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Rates of Substitution in Cis and Trans Ruthenium(II) Aquotetraammines

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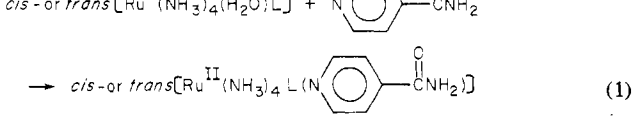
When NH_3 in $Ru(NH_3)_5H_2O^{2+}$ is replaced by a π-acid ligand which is at most a moderately strong σ donor, the lability of the coordinated water, as measured by the rate at which isonicotinamide replaces it, is greatly reduced. Certain other ligands, whose characteristics are harder to define, are strongly labilizing. The order of increasing lability for the series *trans*-$[Ru^{II}(NH_3)_4L(H_2O)]$ is as follows for L: CO = N_2, isn, py, imN $\approx$ NH_3, OH^-, CN^-, SO_3^{2-}, imC. The range in the second-order specific rate covered in this series is $<3 \times 10^{-6}$ M^{-1} s^{-1} (L = CO) to 60 M^{-1} s^{-1} (L = imC). For the π-acid ligands preceding NH_3 in the series, there is a good correlation between the specific rate and the value of E_f for the Ru(III)–Ru(II) couple, a correlation which extends also to cases of multisubstitution. For the strongly labilizing ligands the correlation fails and, moreover, in such cases the effects are strongly trans directed, in contrast to those observed for the delabilizing ligands.

Introduction

The unusual reactivity displayed by ruthenium(II) in the aquopentaammine complex toward ligands capable of accepting back-donation of πd electrons raised the question of how these ligands modify the substitution rates of the ruthenium(II) center. The rate of substitution of water in $[Ru(NH_3)_5H_2O]^{2+}$ by a variety of ligands (e.g., nitrogen bases, nitriles, N_2, etc.), apart from steric and electrostatic effects, is found to be insensitive to the properties of the incoming ligand, indicating that bond breaking is more important than bond formation in the activated complexes involved.[1]

The present study is devoted to exploring the lability of the Ru^{II}–OH_2 bond when one NH_3 in $[Ru(NH_3)_5H_2O]^{2+}$ is replaced by another auxiliary ligand, L. The general reaction considered is the rate of formation of *cis*- or *trans*-$[Ru^{II}(NH_3)_4(isn)L]$ (where isn = isonicotinamide)[2] from the corresponding aquo complex (eq 1). Isonicotinamide was



(1)

chosen as the incoming nucleophile because of its stability and its high solubility and because of the fact that the absorption characteristics of its Ru(II) complexes provide a convenient means of monitoring the reactions studied.

The effect of multisubstitution of NH_3 has also been explored to some extent.

Experimental Section

1. Chemicals and Reagents. (a) Organic Ligands. Imidazole (imN) (Aldrich), pyridine (py) (MCB spectral quality), and pyrazine (pyr) (puriss grade 99+%) were used as supplied. The 2,2′-bipyridine (bpy) and the 2,2′,2″-terpyridine (terpy) (G. F. Smith) were recrystallized from ethanol. Isonicotinamide (isn) (Aldrich) was twice recrystallized from water before use. Methylpyrazinium (Mepyr) *p*-toluenesulfonate was prepared by a method outlined by Magnuson.[3] Except for the preparations to be described, all other chemicals were reagent grade and were used as supplied.

(b) Ruthenium Complexes. $[Ru(NH_3)_5Cl]Cl_2$ was prepared by the method of Vogt et al.,[4] and *cis*- and *trans*-$[Ru(NH_3)_4Cl_2]Cl$ were prepared following the methods of Gleu et al.[5]

***trans*-[Ru(NH$_3$)$_4$(SO$_4$)L]Cl (L = imN, py, isn)** were prepared from their corresponding sulfur dioxide complexes[6] by oxidation with hydrogen peroxide. A typical procedure is the following. To 0.28 mmol of *trans*-$[Ru(NH_3)_4(SO_2)(isn)](CF_3SO_3)_2$ (183 mg)[6] or *trans*-$[Ru(NH_3)_4(SO_2)(isn)](BF_4)_2$ (150 mg) dissolved in 3–5 ml of 1 M HCl 30% H_2O_2 was added dropwise with vigorous stirring until the yellow-orange color disappeared. An equal volume of concentrated HCl was immediately added to the resulting solution, followed by 8 volumes of acetone. A pale yellow solid $[Ru(NH_3)_4(SO_4)(isn)]Cl$ was formed. After cooling of the mixture at −5 °C, the solid was filtered, washed with ethanol and ether, and dried in a vacuum desiccator.

The solid was purified as follows. A sample of 100 mg of the crude *trans*-$[Ru(NH_3)_4(SO_4)(isn)]Cl$ was dissolved in 3 ml of 1 M HCl and reprecipitated by adding 20 ml of reagent grade acetone. Anal. Calcd for $[Ru(NH_3)_4(SO_4)(isn)]Cl \cdot 2H_2O$: C, 15.7; H, 4.48; N, 18.3; Ru, 22.0; S, 7.0; Cl, 7.7. Found: C, 15.8; H, 4.4; N, 18.47; Ru, 21.7; S, 7.1; Cl, 8.6. Yields for the series of complexes prepared varied from 60 to 90%.

In the synthetic procedures to follow ruthenium(II) ammines and ruthenium(II) aquoammine solutions were always handled under an argon atmosphere to prevent air oxidation.

***trans*-[Ru^{II}(NH$_3$)$_4$L(H$_2$O)] ions** were generated from the corresponding *trans*-$[Ru(NH_3)_4L(SO_4)]Cl$ salts by dissolving a known amount and reducing with zinc amalgam for 30 min in an argon atmosphere. It has been shown that coordinated sulfate aquates from the coordination sphere of ruthenium(II) very rapidly ($t_{1/2} < 1$ s).[7]

***cis*- and *trans*-[Ru(NH$_3$)$_4$(H$_2$O)(OH)]$^+$** were generated by reducing acidic solutions (ca. pH 1) of the corresponding *cis*- and *trans*-$[Ru(NH_3)_4Cl_2]Cl$ complexes (0.02 M) with zinc amalgam for 30 min. The hydroxyaquo species were obtained by raising the pH of the solutions to >13 by adding a quantitative amount of a deoxygenated solution of 1 M NaOH.

