 2 °C) in acidic aqueous solution (0.001 M HCl) maintained at 0.2 M ionic strength with NaCl except where noted. Solutions used to measure extinction coefficients were prepared gravimetrically with quantitative dilution. Infrared spectra were obtained with a Perkin-Elmer 283 infrared spectrometer.

Syntheses. Cis complexes of the type [*cis*-$Ru(NH_3)_4(L)X]X_2$ (where L is pyridine (py), isonicotinamide (isn), or acetonitrile (acn) and X^- is Cl^-, Br^-, or I^-) were prepared by a procedure modified from that of Allen[7a] as described here for [*cis*-$Ru(NH_3)_4(isn)Cl]Cl_2$. *cis*-$Ru(NH_3)_4(H_2O)_2^{2+}$ was generated from [*cis*-$Ru(NH_3)_4Cl_2]Cl$ (0.10 g, 3.6×10^{-4} mol) in water (5 mL) by reduction with excess zinc amalgam under an argon atmosphere. To the resulting solution was added an equimolar amount of isonicotinamide (0.024 g) dissolved in deaerated water. After 30 min of reaction time, the zinc amalgam was removed from the solution and 1.5 mL of 3 M aqueous HCl was added. Addition of several drops of 30% aqueous hydrogen peroxide resulted in the formation of the Ru(III) species, *cis*-$Ru(NH_3)_4(isn)Cl^{2+}$. After overnight cooling, the solid formed was collected by filtration, then washed successively with ethanol and ether. The yield of [*cis*-$Ru(NH_3)_4(isn)Cl]Cl_2$ after recrystallization from 0.15 M HCl was 0.062 g (43%). The perchlorate salt was prepared for analysis by dissolving in redistilled water and precipitating with perchloric acid to give [*cis*-$Ru(NH_3)_4(isn)Cl][ClO_4]_2\cdot H_2O$.

Anal. Calcd for $C_6H_{20}N_6O_{10}Cl_3Ru$: C, 13.25; H, 3.71; N, 15.46; Ru, 18.6. Found: C, 13.39; H, 3.77; N, 15.33; Ru, 18.5. When X^- = Br^- or I^-, hydrobromic acid or hydriodic acid were used instead of hydrochloric acid in the appropriate places in the procedure.

Trans complexes of the type [*trans*-$Ru(NH_3)_4(L)X]X_2$ were prepared according to the procedure described here for [*trans*-$Ru(NH_3)_4(py)Cl]Cl_2$. [*trans*-$Ru(NH_3)_4(SO_4)py]Cl$ (0.050 g, 1.3×10^{-4} mol), prepared from [*trans*-$Ru(NH_3)_4(SO_2)Cl]Cl$ according to Isied's procedure,[6] was dissolved in a minimum volume of deaerated 0.15 M aqueous HCl, and several pieces of zinc amalgam were added to the solution. After about a 20-min reaction, 1 M $BaCl_2$ solution was added dropwise to precipitate $BaSO_4$, then the solution was filtered to remove the excess zinc amalgam and solid $BaSO_4$. The orange filtrant was then oxidized by addition of excess acidic H_2O_2 (a few drops of a solution prepared from equal volumes of 3 M HCl and 30% aqueous H_2O_2) to give a pale yellow solution. Solid product was recovered from solution by adding a large volume of acetone (~100 mL), collecting the resulting pale yellow precipitate by filtration, and washing with ethanol, then ether. Recrystallization from 0.2 M HCl gave 0.032 g (60% yield) of [*trans*-$Ru(NH_3)_4(py)Cl]Cl_2$.

Anal. Calcd for $C_5H_{17}N_5Cl_3Ru$: C, 16.93; H, 4.83; N, 19.75. Found: C, 16.86; H, 4.90; N, 19.60.

Trans complexes where X^- = Br^- were prepared analogously except that HBr was substituted for HCl in the procedure described. The procedure for the trans iodo complex was different in the sense that zinc reduction was not necessary to effect the substitution of I^- for the sulfate of [*trans*-$Ru(NH_3)_4(py)SO_4]Cl$. Addition of saturated NaI solution (several drops) to aqueous [*trans*-$Ru(NH_3)_4(py)SO_4]Cl$ (0.050 mg in 0.5 mL of H_2O) led to a rapid color change from yellow to blue. A blue solid [*trans*-$Ru(NH_3)_4(py)I]I_2$ precipitated on cooling and was collected by filtration and washed with ethanol then ether.

Attempts to make the trans acetonitrile complex [*trans*-$Ru(NH_3)_4(CH_3CN)SO_4]Cl$ via Isied's procedures[6] proved unsuccessful, so a procedure analogous to that used for the cis complexes (vide infra) was used to prepare [*trans*-$Ru(NH_3)_4(CH_3CN)Cl]Cl_2$ directly from [*trans*-$Ru(NH_3)_4Cl_2]Cl$. The IR spectra (KBr pellets) of the two acetonitrile complexes are closely analogous to that reported previously for the pentaammine complex $[Ru(NH_3)_5CH_3CN][ClO_4]_3$ (two medium-intensity bands in the nitrile region, ν_{CN} at 2286 cm^{-1} and a weaker combination band at 2313 cm^{-1}).[15] The cis complex shows two bands at 2289 and 2319 cm^{-1} with the lower frequency band being the stronger while the trans complex shows bands at 2288 and 2318 cm^{-1} but with the relative intensities reversed.

