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PROPERTIES AND REACTIONS OF RUTHENIUM(II) AMINE COMPLEXES

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CONTENTS

ABBREVIATIONS

deg	degenerate	phen	1,10-phenanthroline
dien	diethylenetriamine	pn	propylenediamine
en	ethylenediamine	py	pyridine
enD	tetra-N-deuteroethylenediamine	sym	symmetrical
Ph	phenyl		

A. INTRODUCTION

In recent years the chemistry of ruthenium(II) amines has received attention from a number of workers. Initially this interest was largely based upon analogies drawn between the low-spin d^6 Ru^{II} complexes and similar Werner-type octahedral complexes of cobalt(III) and rhodium(III). In 1965, while exploring new synthetic routes to Ru^{II} and Ru^{III} ammines, Allen and Senoff[1] isolated the complex ion $Ru(NH_3)_5N_2^{2+}$. the first stable molecular nitrogen complex to [illegible] definitively characterized. The stability of the metal–N_2 bond is largely the result of the ability of the Ru^{II} d_π electrons to participate strongly in π-backbonding, a feature less prominent in the corresponding Co^{III} and Rh^{III} complexes.

The present review will concentrate on the recent developments in the reactions and properties of ruthenium(II) amine complexes and will also touch briefly on the chemistry of some Ru^{III} amines relevant to the main topic. The earlier sections will concentrate on the properties of complexes with π-acceptor ligands while the later sections will discuss some substitution and redox reactions of Ru^{II}. Since the article is not primarily concerned with the chemistry of the amine ligands but of the other ligands and the complexes as a whole, discussion will be limited to those species in which three or more Ru^{II} coordination sites are occupied by ammonia or by some ammonia derivative such as ethylenediamine. For a general review on ruthenium chemistry, the reader is referred to a recent monograph by Griffith[2].

B. COMPLEXES NOT HAVING π-ACCEPTOR LIGANDS

Hexaammineruthenium(II) can be prepared by several routes. The action[3] of zinc dust with ammonia and ammonium chloride on aqueous $RuCl_3$ gives $[Ru(NH_3)_6]Cl_2$ in the form of air-sensitive orange crystals. The salts of $Ru(en)_3^{2+}$ (en = ethylenediamine), $Ru(pn)_3^{2+}$ (pn = propylenediamine) and $Ru(dien)_2^{2+}$ (dien = diethylenetriamine) have been prepared[4,5] by analogous methods. In deaerated aqueous solution, $Ru(NH_3)_6^{2+}$ is relatively stable but does undergo stepwise acid catalyzed aquation (see below) ultimately giving several species unidentified at present but undoubtedly polynuclear in nature. One of these which is formed in strong HCl solutions has a brilliant blue color (λ_{max} 590 nm), is stable to aqueous O_2, but is oxidized by Co^{III} ammines[6] (including $Co(NH_3)_6^{3+}$), Ce^{IV}, or Cl_2.

Infrared spectra have been recorded and partially assigned for $[Ru(NH_3)_6]X_2$ (ref. 7, 8) for $[Ru(en)_3]X_2$ (ref. 9) for the completely deuterated analogs[7,9], and for the corresponding Ru^{III} complexes[7,9]. The spectra of $[Ru(NH_3)_6]Cl_2$ and $[Ru(NH_3)_6]Cl_3$ are compared in Table 1. The absorption maxima are typical of hexaammine complexes, and the assignments are non-controversial with the exception of the Fairey and Irving[8] report of a Ru–N stretching frequency at 437 cm^{-1} for $[Ru(NH_3)_6]Cl_2$. A band at a frequency this high would be consistent with the relative stability of the diamagnetic Ru^{II} hexaammine, despite the fact that the metal is only dipositive. However, Allen and Senoff[7] in subsequent work were unable to detect an absorption in this region even with "very concentrated" mulls. Ruthenium(II)–ammonia stretching frequencies have been reported for several other Ru^{II} complexes; however, in each example, a π-acceptor ligand also occupies a coordination site. In these cases, electron delocalization into the π-acceptor ligand increases the metal electronegativity toward the σ-donor ammonia ligands, a feature which should be reflected in higher $M-NH_3$ stretching frequencies. Examples are the N_2 complexes $[Ru(NH_3)_5N_2]X_2$, where $\nu(Ru-NH_3)$ ranges from 388 to 454 cm^{-1} depending[10] on the identity of X^-, and the nitrosyl ammine complex[8] $[Ru(NH_3)_5NO]Cl_3$, $\nu(Ru-NH_3) = 481$ cm^{-1}.

Wilmshurst[11] has derived an empirical linear relationship between the electronegativity of the metal ion and the square of either the NH_3 symmetric deformation frequency or the NH_3 rocking frequency. Qualitatively it can be seen that both $\delta(NH_3$ sym) and $\rho(NH_3)$ (Table 1) are lower for Ru^{II} than for Ru^{III} hexaammine as would be predicted from the Wilmshurst relationship. On a more quantitative basis, such a consideration would be essentially useless for the ruthenium hexaammine data owing to the marked changes in band positions resulting from the use of different anions[7].

The electronic spectra for a series of hexaamineruthenium(II) complexes are given in Table 2. The maxima reported are not peaks but are well defined shoulders. Fair agreement is found between references 12 and 5 for $Ru(NH_3)_6^{2+}$ and $Ru(en)_3^{2+}$ band positions and for $Ru(NH_3)_6^{2+}$ extinction coefficients. However, the reason for the striking discrepancy in the reported $Ru(en)_3^{2+}$ extinction coefficients is not apparent to this reviewer. Elsbernd and Beattie[67] have recently resolved $(-)_{350}Ru(en)_3^{3+}$ which can be reduced to $(-)_{375}Ru(en)_3^{2+}$ (both ions apparently having the D configuration). The absorption spectra and extinction coefficients of these species are consistent with those reported for the racemic com-

TABLE 1

OBSERVED VIBRATIONAL FREQUENCIES FOR $[Ru(NH_3)_6]Cl_2$ AND $[Ru(NH_3)_6]Cl_3$ (in cm^{-1})[a]

Vibration	$[Ru(NH_3)_6]Cl_3$[b]	$[Ru(NH_3)_6]Cl_2$[b]	$[Ru(NH_3)_6]Cl_2$[c]
$\nu(NH)$	[d]	[d]	3300 s 3195 s
$\delta(NH_3)$, deg.	1612 s, br	1607 s, br	1610 m
$\delta(NH_3)$, sym.	1362 m 1338 s 1316 vs	1217 vs	1220 s
$\rho(NH_3)$	788 s	765 s	769 s
$\nu(RuN)$	(474)[e] w 464 w 452 w		437 w

[a] Nujol mulls, s = strong, vs = very strong, w = weak, m = medium, br = broad.
[b] Ref. 7.
[c] Ref. 8.
[d] Region of broad absorption.
[e] Band position uncertain.

TABLE 2

ABSORPTION MAXIMA IN THE UV-VIS SPECTRA OF RUTHENIUM HEXAAMINES IN AQUEOUS SOLUTION

Compound	λ *[nm]*	ε *[M^{-1} cm^{-1}]*	*Ref.*
$Ru(NH_3)_6{}^{3+}$	~320	~100	12
	275	475 ± 10	
$Ru(en)_3{}^{3+}$	310	360 ± 25	12
$Ru(NH_3)_6{}^{2+}$	~400, (385)	~30, (39)	12 (5)
	275, (275)	624 ± 10, (670)	
$Ru(en)_3{}^{2+}$	370, (370)	120 ± 10, (40)	12 (5)
	302, (301)	1020 ± 10, (91)	
$Ru(pn)_3{}^{2+}$	368	55	5
	299	120	
$Ru(dien)_2{}^{2+}$	362	95	5
	295	76	

plexes reported by Meyer and Taube[12]. For the Ru^{II} complexes, Schmidtke and Garthoff[5] have assigned the longer wavelength band to the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition and the shorter wavelength absorption to the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition. Using the approximations of Tanabe and Sugano[13], they have also calculated Δ values for the $t_{2g}-e_g$ orbital splitting as 27,100 cm^{-1} for $Ru(NH_3)_6{}^{2+}$ and 28,100 cm^{-1} for $Ru(en)_3{}^{2+}$. These values are to be compared with 21,000 cm^{-1} for[14] $Ru(H_2O)_6{}^{2+}$ and with 34,000 cm^{-1} and 34,600 cm^{-1} for the respective isoelectronic rhodium(III) ions[15], $Rh(NH_3)_6{}^{3+}$ and $Rh(en)_3{}^{3+}$. The magnitude of the $Ru(NH_3)_6{}^{2+}$ octahedral splitting, larger than that of either[16] $Co(NH_3)_6{}^{3+}$ or $Cr(NH_3)_6{}^{3+}$, suggests the probable reason for the relative kinetic inertness of the Ru(II)–NH_3 bonds.

No compound of the type $Ru^{II}(NH_3)_5X$ or $Ru^{II}(NH_3)_4X_2$ (where X is not a π-acceptor ligand or an amine) has been characterized in the solid state. Complexes of this composition have been generated in aqueous solution by reduction of the Ru^{III} analog[17,18]; however, the lability of the X ligand (see below) leads to rapid equilibration with the solvent. Consequently, the reactions and properties of $Ru^{II}(NH_3)_5X$ in solution will reflect the equilibrium mixture of $Ru^{II}(NH_3)_5X$ and $Ru(NH_3)_5S^{2+}$ (S = solvent).