***cis*-[Ru^{II}(NH$_3$)$_4$(H$_2$O)L] (L = imN, py, isn)** were prepared in solution by adding an equimolar amount of solutions of the heterocyclic ligand L in 0.2 M NaOH to *cis*-$[Ru(NH_3)_4(H_2O)(OH)]^+$ and allowing the reaction to proceed for 15 min. A 5% excess of L was then added to ensure complete reaction. Acidification to pH 5.5 produced the *cis*-$[Ru^{II}(NH_3)_4(H_2O)L]$ complex.

***cis*- and *trans*-Ru(NH$_3$)$_4$(Mepyr)Cl$_3$ Complexes.** A 15-mg (0.055-mmol) amount of *cis*-$Ru(NH_3)_4Cl_3$ was dissolved in 5 ml water containing a few drops of 0.1 M HTos and reduced over Zn(Hg) in a stream of argon for 30 min in the dark. The Zn(Hg) was removed, 150 mg (0.56 mmol) of MepyrTos (Tos = tosylate) was added, and the solution was left in an argon stream for 2 h. The solution was then concentrated to near dryness by rotary evaporation and added to 2 ml of concentrated HCl and 10 ml of ethanol. After cooling of the mixture at −10 °C the solid which formed was collected by filtration and washed with ethanol and ether. The trans compound was prepared similarly from the corresponding *trans*-tetraammine salt.

The *cis*- and *trans*-$[Ru(NH_3)_4(Mepyr)H_2O]^{3+}$ ions were prepared in solution from their corresponding tetraammine salts as follows. To 10 ml of 0.1 M HTos, 9 mg (0.033 mmol) of $Ru(NH_3)_4Cl_3$ was added. The resulting solution was reduced over Zn(Hg) for 30 min after which the Zn(Hg) was removed and 18 mg (0.068 mmol) of MepyrTos was added. The solution was left in a stream of argon for 2–3 h in the dark. The visible spectrum shows that only one $Mepyr^+$ ion is substituted under these conditions. Note: these compounds are light sensitive.

It should be noted that the solid compounds *cis*- and *trans*-$Ru(NH_3)_4(Mepyr)Cl_3$ prepared as described above have Cl^- coordinated to Ru(II), and aquation is slow enough so that cyclic voltammetry on freshly prepared solutions does not yield potentials for the aquo species. The aquo ions, prepared as solution species, were therefore used for the cyclic voltammetry measurements; the rates of substitution

by isn are slow enough so that the same results were obtained whether the solid chloro complexes or the aquo species were used.

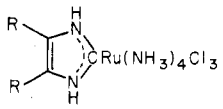
trans-**[Ru(NH$_3$)$_4$(H$_2$O)CO]Br$_2$.** Argon was bubbled through a solution of *trans*-[Ru(NH$_3$)$_4$Cl$_2$]Cl (0.1 g, 0.36 mmol, in 9 ml of water and 1 ml of 90% formic acid) which was maintained at 60 °C. After 30 min a few pieces of zinc amalgam were introduced and carbon monoxide was bubbled through the solution for 2 h at 60 °C. The solution was filtered and the filtrate was added to 10 ml of a saturated solution of NaBr and then cooled in ice. The white solid, [Ru(NH$_3$)$_4$(H$_2$O)CO]Br$_2$, which formed was collected by filtration, washed with ethanol and ether, and then vacuum dried; yield 43 mg, 26%.

cis-**[Ru(NH$_3$)$_4$(H$_2$O)(CO)]X$_2$** was prepared following the method of Allen et al.[8]

cis- **and** *trans*-**[Ru(NH$_3$)$_4$(H$_2$O)(N$_2$)]Cl$_2$** were prepared by the nitrous oxide method used by Armor[9] for the preparation of [Ru(NH$_3$)$_5$(N$_2$)]Br$_2$. Some modifications were introduced because the *cis*- and *trans*-aquodinitrogentetraammines are more soluble than the pentaamminedinitrogen complex.

One-tenth gram of *cis*- or *trans*-[Ru(NH$_3$)$_4$Cl$_2$]Cl (0.36 mmol) was dissolved in 60 ml of 0.1 M HCl and saturated with nitrous oxide for 0.5 h. Excess Cr^{2+} ion (more than 3 equiv) in 0.1 M HCl was added and the reaction was allowed to proceed for 1 h. The solution was then concentrated by rotary evaporation at room temperature to 1 ml. It was filtered and washed well with ethanol and ether. At this stage the uv spectrum of the solution showed it to contain a mixture of the mononuclear and binuclear complexes (λ_{max} for the mononuclear complex 221nm; λ_{max} for the binuclear complex 265 nm). A sample of the complex (60 mg) was dissolved in water and loaded on an ion-exchange column (Bio-Rad AG-50W-X2, 100–200 mesh). The mononuclear complex was eluted with 50 ml of 1.2 M HCl. This solution was again concentrated by rotary evaporation to 1 ml. The solid which formed was filtered and washed with ethanol and ether. The uv spectrum showed only λ_{max} 221 nm ($\epsilon \sim 10^4$ M^{-1} cm^{-1}).

Carbon-Bound Imidazole Complexes



For R = H the imidazole complex was synthesized using the method of Sundberg[10] and the 4,5-dimethylimidazole complex[10] was generously provided by R. Sundberg.

K$_3$[Ru(C$_2$O$_4$)$_3$] and K$_2$[RuCl$_5$(H$_2$O)] were prepared by methods described by Creutz.[11]

Cs[Ru(en)Cl$_4$]. The preparation of H[Ru(en)Cl$_4$] was carried out using a method outlined by Broomhead.[12] Addition of saturated cesium chloride to the product solution resulted in the precipitation of Cs[Ru(en)Cl$_4$].

[Ru(en)(terpy)(H$_2$O)](ClO$_4$)$_2$. In a Zwickel flask[19] 79 mg of Cs[Ru(en)Cl$_4$] was dissolved in 35 ml of water and added to 45.5 mg of terpyridine in 5 ml of 50% ethanol. A few pieces of zinc amalgam were added and argon was bubbled through the solution for 1 h. The solution was transferred under argon and concentrated to 10 ml by rotary evaporation, and NaClO$_4$ solution was added to it. A pinkish brown precipitate formed which was filtered and washed with a 1:4 mixture of ethanol and ether. The yield was low, ca. 5%, because the compound was difficult to crystallize.

Cs[RuCl$_4$(bpy)]. A sample of 150 mg of bpyH[RuCl$_4$(bpy)], prepared by the method of Dwyer and co-workers,[14] was dissolved in 5 ml of 6 M trifluoromethanesulfonic acid and then filtered. Two milliliters of saturated cesium chloride was added to the filtrate. The yellow solid which formed was collected by filtration and washed with ethanol and ether.