Rate Studies. First-order rate constants for reactions occurring subsequent to an electron transfer reaction at the electrode were obtained from the CV curves according to the method of Nicholson and Shain.[3,10a,16] Cyclic voltammograms were obtained for freshly prepared solutions ~1×10^{-3} M in the Ru(III) complexes for various calibrated scan speeds. The rate constants are obtained from the ratio of the peak currents of reverse scan to those of forward scan (corrected for residual currents) for the reversible wave according to theoretical relationships.

Results and Discussion

Synthesis. The stereoretentive substitution behavior of ruthenium(II) ammine substitution reactions and the relative labilities of aquo, halide, and other anionic ligands when coordinated to Ru(II) are the keys to the syntheses described here.[4,17] Thus, various relatively substitution inert tetraammineruthenium(III) species can be prepared by stereospecific pathways, and reduction to Ru(II) followed by oxidation back to Ru(III) allows the replacement of coordinated halide or sulfate to give desired complexes. Examination of various reaction products by ion exchange chromatography gave no indication of any cis ⇄ trans isomerism. Preparation of the iodo complexes *trans*-$Ru(NH_3)_4(L)I^{2+}$ from *trans*-$Ru(NH_3)_4(L)SO_4^+$ did not require the zinc reduction step; however, it is possible that the substitution occurs via the catalytic formation of Ru(II) from some reduction by I^-. Similar redox catalysis may also account for qualitative observations that the iodo complexes $Ru(NH_3)_4LI^{2+}$ are much more labile to halide substitution than are the analogous Br^- complexes. It was noted, when attempting to determine extinction coefficients for the $[Ru(NH_3)_4(L)X]X_2$ salts in pH 3, 0.2 M NaCl solution, that the spectra were stable for a period of hours for X^- = Br^- but underwent slow changes indicating replacement of I^- by Cl^- in the coordination sphere when X^- = I^-. For this reason, visible-region extinction coefficients for the iodo complexes were measured in pH 3, 0.2 M NaI solution under which conditions the spectra were stable.

Reduction Potentials. Cyclic voltammograms of the complex *cis*-$Ru(NH_3)_4(py)Cl^{2+}$ in 0.1 M HpTS/0.1 M KpTS aqueous solution are illustrative of the behavior of each of these halide complexes. For a relatively fast scan (2.5 V/s), the cathodic and anodic waves each show single peaks with a separation of 60 mV, i.e., very close to that predicted for reversible behavior. A slower scan (e.g., 0.5 V/s) shows two anodic peaks, one separated from the cathodic peak by approximately 60 mV and a smaller one appearing at a more positive potential. This second anodic peak is increasingly prominent at even slower scan rates. Repetitive scans at the slower rates also show a growing in of a new cathodic peak at a more positive potential than the single peak seen in the first scan. These data can be interpreted in terms of the sequence of events described in Scheme I. A similar scheme has been proposed[10a,19] for the cyclic voltammetry of the corresponding pentaammine complex $Ru(NH_3)_5Cl^{2+}$. Formal reduction potentials for the couples $Ru(NH_3)_4(L)X^{2+/+}$ obtained from the reversible cathodic and anionic waves of the fast-scan CV are listed in Table I. In addition, formal reduction potentials for the aquo analogues $Ru(NH_3)_4(L)H_2O^{3+/2+}$ can be obtained from the new anodic and cathodic peaks appearing for repetitive cyclic scans at slow scan rates and displaying reversible behavior. These values are listed in Table II, and it is a reassuring confirmation of Scheme I that the E_f values obtained in this manner for L = py and L = isn reproduce those

Scheme I

$$\textit{cis}\text{-Ru(NH}_3)_4\text{(py)Cl}^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \textit{cis}\text{-Ru(NH}_3)_4\text{(py)Cl}^{+} \qquad (3)$$

$$\left.\begin{matrix}-\text{Cl}^-\\+\text{H}_2\text{O}\end{matrix}\right\downarrow k_1 \qquad (4)$$

$$\textit{cis}\text{-Ru(NH}_3)_4\text{py(H}_2\text{O)}^{3+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \textit{cis}\text{-Ru(NH}_3)_4\text{(py)(H}_2\text{O)}^{2+} \qquad (5)$$

Table I. Electronic Spectra and Formal Reduction Potentials of Haloammine Complexes of Ruthenium(III) in Aqueous Solution