The ion $Ru(NH_3)_5H_2O^{2+}$ is very susceptible to air oxidation and undergoes rapid substitution reactions at the sixth coordination position. It also undergoes a much slower decomposition in aqueous solution to form ultimately the same products as the $Ru(NH_3)_6{}^{2+}$ decomposition[6]. The pK_a for reaction (1) has been measured[6] and found to be 10.7 (25°, $\mu = 0.2$) much larger, as expected, than the value found[19] for $Ru(NH_3)_5H_2O^{3+}$ (pK_a = 4.2, 25°). The electronic

$$Ru(NH_3)_5H_2O^{2+} \rightleftharpoons Ru(NH_3)_5OH^+ + H^+ \tag{1}$$

spectrum has been obtained[6] and is qualitatively similar to that of $Ru(NH_3)_6{}^{2+}$.

C. COMPLEXES WITH π-ACCEPTOR LIGANDS

(i) N_2 as a ligand

In 1965, Allen and Senoff[1] isolated $[Ru(NH_3)_5N_2]X_2$ ($X = Br^-, I^-, BF_4^-$, or PF_6^-) from a reaction mixture of aqueous ruthenium trichloride and hydrazine hydrate at 25°. This species was the first stable molecular nitrogen–metal complex to be definitively characterized and has since been found to be the product of a variety of reactions which have been summarized previously[20]. Other ruthenium(II) amine N_2 complexes recently reported include $[[Ru(NH_3)_5]_2N_2]^{4+}$, *cis*-$Ru(en)_2(N_2)_2^{2+}$, *cis*-$Ru(en)_2N_3N_2^+$, *cis*-$Ru(en)_2(H_2O)N_2^{2+}$, and $Ru(NH_3)_4(N_2)_2^{2+}$ (*vide infra*).

The infrared spectrum of $[Ru(NH_3)_5N_2]X_2$ shows an intense and sharp absorption in the region 2100–2170 cm^{-1}, the exact position being dependent on the identity[10] of X. A similar band appears in other N_2 complexes[21] and has been assigned to the N–N stretching frequency $\nu(NN)$ of coordinated N_2. The marked shift from $\nu(NN)$ of free N_2 (2330 cm^{-1}, Raman) indicates a decrease in the N–N bond order caused by π-backbonding from Ru^{II} *d*-orbitals into π^*N_2 orbitals. The intensity of the N–N stretching absorption implies that the N_2 is in an unsymmetrical environment coordinated at one end rather than in a symmetrical π-bond configuration. This conclusion is confirmed by X-ray crystallographic studies[22] which show the Ru–N–N triad to be linear. Unfortunately, crystal degeneracy allowed measurement of only approximate bond lengths for $Ru–N_2$ (~2.11 Å) and N–N (~1.12 Å).

Coordinated N_2 has proved to be inert to reduction by common reducing agents in every case where a stable N_2 complex has been isolated[23]. The same is true[24] for $Ru(NH_3)_5N_2^{2+}$ despite the early report that $NaBH_4$ reduced the coordinated N_2 to NH_3 in high yield. Oxidation of $Ru(NH_3)_5N_2^{2+}$ leads to immediate decomposition to give free N_2 in nearly quantitative yield. The other product is the pentaammine ruthenium(III) moiety $Ru(NH_3)_5X^{2+}$. Other reactions[10] of $Ru(NH_3)_5N_2^{2+}$ probably involve the initial loss of N_2 followed by reactions characteristic of the intermediate pentaammineruthenium(II) species [*e.g.* $Ru(NH_3)_5H_2O^{2+}$ in aqueous solution] thus generated. Representative are the reactions with ammonia to give $Ru(NH_3)_6^{2+}$ and the reaction with concentrated hydrochloric acid and air to give[25] $[Ru(NH_3)_5Cl]Cl_2$. When $Ru(NH_3)_5N_2^{2+}$ is warmed in aqueous pyridine, $Ru(NH_3)_4py_2^{2+}$ is the major product[10]. Since it has been recently demonstrated[17] that $Ru(NH_3)_5H_2O^{2+}$ or $Ru(NH_3)_5py^{2+}$ when heated in aqueous pyridine under similar conditions give a *cis*/*trans* mixture of $Ru(NH_3)_4py_2^{2+}$, it appears probable that again the initial step is loss of N_2 to give $Ru(NH_3)_5H_2O^{2+}$ which is responsible for further reactions.

The diruthenium ion $[(Ru(NH_3)_5)_2N_2]^{4+}$ is the only characterized complex in which N_2 acts as bridging ligand. The species is formed in the aqueous solution reaction between $Ru(NH_3)_5H_2O^{2+}$ and N_2 and it has been shown that the ion can be formed directly[26] from $Ru(NH_3)_5N_2{}^{2+}$ and $Ru(NH_3)_5H_2O^{2+}$. It has at best a weak and poorly defined i.r. band in the triple bond stretching region, but does have a strong Raman band[27] at 2100 cm^{-1}. This result is interpreted as indicating a linear structure, essentially $[(NH_3)_5Ru{-}N{\equiv}N{-}Ru(NH_3)_5]^{4+}$ rather than a bent diazo structure. The $\nu(NN)$ of bridging N_2 is not markedly smaller than that of non-bridging coordinated N_2 (*vide supra*) suggesting that the $N{\equiv}N$ bond force constant is not significantly smaller. As in other N_2 complexes, the bridging N_2 is inert to reduction by common reducing agents. Oxidative decomposition gives N_2 in 95% yield[26].

The dinitrogen complex $Ru(en)_2(N_2)_2{}^{2+}$ was isolated as a transient intermediate[28] in the reaction of nitrous acid with $Ru(en)_2N_3N_2{}^{+}$. Unlike $Ru(NH_3)_5N_2{}^{2+}$ the dinitrogen complex is quite unstable having a decomposition half-life of seconds under the reaction conditions at 0°. The solid isolated by tetraphenylborate addition to the reaction mixture was a mixture of the salts of $Ru(en)_2(H_2O)N_2{}^{2+}$ and $Ru(en)_2(N_2)_2{}^{2+}$. However, within minutes only the mono nitrogen complex remained. The infrared spectrum of this solid had two i.r. bands at 2220 and 2190 cm^{-1} attributed to the dinitrogen species, and a third band at 2130 cm^{-1} attributed to *cis*-$Ru(NH_3)_4(H_2O)N_2$. Since the π-backbonding from Ru^{II} to N_2 is important to the stability of the metal N_2 bond, it is not unreasonable that a species having two nitrogens which must then share the ruthenium electron density would be less stable. The smaller decrease of the $\nu(NN)$ of the dinitrogen species from the free ligand (symmetric and assymmetric stretch) is evidence of the lesser π-backbonding into the individual N_2 ligands. The complex ion $Ru(NH_3)_4(N_2)_2{}^{2+}$ has also been reported[29] and is somewhat more stable toward thermal decomposition than *cis*-$Ru(en)_2(N_2)_2{}^{2+}$. The presence of two infrared bands in the triple bond region (2220 and 2185 cm^{-1}) suggest a *cis* configuration for this ion also.

(*ii*) *Aromatic nitrogen heterocycles as ligands*

Pentaammine–ruthenium(II) complexes of pyridine, substituted pyridines and other aromatic nitrogen heterocycles were synthesized by Zn(Hg) reduction of aqueous $Ru(NH_3)_5Cl^{2+}$ in the presence of excess ligand[30]. Oxidation with Ag^{I} or Ce^{IV} gave the corresponding Ru^{III} complex ion. Both *cis*- and *trans*-tetraamminebis(pyridine)–ruthenium(II) salts have also been made[17]. Most of the Ru^{II} complexes are relatively stable in the solid state but in aqueous solution are oxidized by O_2 and undergo slow aquation (more rapid in acid solution, *vide infra*). Characteristic spectral features of each are an intense metal-to-ligand charge transfer (CT) absorption band in the visible (408 nm, $\varepsilon = 7.78\times10^3$ for $Ru(NH_3)_5py^{2+}$) and a somewhat less intense UV band (244 nm, $\varepsilon = 4.57\times10^3$ for $Ru(NH_3)_5py^{2+}$) corresponding to an aromatic ligand $\pi \rightarrow \pi^*$ absorption (Fig. 1). The intensity and breadth of the CT band obscures additional spectral features (*e.g.* $d \rightarrow d$ bands) which might be expected for these complexes. A number of the Ru^{III} analogues have been synthesized[30,17] and these are devoid of absorption bands in the visible but show the ligand absorptions in the UV ($\lambda_{\max} = 253$ nm, $\varepsilon = 4.57 \times 10^3$ for $\text{Ru(NH}_3)_5\text{py}^{3+}$).

The CT band frequency is quite sensitive to the nature of pyridine ring substituents. As expected for a metal-to-ligand transition, electron withdrawing substituents result in a lower band frequency with para groups clearly having the larger effect (Table 3). For a series of unsubstituted aromatic nitrogen heterocycles (L), a roughly linear correlation has been drawn between the energy of the lowest unoccupied molecular orbital of the free ligand (determined via polarographic techniques) and the frequency of the CT band maximum for $\text{Ru(NH}_3)_5\text{L}^{2+}$ (Table 4). The linearity of this dependence is perhaps fortuitous; however, dependence between the energy of the unoccupied ligand orbitals and the charge transfer frequency can certainly be expected.