[Ru(H$_2$O)(bpy)(terpy)](ClO$_4$)$_2$.[14] To 20 ml of 50% ethanol 106 mg of Cs[RuCl$_4$(bpy)] and 50 mg of terpyridine were added and the solution was heated to dryness on a steam bath. Then 20 ml of 75% ethanol was added and heating was continued until the volume of solution was about 7 ml. The solution was filtered and 3 ml of saturated NaClO$_4$ was added to the filtrate. After cooling of the mixture, the brown crystalline solid which formed was collected by filtration, washed with a solution of 1:3 ethanol–ether and then with ether, and vacuum dried. The yield was 76 mg, 54%.

(c) Pyrazine-Bridged Compounds. μ-Pyrazine-*cis*-diaquooctaamminediruthenium(II) *p*-Toluenesulfonate. Three milliliters of water was degassed with a stream of argon for 30 min, and 0.54 mmol (150 mg) of *cis*-[Ru(NH$_3$)$_4$Cl$_2$]Cl, 1 drop of concentrated CF_3COOH, and 20 mg of pyrazine were then added. After the solid dissolved, a few pieces of zinc amalgam were added. Argon was bubbled through the solution for 2 h. The solution was quickly filtered and 5 ml of saturated sodium *p*-toluenesulfonate solution was added to it. The solution was cooled overnight in the refrigerator. The dark violet crystalline solid was collected by filtration, washed with 1:3 ethanol–ether and then with ether, and vacuum dried. The yield was 175 mg, 56%.

μ-Pyrazine-*cis*-diaquooctaamminediruthenium(II,III) *p*-Toluenesulfonate. A slurry of 56 mg of the pyrazine-bridged ruthenium(II) complex described above and 13.4 mg of silver(I) *p*-toluenesulfonate was stirred for 30 min in 4 ml of water. The resulting solution was filtered to remove silver metal, and an equal volume of saturated sodium *p*-toluenesulfonate solution was added to the filtrate. After cooling of the mixture, a solid similar to the one described above was formed. It was also treated in a similar way. The yield was 15 mg, 23%.

μ-Pyrazine-*cis*-aquotetraammineruthenium(II)pentaammine-rhodium(III) *p*-Toluenesulfonate. The rhodium complex [Rh(NH$_3$)$_5$pyr](ClO$_4$)$_3$ was made according to the method of Creutz.[15] The perchlorate salt was reprecipitated as a *p*-toluenesulfonate salt. To make the binuclear complex, 36 mg of *cis*-[Ru(NH$_3$)$_4$(H$_2$O)$_2$](C$_7$H$_7$SO$_3$)$_2$ and 40 mg of [Rh(NH$_3$)$_5$pyr](C$_7$H$_7$SO$_3$)$_3$ were dissolved in 4 ml of water and degassed for 15 min. Two pieces of zinc amalgam were introduced and argon bubbling was continued for 4 h. The solution was then filtered and added to an equal volume of saturated sodium tosylate solution. After cooling of the mixture in a refrigerator, a pink solid formed. It was collected by filtration, washed with ethanol and ether, and vacuum dried.

2. Electrochemical Measurements. Formal potentials E_f were obtained by cyclic voltammetry. The formal potentials were taken as the mean of the cathodic and anodic peak potentials. Potentials were measured with respect to SCE at 25 °C and converted to NHE by adding 0.242 V. As the electrode, a Pt button (Beckman Instruments) or a hanging mercury drop was used. The experiments were done in an H-cell with the two sides filled with a supporting electrolyte and enough of the compound was added to one arm to make a solution millimolar in complex. Normally sweep rates of 50/100 mV s^{-1} were used. For fast scans (10–100 V/s) the output was connected to an HP Model 130 Br oscilloscope and pictures were taken of the traces on a 146-L Polaroid film. Except in a few cases (see Results) reversible oxidation–reduction waves were obtained with peak separations of about 60 mV.

3. Kinetic Studies. Whenever possible, all-glass connections were used to transfer air-sensitive materials. For very air-sensitive compounds, this was conveniently done by using a Zwickel flask.[19] For a typical experiment one of the reactants was separately degassed with argon in a flask, tightly covered with a serum cap, and vented through a syringe needle. To initiate the reaction, a syringe well flushed with argon was used to draw a small volume of solution (ca. 0.5–1.0 ml) from this flask and was then injected quickly into the Zwickel flask.[19] A time span of several seconds was allowed for mixing, after which the solution was transferred under argon pressure into an attached cell. Stopcocks on the cell adapter were closed and the cell and adapter were placed in the Cary 15 cell compartment thermostated at 25 °C.

For less air-sensitive materials 5 ml of one of the reactants was degassed for 15 min directly in a 2.0-cm spectrophotometric cell with argon introduced by means of a syringe needle led through a tight rubber septum cap. The cell was placed in a thermostated Cary 15 cell compartment and allowed to equilibrate for 20–30 min at 25 °C. The second reactant was also allowed to come to temperature by immersing it directly in the constant-temperature water bath. To initiate reaction 0.25 ml of this reactant was quickly transferred into the spectrophotometric cell by using a gastight syringe. The progress of the reaction was followed by repetitive scans as a function of time or by observing the change in absorbance at a single wavelength characteristic of the product.

For the fast reactions ($t_{1/2} < 1$ s) a stopped-flow instrument[16] was used. For the slow reactions ($t_{1/2} > 4$ h) a weighed amount of complex was dissolved in a solution of known concentration of isonicotinamide at pH 5.5. This was transferred to a quartz 1-cm spectrophotometric cell which was glass-sealed. The change in absorption was scanned over different time intervals for periods of days. If the reaction was not complete within 1 week, the solution was warmed on a steam bath

Table I. Uv-Visible Band Maxima of *cis*- and *trans*-$[Ru^{II}(NH_3)_4L(H_2O)]$[a] and $[Ru^{II}(NH_3)_4L(isn)]$[b] Complexes

L	$\lambda_{max,cis}$, nm		$\lambda_{max,trans}$, nm	
	$[Ru^{II}(NH_3)_4L(H_2O)]$	$[Ru^{II}(NH_3)_4L(isn)]$	$[Ru^{II}(NH_3)_4L(H_2O)]$	$[Ru^{II}(NH_3)_4L(isn)]$
imN[c]	280 sh, 255	478	290 sh, 260	481
py[c]	396	468, 385	405	470
isn[c]	485	482, 418	476	493
N_2[d]	222	*f*	218	*f*
CO	300 sh, 270	340 sh	281	*f*
OH^-		495		511
$[Ru^{III}(NH_3)_4(H_2O)pyr]^{3+}$ [e]	521	550, 415		
$[Rh^{III}(NH_3)_5pyr]^{3+}$ [e]	524	528, 400		
$Mepyr^+$ [e]	540	555, 373		