Compound	λ_{max}[a] ($\epsilon \times 10^{-3}$)[b]	E_f[c]
$[Ru(NH_3)_5Cl]Cl_2$	328 (1.9)[d]	−0.04
[*trans*-$Ru(NH_3)_4Cl_2$]Cl	331 (5.0)[e] 295 sh (0.7)[e]	−0.16
[*cis*-$Ru(NH_3)_4Cl_2$]Cl	350 (1.5)[e] 308 (1.3)[e]	−0.11
[*trans*-$Ru(NH_3)_4(py)Cl$]Cl_2	346 (2.7) 251 (4.4)	0.20
[*cis*-$Ru(NH_3)_4(py)Cl$]Cl_2	340 (2.1) 262 (4.1)	0.17
[*trans*-$Ru(NH_3)_4(isn)Cl$]Cl_2	347 (3.4) 301 sh (3.1) 263 (4.9)	0.29
[*cis*-$Ru(NH_3)_4(isn)Cl$]Cl_2	343 (2.8) 298 sh (3.8)	0.23
[*trans*-$Ru(NH_3)_4(acn)Cl$]Cl_2	353 (1.4) 286 (0.30)	0.32
[*cis*-$Ru(NH_3)_4(acn)Cl$]Cl_2	350 (1.5) 280 sh (0.24)	0.31
$[Ru(NH_3)_5Br]Br_2$	398 (1.8)[d]	−0.02 −0.03[f]
[*trans*-$Ru(NH_3)_4(py)Br$]Br_2	424 (2.0) 350 (0.88) 260 sh (3.00)	0.19
[*cis*-$Ru(NH_3)_4(py)Br$]Br_2	425 (1.4) 263 (3.3)	0.19
[*trans*-$Ru(NH_3)_4(isn)Br$]Br_2	430 (1.8) 340 sh (2.1) 267 (5.0)	0.30
[*cis*-$Ru(NH_3)_4(isn)Br$]Br_2	430 (1.0) 350 sh (1.6) 278 (3.7)	0.24
$[Ru(NH_3)_5I]I_2$	540 (2.1)	
[*trans*-$Ru(NH_3)_4(py)I$]I_2	597 (1.9)[g] 350 (1.0) 260 sh (3.0)	0.23
[*cis*-$Ru(NH_3)_4(py)I$]I_2	600 (2.1)[g] 272 sh (3.7)	0.18
[*trans*-$Ru(NH_3)_4(isn)I$]I_2	604 (2.6)[g] 300 sh (3.5)	0.29
[*cis*-$Ru(NH_3)_4(isn)I$]I_2	607 (2.3)[g] 315 sh (3.4)	0.26
[*trans*-$Ru(NH_3)_4(py)SO_4$]Cl	328 (3.2) 252 (5.0)	
[*trans*-$Ru(NH_3)_4(isn)SO_4$]Cl	330 (3.8) 266 (5.4)	

[a] Spectral maxima in nm, spectra obtained for dilute aqueous solutions at 25 °C. Solution concentrations were [Ru] $\sim 10^{-3}$ M, pH 3/0.199 M NaCl except where noted. Abbreviations are py = pyridine, isn = isonicotinamide, and acn = acetonitrile. [b] Extinction coefficient in M^{-1} cm^{-1}. [c] Formal reduction potentials in V vs. the NHE. All values are ±0.01 V as obtained under reversible conditions from CV (separation of cathodic and anodic waves was 60–75 mV in each case). Complex concentrations were 1×10^{-3} M in aqueous solution with 0.1 M HpTS and 0.1 M KpTS as supporting electrolytes. [d] J. Stritar, Ph.D. Dissertation, Stanford University, 1967. [e] Reference 7b. [f] Reference 9. [g] Extinction coefficients for visible-region bands obtained in 0.199 M NaI/0.001 M HI aqueous solution.

Table II. Formal Reduction Potentials for Aquotetraammineruthenium Complexes *cis*- and *trans*-$Ru(NH_3)_4(L)H_2O^{3+/2+}$

	E_f[a]	
L	Cis	Trans
NH_3	0.07[b]	0.07[b]
H_2O	0.10[c,d]	0.08[d]
Cl^-	0.00[e] (0.03)[c]	−0.05[e] (−0.05)[c]
py	0.28[e] (0.27)[d]	0.33[e] (0.33)[d]
isn	0.34[e] (0.34)[d]	0.41[e] (0.42)[d]
acn	0.39[e]	0.49[e]

[a] Formal reduction potential in volts vs. NHE. New values reported here were determined in 0.1 M HpTS/0.1 M KpTS aqueous solution at 25 °C. [b] Reference 3. [c] Reference 19; pH 2, 0.3 M CH_3SO_3Na. [d] Reference 6, in 0.1 M $NaBF_4$ aqueous solution. [e] Obtained from reversible cathodic and anodic peaks of new species seen in repetition scan CV as described in the text.

values obtained[6] from the CV of the aquo complexes prepared independently (Table II).

The formal reduction potentials listed in Tables I and II for the mixed-ligand complexes indicate two general characteristics. First, E_f is surprisingly independent of the identity of the halide ion X^-. For the pentaammine complexes, substitution of Cl^- or Br^- for the H_2O of $Ru(NH_3)_5H_2O^{3+}$ reduces E_f by about 0.10 ± 0.01 V. A comparable effect is noted for substitution of Cl^-, Br^-, or I^- for the H_2O of *cis*- or *trans*-$Ru(NH_3)_4(py)H_2O^{3+}$ although there are clearly some subtle effects regarding whether the halide is in the cis or trans configuration to the unsaturated ligand of $Ru(NH_3)_4(acn)X^{2+}$ and $Ru(NH_3)_4(isn)(X)^{2+}$. The relative insensitivity of E_f to the nature of X^- is somewhat surprising given the contrasting properties of Ru(II) and Ru(III) with regard to metal–ligand π bonding. For example, the π acceptor nature of the pentaammineruthenium(III) center is illustrated by the much greater acidity of $Ru(NH_3)_5H_2O^{3+}$ than of the rhodium(III) analogue (pK_a's 4.2[22] and 6.8,[23] respectively). Thus, while coordination of X^- decreases E_f compared to those complexes having H_2O or NH_3 in the same site (i.e., $Ru(NH_3)_4(L)X^{2+}$ vs. $Ru(NH_3)_4(L)H_2O^{2+}$, Tables I and II), the relative insensitivity of E_f to whether X^- is Cl^-, Br^-, or I^- implies that the differences in the Ru(III)–X bonding for each of these anions are paralleled by similar differences in the Ru(II)–X bonding. The low-spin, d^6 Ru(II) center is unlikely to participate in significant π bonding with the halides, and the implication is that there are but small differences in the Ru(III)–X π bonding for these three anions. As the extent of π overlap should be a function of the donor orbital size, the insensitivity of E_f to X^- can be further interpreted as suggesting that the π bonding may be but a minor component of the overall metal–halide bonding for these anions. Such a conclusion may not be surprising given that the accumulation of thermodynamic and kinetic data which have implied ligand to Ru(III) π bonding were largely collected for ligands involving nitrogen or oxygen coordinating atoms. The smaller π orbitals of these may match more closely the partially filled $d\pi$ orbitals of the d^5 Ru(III). Thus it is notable that E_f for the $Ru(NH_3)_5OH^{2+/+}$ couple is −0.42 V,[9] 0.38 V more negative than that for $Ru(NH_3)_5Cl^{2+/+}$.