TABLE 3

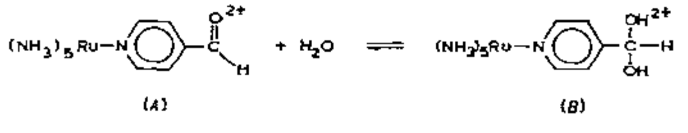
EFFECT OF SUBSTITUENTS ON THE CHARGE TRANSFER BAND MAXIMA FOR THE COMPLEXES $\text{Ru(NH}_3)_5\text{(py-X)}^{2+}$ [a]

Substituent (X)	σ[b]	$\lambda_{\max}(\log \varepsilon_{\max})$ *(nm)*
p-CH_3	−0.17	398
H	0.00	407 (3.89)
p-CH_2OH	—	412
p-CH(OH)_2	—	420
p-CO_2^-	0.00	457
p-CONH_2	0.27	479 (4.02)
p-CO_2CH_3	0.39	497 (4.10)
p-CO_2H	0.405	497
p-CHO	~0.5	545 (3.97)
m-CH_3	−0.069	404
m-CO_2CH_3	0.32	417 (3.77)
m-I	0.35	426
m-Cl	0.37	426
m-Br	0.39	427
m-CONH_2	0.28	427 (3.78)

[a] Data from ref. 30.

[b] Hammett substituent constant σ.

The sensitivity of the CT band to pyridine substituents provides a probe for the investigation of substituent reactions. An example is the aldehyde function of pentaammine(p-formylpyridine) ruthenium(II) which is partially hydrated in aqueous solution (Eqn. 2)[30]. The hydration equilibrium constant K_2 can be estimated from the



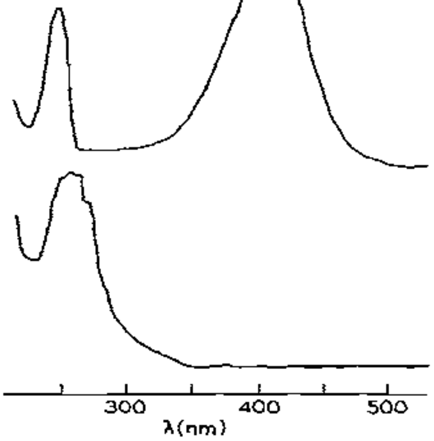
(2)

TABLE 4

CORRELATION OF $E_{\frac{1}{2}}$ (FREE LIGAND) TO CHARGE TRANSFER BAND OF $Ru(NH_3)_5L^{2+}$, WHERE L IS AN AROMATIC NITROGEN HETEROCYCLE. (PERCHLORATE SALTS IN H_2O)[a]

Ligand	$E_{\frac{1}{2}}$ *(L) (volts)*	$\lambda_{max}(\log \varepsilon_{max})$	*Frequency* *(× 10⁴ cm⁻¹)*
pyridine	−2.01	407 nm (3.89)	2.45
pyrimidine	−1.78	445 (3.78)	2.25
pyridazine	−1.60	467 (3.99)	2.14
pyrazine	−1.57	472 (4.03)	2.12
s-triazine	−1.46	471 (3.70)	2.13
pyrazine (H^+)		529 (4.08)	1.89
pyridazine (H^+)		556 (3.96)	1.83
pyrimidine (H^+)		~463	~2.16

[a] Data from ref. 30.



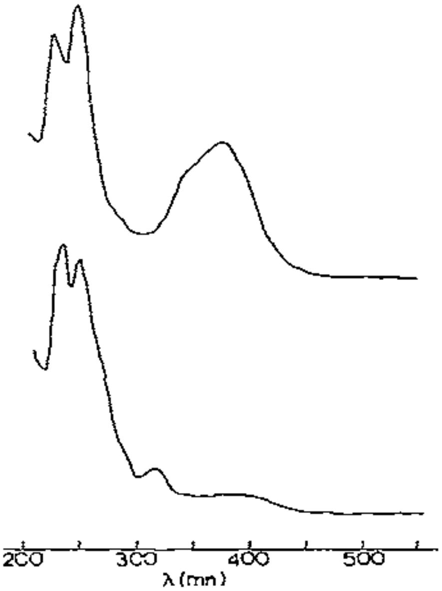


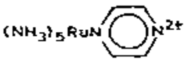
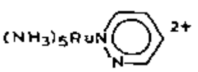
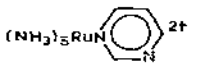
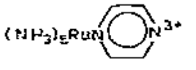
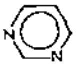
Fig. 1. Electronic spectra of $Ru(NH_3)_5py^{2+}$ (upper) and $Ru(NH_3)_5py^{3+}$ (lower) in aqueous solution.

Fig. 2. Electronic spectra of $Ru(NH_3)_5(PhCN)^{2+}$ (upper, 5.6×10^{-4} *M*) and $Ru(NH_3)_5(PhCN)^{3+}$ (lower, 8.0×10^{-5} *M*) in aqueous solution.

contributions to the visible spectrum by the CT bands for *A* (545 nm) and *B* (420 nm). In this manner a value $K_2 = 0.20$ was measured for Eqn. (2) which is substantially less than the hydration constants $K = 0.84$ for the free ligand and $K = 0.88$ for the protonated free ligand (all three equilibria measured in D_2O at 37°). The purely electrostatic effect on the equilibrium owing to cation coordination apparently favors hydrate formation, since *K* for protonated *p*-formylpyridine is larger than for the free ligand. Effect of Ru^{II} coordination on the hydrate formation is opposite from that expected for purely electrostatic considerations. Consequently, Ru^{II} coordination must favor the aldehyde carbonyl form over that of the hydrate because the unsaturated carbonyl is more strongly involved in the π-bonding interaction between metal $d\pi$ orbitals and the aromatic ligand π^* orbitals.

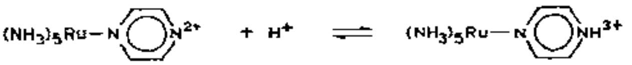
TABLE 5

pK_a MEASUREMENT AT 25°

Compound[a]	$[H^+]_{-\frac{1}{2}}$[b]	$-\log\,[H^+]_{-\frac{1}{2}}$
	0.0032[c]	2.5 ± 0.1
	0.93[d]	0.03 ± 0.05
	~1.0[d]	0.00
	~6*M*[c]	−0.8
Free Ligands		
		2.33
		1.3
		0.6

[a] Data from ref. 30.
[b] $[H^+]_{-\frac{1}{2}}$ = acid concentration where $[B] = [BH^+]$
[c] $HClO_4$
[d] HCl

In strong acid solution of $Ru(NH_3)_5L^{2+}$, it is possible to measure the equilibrium constants (Table 5) for the reversible protonation of the complexes where L is pyrazine, pyridazine or pyrimidine (*e.g.*, Eqn. 3). The protonation equilibria can be observed

 (3)

spectrophotometrically by the bathochromic shift of the respective CT band on complex protonation (Table 4) and by less dramatic changes in the rest of the spectrum[30]. The pK_a of pentaamminepyrazineruthenium(II) is 2.5 ± 0.1 showing that coordination to the dipositive Ru^{II} center makes pyrazine nearly two orders of magnitude more basic than free pyrazine (pK_a = 0.6). In contrast, the Ru^{III} analog is substantially less basic than free pyrazine (Table 5). Here again is evidence that the 4-position of the aromatic ring is affected more strongly by Ru^{II}-π-back bonding than by the electrostatic effect of metal cation coordination. For the Ru^{III} complex, the electrostatic effect apparently predominates.

A series of dinuclear ruthenium ammine complexes having a pyrazine bridge [(NH$_3$)$_5$Ru–N  N–Ru(NH$_3$)$_5$]$^{n+}$, (n = 4, 5, or 6) have been characterized by Creutz and Taube[31]. The 4+ ion which has two Ru^{II} centers had a very intense CT band at 547 nm. One equivalent oxidation of this species gives the 5+ ion which has a less intense CT band in approximately the same position (565 nm) as the 4+ ion. This species, however, has a second CT band in the near infrared (1,570 nm) which has been interpreted to be a charge transfer from a Ru^{II} center to the Ru^{III} center coordinated to the same pyrazine.

(*iii*) *Organonitriles as ligands*

Organonitrile complexes of the types Ru(NH$_3$)$_5$(RCN)$^{2+}$ and Ru(NH$_3$)$_4$(RCN)$_2$$^{2+}$ have been synthesized by the methods used to prepare the respective pyridine complexes[32,33]. The complexes include L = substituted benzonitrile, cyanopyridines, acetonitrile or acrylonitrile. Many of the mononitrile complexes can be oxidized by Ag^{I} or Ce^{IV} to the corresponding Ru^{III} ion, Ru(NH$_3$)$_5$L^{3+}. In general, the Ru^{II} salts are stable in the solid state but in aqueous solution are slowly oxidized by O$_2$ and undergo slow decomposition to aquoammines. Pentaammine(benzonitrile)ruthenium(II) is more stable toward aquation than either *cis*- or *trans*-tetraammine bis(benzonitrile)ruthenium(II). The *cis* isomer is more stable than the *trans* which cannot be recrystallized without partial decomposition to a mono-nitrile species, presumably Ru(NH$_3$)$_4$(H$_2$O) (PhCN)$^{2+}$. The greater stability of the *cis* over the *trans* isomer is very likely due to the competition between the *trans* nitriles for the same sets of metal π-electrons.