[a] Spectra of the aquo ions were taken in ca. 0.1 M CF_3SO_3H (except for L = OH where the medium was 0.5 M NaOH). The extinction coefficients are within 10% of the values reported for their pentaammine analogues. [b] For the isn complexes, spectra were taken in excess isonicotinamide solution (>0.1 M); the short wavelengths (below 300 nm) were masked by the isonicotinamide π-π^* absorptions. [c] See ref 1 for the pentaammine analogue. [d] See ref 9 for the pentaammine analogue. [e] See ref 15 for the pentaammine analogue. [f] Band assignment discussed in the text.

for 20 min to obtain A_∞, the absorbance of the fully formed product. Ionic strength was maintained between 0.01 and 0.03 M (with HCl–NaCl and CF_3CO_2H–CF_3CO_2Na) for all experiments unless otherwise stated. The temperature was 25 ± 1 °C for all experiments.

Pseudo-first-order rate constants were determined graphically from plots of log $(A_\infty - A_t)$ vs. time (where A_∞ and A_t are the final absorbance and that at time t, respectively) yielding values of k_{obsd}. The ligand concentration exceeded that of Ru(II) by at least a factor of 10. Good psuedo-first-order behavior was observed in all cases, showing that the reactions are first order in ruthenium(II) concentration. By changing the initial concentration of ligand, the reaction order in ligand was determined, and where appropriate, second-order specific rates were calculated. When secondary reactions interfered with the determination of A_∞, the Guggenheim treatment of the data[17] was used. Under the high isonicotinamide concentrations used (ca. 0.1 M), there was no need to correct for the aquation rate of the product, $[Ru^{II}(NH_3)_4(isn)L]$, except in the case of L = imC and 4,5-imC, the C-bound imidazoles (see Results).

Results

1. Characterization of the Complexes. *cis*- and *trans*-$[Ru^{II}(NH_3)_4(H_2O)L]$. The complexes were identified by their uv–visible spectra (Table I). As expected, these show only small differences in the position of λ_{max} and in extinction coefficients from the more fully characterized pentaammine series. The measured reduction potentials are also very similar to those of the corresponding pentaammine complexes (Table II).

In assigning cis and trans configurations we rely on published reports that no cis–trans rearrangements have been observed for similar Ru(II) complexes.[18]

L = N_2, CO. The purified N_2 complexes were identified by their ir (ν_{NN} 2101, 2105 cm^{-1} for *cis*-$[Ru(NH_3)_4(N_2)(H_2O)]Br_2$ and 2098 cm^{-1} for *trans*-$[Ru(NH_3)_4(N_2)(H_2O)]Cl_2$) and uv ($\lambda_{max}$ 221 nm, $\epsilon \sim 1.3 \times 10^4$ M^{-1} cm^{-1}) spectra. It was necessary to purify these compounds from the μ-dinitrogen complexes (λ_{max} 265 nm) by ion-exchange chromatography. The *cis*- and *trans*-$[Ru(NH_3)_4(CO)(H_2O)]^{2+}$ complexes were identified by elemental analysis and uv and ir spectra (ν_{CO} for *trans*-$[Ru(NH_3)_4(CO)(H_2O)]Br_2$ 1922 cm^{-1} and for *cis*-$[Ru(NH_3)_4(CO)(H_2O)]Cl_2$ 1920 cm^{-1}).[8]

Bipyridine and Terpyridine Complexes. The uv–visible spectrum for $[Ru(terpy)(bpy)(H_2O)](ClO_4)_2$ agreed with that reported by Davies[14] (Table III). The $[Ru(terpy)(en)(H_2O)]^{2+}$ complex was best prepared by reducing $[Ru(en)Cl_4]^-$ with zinc analgam in the presence of an equimolar amount of terpy in aqueous ethanol. The uv–visible spectra of the $[Ru(terpy)(en)(H_2O)]^{2+}$ and its product of reaction with isonicotinamide are reported in Table III.

Table II. Reduction Potentials[a] for *cis*- and *trans*-$[Ru^{II/III}(NH_3)_4(H_2O)L]$ and Related Complexes[h]

L	E_f, V	
	cis-$[Ru^{II/III}(NH_3)_4(H_2O)L]$	*trans*-$[Ru^{II/III}(NH_3)_4(H_2O)L]$
OH^- [b]	−0.038	−0.12
NH_3	+0.08	+0.08
H_2O	+0.10	+0.08
imN[c]	+0.10	+0.19
4,5-imC[d]		+0.13
imC		
py	+0.27	+0.33
isn	+0.34	+0.42
$S(CH_3)_2$	+0.48	
SO_2		+0.67[e]
		+0.28[e]
$Mepyr^+$	+0.77	+0.70
N_2[f]	+0.94	+1.30
CO[g]	+1.09	+1.14
	+1.34	+1.40
$[Ru^{III}(NH_3)_4(H_2O)pyr]$	+0.64	
$[Rh^{III}(NH_3)_5pyr]$	+0.62	

[a] Potentials are vs. NHE, measured by cyclic voltammetry using a Pt button electrode in 0.1 M HBF_4, unless otherwise specified. [b] In 0.1 M NaOH. [c] In 0.1 M $NaC_7H_7SO_3$, 10^{-3} M HCl. [d] In 0.1 M KCl, 10^{-3} M HCl. [e] The value +0.67 V is measured in 2 M HBF_4, when the complex is predominantly in the SO_2 form; the value +0.28 V is measured in 0.1 M HCO_3^-, when the complex is predominantly in the SO_3^{2-} form. [f] Value reported is for oxidation wave; no reduction wave was observed. [g] Two waves were observed for both the cis and the trans CO complexes the origins of which are unclear. [h] Conditions specified in footnote *a* apply also to measurements on $[Ru(terpy)(bpy)H_2O]^{2+}$ and $[Ru(terpy)(en)H_2O]^{2+}$ for which values of E_f = +1.05 and +0.52 V, respectively, are measured.