E_f is much more responsive to the nature of the neutral ligand L and follows the order L = $NH_3 \sim H_2O <$ py < isn < acn. A similar order was seen with the pentaammine complexes $Ru(NH_3)_5L^{3+/2+}$ and was attributed to the combination of the decreasing σ-donor character of the ligands along this series (thus destabilizing the +3 oxidation state relative to the +2 oxidation state) and the increasing π-acceptor ability along the same series of ligands (with the same net effect). The stereochemistry also exerts an influence on E_f and a consistent but not compelling pattern is seen in the data of Tables I and II. For complexes $Ru(NH_3)_4(L)X$ where X^- is I^-, Br^-, Cl^-, or H_2O and L is a π-acceptor ligand py, isn, or acn, E_f of the trans complex is more positive than that of the cis analogue. In contrast if X is Cl^- or H_2O and L is Cl^- or H_2O, E_f of the trans configuration is the more negative. With one or two exceptions similar patterns are also seen with the $Ru(NH_3)_4(H_2O)L$ complex reported by Isied.[6] While one is tempted to invoke cooperative interactions between the π-acceptor organic ligands and the π-donor ligands as an explanation for these stereochemical effects, it is notable that the poorer π-donor H_2O gave the larger trans/cis E_f differences when appearing in the same coordination sphere as py, isn, or acn. Thus differences in the σ-bonding interactions or solvation phenomena may be dominant influences.

Spectra of Ru(III) Complexes. The electronic spectra of various $Ru(NH_3)_4LX^{2+}$ complexes are summarized in Table I. In each case, the longest wavelength band listed can be assigned as a ligand to metal charge transfer (LMCT) and can be conceptualized as the following transformation

$$Ru^{III}(X^-) \xrightarrow{h\nu} [Ru^{II}(X\cdot)]^* \qquad (6)$$

The position of this band is markedly a function of X^- but only modestly a function of L. When $X^- = Cl^-$, the LMCT λ_{max} falls into the range 328–353 nm for the complexes reported here, when $X^- = Br^-$ the range is 398–430 nm, and when $X^- = I^-$ it is 540–607 nm. Consistent with eq 6, the relative oxidizability of X^- is a dominant energetic factor, the gas-phase ionization potentials of X^- following the series Cl^- (3.61 eV) > Br^- (3.36 eV) > I^- (3.06 eV).[18] Complexes where L is an unsaturated nitrogen ligand display lower energy LMCT bands than when L is NH_3; however, for a particular X^- there are only small differences between the cis and trans configurations.

The "Ru(II)" species produced instantaneously by eq 6 differs from the $Ru^{II}(X^-)$ produced by the reversible reduction of the analogous complex at the electrode owing to the nature of the sixth ligand ($X\cdot$ vs. X^-) and the role of Franck–Condon contributions to the energy (E(CT)) of the electronic transition. For the series $Ru(NH_3)_4(L)Cl^{2+}$ in either the cis or the trans configuration, E(CT) follows the order L = NH_3 > py > isn > CH_3CN, the same pattern seen for E_f for an analogous series. In addition, comparison of E(CT) values (in the appropriate units) for the halopentaammine to those of the $Ru(NH_3)_4(L)X^{2+}$ series shows that the differences are 70–80% of the E_f differences for the same complexes. For example, the E(CT) difference between $Ru(NH_3)_5Cl^{2+}$ and *trans*-$Ru(NH_3)_4(acn)Cl^{2+}$ is 0.27 V while the E_f difference for the same complexes is 0.36 V, a ratio of 0.75. Thus, the excited state "Ru(II)" of eq 6 is much like the Ru(II) formed in an equilibrium process, and Franck–Condon distortions are relatively small. Given that the metal-acceptor orbital in the electronic transition is a $d\pi$ orbital[20] (t_{2g} in O_h symmetry), modest Franck–Condon effects are not surprising.