The electronic spectra of the ions Ru(NH$_3$)$_5$(PhCN)$^{2+}$ and Ru(NH$_3$)$_5$(PhCN)$^{3+}$ are shown in Fig. 2. These are representative for the pentaammine complexes of other substituted benzonitriles. The longest wavelength absorption (376 nm) of the Ru^{II} complex is apparently a metal-to-ligand CT band while the higher energy absorptions (230 and 249 nm) are probably ligand π-π^* absorptions.

Infrared spectral data for the CN stretching frequencies [ν(CN)] for substituted benzonitrile Ru^{II} and Ru^{III} complexes are summarized in Table 6. These data demonstrate that in each case, coordination to Ru(NH$_3$)$_5$$^{2+}$ decreases ν(CN) with $\delta\nu$(CN) ranging from -31 to -57 cm^{-1}. Such behavior parallels the large decrease in ν(NN) from free N$_2$ to Ru(NH$_3$)$_5$N$_2$$^{2+}$ and is in sharp contrast to the typical ν(CN) increase on coordination of organonitriles to most metal cations and other Lewis acids[34]. Coordination to Ru^{III} does increase ν(CN) in each case.

TABLE 6

RUTHENIUM AMMINE COMPLEXES OF ORGANONITRILES, CN STRETCHING FREQUENCIES (IN CM^{-1})[a]

	ν(CN)		
R–	*RCN*	*$[Ru(NH_3)_5(RCN)]Br_2$*	*$[Ru(NH_3)_5(RCN)]Br_3$*
C_6H_5–	2231 s	2194 s	2268 m
p-CH_3–C_6H_4–	2230 s	2198 s	2263 m
p-Cl–C_6H_4–	2228 s	2192 s	2264 m
p-CH_3O–C_6H_4–	2217 s	2194 s[b,c]	2260 s[b,d]
p-HO_2C–C_6H_4–	2231 s	2172 s	2275 m, 2205 m
C_6F_5–	2246 s	2189 s	—
CH_3–	2254 s	2239 s[b,c]	2286 m[b,d]
4-py–	2243 s	2179 s[b]	—

[a] Data from ref. 32, abreviations: s = strong, m = medium.

[b] Ref. 33.

[c] BF_4^- salt.

[d] ClO_4^- salt.

Negative $\delta\nu$(CN) on $Ru(NH_3)_5^{2+}$ coordination undoubtedly results from a lower C–N bond order caused by metal electron backbonding into nitrile π^* orbitals. Consonant with this explanation is the observation that a more negative $\delta\nu$(CN) occurs with electron withdrawing phenyl substituents. The Ru^{II} ammines are the only cationic organonitrile complexes involving monodentate organonitriles for which negative stretching frequency shifts have been reported[32,34]. The only other well characterized example for which metal coordination to a monodentate organonitrile results in a decreased ν(CN) is the recent report[35] of $CoH(Ph_3P)_3(CH_3CN)$, $\nu(CN) = 2210$ cm^{-1}, $\delta\nu(CN) = -45$ cm^{-1}, also an analog to an N_2 complex, $CoH(Ph_3P)_3N_2$. The difference in the sign of $\delta\nu$(CN) between the Ru^{II} and Ru^{III} complexes is again an example of the tendency of $Ru(NH_3)_5^{2+}$ backbonding to predominate over the electrostatic effect of the dipositive center, the opposite remains true for $Ru(NH_3)_5^{3+}$ coordination.

The infrared spectrum of *cis*-$Ru(NH_3)_4(PhCN)_2^{2+}$ in the nitrile stretching region is strikingly similar to the N≡N stretching region for reported dinitrogen complexes[28,29]. A doublet (2232 cm^{-1} and 2219 cm^{-1} for the $ZnBr_4^{2-}$ salt) is observed (Fig. 3) and both bands occur at higher frequency than that for the mononitrile complex $Ru(NH_3)_5(PhCN)^{2+}$. A similar spectral pattern was observed for the *cis* bis-nitrile complexes synthesized from pentafluorobenzonitrile and from acrylonitrile[33]. In contrast to the *cis* complexes, *trans*-$Ru(NH_3)_4(PhCN)_2^{2+}$ has but a single sharp absorption in the nitrile region (2213 cm^{-1} for the perchlorate salt).

Reduction of aqueous $[Ru(NH_3)_5Cl]Cl_2$ in a large excess of 4-cyanopyridine gives a mixture of two products[33], the major one (*C*) having a visible absorption at 421nm, the minor product (*D*) having a band at 510 nm. When the synthesis is carried out in strong acid, *C* is the only product. This material can be reversibly protonated to give a new band at 529 nm while the absorption maximum of *D* is

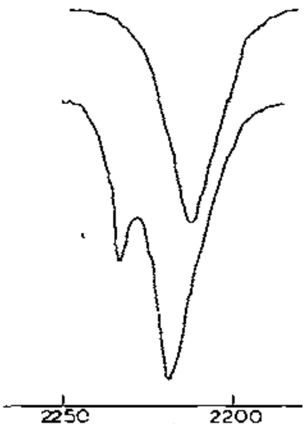
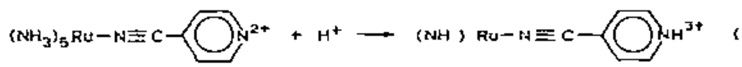


Fig. 3. Nitrile stretching bands for *trans*-$[Ru(NH_3)_4(PhCN)_2](ClO_4)_2$ (upper) and for *cis*-$[Ru(NH_3)_4(PhCN)_2]ZnBr_4$(lower).

unaffected by either acid or base. Two linkage isomer products can be envisioned involving $Ru(NH_3)_5{}^{2+}$ coordination either to the pyridine nitrogen or to the nitrile nitrogen. The effect of substituents on the CT band of the pyridine complexes (Table 3) suggests that *D* is the pyridine bound complex. Consistent with this view is the acid-base behavior of *C* which, if nitrile bound, would have a free pyridine nitrogen for protonation (Eqn. 4). The corresponding nitrile coordinated isomer of 2-cyanopyridine and 3-cyanopyridine have also been made. For each of these complexes,


(4)

the protonation equilibrium constants were determined by the procedure[30] used to measure the pK_a of $Ru(NH_3)_5(pyrazine)^{2+}$. Each of these complexes was found to be more basic than the free ligand, whether the base site is ortho, meta or para to $Ru(NH_3)_5{}^{2+}$ coordinated nitrile (Table 7). Ligand basicity enhancement as reflected by ΔpK_a is larger in the 2- and 4-positions than in the 3-position. Such a pattern of alternation about the aromatic ring is commonly found for the effect

TABLE 7

pK_a's OF $Ru(NH_3)_5$ (CYANOPYRIDINE)$^{2+}$ COMPLEXES[a]

Ligand	pK_a *(complex)*	pK_a *(free ligand)*	$\Delta pK_a{}^b$
4-NC–py	2.72	1.86[c]	+0.86
3-NC–py	1.75	1.35[c]	+0.40
2-NC–py	0.80	−0.26[d] (20°)	+1.06

[a] Ref. 33.
[b] $\Delta pK_a = pK_a\,(\text{complex}) - pK_a\,(\text{free ligand})$, $T = 25°$.
[c] Ref. 64.
[d] Ref. 65.

of a π-interacting substituent on the reactivity and/or properties of the ring position. A purely inductive effect would be expected to have a sequentially diminishing importance as one proceeded to more remote positions on the ring[36].

(iv) *Nitrosyl complexes*

More ruthenium nitrosyl complexes have been characterized than of any other metal, and most can be formally categorized as a complex of Ru^{II} and NO^+. The ruthenium–nitrosyl linkage is exceptionally stable in diverse compounds and is arrived at by numerous routes. It is quite inert to substitution and stabilizes the Ru^{II} against oxidation or reduction. Ruthenium ammine nitrosyl complexes have been synthesized by several routes. Reaction of $[Ru(NH_3)_5Cl]Cl_2$ with aqueous nitrous acid or with $S_2O_8^{2-}$ in ammonia solution[37] leads to the isolation of $Ru(NH_3)_5NO^{3+}$ salts. Treatment of this species with base gives $Ru(NH_3)_4(OH)NO^{2+}$ which on treatment with the appropriate hydrohalic acid[38], HX, gives $Ru(NH_3)_4X(NO)^{2+}$. These tetraammine complexes have been shown by X-ray studies to have the *trans*-configuration[39]. The *trans*-$[Ru(NH_3)_4Cl(NO)]Cl_2$ can also be made by heating[40] solid $[Ru(NH_3)_5NO]Cl_3$. Direct reaction of NO(g) and aqueous $Ru(NH_3)_6{}^{3+}$ also gives $Ru(NH_3)_5NO^{3+}$, apparently via an electrophilic substitution mechanism[41]. Oxidation of ruthenium(III) ammines by aqueous perchloric acid also leads to nitrosyl ruthenium ammine complexes[42].

The synthesis of *trans*-$Ru(NH_3)_4(OH)NO^{2+}$ from $Ru(NH_3)_5NO^{3+}$ indicates a strong *trans*-directing influence of the NO^+ ligand. This fact was borne out in the X-ray structure[43] which showed the *trans*-Ru–NH_3 bond (2.19 Å) to he significantly longer than the *cis*-Ru–NH_3 bond (2.09 Å). In the same study, the strength of the Ru–NO π-bonding is pointedly illustrated by the exceptionally short metal–NO bond distance (1.80 Å).