Table III. Uv-Visible Band Maxima of Aquo- and isn-Substituted Ruthenium(II) Complexes with Polydentate Ligands[a]

Complex	λ_{max}, nm
$[Ru(terpy)(bpy)(H_2O)]^{2+}$	478, 350 sh, 312, 288, 279, 272 sh, 228 sh[b]
$[Ru(terpy)(en)(H_2O)]^{2+}$	514, 476, 360 sh
$[Ru(bpy)(terpy)(isn)]^{2+}$	460 sh, 430, 360 sh
$[Ru(terpy)(en)(H_2O)]^{2+}$	505, 472, 398, 370 sh

[a] Spectra of the aquo ions were taken in 0.1 M CF_3SO_3H; for the isn complexes, spectra were taken in excess isonicotinamide (>0.1 M); the short wavelengths (below 300 nm) were masked by the isn π-π^* absorptions. [b] Previously prepared by Davies et al.[14a]

C-Bound Imidazole Complexes. The series of C-bound imidazole complexes have been characterized by Sundberg et al.[10] The λ_{max} absorption characteristics of the complexes are shown on Table IV.

Pyrazine-Bridged Compounds. *cis*-$[(H_2O)(NH_3)_4Ru$-μ-pyr-$Ru(NH_3)_4(H_2O)]^{5+}$. The mixed-valence ion was identified by its near-ir spectrum (λ_{max} 1525 nm).

cis-$[(H_2O)(NH_3)_4Ru\mu$-pyr-$Rh(NH_3)_5]^{5+}$ was identified by its uv–visible spectrum in comparison to that of the decaammine ion.[15] The high charge on the ion was confirmed by its ion-exchange behavior (4 M HCl was required to elute it from a cation-exchange resin, AG-50W-X2, 200–400 mesh).

***cis*- and *trans*-$[Ru^{II}(NH_3)_4(isn)L]$.** Table I shows the uv–visible spectra of the products of the reaction of the above

Table IV. Band Maxima and Extinction Coefficients for Carbon-Bound Imidazole Complexes of Ruthenium

Complex	λ, nm (ε, M^{-1} cm^{-1})	Ref
trans-$[Ru(NH_3)_4(imC)Cl]Cl_2$	480 (1.6 × 10^3)	10
trans-$[Ru(NH_3)_4(imC)(H_2O)]^{2+}$	224 (5.7 × 10^3), 262	10
trans-$[Ru(NH_3)_4(4,5\text{-}imC)Cl]Cl$	600 (4.7 × 10^3), 250 sh	10
trans-$[Ru(NH_3)_4(4,5\text{-}imC)(H_2O)]^{2+}$	262 (8.3 × 10^3), 250 sh, 230	10
trans-$[Ru(NH_3)_4(imC)(isn)]^{2+}$	462 (~8 × 10^3)	This work
trans-$[Ru(NH_3)_4(4,5\text{-}imC)(isn)]^{2+}$	470 (~8 × 10^3)	This work

binuclear ions with isonicotinamide.

It should be noted that though few of the complexes were characterized by isolation and analysis of solids containing them, purity for present purposes is ensured by the preparative method. There is a large decrease in rate for the replacement of OH^- from Ru(II) as compared to that for H_2O in a species such as $[Ru(NH_3)_4(H_2O)OH]^+$; furthermore, for most entering ligands L, the sole exception for the present series being imidazole, once one H_2O in $[Ru(NH_3)_4(H_2O)_2]^{2+}$ is replaced by L, the rate of replacement of the second is diminished by a large factor. Purity is attested to also by the fact that substitution by isn in $[Ru(NH_3)_4LH_2O]^{2+}$ proved in every case to be nicely first order, and there was no evidence for any of the systems that an impurity showing a different reactivity was present in significant amount.

2. Rates of Substitution of Isonicotinamide. (a) *cis*- and *trans*-$[Ru^{II}(NH_3)_4(H_2O)L]$ (L = imN, py, isn, N_2, CO). Experiments were generally conducted in isonicotinamide solutions titrated to pH 5.5. Under these conditions the ruthenium(II) complexes are predominantly in the aquo form, $[Ru(NH_3)_4L(H_2O)]^{2+}$, and isonicotinamide is in the unprotonated form. Thus small contributions from subsidiary paths involving protonated ligands or the hydrolyzed complexes can be neglected. The specific rate k is defined by the rate law

$$\frac{d}{dt}[Ru^{II}(NH_3)_4L(isn)] = k[Ru^{II}(NH_3)_4L(H_2O)][isn]$$

Table V summarizes the kinetics results obtained. Most of the values reported are the average of replicate determinations. In most but not all cases the concentration of isn was varied. As expected on the basis of other experience, the rate proved to be first order in [isn]. Because of the survey nature of this study, rates were not determined with meticulous care, and the slower rates may be in error by as much as 25%. This error is minor when compared to the several orders of magnitude by which the rates vary. For some of the very slow substitution reactions, only upper limits on the rates could be set.

(b) Ruthenium Complexes with Polydentate Amines. Kinetics of the ruthenium(II) compounds with terpy, en, and bpy ligands were treated similarly to those of the *cis*- and *trans*-tetraammine series. Table V summarizes the kinetic data obtained.

(c) C-Bound Imidazole Complexes. For the 4,5-imC complex the stopped-flow apparatus was used to measure the rate of the substitution reaction at high isonicotinamide concentration (ca. 0.1 M) where the reverse reaction is negligible. The value of k at 25 °C was measured as 58 ± 3 M^{-1} s^{-1}. For the unsubstituted C-bound imidazole complex (imC), experiments were carried out using the Cary 15 spectrophotometer. Table VI summarizes the observed rates with different isonicotinamide concentrations. At these ligand concentrations the reverse path had to be corrected for; thus, $k = k_1[L] + k_{-1}$, where k_1 corresponds to the forward reaction and k_{-1} to the reverse reaction. Values for k_1, k_{-1}, and K_{eq} for the reaction *trans*-$[Ru(NH_3)_4(imC)(H_2O)]^{2+}$ + isn = *trans*-$[Ru(NH_3)_4(imC)(isn)]^{2+}$ are 74 ± 21 M^{-1} s^{-1}, 1.2 × 10^{-1} s^{-1}, and 6 × 10^2 M^{-1}, respectively.