Kinetics of Ru(II) Substitution. Analysis of peak current ratios of the anodic and cathodic waves at various scan speeds according to the method of Nicholson and Shain[3,10,16] gives rate constants for the first-order processes (e.g., eq 4) decreasing the intensity of the anodic wave for the Ru(II) species $Ru(NH_3)_4(L)X^+$. These rate constants are summarized in Table III. The experimental uncertainties listed are relatively large and a realistic estimate of the problems inherent to the method, and perhaps to our apparatus, suggests that rate constants obtained in this way have a normal uncertainty of 15–20%. Our value for $Ru(NH_3)_5Cl^+$ agrees reasonably well with the rate constant reported by Kuempel et al.,[10] which agrees with the rate constant (4.7 s^{-1} at 20 °C) by a pulse radiolysis technique.[21] The rate constant for chloride aquation from $Ru(NH_3)_5Cl^{2+}$ obtained by Elson et al. by the peak to peak current ratio method[19] is somewhat larger and an even larger number (17 s^{-1}) was calculated in another manner from CV data by these workers. The source of these discrepancies is unclear; however, the new data reported here were obtained from several different preparations of $[Ru(NH_3)_5Cl]Cl_2$ and were measured independently by several workers in this laboratory. A large discrepancy is also noted between the rate constants for Cl^- aquation from *trans*-$Ru(NH_3)_4Cl_2^+$ reported new here and those reported previously by Elson et al.[19] although in each set of measurements the lability followed the order *cis*-$Ru(NH_3)_4Cl_2^+$ > $Ru(NH_3)_5Cl^{2+}$ > *trans*-$Ru(NH_3)_4Cl_2^+$. The reversible cathodic and anodic peaks chosen for our rate analysis agree with those of Elson et al.[19] The source of the disagreements from one laboratory to another is not clear; however, the rate data reported in this article were internally self-consistent and reproducible and the ensuing discussion will be largely concerned with comparisons among these data.

Table III. Rate Constants Determined by CV for Aquation of Halide from the Cis or Trans Tetraammineruthenium(II) Complexes $Ru(NH_3)_4LX^+$ in Aqueous Solution

$$Ru(NH_3)_4(L)X^+ + H_2O \xrightarrow{k_{obsd}} Ru(NH_3)_4(L)H_2O^{2+} + X^-$$

L	X^-	$k_{obsd}{}^a$ (s^{-1})	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
NH_3	Cl^-	5.1 ± 0.8^b		
		$(6.3 \pm 0.3)^{b,c}$	12 ± 3^c	-16 ± 6^c
		$(10 \pm 4)^{b,d}$		
Cis Cl^-	Cl^-	$\sim 32^b$		
		$(\sim 73)^{b,d}$		
Trans Cl^-	Cl^-	0.9 ± 0.1^b		
		$(4.4 \pm 2.1)^{b,d}$		
Cis py	Cl^-	0.40 ± 0.05 (25 °C)^b	14 ± 3	-13 ± 9
		0.8 ± 0.1 (33 °C)^b		
		1.4 ± 0.1 (40 °C)^b		
Trans py	Cl^-	0.85 ± 0.2 (18 °C)^b		
		1.5 ± 0.3 (25 °C)^b	17 ± 3	-1 ± 9
		3.0 ± 0.2 (33 °C)		
		7.0 ± 0.2 (40 °C)^b		
Cis isn	Cl^-	0.13 ± 0.03		
Trans isn	Cl^-	0.23 ± 0.05 (18 °C)^b		
		0.50 ± 0.03 (25 °C)^{b,c}	17 ± 3	-3 ± 9
		0.9 ± 0.1 (33 °C)^b		
		2.1 ± 0.1 (40 °C)^b		
Cis acn	Cl^-	0.18 ± 0.03^e		
Trans acn	Cl^-	0.10 ± 0.03^e		
NH_3	Br^-	3.4 ± 0.7^b		
		$(5.4 \pm 0.4)^{b,c}$	14 ± 3^c	-10 ± 6^c
Cis py	Br^-	0.40 ± 0.03^e		
Trans py	Br^-	2.1 ± 0.4^e		
Cis isn	Br^-	0.18 ± 0.03^e		
Trans isn	Br^-	0.43 ± 0.04^e		
Cis py	I^-	0.75 ± 0.15^e		
Trans py	I^-	0.9 ± 0.2^e		
Cis isn	I^-	0.14 ± 0.04^e		
Trans isn	I^-	0.5 ± 0.3^e		

[a] First-order rate constant calculated from ratios of anodic to cathodic peak currents according to ref 16. Reactions were carried out in 25 °C, deaerated, 0.1 M HpTS/0.1 M KpTS aqueous solution except where noted. Rate constants in parentheses are those obtained in other laboratories. [b] Rate measured at dropping mercury electrode. [c] Reference 9, 0.171 M HpTS aqueous solution. [d] Reference 19, pH 2, 0.3 M CH_3SO_3Na. [e] Rate measured at platinum ball electrode.

In general the following trends are apparent for the data in Table III. (1) The first-order substitution rate constants (k_{obsd}) for the Ru(II) complexes $Ru(NH_3)_4(L)X^+$ are relatively insensitive to whether X^- is Cl^-, Br^-, or I^-. The stereochemistry of a particular complex (cis or trans) has a greater rate effect. (2) The general pattern for k_{obsd} shows the complexes containing the π-acid nitrogen bases to be less labile than the pentaammine complexes, the orders observed being L = NH_3 > py > isn > acn for the trans species and L = NH_3 > py > acn ≃ isn for the cis. (3) Although the activation parameters reflect the large uncertainties inherent to the rate data, within the generous error limits there are no significant differences among the systems reported in Table III, with $\Delta H^\ddagger$ and $\Delta S^\ddagger$ falling within the ranges 15 ± 3 kcal/mol and −9 ± 8 eu respectively.