The *trans* effect in these complexes has also been the subject of several infrared spectral studies[8,38,40]. The identity of the *trans* ligand affects the M–NO and N–O stretching frequencies (Table 8); however, the solid state effects of different spectral media and counter ions detract from the significance of differences found in the N–O frequency. From the ν(Ru–NO) data in Table 8, Mercer and coworkers[38] have concluded that the influence of the *trans* ligand in decreasing ν(Ru–NO) follows the order $I^- > Br^- > NH_3 > Cl^- > OH^-$, an order close to that found for the *trans* effect in Pt^{II} substitution reactions[44]. Another feature of the nitrosyl ammine complex infrared spectra is the magnitude of the coordinated ammonia symmetrical deformation frequencies (*e.g.*, 1303 cm^{-1} for[38] $[Ru(NH_3)_5NO]Cl_3$ which are substantially higher than found for $[Ru(NH_3)_6]Cl_2$ (Table 1) and rather close to that observed for the Ru^{III} hexaammine. Clearly if the Wilmshurst relationship (above) holds true for these complexes, electron delocalization from the metal into NO orbitals results in a large increase in Ru^{II} afinity toward the sigma bonding NH_3.

TABLE 8

Trans-EFFECT ON INFRARED FREQUENCIES (CM^{-1}) FOR THE NITROSYL COMPLEXES *trans*-$[Ru(NH_3)_4(NO)X]Y_2$[a]

X	*Y*	*ν(Ru–NO)*	*ν(N–O)*
NH_3	Cl^- [b]	602	1903
OH^-	Cl^-	628	1834
OH^-	Br^-	624	1840
OH^-	I^-	624	1840
OD^-	I^-	621	1830
Cl^-	Cl^-	608	1880
Br^-	Bt^-	591	1870
I^-	I^-	572	1862

[a] Ref. 38, polyethylene solid matrix, data from ref. 8 agree well with these except for ν(Ru–NO) when $X = OH^-$ owing to a different band being assigned as ν(Ru–NO).

[b] Trichloride salt.

(v) *Other π-acceptor ligands*

Several Ru^{II} ammine complexes of SO_2, $HSO_3{}^-$ and $SO_3{}^{2-}$ have been characterized. The reaction of $HSO_3{}^-$ with hot aqueous $Ru(NH_3)_5OH^{2+}$ gives the bis(bisulfite) complex, *trans*-$Ru(NH_3)_4(SO_3H)_2$, which can be converted into *trans*-$Ru(NH_3)_4(SO_2)Cl^+$ by the reaction with hot HCl[45]. The SO_2 complex is quite stable, but can be oxidized by aqueous $HICl_2$ to give[46] *trans*-$Ru(NH_3)_4Cl_2{}^+$. Reaction with aqueous NH_3 is reported to convert *trans*-$Ru(NH_3)_4(SO_2)Cl^+$ to the unstable pentaammine[47] $Ru(NH_3)_5SO_3 \cdot H_2O$. Reaction with acid converts the last species to $Ru(NH_3)_5SO_2{}^{2+}$ which itself is a strong acid (Eqn. 5)[47].

$$Ru(NH_3)_5SO_2{}^{2+} + H_2O \rightleftharpoons Ru(NH_3)_5SO_3H^+ + H^+ \tag{5}$$

An X-ray structure determination[48] carried out on the complex *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ shows the SO_2 to be coordinated via the sulfur. The Ru–SO_2 distance is quite short (2.072 Å), indicating a strong Ru–S bond. The same workers carried out some infrared spectral studies on the Ru^{II}–SO_2 complexes and reported that both the symmetric and assymmetric S–O stretching vibrations were decreased in the complex compared to solid SO_2. The change was larger for the symmetric S–O stretch where decreases of 30–49 cm^{-1} were observed. Such decreases though relatively small would be predicted if there is significant backbonding from the Ru^{II} d_π orbitals into $SO_2\pi^*$ orbitals.

The carbonyl complex ion $Ru(NH_3)_5CO^{2+}$ is the product of the direct reaction of aqueous $Ru(NH_3)_5H_2O^{2+}$ and carbon monoxide[49]. The infrared spectrum of the yellow iodide salt (Table 9) shows a strong band at 1955 cm^{-1} which may be assigned to the C–O stretching frequency. Since this value is perhaps lower than anticipated for a 2+ metal ion–carbonyl complex, it is taken as evidence for unusual metal–ligand π bonding. The complex is reported to be quite stable in aqueous solution.

TABLE 9

SHIFTS IN ν(X–Y) (IN CM^{-1}) FOR COMPLEXES OF THE TYPE $(NH_3)_5Ru(II)–X\equiv Y–R$

R–X≡Y	*ν (free ligand)*	*ν (coord. ligand)*	*δν*	*Ref.*
N_2	2330	2129[a]	−201	10
CO	2143	1955[a]	−188	49
NO^+ [e]	2220	1903[b]	−317	38
$C_6H_5–CN$	2231	2194[c]	−37	32
$CH_3–CN$	2254	2239[c]	−15	33
$CH_3–NC$	2166	2095[d]	−71	33

[a] I_2 salt.
[b] Cl_2 salt.
[c] Br_2 salt.
[d] $(ClO_4)_2$ salt.
[e] Ref. 66.

The methyl isocyanide complex, $Ru(NH_3)_5(CH_3NC)^{2+}$, has also been synthesized by the direct reaction of aqueous $Ru(NH_3)_5H_2O^{2+}$ and CH_3NC[33]. It was isolated as the white perchlorate salt and had a ν(NC) significantly decreased from that of the free ligand. Table 9 summarizes the infrared stretching frequencies ν(XY) for several of these complexes $Ru^{II}–X\equiv Y–R$ where the Ru–X–Y linkage is presumed to be linear.

D. SUBSTITUTION REACTIONS

Studies of ruthenium(II) amine substitution reactions are few. The known reactions appear to define two categories. Ligands which are potential π-donors (*e.g.* Cl^- or H_2O) are quite labile, while amines and those ligands which are good π-acids (*e.g.*, py, N_2) are much less labile; however, this generalization holds true only in solutions which are not strongly acidic. All studies reported have been done in aqueous solution.

Aquation rates of pentaammineruthenium(II) complexes, $Ru^{II}(NH_3)_5L$ (where the binding atom of L is oxygen), have been measured by Stritar[50] (Table 10). These species were generated by outersphere reduction of the Ru^{III} analo-

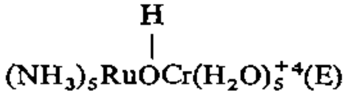
TABLE 10

RATE CONSTANTS[a] FOR $Ru^{II}(NH_3)_5X$ AQUATIONS

L	*k (sec⁻¹)*		
	X = L	*X = LH⁺*	*X = L–Cr^III(H₂O)₅*
HCO_2^-	1.28	20.1	2.4
$CH_3CO_2^-$	<5	17.5	25.5
$CF_3CO_2^-$	5.3		>600
OH^-			$10.5+(4.5\times10^3)\ [H^+]$

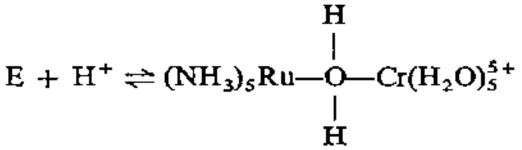
[a] $T = 25°$, $\mu = 0.1–0.5\ M\ ClO_4^-$, ref. 50.

gues by Eu^{II} or V^{II} in a stopped-flow spectrometer, and the aquation rates were determined by following the disappearance of the transient $Ru^{II}(NH_3)_5L$ intermediate. In contrast, chromous reduction of $Ru^{III}(NH_3)_5L$ gives the bridged intermediate[50] $(NH_3)_5Ru^{II}$–L–$Cr^{III}(H_2O)_5$. Chromium(III) complexes are relatively unreactive to aquation, so decomposition of the bridged intermediate occurs by Ru–L bond cleavage giving the complex $Cr^{III}(H_2O)_5L$ as the leaving group. The data in Table 10 are insufficient to indicate trends for ligands of like charge, but it is apparent that protonation or attachment of the Cr^{III} moiety increases the Ru^{II}–L bond lability, electrostatic effects being a logical rationalization for this trend. The two term rate expression for decomposition of the bridged intermediate



$$(NH_3)_5Ru\overset{\overset{H}{|}}{O}Cr(H_2O)_5^{+4}\ (E)$$

have been attributed to a pathway involving reactions 6–8.



$$E + H^+ \rightleftharpoons (NH_3)_5Ru—\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{O}}—Cr(H_2O)_5^{5+} \qquad (6)$$

(EH$^+$)

$$H_2O + E \rightarrow [Ru(NH_3)_5H_2O]^{2+} + [Cr(H_2O)_5OH]^{2+} \qquad (7)$$

$$H_2O + EH^+ \rightarrow [Ru(NH_3)_5H_2O]^{2+} + [Cr(H_2O)_6{}^{3+} \qquad (8)$$

Stritar observed no reaction intermediate in the V^{II} or Cr^{II} reductions of $Ru(NH_3)_5X^{2+}$ ($X = Cl^-, Br^-, I^-$) under the conditions used to obtain the data of Table 10. This fact implies that neither the outer-sphere reduction product, $Ru(NH_3)_5X^+$, nor the inner sphere reduction product $(NH_3)_5Ru$–X–$Cr(H_2O)_5{}^{4+}$ has a lifetime of sufficient length to be detected by the stopped-flow method. An alternate possibility would be that the spectral properties of the two intermediates are not sufficiently different from those of the final product $Ru(NH_3)_5H_2O^{2+}$ to be detectable.