Table V. Rates of Substitution of Isonicotinamide in *cis*- and *trans*-$[Ru(NH_3)_4(H_2O)L]^{2+}$ and Related Complexes[a]

L	[isn], M	k_{obsd}, s^{-1}	k_{obsd}/[isn], M^{-1} s^{-1}
	cis-$[Ru(NH_3)_4(H_2O)L]^{2+}$ [c]		
imN	0.067	6.7 × 10^{-3}	1.0 × 10^{-1}
	0.08	5.6 × 10^{-3}	0.7 × 10^{-1}
py	0.08	1.6 × 10^{-3}	2.0 × 10^{-2}
	0.02	3.6 × 10^{-3}	1.8 × 10^{-2}
isn	0.095	6.1 × 10^{-5}	6.4 × 10^{-3}
	0.48	2.0 × 10^{-4}	4.2 × 10^{-3}
N_2	0.5	6 × 10^{-6}	1.2 × 10^{-5}
	1.0	1.3 × 10^{-5}	1.3 × 10^{-5}
CO	1.0	4 × 10^{-6}	4 × 10^{-6}
$[Rh(NH_3)_5pyr]^{3+}$	0.72		1.2 × 10^{-4}
$[Ru(NH_3)_4(H_2O)pyr]^{3+}$	0.72		5.3 × 10^{-5}
$Mepyr^+$	1.0		5 × 10^{-6}
	trans-$[Ru(NH_3)_4(H_2O)L]^{2+}$		
imN	0.09	1.3 × 10^{-2}	1.4 × 10^{-1}
	0.45	4.1 × 10^{-2}	0.91 × 10^{-1}
py	0.09	1.1 × 10^{-3}	1.2 × 10^{-2}
	0.20	1.8 × 10^{-3}	0.90 × 10^{-2}
isn	0.45	1.6 × 10^{-3}	3.5 × 10^{-3}
	0.09	3.1 × 10^{-4}	3.5 × 10^{-3}
N_2	0.5		<0.5 × 10^{-5} [b]
	1.0		<0.5 × 10^{-5} [b]
CO	1.0		<3 × 10^{-6} [b]
	$[Ru(terpy)(en)(H_2O)]^{2+}$		
	0.20	6.0 × 10^{-3}	3.0 × 10^{-2}
	0.02	6.8 × 10^{-4}	3.4 × 10^{-2}
	$[Ru(terpy)(bpy)(H_2O)]^{2+}$		
	0.75	5.0 × 10^{-5}	7 × 10^{-5}
	0.50	3.5 × 10^{-5}	7 × 10^{-5}

[a] At 25 °C. [b] Upper limits only because other reactions interfere. [c] For the substitution ratio of *cis*-$[Ru(NH_3)_4(S(CH_3)_2)H_2O]^{2+}$ a specific rate of ~6 × 10^{-3} M^{-1} s^{-1} has been observed.[13]

Table VI. Observed Rates of Substitution of Isonicotinamide on the *trans*-$[Ru(NH_3)_4(imC)(H_2O)]^{2+}$ Ion[a]

10^3[isn], M	k_{obsd}, s^{-1}	k_{obsd}/[isn],[b] M^{-1} s^{-1}
1.8	0.271	150
1.8	0.257	142
1.4	0.219	156
0.9	0.195	216

[a] At 25 ± 1 °C. [b] To interpret data, the reverse reaction must be allowed for; see text.

Table VII. Rates[a] of Substitution of Isonicotinamide on *cis*-[b] and *trans*-$[Ru(NH_3)_4(OH)(H_2O)]^+$ [c] Ions

[NaOH], M	10^3[isn], M	k, M^{-1} s^{-1}: *cis*-$[Ru(NH_3)_4(OH)(H_2O)]^+$	k, M^{-1} s^{-1}: *trans*-$[Ru(NH_3)_4(OH)(H_2O)]^+$
0.29	9.5	0.56	0.51
0.29	19	0.47	0.57
0.48	19	0.48	0.63
	5.5	0.48 (pH 11.7)	0.46 (pH 11.4)

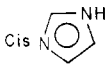
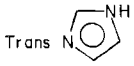
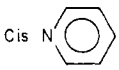
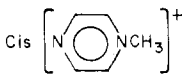
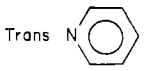
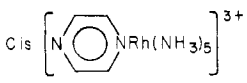
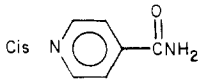
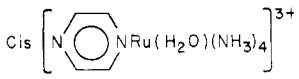
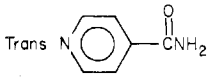
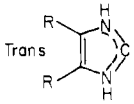
[a] At 25 °C; ionic strength 0.50 M with added NaCl. [b] $[cis\text{-}[Ru(NH_3)_4(H_2O)_2]^{2+}] = 0.7 \times 10^{-4}$ M. [c] $[trans\text{-}[Ru(NH_3)_4(H_2O)_2]^{2+}] = 0.95 \times 10^{-4}$ M.

(d) $[Ru(NH_3)_4OH_2(OH)]^+$ Ions. Table VII summarizes the results on the rates of substitution in these aquo ions by isn.

Discussion

Two series of ruthenium(II) complexes are surveyed in this report. In one, a single ammonia in aquopentaammineruthenium(II) is replaced by a different ligand and the effect

Table VIII. Rates of Substitution of Isonicotinamide in *cis*- and *trans*-$[Ru(NH_3)_4(H_2O)L]^{2+}$ Ions

L	k, M^{-1} s^{-1}	L	k, M^{-1} s^{-1}
	Delabilizing Groups[a]		
Cis 	0.85×10^{-1}	Cis $(CH_3)_2S$	6×10^{-3} [c]
		Cis N_2	1.2×10^{-5}
Trans 	1.2×10^{-1}	Trans N_2	$<0.5 \times 10^{-5}$
		Cis CO	4×10^{-6}
		Trans CO	$<3 \times 10^{-6}$
Cis 	1.9×10^{-2}	Cis 	5×10^{-6}
Trans 	1.0×10^{-2}	Cis 	1.2×10^{-4}
Cis 	5.3×10^{-3}	Cis 	5.3×10^{-5}
Trans 	3.5×10^{-3}		
	Labilizing Groups[a]		
Cis OH^-	0.5	Trans CN^- [b]	~7
Trans OH^-	0.6	Trans SO_3^{2-}	25
Trans 	~60		

[a] The substitution of isn into $[Ru(NH_3)_5H_2O]^{2+}$ is governed by a specific rate of 1.0×10^{-1} M^{-1} s^{-1}. [b] Estimated from rate of loss of ammonia from $[Ru(NH_3)_5CN]^+$ and the corresponding rates for $[Ru(NH_3)_5SO_3]$ aquation and $[Ru(NH_3)_4SO_3OH_2]$ substitution. [c] Reference 13.

of this substitution on the lability of the water molecule completing the coordination sphere is measured. Within this series, to some extent the effect of placing the ligand cis rather than trans to the disposable water molecule has been examined and, as well, whatever special effect may obtain when the "different" ligand undergoes valence isomerization (e.g., N-bound to C-bound imidazole). In the second, and this series is very limited in extent, the effect of multisubstitution of ammonia by π-acid ligands is examined. The lability of the water being replaced is in every case being assessed by measuring the rate at which isonicotinamide substitutes for it. Other work has indicated that substitution in ruthenium(II) ammines involves mainly bond breaking rather than bond making. The second-order specific rates recorded, while hardly providing a quantitative measure of the change in activation energy for the dissociation of a water molecule by an SN1 mechanism, do probably at least provide a correct ordering with respect to the ease at which this process occurs.