A dissociative mechanism (eq 7 and 8) has been

$$Ru(NH_3)_5H_2O^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ru(NH_3)_5{}^{2+} + H_2O \qquad (7)$$

$$Ru(NH_3)_5{}^{2+} + N \xrightarrow{k_N} Ru(NH_3)_5N^{2+} \qquad (8)$$

argued[6,7a,11,12] for the reactions of various nucleophiles N with $Ru(NH_3)_5H_2O^{2+}$ and with aquotetraammines $Ru(NH_3)_4$-

$(L)H_2O^{2+}$ (eq 2). This proposal is based on the relative insensitivity of the rate parameters k_2, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ to the nature of N (with the exception of some steric considerations). The observed rates are first order each in $[Ru(NH_3)_5H_2O^{2+}]$ and [N] (eq 9) but this is easily accommodated by the rate

$$\text{observed rate} = k_2[Ru(NH_3)_5H_2O^{2+}][N] \tag{9}$$

$$\text{rate} = \frac{k_f k_N [Ru(NH_3)_5H_2O^{2+}][N]}{k_r + k_N[N]} \cong \frac{k_f k_N}{k_r}[Ru(NH_3)_5H_2O^{2+}][N] \quad \text{if } k_r >> k_f[N] \tag{10}$$

law for the mechanism (eq 10) if $k_N[N] << k_r$.

Accordingly, k_2 equals the ratio $k_f k_N/k_r$, and variations in k_2 can be attributed to small variations in the k_N step, the nucleophilic capture of the coordinatively unsaturated $Ru(NH_3)_5^{2+}$. However, since the rate parameters are quite insensitive to the identity of N[11,12] the dominant contribution to the activation energy must be the k_f term. A direct measurement of k_f has not been made; however, aquation rates measured[10,20,25] for several ligands X^- (eq 1) and Y (eq 11)

$$Ru(NH_3)_5Y^{2+} + H_2O \rightarrow Ru(NH_3)_5H_2O^{2+} + Y \tag{11}$$

were the basis of the estimate[11] of $\sim 10\ s^{-1}$ for k_f. Notably, when Y = NH_3, ligand aquation is very slow ($\sim 10^{-5}\ s^{-1}$),[11] and qualitative observations indicate the π-unsaturated ligands such as pyridine and acetonitrile are no more labile than NH_3.[26,27] Thus the labile ligands are ones with unshared electron pairs on the coordinating atom, and it is likely that the net interaction of these electron pairs with the low-spin d^6 metal centers is repulsive.[4a] Notably similar lability differences between such ligands and NH_3 is observed for the aquation of the analogous cobalt(III) series which also have been proposed as dissociative in character.[28,29]

One striking difference between Ru(II) and other d^6 metal centers such as Co(III) and Rh(III) is the relative π-donor strength of Ru(II) toward π-unsaturated nitrogen ligands.[4] Thus, it has been of interest to examine[6,7a] the effect of various ligands L on the lability of H_2O in complexes such as $Ru(NH_3)_4L(H_2O)^{2+}$ (eq 2). However, the second-order rate constants k_2(L) obtained in such cases reflect the ratio ($k_2(L) = k_f k_N/k_r$) of the rate constants for three processes, all three of which may be functions of the ligand L. Thus the lability of X^- in a reaction such as eq 1 provides a more direct measure of the effect of changing the nonlabile ligands.

At this point it is worth noting that the conclusion that the k_f step is the dominant contributor to the activation energy of eq 2 is consistent with the activation parameters for eq 1 and 2 with various L and N. For each L and N not having unusual steric properties, the activation parameters which have been measured for eq 2 fall into the ranges $\Delta H^{\ddagger} = 16 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = -9 \pm 5$ eu.[7a,11,12] Although some subtle interpretations can be made concerning various trends within these ranges, it is particularly significant that these values fall close to the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ ranges noted for the direct aquation of the halide anions (Table III and vida supra). Thus a consistency of mechanism is suggested.

A ligand such as L may be expected to exert a variety of steric, electrostatic, and electronic effects on the lability of X^- or Y in $Ru(NH_3)_4(L)X^+$ or $Ru(NH_3)(L)Y^{2+}$. These various effects may be competitive. For example, the electrostatic effect of an anionic ligand L would be expected to increase the lability of X^- over the case where L is an uncharged ligand, and most of the anionic L's which have been investigated in the context of X^- or Y lability (vide infra) have an activating effect. Yet, while k_{obsd} for *cis*-$Ru(NH_3)_4Cl_2$ is consistent with this pattern, *trans*-$Ru(NH_3)_4Cl_2$ is less labile than $Ru(NH_3)_5Cl^+$ under the same conditions (Table III).

The results of Isied and Taube[6] and of Allen[7a] can be combined to give the following series for the labilizing effect of L in the reaction of N with *trans*-$Ru(NH_3)_4(L)H_2O^{2+}$: CO $\sim$ N_2 $\ll$ isn < py $\sim$ H_2O < imN $\sim$ NH_3 < OH^- < CN^- < SO_3^{2-} < imC, where imN and imC are N- and C-coordinated imidazole, respectively. A less-extensive series for the analogous cis complex follows the order:[6,7a] CO < N_2 $\ll$ isn < py < imN $\sim$ NH_3 $\sim$ H_2O < OH^-. Given that k_f is the dominant energetic component of k_2, it is probable that this is also the order for the lability of H_2O in these complexes. This argument is supported by our observation that the lability of X^- from $Ru(NH_3)_4(L)X^+$ follows the order L = isn < py < NH_3 for both the cis and trans configurations. Thus the rate data reported here can be included to expand the trans series to give CO $\sim$ N_2 $\ll$ acn < isn < Cl^- $\sim$ py $\sim$ H_2O < imN $\sim$ NH_3 < OH^- < CN^- < SO_3^{2-} < imC and the cis series to give CO < N_2 $\ll$ isn $\sim$ acn < py < imN $\sim$ NH_3 $\sim$ H_2O < Cl^- $\sim$ OH^-.