From the results of electrochemical studies, Itzkovitch and Page[51] have reported a second order rate constant ($k_d = 4.2 \times 10^{-2}$ mole^{-1} · sec^{-1}) for the formation of the complex $[Ru(NH_3)_5]_2N_2{}^{4+}$ from $Ru(NH_3)_5OH_2{}^{2+}$ and $Ru(NH_3)_5N_2{}^{2+}$ in aqueous solution (25°). The first order rate constant reported for the formation of $Ru(NH_3)_5N_2{}^{2+}$ from $Ru(NH_3)_5H_2O^{2+}$ in N_2-saturated aqueous solution was $k_m = 4.4 \times 10^{-5} \cdot \text{sec}^{-1}$ (25°). When k_m' is divided by the N_2 concentration in the saturated solution (6.2×10^{-4} M), a second order rate constant is obtained, $k_m = 7.1 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$, which is remarkably close to k_d. This result implies that coordinated N_2 is nearly as reactive as free N_2 if the formation of $Ru(NH_3)_5N_2^{2+}$ is indeed second order, a reaction feature not demonstrated in this study.

The stereochemistry of the substitution reactions of the labile dichlorotetraammineruthenium(II) ions has been studied[17]. These ions were generated by Cr^{II} or by Zn(Hg) reduction of *cis*- or *trans*-$Ru(NH_3)_4Cl_2^+$ in an aqueous pyridine-pyridinium hydrochloride buffer. The corresponding tetraamminebis(pyridine)-ruthenium(II) ions were isolated in nearly quantitative yield and found to be stereochemically pure with a configuration (*i.e.*, *cis* or *trans*) identical to the initial dichloro species. Stereospecific $Ru(NH_3)_4py_2^{2+}$ formation requires that all steps (formation of both Ru^{II}–py bonds, as well as any prior chloride replacement by solvent) be stereospecific in the reaction sequence.

Retention of configuration in octahedral substitutions is consistent with either a dissociative pathway via an intermediate maintaining the other ligands in a square pyramid[52], or with associative or interchange mechanisms occurring by *cis* attack[53]. Dissociation leading to trigonal bypyramid intermediates is expected to result in isomerization for at least one of the isomers, and therefore appears less likely. The loss of $Cr(H_2O)_5Cl^{2+}$ from the probable Cr^{II} reduction intermediate $[(H_2O)_5Cr\text{–}Cl\text{–}Ru(NH_3)_4Cl]^{3+}$ might be expected to generate a pentacoordinate Ru^{II} species, as the bulky leaving group makes concerted *cis* attack by pyridine unlikely. If a true pentacoordinate Ru^{II} intermediate is indeed produced, the reaction stereospecificity suggests that it would be a square pyramid.

Retention is also the rule for aquation of the rhodium(III) complexes[53], $RhA_4Y_2^+$, and the ruthenium(III) complexes[54], $RuA_4Y_2^+$ ($A = NH_3$ or $en_{\frac{1}{2}}$, $Y = Cl^-$, Br^-, or I^-). In the only ruthenium(II) case for which stereochemical information has been previously reported[55], anion substitution for pyridine in optically active *cis*-$Ru(phen)_2py_2^{2+}$ (phen = 1,10-phenanthroline) gives *cis*-$Ru(phen)_2pyY^+$ with complete retention of the absolute configuration. Prolonged heating in LiCl solution, however, leads to racemic *cis*-Ru(*o*-phen)$_2$Cl$_2$. In contrast to the chloroammine Ru^{II} complexes, none of the above thermal reactions are rapid at room temperature.

In aqueous solutions which are not strongly acidic, Ru^{II} amine complexes of π-acceptor ligands are relatively unreactive and undergo substitution very slowly or not at all. This is also true of hexaamine species such as $Ru(NH_3)_6^{2+}$ which has a decomposition half-life of days in 1M NaOH solution[56]. One noteable exception to the generality is the dinitrogen complex[28] *cis*$(Ru(en)_2(N_2)_2^{2+}$ which rapidly loses one N_2 even at 0°. Other nitrogen complex ions such as $Ru(NH_3)_5N_2^{2+}$ and $[Ru(NH_3)_5]_2N_2^{4+}$ are quite stable in neutral or slightly acidic aqueous solution[57]. The first aquation step of $Ru(NH_3)_6^{2+}$ (Eqn. 9) has been studied[56] in acid solution and found to follow the rate law, $v = k[H^+]\,[Ru(NH_3)_6^{2+}]$, where at

$$Ru(NH_3)_6^{2+} + H_3O^+ \rightarrow Ru(NH_3)_5(H_2O)^{2+} + NH_4^+ \qquad (9)$$

25° $k = (1.24 \pm 0.03) \times 10^{-3}$ $M^{-1} \cdot sec^{-1}$ ($\Delta H^{\neq} = 19.3 \pm 0.4$ kcal · mole^{-1},

$\Delta S^{*} = -7.2 \pm 0.4$ *e.u.*). Thus, even in one molar toluenesulfonic acid, the aquation of $Ru^{II}(NH_3)_5L$ is a factor of 10^3–10^4 slower for $L = NH_3$ than for $L =$ the oxygen bases listed in Table 10.

The primary aquation steps of $Ru(NH_3)_5py^{2+}$ have also been demonstrated to have a rate dependence on acid concentration[56]. Initial aquation of this complex could be expected to lead to one of three complexes (Eqn. 10) depending on which ligand is replaced.

$$\begin{tikzcd}
 & NH_4^+ + cis-Ru(NH_3)_4(H_2O)py^{2+} \\
H_3O^+ + Ru(NH_3)_5py^{2+} \arrow[ur, "10a"] \arrow[r, "10b"] \arrow[dr, "10c"] & NH_4 + trans-Ru(NH_3)_4(H_2O)py^{2+} \\
 & pyH^+ + Ru(NH_3)_5(H_2O)^{2+}
\end{tikzcd} \tag{10}$$

Ion exchange studies indicate that 10*c* predominates but that all three products were produced in aqueous HCl. Exact ratios could not be measured because of subsequent decomposition of reaction intermediates. When $(Ru(NH_3)_5py^{2+}$ is heated in an aqueous pyridine buffer solution[17], the products of Ru^{II}–ligand bond cleavage is a mixture of *cis*- and *trans*-$Ru(NH_3)_4py_2{}^{2+}$ in the approximate ratio 7:3. This result suggests that reactions 10*a* and 10*b* have competitive rates and that the pyridine does not have a strong directing influence on NH_3 lability (8:2 would be the statistical distribution). In this case, 10*c* is swamped in the pyridine buffer by the reverse reaction to give starting material. It should be emphasized that the experimental conditions of this study (ph ~ 5, 60°) were markedly different from those for which kinetics[56] were measured (pH < 3, 25°). Since the rate studies indicate the possibility of multiple pathways for $Ru(NH_3)_5py^{2+}$ aquation, careful product studies under a variety of conditions are needed to elucidate the stoichiometries of these.

For the ion $Ru(NH_3)_5py^{2+}$ in one molar acid, reaction 10*c* is a factor of ten slower than aquation of $Ru(NH_3)_6{}^{2+}$ (Eqn. 9) under similar conditions[56]. Perhaps a more significant comparison is that the sum of (10*a*) and (10*b*) is a factor of 20 slower than (9). On comparison of the reaction patterns for $Ru(NH_3)_6{}^{2+}$ and $Ru(NH_3)_5py^{2+}$, it is clear that the π-backbonding with pyridine deactivates the Ru^{II} center toward the acid catalyzed aquation. This deactivation is further illustrated by the effect of pyridine substituents on the rate of 10*c*. A plot of the aquation rate versus the Hammett substituent constant (Fig. 4) is roughly linear giving $\rho = -2.3$. While linearity may not prove significant for this scant data, the negative ρ clearly indicates that electron withdrawing substituents, which should increase the backbonding interaction, stabilize the complex toward aquation.