The data on the effect of replacing one NH_3 in $[Ru(NH_3)_5H_2O]^{2+}$ on the lability of the water molecule are summarized in Table VIII. The order of increasing enhancement of the lability of the water molecule located trans to the group in question is as follows: $CO = N_2 <$ isn $<$ py $<$ imN $\sim$ $NH_3 < OH^- < CN^- < SO_3^{2-} <$ imC. This ordering, at least for the limited comparison which can be made, shows some striking contrasts to that registered for the trans effect in Pt(II) complexes:[20] py $= NH_3 = H_2O \ll$ CO. In neither series is the so-called "trans effect" fully understood, and thus the fact that differences exist should of itself not be astonishing. It would be more astonishing if in the octahedral and in the square-planar cases, where the initial states and, in all likelihood, the activated complexes have different geometries, a close parallelism existed. Furthermore, Ru(II) in the present series and Pt(II) as it is dealt with in the usual discussions of the trans effect differ substantially in their propensity for back-bonding interactions.

The ligands to the left of NH_3 have in common the property that they are rather good π acids and are weak to only moderately strong σ donors. For these, there is a rather good correlation of substitution rate with the value of $E°$ for the Ru(III)–Ru(II) half-reaction. The data are shown plotted in Figure 1. A relation of this kind is expected to have some validity if there is a monotonous change in σ-donating power of the ligand as the π-acid character changes over the series. The connection exists because the π acids withdraw πd-electron density from Ru(II); this stabilizes Ru(II) relative to Ru(III), accounting for the trend in $E°$, and increases the effective charge on Ru(II), accounting for the change in lability of the water molecule.

The comparison of the effect of the π acid when in a cis rather than a trans position has not been made in detail. For a moderately strong π acid such as isonicotinamide, the effect is observed as being little different at the two positions, and this has been observed to be the case also for pyridine.[21] Isonicotinamide in acting on, for example, the d_{zx} orbital is not expected to affect the πd-electron density significantly more in the z direction than it does in the x. The effects on πd-electron density are of course not directly translatable into differences in rates of substitution, because the interactions in the activated complexes have not been taken into account. Just what these are will depend on the geometry of the activated complex. This is not known from independent studies, and the cis vs. trans kinetic stabilization by π acids has not been studied sufficiently to illuminate the subject.

In the terpy cases, the rates are somewhat higher than expected from the correlation of rate with E_f. This may well reflect a geometric constraint which makes the activated complex when terpy is present more accessible than it is in the other cases.

A point of specific interest, which is important for the subject of mixed-valence complexes, is that the lability of H_2O on Ru(II) is almost as strongly affected by $[(NH_3)_5Rh(pyr)]^{3+}$

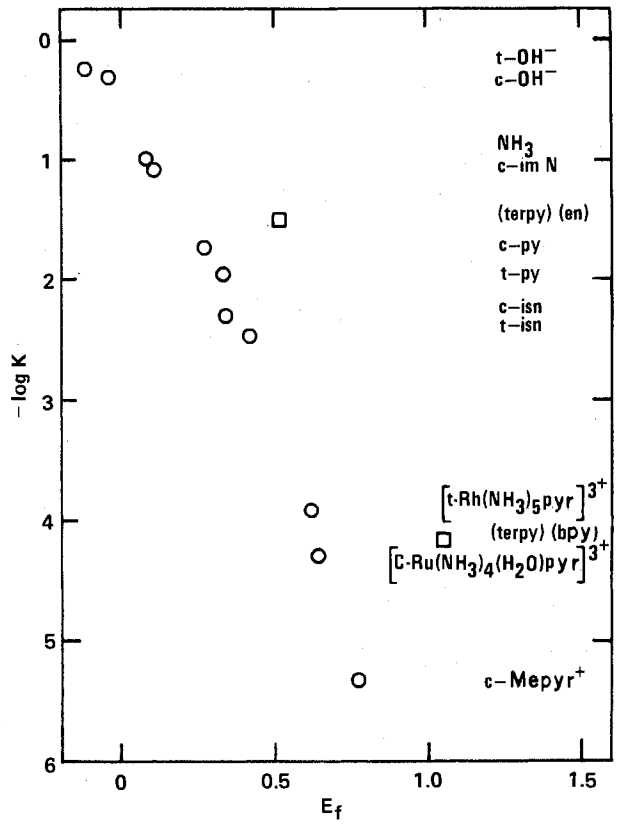


Figure 1. Specific rates (M^{-1} s^{-1}) at 25 °C for the substitution of H_2O in Ru(II) complexes as a function of E_f for the Ru(III)-Ru(II) couple. The supplementary ligands in each case are comprised by four NH_3 molecules, except in the case of [(Ru(terpy)-(en)H_2O^{2+}] and [Ru(terpy)(bpy)H_2O^{2+}].

as it is by $[(NH_3)_4(H_2O)Ru(pyr)]^{3+}$ (Table V). In the former case, the Ru(II) valence is obliged to remain localized, while in the latter, electron exchange between Ru(II) and Ru(III) takes place. If the exchange is rapid enough to endow a Ru(II) center with Ru(III) character, a decrease in the lability of a water molecule is expected. For such an effect to be significant, a rate of electron exchange in excess of 10^{13} s^{-1} would be needed—note that the uncertainty broadening for a state of lifetime of 10^{-13} s is less than 1 kcal mol^{-1}. The comparison of the effects of the two ligands shows that Ru(II) character has been only slightly altered by introducing the possibility of valence delocalization. Other work has shown[11,22] that the rate of electron transfer exceeds 10^{12} s^{-1} in the Ru(II)–Ru(III) mixed-valence species, and thus, by considering all the observations, a rate of electron transfer of the order of 10^{13} s^{-1} is indicated.

As another item of specific interest, it should be noted that the product of the reaction of *cis*-$[Ru(NH_3)_4(N_2)H_2O]^{2+}$ with isn is the diisonicotinamide complex. Replacing H_2O by the π acid isn so weakens the Ru^{II}–N_2 bond that the ligand is rapidly lost, to be replaced eventually by isn.

The labilizing effects of certain ligands—among those thus far encountered, SO_3^{2-}, imC, and CN^- are notable—are more difficult to understand than are the delabilizing effects discussed in the earlier paragraphs. For the labilizing groups, OH^- excepted, there is a strongly trans-directed effect. In fact, for the SO_3^{2-} case, it has been shown[6] that while this ligand labilizes trans, it delabilizes cis. Just how the trans-labilizing groups produce the effects they do is by no means clear to us. The complexes with the labilizing ligands, it should be noted, do not fit the correlation implied by Figure 1.