The trans series is perplexing in the context that strong π-acceptor ligands lie at both ends, thus π acidity alone is not a determining factor. π back-bonding should serve the dual role of increasing the effective charge of the metal center and decreasing the potential repulsion between the metal dπ electrons and the unshared electron pair on the leaving group. Both effects should decrease ligand lability in a manner consistent with the observations for the relatively weak σ-donor, uncharged π-acid ligands: py, isn, acn, etc. The ligands, CN^-, SO_3^{2-}, etc., which are good π acids yet labilize the metal center toward aquation are also good σ donors[30,31] thus destabilizing the metal–ligand σ bond in a position trans to L. This admittedly is an argument based on ground-state properties, and it is essential not to lose the view that relative rates are determined by the energy differences between the ground and the transition states. However, a dissociative mechanism, if valid over the wide reactivity ranges seen here, allows one the luxury of considering differences in ground-state bond energies as being directly reflected in reaction activation energies.[32] In this context ground-state structural trans effects of SO_3^{2-} and similar ligands have been argued to be reflected in the kinetic trans effects of cobalt(III) complexes.[33] Thus we would argue that trans labilization among the ruthenium(II) ammine complexes by ligands such as SO_3^{2-} is a reflection of that ligand's σ-donor strength[34] (perhaps enhanced by synergistic effects)[7a] and that delabilizing effects of π-acid ligands such as isonicotinamide or dinitrogen in the trans position are reflection of the poor σ-donor character of these ligands (relative to NH_3) combined with the general increase in the effective charge of the metal center owing to π back-bonding.

Accurate structural information is not available for the various Ru(II) complexes for which kinetic information is available, and it is difficult to evaluate the ground-state structure effects of the various ligands L. Nonetheless, it is interesting that the NO_2^- ligand which is proported to be trans labilizing[35] shows a lengthening of the trans Ru(II)–NH_3 bond (2.199 Å)[34] but a shortening of the cis Ru(II)–NH_3 bonds (2.127 Å, average)[34] in $Ru(NH_3)_5NO_2^+$ relative to the Ru(II)–NH_3 bond lengths in $Ru(NH_3)_6^{2+}$ (2.144 Å).[36] These observations are consistent with the expected effects of a good σ-donor ligand which also is a π acceptor. It is clear that more structural information is necessary before meaningful correlations can be extended.

A more complete view of ligand effects on the lability of the Ru(II) complexes must include the potential role of cis L.[37] The substitution mechanisms have been shown to be dissociative in the case of $Ru(NH_3)_5H_2O^{2+}$ and stereoretentive in the cases of *cis*- and *trans*-$Ru(NH_3)_4(H_2O)_2^{2+}$.[17] Activation parameters, etc., suggest a similar mechanism for the aquation of X^- from $Ru(NH_3)_4(L)X^+$. Thus the structure of the activated complex formed by a step such as eq 7 is likely to be tetragonal pyramid with the ligand originally trans to the leaving ligand remaining in the stereochemically unique, apical position. The plane constituting the cis ligands might be expected to move somewhat below the metal atom, filling in (to some degree) the space vacated by the leaving group. A qualitative examination of the metal–ligand π interactions in this intermediate indicates that there is little change between the ground state and the activated complex in the general symmetry of these interactions for the trans ligands. Changes in σ and π bonding for this ligand can be attributed principally to effects on the metal orbital electron densities due to the presence or absence of X^-. However, movement of the cis ligand plane to a position below the metal atom changes the potential π symmetry interactions of these ligands with the metal. Some decreases in the π overlap with the d_{xy}, d_{xz}, and d_{yz} orbitals may result (thus decreasing back-bonding to the π-acid cis ligands); however, a more significant perturbation may be the possibility (in the square-pyramidal intermediate) of π overlap between cis L and the unfilled d_{z^2} orbital.[38] In this context, it is interesting to note that the only cis ligands demonstrated to have labilizing effects (in comparison to NH_3) are the potential π donors Cl^- and OH^-. As in the trans series the π-acid, weak σ-donor ligands such as py, isn, etc., are delabilizing when in the cis position.

Lastly, the data in Table III provide an interesting anomaly to be considered. Although for L = py or isn the lability of *cis*-$Ru(NH_3)_4(L)X^+$ is about one-third that of *trans*-$Ru(NH_3)_4(L)X^+$ (eq 1), both *cis*-$Ru(NH_3)_4(py)H_2O^{2+}$ and *cis*-$Ru(NH_3)_4(isn)H_2O^{2+}$ are more reactive toward py[7a] or isn[6] (eq 2), respectively, than are the trans analogues. Two possible explanations are (1) a special interaction between the halide and an aromatic heterocycle lying cis to it leading to decreased reactivity relative to the aquo complexes or (2) the presence of a cis py or isn is rate accelerating relative to trans py or isn in the trapping of the coordinatively unsaturated intermediate by py or isn (eq 8, k_N). Without directly measuring the H_2O exchange rates this question cannot be answered confidently; however, it appears than an aromatic ligand in the cis position does not represent a major steric barrier to an incoming aromatic heterocycle but instead may have a net attractive interaction.