The acid catalysis of the $Ru(NH_3)_5py^{2+}$ and the $Ru(NH_3)_6{}^{2+}$ aquations is not paralleled in the chemistry of other metal amine complexes (*e.g.*, Ni^{II} amine[58]). Structural inspection of $Ru(NH_3)_6{}^{2+}$ reveals no base sites with the exception of

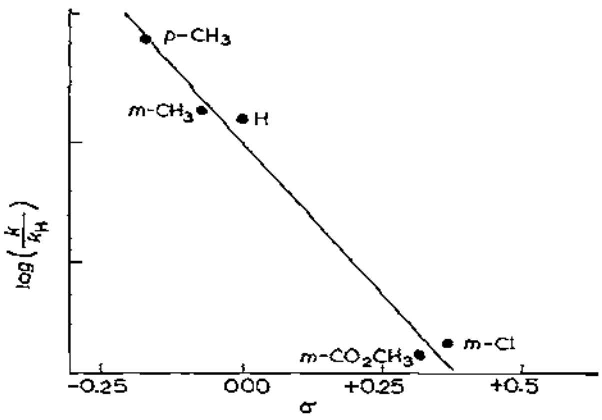


Fig. 4. Plot of log (k/k_H) *vs.* Hammett substituent constant σ for reaction 10*c*.

the filled t_{2g} metal orbitals which provide electron density at the faces of the octahedron. Consequently, it was proposed that the initial step is a direct engagement of the t_{2g} electrons by the proton (Eqn. 11) giving what could be construed as a Ru^{IV} hydride heptacoordinate intermediate. This reaction could be rate-determining, or it may be a preequilibrium followed by a rate determining substitution (Eqn. 12) and loss of a proton (Eqn. 13). It is not

$$Ru(NH_3)_6{}^{2+} + H^+ \rightleftharpoons Ru(NH_3)_6H^{3+} \tag{11}$$

$$Ru(NH_3)_6H^{3+} + H_2O \rightarrow Ru(NH_3)_5(H_2O)H^{3+} + NH_3 \tag{12}$$

$$Ru(NH_3)_5(H_2O)H^{3+} \rightleftharpoons Ru(NH_3)_5H_2O^{2+} + H^+ \tag{13}$$

obvious how a heptacoordinate hydride intermediate would have unusual lability; however, a proton sitting on the face or edge of the octahedron potentially could engage the electrons of a partially broken bond between the Ru^{II} and an adjacent NH_3, thereby lowering the energy of the transition state. A similar argument could be presented for the aquation of $Ru(NH_3)_5py^{2+}$. If a hydride intermediate does intervene in the reaction sequence, this intermediate does not react with acid (Eqn. 14) as no significant oxidation of Ru^{II} occurs during the aquation.

$$Ru(NH_3)_6H^{3+} + H^+ \rightarrow Ru(NH_3)_6{}^{4+} + H_2 \tag{14}$$

Another aquation mechanism whose kinetics are indistinguishable from the one discussed above would involve electrophilic attack of H^+ on a Ru^{II} coordinated ligand leading to greatly increased lability. Such a mechanism appears quite feasible for $Ru(NH_3)_5py^{2+}$ due to the availability of pyridine π electrons as a base site but is less conceivable for $Ru(NH_3)_6{}^{2+}$ where all ligand electrons are in sigma bonding orbitals. Either mechanism could involve a preliminary equilibrium between the protonated and unprotonated forms of the complex; however, attempts to detect a significant concentration of a protonated complex in strong acid were unsuccessful[56].

E. REDOX REACTIONS

The Ru^{II} amines are weak reducing agents as shown by the Ru^{II}/Ru^{III} couples (Table 11). The hexaamines react with metal ion oxidants (*e.g.*, Eqn. 15)

TABLE 11

STANDARD ELECTRODE POTENTIAL FOR Ru^{II}/Ru^{III} COUPLES[a] (25°)

		$E°$ *(v)*
$Ru(NH_3)_6^{3+} + e^-$	$\rightarrow Ru(NH_3)_6^{2+}$	0.10 ± 0.01
$Ru(NH_3)_5H_2O^{3+} + e^-$	$\rightarrow Ru(NH_3)_5(H_2O)^{2+}$	0.16 ± 0.01
$Ru(en)_3^{3+} + e^-$	$\rightarrow Ru(en)_3^{2+}$	0.21 ± 0.005
$Ru(H_2O)_6^{3+} + e^-$	$\rightarrow Ru(H_2O)_6^{2+}$	0.22 ± 0.03[b]

[a] Ref. 12.
[b] Ref. 14.

without scission of the Ru^{II} amine bonds. In appearance, the reduction proceeds *via* an "outer

$$Co(NH_3)_5X^{2+} + Ru(NH_3)_6^{2+} + 5H^+ \rightarrow Co^{2+}(aq) + \\ + Ru(NH_3)_6^{3+} + X^- + 5NH_4^+ \qquad (15)$$

sphere" electron transfer step[6], that is, the inner coordination shells of the reactants remain intact in the redox step transition state. Outer sphere electron transfer pathways characterize both the oxidations of the Ru^{II} and the reductions of the Ru^{III} hexaammines and tris(ethylenediamine) complexes. This behavior is the result of the relative inertia of the Ru^{II} and Ru^{III} amine bonds. The isolation of the hexaamine product does not, however, unambiguously exclude an inner sphere type pathway where the bridging ligand occupies a site on an intermediate heptacoordinate ruthenium species but is substantially more labile than the amines in both Ru^{II} and Ru^{III}. There are no published experimental data concerning the hexaammineruthenium(II) reductions of metal complexes which distinguish an inner sphere mechanism of this type from the presumed outer sphere pathway.

In contrast to oxidations by $Ru(NH_3)_6^{3+}$, the Cr^{II} reduction of aqueous $Ru(NH_3)_5Cl^{2+}$ proceeds via an inner sphere pathway resulting in chloride transfer[18] (Eqn. 16). The metal ion reductions

$$Ru(NH_3)_5Cl^{2+} + Cr^{2+} \rightarrow (NH_3)_5Ru\text{–}Cl\text{–}Cr(H_2O)_5^{4+} \xrightarrow{H_2O} \\ Ru(NH_3)_5(H_2O)^{2+} + Cr(H_2O)_5Cl^{2+} \qquad (16)$$

of numerous Ru^{III} ammines $Ru(NH_3)_5X^{2+}$ have been studied by Taube and coworkers[6,50,59]. A detailed accounting of this work is beyond the scope of the review.

The self exchange rates for the couples $Ru(NH_3)_6{}^{2+}/Ru(NH_3)_6{}^{3+}$ and $Ru(en)_3{}^{2+}/Ru(en)_3{}^{3+}$ have been studied by taking advantage of an optical density change in overtone N–H stretching absorptions (near I.R.) when the deuterated 3+ complex [*e.g.* $Ru(ND_3)_6{}^{3+}$] is reduced by the protonated 2+ complex[12] [*e.g.*, $Ru(NH_3)_6{}^{2+}$]. The rate data were subject to some reproducibility problems; however, it was shown that at 25° and $\mu = 0.013$ the $Ru(en)_3{}^{2+,3+}$ couple ($k_2 < 2\times 10^2$ $M^{-1}\cdot sec^{-1}$) exchanges at a rate slower than the $Ru(NH_3)_6{}^{2+,3+}$ couple ($k_2 = 8.2\times 10^2\ M^{-1}\cdot sec^{-1}$).

Fast exchange between Ru^{II} and Ru^{III} provides a catalytic pathway for Ru^{III} substitution reactions[18]. Traces of $Ru(NH_3)_5H_2O^{2+}$ in aqueous $Ru(NH_3)_5X^{2+}$ ($X = Cl^-, Br^-, I^-$) result in the rapid equilibration of the sixth coordination position with the solvent medium (Eqn. 17). In contrast, the room temperature aquation of

$$H_2O + Ru(NH_3)_5X^{2+} \rightleftharpoons Ru(NH_3)_5H_2O^{3+} + X^- \tag{17}$$

$Ru(NH_3)_5Cl^{2+}$ has a half-life exceeding 10^5 sec, necessarily resulting in a very slow uncatalyzed equilibration. Ru^{II}/Ru^{III} exchange is also catalytically important in the H/D exchange of NH_3 coordinated to Ru^{II} in D_2O solution. Uncatalyzed H/D exchange folows a rate pattern, $R = k[OD^-]H_a$, where H_a is the sum of H and D in the complex[12]. The reported rate constant for $Ru(NH_3)_6{}^{2+}$ ($k = 1.3\times 10^7$ l/g-atom · sec) is substantially slower than that for $Ru(NH_3)_6{}^{3+}$ [$(235 \pm 35)\times 10^7$ l/g-atom · sec]. In the presence of trace $Ru(NH_3)_6{}^{3+}$, the H/D exchange on $Ru(NH_3)_6{}^{2+}$ is catalyzed, and concentration manipulations can give conditions where either Ru^{II}/Ru^{III} electron transfer or H/D exchange on $Ru(NH_3)_6{}^{3+}$ is rate determining.

Meyer and Taube[12] have investigated the rates of $Ru(NH_3)_6{}^{2+}$ and $Ru(en)_3{}^{2+}$ oxidation by aqueous Fe^{III}. These outer sphere reactions were greatly enhanced by added Cl^-. The oxidations by $FeCl^{2+}$ were too rapid to measure with the stopped-flow techniques employed, being more reactive than Fe^{3+} by factors of >50 for $Ru(NH_3)_6{}^{2+}$ and >120 for $Ru(en)_3{}^{2+}$. In contrast to the rate acceleration observed when Cl^- occupies an Fe coordination position, oxidation of $Ru(NH_3)_6{}^{2+}$ or $Ru(en)_3{}^{2+}$ by $FeOH^{2+}$ was shown to be a factor of 6 slower than the corresponding Fe^{3+} oxidations (Table 12). These rate differences emphasize the importance of factors other than electrostatic effects which influence outer sphere reaction rates.