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Registry No. *cis*-$[Ru(NH_3)_4(imN)(H_2O)]^{2+}$, 60168-56-1; *cis*-$[Ru(NH_3)_4(py)(H_2O)]^{2+}$, 26540-33-0; *cis*-$[Ru(NH_3)_4(isn)(H_2O)]^{2+}$, 60168-57-2; *cis*-$[Ru(NH_3)_4(N_2)(H_2O)]^{2+}$, 60208-48-2; *cis*-$[Ru(NH_3)_4(CO)(H_2O)]^{2+}$, 60183-85-9; *cis*-$[Ru(NH_3)_4(OH)(H_2O)]^{+}$, 60168-58-3; *cis*-$[[Ru(NH_3)_4[Ru(NH_3)_4(H_2O)(pyr)](H_2O)]]^{5+}$, 60238-64-4; *cis*-$[[Ru(NH_3)_4[Ru(NH_3)_5(pyr)](H_2O)]]^{5+}$, 60238-65-5; *cis*-$[Ru(NH_3)_4(Mepyr)(H_2O)]^{3+}$, 60208-49-3; *trans*-$[Ru(NH_3)_4(imN)(H_2O)]^{2+}$, 60251-41-4; *trans*-$[Ru(NH_3)_4(py)(H_2O)]^{2+}$, 26518-89-8; *trans*-$[Ru(NH_3)_4(isn)(H_2O)]^{2+}$, 60208-50-6; *trans*-$[Ru(NH_3)_4(N_2)(H_2O)]^{2+}$, 60208-51-7; *trans*-$[Ru(NH_3)_4(CO)(H_2O)]^{2+}$, 60168-59-4; *trans*-$[Ru(NH_3)_4(OH)(H_2O)]^{+}$, 60208-52-8; *cis*-$[Ru(NH_3)_4(imN)(isn)]^{2+}$, 60208-53-9; *cis*-$[Ru(NH_3)_4(py)(isn)]^{2+}$, 60208-54-0; *cis*-$[Ru(NH_3)_4(isn)_2]^{2+}$, 50573-21-2; *cis*-$[Ru(NH_3)_4(N_2)(isn)]^{2+}$, 60208-55-1; *cis*-$[Ru(NH_3)_4(CO)(isn)]^{2+}$, 60168-46-9; *cis*-$[Ru(NH_3)_4(OH)(isn)]^{+}$, 60168-47-0; *cis*-$[[Ru(NH_3)_4[Ru(NH_3)_4(H_2O)(pyr)](isn)]]^{5+}$, 60238-66-6; *cis*-$[[Ru(NH_3)_4[Ru(NH_3)_5(pyr)](isn)]]^{5+}$, 60238-67-7; *cis*-$[Ru(NH_3)_4(Mepyr)(isn)]^{3+}$, 60168-48-1; *trans*-$[Ru(NH_3)_4(imN)(isn)]^{2+}$, 60168-49-2; *trans*-$[Ru(NH_3)_4(py)(isn)]^{2+}$, 60168-50-5; *trans*-$[Ru(NH_3)_4(isn)_2]^{2+}$, 34383-39-6; *trans*-$[Ru(NH_3)_4(N_2)(isn)]^{2+}$, 60168-51-6; *trans*-$[Ru(NH_3)_4(CO)(isn)]^{2+}$, 60208-46-0; *trans*-$[Ru(NH_3)_4(OH)(isn)]^{+}$, 60208-47-1; $[Ru(NH_3)_5(H_2O)]^{2+}$, 21393-88-4; *cis*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$, 29946-00-7; *trans*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$, 42230-44-4; *trans*-$[Ru(NH_3)_4(H_2O)(4,5\text{-imC})]^{2+}$, 60168-52-7; *cis*-$[Ru(NH_3)_4(H_2O)(S(CH_3)_2)]^{2+}$, 60168-53-8; *trans*-$[Ru(NH_3)_4(H_2O)(SO_2)]^{2+}$, 51175-03-2; *trans*-$[Ru(NH_3)_4(H_2O)(Mepyr)]^{3+}$, 60168-54-9; $[Ru(terpy)(bpy)(H_2O)]^{2+}$, 20154-63-6; $[Ru(terpy)(en)(H_2O)]^{2+}$, 60168-55-0; $[Ru(bpy)(terpy)(isn)]^{2+}$, 60153-95-9; $[Ru(terpy)(en)(isn)]^{2+}$, 60153-96-0; *trans*-$[Ru(NH_3)_4(imC)(isn)]^{2+}$, 60153-97-1; *trans*-$[Ru(NH_3)_4(4,5\text{-imC})(isn)]^{2+}$, 60168-78-7; *trans*-$[Ru(NH_3)_4(imC)(H_2O)]^{2+}$, 60153-98-2; *cis*-$[Ru(NH_3)_4(Mepyr)Cl]Cl_2$, 60153-99-3; *trans*-$[Ru(NH_3)_4(Mepyr)Cl]Cl_2$, 60208-19-7; *cis*-$[Ru(NH_3)_4Cl_2]Cl$, 22327-28-2; *trans*-$[Ru(NH_3)_4Cl_2]Cl$, 29871-95-2; $Cs[Ru(en)Cl_4]$, 60184-03-4; $Cs[RuCl_4(bpy)]$, 60184-04-5; μ-pyrazine-*cis*-diaquooctammine-diruthenium(II) *p*-toluenesulfonate, 60184-06-7; *cis*-$[Ru(NH_3)_4(H_2O)_2](C_7H_7SO_3)_2$, 60184-07-8; $[Ru(NH_3)_5pyr](C_7H_7SO_3)_3$, 41557-34-0; *trans*-$[Ru(NH_3)_4(SO_4)(isn)]Cl$, 60209-67-8.

References and Notes

(1) R. E. Shepherd and H. Taube, *Inorg. Chem.*, **12**, 1392 (1973).
(2) Abbreviations: isn, isonicotinamide; py, pyridine; pyr, pyrazine; $Mepyr^+$, methylpyrazinium ion; imN, N-bound imidazole; imC, C-bound imidazole; 4,5-imC, 4,5-dimethylimidazole (C-2 bound); en, ethylenediamine; bpy, 2,2′-bipyridine; terpy, 2,2′,2″-terpyridine; SCE, standard calomel electrode; NHE, normal hydrogen electrode.
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