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Registry No. $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1; [*trans*-$Ru(NH_3)_4Cl_2]Cl$, 63251-19-4; [*cis*-$Ru(NH_3)_4Cl_2]Cl$, 22327-28-2; [*trans*-$Ru(NH_3)_4(py)Cl]Cl_2$, 63251-20-7; [*cis*-$Ru(NH_3)_4(py)Cl]Cl_2$, 63251-21-8; [*trans*-$Ru(NH_3)_4(isn)Cl]Cl_2$, 63251-12-7; [*cis*-$Ru(NH_3)_4(isn)Cl]Cl_2$, 63323-69-3; [*trans*-$Ru(NH_3)_4(acn)Cl]Cl_2$, 63251-13-8; [*cis*-$Ru(NH_3)_4(acn)Cl]Cl_2$, 63323-70-6; $[Ru(NH_3)_5Br]Br_2$, 16446-65-4; [*trans*-$Ru(NH_3)_4(py)Br]Br_2$, 63251-14-9; [*cis*-$Ru(NH_3)_4(py)Br]Br_2$, 63323-71-7; [*trans*-$Ru(NH_3)_4(isn)Br]Br_2$, 63251-15-0; [*cis*-$Ru(NH_3)_4(isn)Br]Br_2$, 63323-72-8; $[Ru(NH_3)_5I]I_2$, 16455-58-6; [*trans*-$Ru(NH_3)_4(py)I]I_2$, 63251-16-1; [*cis*-$Ru(NH_3)_4(py)I]I_2$, 63323-73-9; [*trans*-$Ru(NH_3)_4(isn)I]I_2$, 63251-17-2; [*cis*-$Ru(NH_3)_4(isn)I]I_2$, 63323-74-0; [*trans*-$Ru(NH_3)_4(py)SO_4]Cl$, 63251-18-3; [*trans*-$Ru(NH_3)_4(isn)SO_4]Cl$, 60209-67-8; *cis*-$Ru(NH_3)_4(Cl)H_2O^{2+}$, 29871-96-3; *cis*-$Ru(NH_3)_4(Cl)H_2O^+$, 63323-75-1; *trans*-$Ru(NH_3)_4(Cl)H_2O^{2+}$, 29871-97-4; *trans*-$Ru(NH_3)_4(Cl)H_2O^+$, 63251-09-2; *cis*-$Ru(NH_3)_4(py)H_2O^{2+}$, 26540-33-0; *cis*-$Ru(NH_3)_4(py)H_2O^{3+}$, 63251-05-8; *trans*-$Ru(NH_3)_4(py)H_2O^{2+}$, 26518-89-8; *trans*-$Ru(NH_3)_4(py)H_2O^{3+}$, 63323-63-7; *cis*-$Ru(NH_3)_4(isn)H_2O^{2+}$, 60168-57-2; *cis*-$Ru(NH_3)_4(isn)H_2O^{3+}$, 63251-06-9; *trans*-$Ru(NH_3)_4(isn)H_2O^{2+}$, 60208-50-6; *trans*-$Ru(NH_3)_4(isn)H_2O^{3+}$, 63323-64-8; *cis*-$Ru(NH_3)_4(acn)H_2O^{2+}$, 63323-65-9; *cis*-$Ru(NH_3)_4(acn)H_2O^{3+}$, 63251-08-1; *trans*-$Ru(NH_3)_4(acn)H_2O^{2+}$, 63251-07-0; *trans*-$Ru(NH_3)_4(acn)H_2O^{3+}$, 63323-66-0; $Ru(NH_3)_5Cl^+$, 29933-34-4; *cis*-$Ru(NH_3)_4Cl_2{}^+$, 25604-36-8; *trans*-$Ru(NH_3)_4Cl_2{}^+$, 29871-95-2; *cis*-$Ru(NH_3)_4(py)Cl^+$, 63251-10-5; *trans*-$Ru(NH_3)_4(py)Cl^+$, 63323-67-1; *cis*-$Ru(NH_3)_4(isn)Cl^+$, 63251-11-6; *trans*-$Ru(NH_3)_4(isn)Cl^+$, 63323-68-2; *cis*-$Ru(NH_3)_4(acn)Cl^+$, 63251-00-3; *trans*-$Ru(NH_3)_4(acn)Cl^+$, 63323-59-1; $Ru(NH_3)_5Br^+$, 63284-61-7; *cis*-$Ru(NH_3)_4(py)Br^+$, 63251-01-4; *trans*-$Ru(NH_3)_4(py)Br^+$, 63323-60-4; *cis*-$Ru(NH_3)_4(isn)Br^+$, 63251-02-5; *trans*-$Ru(NH_3)_4(isn)Br^+$, 63323-61-5; *cis*-$Ru\text{-}(NH_3)_4(py)I^+$, 63251-03-6; *trans*-$Ru(NH_3)_4(py)I^+$, 63357-02-8; *cis*-$Ru(NH_3)_4(isn)I^+$, 63251-04-7; *trans*-$Ru(NH_3)_4(isn)I^+$, 63323-62-6.

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