When $Ru(NH_3)_5H_2O^{2+}$ is the reductant, the relative reactivities of Fe^{3+} and $FeOH^{2+}$ are inverted, $FeOH^{2+}$ being the more reactive by a factor of six (Table 12). On the basis of ligand substitution rate considerations, these oxidations have also been tentatively assigned to the "outer sphere" category. In light of the lower reactivity of the $FeOH^{2+}/Ru(NH_3)_6{}^{2+}$ system compared with the $Fe^{3+}/$

TABLE 12

REDOX RATES INVOLVING Ru^{II} AMINE REDUCTANTS[a]

Reaction	k_2 *($M^{-1}sec^{-1}$)*	*$\Delta H^{\neq}$ (kcal/mole)*	*$\Delta S^{\neq}$ (e.u.)*
$Ru(en)_3^{2+} + Ru(enD)_3^{3+}$ [b]	2×10^2		
$Ru(NH_3)_6^{2+} + Ru(ND_3)_6^{3+}$ [b]	8.2×10^2	10.3	−11
$Ru(NH_3)_6^{2+} + Fe^{3+}$ [c]	31×10^4	3.2	−22
$Ru(NH_3)_6^{2+} + FeOH^{2+}$ [c]	5.0×10^4		
$Ru(NH_3)_5OH_2^{2+} + Fe^{3+}$ [c]	8.0×10^4		
$Ru(NH_3)_5OH_2^{2+} + FeOH^{2+}$ [c]	48.0×10^4		
$Ru(en)_3^{2+} + Fe^{3+}$[c]	9.4×10^4	4.3	−22
$Ru(en)_3^{2+} + FeOH^{2+}$[c]	1.5×10^4		

[a] Ref. 12. [b] 25°, $\mu = 0.013$. [c] 10°, $\mu = 0.10$.

TABLE 13

RATES FOR THE REDUCTION OF SOME REPRESENTATIVE Co^{III} COMPLEXES BY $Ru(NH_3)_6^{2+}$

Oxidant	*k ($M^{-1} \cdot sec^{-1}$)*[a]
$Co(NH_3)_6^{3+}$	0.011
$Co(NH_3)_5OH_2^{3+}$	3.0
$Co(NH_3)_5OH^{2+}$	0.04
$Co(NH_3)_5NO_3^{2+}$	34
$Co(NH_3)_5N_3^{2+}$	1.2
$Co(NH_3)_5Cl^{2+}$	260
$Co(NH_3)_5Br^{2+}$	1,600
$Co(NH_3)_5I^{2+}$	6,700
cis-$Co(NH_3)_4(H_2O)_2^{3+}$	270
trans-$Co(en)_2Cl_2^{+}$	9,000
cis-$Co(en)_2Cl_2^{+}$	880
trans-$Co(NH_3)_4(OAc)_2$	$3.0 + 36[H^+]$
cis-$Co(NH_3)_4(OAc)_2$	$0.6 + 12[H^+]$
cis-$Co(en)_2(H_2O)Cl^{2+}$	231[b]
cis-$Co(en)_2(NH_3)Cl^{2+}$	12[b]
cis-$Co(en)_2(NH_2C_2H_5)Cl^{2+}$	32[b]
cis-$Co(en)_2pyCl^{2+}$	657[b]

[a] $\mu = 0.20$, $T = 25°$, ref. 61.
[b] $\mu = 0.10$, $T = 25°$, ref. 60.

$Ru(NH_3)_6^{2+}$ couple, the enhanced reactivity of $FeOH^{2+}$ with $Ru(NH_3)_5OH_2^{2+}$ raises the possibility that proton transfer from Ru^{II} OH_2 to $FeOH^{2+}$ accompanies electron transfer.

The $Ru(NH_3)_6^{2+}$ reduction rates for a series of tetraamine and pentaamine cobalt(III) complexes, $Co^{III}(NH_3)_4L_2$ and $Co^{III}(NH_3)_5L$ are summarized in Table 13. Despite the "outer sphere" nature of the products (Eqn. 15), a rate difference of nearly 10^6 is found between the $Ru(NH_3)_6^{2+}$ reductions of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5I^{2+}$, pointedly illustrating the rate dependence on the Co^{III} coordination[60,61]. That the effect is not purely electrostatic is evident from the lower reactivity of $Co(NH_3)_5OH^{2+}$ compared with $Co(NH_3)_5OH_2^{3+}$. Comparison of the Ru^{II} reductions of $Co(NH_3)_5Cl^{2+}$ and $Co(en)_2NH_3Cl^{2+}$ show a rate ratio of about 100 to 1, further emphasizing the marked rate effects resulting from relatively subtle changes on the Co^{III} coordination sphere. The ferrous ion reductions of the latter two Co^{III} species proceed via an inner sphere pathway[60] (bridging Cl^-) yet show comparable relative rate differences. Consequently, the sensitivity of the relative rates toward the nature of the nonbridging Co^{III} ligands is not strictly a property of the $Ru(NH_3)_6{}^{2+}$ reductant or of the mechanism (inner sphere or outer sphere).

Unlike $Ru(NH_3)_6{}^{2+}$, $Ru(NH_3)_5OH_2{}^{2+}$ potentially could act as an inner sphere reductant, as the lability of the aquo ligand could open a "normal" coordination position to a bridging ligand. The $Ru(NH_3)_5OH_2{}^{2+}$ reduction of $Co^{III}(NH_3)_5L$ via an inner sphere pathway would be predicted to result in ligand transfer, as the Ru^{III} moiety is relatively inert while Co^{II} is labile. However, the catalysis of Ru^{III} substitutions by trace Ru^{II} complicates the analysis, and consequently the isolation of the product $Ru^{III}(NH_3)_5L$ is not an unambiguous result indicative of an inner sphere mechanism. Endicott and Taube[6] have isolated the product $Ru(NH_3)_5I^{2+}$ from the $Ru(NH_3)_5OH_2{}^{2+}$ reduction of $Co(NH_3)_5I^{2+}$ in a yield (~5%) exceeding by a factor of 1.5 the equilibrium concentration conservatively predicted for the reaction system. On this basis, they suggested that perhaps the outer- and inner-sphere paths were proceeding at competitive rates. Isolation of $Ru(NH_3)_5I^{2+}$ in excess of the predicted equilibrium concentration is a powerful argument for a redox pathway (*i.e.*, inner sphere) which generates $Ru(NH_3)_5I^{2+}$. However, the relative closeness of the product concentration to the equilibrium predicted value requires that K_{eq} be accurately known. The constants for equilibrium (17) ($X^- = Cl^-$, Br^-, or I^-) are apparently quite sensitive to environment[6,19,53] as demonstrated by differences in the value for $X^- = Cl^-$ obtained by Endicott and Taube[6] ($K = 70 \pm 6$ M^{-1} at 25°, $\mu = 0.11$ M, $Cl^-/ClO_4{}^-$ medium) and found by extrapolation of data by Broomhead, Basolo and Pearson[19] ($K = 140 \pm 15$ M^{-1} at 25°, $\mu = 0.11$ M, *p*-toluene sulfuric acid medium). In this context, the isolation of $Ru(NH_3)_5I^{2+}$ in the above experiment cannot at present be considered a truly definitive example of an inner sphere reduction by a Ru^{II} ammine.

The Ru^{II} ammines are also oxidized by perchlorate ion to the corresponding Ru^{III} ammines[18], the rates following the order[6]

$$-\frac{d[Ru^{II}]}{dt} = k_3[ClO_4{}^-]\,[Ru^{II}].$$

The aquo complex $Ru(NH_3)_5OH_2{}^{2+}$ ($k_3 \cong 2.6\times10^{-2}$ $M^{-1}\cdot sec^{-1}$) is nearly two orders of magnitude more reactive than $Ru(NH_3)_6{}^{2+}$ ($k_3 = 3\times10^{-4}$ $M^{-1}\cdot sec^{-1}$) at 25°. The lability of the aquo ion, potentially allowing a normal coordination position for $ClO_4{}^-$, is undoubtedly respousible for the greater reactivity of $Ru(NH_3)_5H_2O^{2+}$. In either case, it is not clear how Ru^{II} would reduce $ClO_4{}^-$ in a path first order in reductant. On the basis of low $ClO_4{}^-$ reactivity toward other one-electron transfer agents, Endicott and Taube[6] have suggested that perhaps the reaction involves oxygen atom transfer from ClO_4^- to Ru^{II} giving an initial Ru^{IV} intermediate which is reduced by a second Ru^{II} to give two equivalents of Ru^{III}. This mechanism requires a seven coordinate intermediate in the oxidation of $Ru(NH_3)_6^{2+}$ since all six ammines are retained in the final product. Another metal ion reduction of ClO_4^- which has been studied is the facile reaction[63] with aqueous Ti^{III}, where a rate study shows the reaction to be first order in $[Ti^{III}]$. In this example a two-electron transfer from the $3d^1$ Ti^{3+} ion appears very unlikely. While the analogy between Ti^{III} and Ru^{II} complexes may be distant, the reactivity of Ti^{III} with ClO_4^- indicates that a one-electron transfer need not be excluded from consideration for the Ru^{II} reaction.

Ru^{II} ammines are oxidized by aqueous O_2 and H_2O_2 to give nearly quantitative yields of the corresponding Ru^{III} ammine[17]. Since the ammine ligands remain intact [*e.g.*, the oxidation of $Ru(NH_3)_5py^{2+}$ gives $Ru(NH_3)_5py^{3+}$], the "outer sphere" definition is applicable. In considering this reaction, one is faced again with the kinetically indistinguishable possibility of some inner sphere type of interaction involving the electron-deficient O_2 and the electron-rich face of the Ru^{II} octahedron. Ru^{II} ammines may also be oxidized by Cl_2 to Ru^{III} ammine; however, the oxidation is difficult to control and can lead to considerable Ru loss to higher oxidation states[6].

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