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Synthesis and Properties of Pentaamminepyridineruthenium(II) and Related Pentaammineruthenium Complexes of Aromatic Nitrogen Heterocycles

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Abstract: The syntheses of pentaammineruthenium(II) and pentaammineruthenium(III) complexes of pyridine and analogous aromatic nitrogen heterocycles are reported here. The pentaammineruthenium(II) complex of each of these heterocyclic ligands has an intense absorption band in the visible region which, on the basis of evidence presented below, is assigned to a metal-to-ligand charge-transfer transition. The pentaamminepyrazineruthenium-(II) complex ion can be protonated in a reversible fashion, presumably at the noncoordinated nitrogen of the 1,4-diazine. The pK_a of this complex demonstrates that the dipositive ion is approximately two orders of magnitude *more basic than the free ligand*. This result and related data are interpreted in terms of ground-state π back-bonding from the ruthenium(II) to the aromatic ligand.

We undertook the present work in the hope that comparison of the reactivity of various ruthenium-(III) complexes, which have low-spin d^5 electronic configurations, to analogous cobalt(III) complexes (low-spin d^6) would improve our understanding of the role of electronic configuration in the mechanism of reductions of these complexes. Pentaammineruthenium(III) complexes of nitrogen heterocycles such as pyridine derivatives are of special interest because it is reported that reductants such as chromium(II) can attack at ligand sites remote from the metal ion center in certain Co(III) analogs.[2]

Remote attack may require transfer of the reducing electron through the conjugated π orbitals of the aromatic ligand. It has been suggested that the ruthenium-(III) complexes having a π-symmetry (t_{2g}) acceptor orbital might demonstrate dramatically different reactivity characteristics in reductions by remote attack from Co(III) analogs having σ-symmetry (or e_g) acceptor orbitals. In the course of investigating these problems, we have synthesized a number of pentaammineruthenium(II) and pentaammineruthenium(III) complexes of aromatic nitrogen heterocycles. These have been found to have interesting physical and spectral properties; their description and interpretation form the subject of this paper.

Results

Spectral Characteristics. The spectrum of pentaamminepyridineruthenium(II) perchlorate in aqueous solution is shown in Figure 1. Characteristic of the spectrum of this complex and of the pentaammineruthenium(II) complexes of related aromatic nitrogen heterocycles is an intense absorption band in the visible range having an extinction coefficient approximately $10^4 \, M^{-1} \text{cm}^{-1}$. Comparison of the spectrum in the visible range for pentaamminepyridineruthenium(II) perchlorate in aqueous solution to the spectra of pentaamminepyridineruthenium(III) perchlorate (Figure 1) and of hexaammineruthenium(II) perchlorate (Table I) in aqueous

(1) (a) NSF Postdoctoral Research Associate, Stanford University; (b) NSF Science Faculty Fellow and Visiting Scholar at Stanford University.
(2) F. R. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **88**, 4745, (1966).

solutions demonstrates that among these the band occurring at 407 mμ is unique to the Ru(II)–pyridine species. Somewhat analogous absorptions have been observed in the spectra of other pyridine complexes with d^6 metal ions. For example, the spectra of pyridine complexes of chloroiridium(III) show intense visible range absorptions which are suggested by Jørgensen[3] to arise from metal-to-ligand charge transfers.

Table I. Spectra of Pentaammineruthenium Complexes

Complex	λ_{max}, mμ (log ϵ_{max})		
$(NH_3)_6Ru^{2+}$ [a]	400 (1.48)	275 (2.80)	
$(NH_3)_6Ru^{3+}$ [a]	320 (2.00)	275 (2.68)	
$(NH_3)_5Ru(py)^{2+}$	407 (3.89)	244 (3.66)	
$(NH_3)_5Ru(py)^{3+}$	262 (3.657)	253 (3.660)	247 (3.653)
Pyridine[b]	253 (3.55)		
Pyridine (H⁺)	255 (3.72)		

[a] T. Meyer, Ph.D. Dissertation, Stanford University, 1966, p 30. [b] (0,0) band of pyridine spectrum: H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 363.

The only other high-intensity absorption apparent in the electronic spectrum of the pentaamminepyridineruthenium(II) complex occurs in the ultraviolet region of the spectrum at 244 mμ. The position of this band and its intensity, ϵ 4.6 $\times$ 10^3 M^{-1} cm^{-1}, are similar to those for free pyridine and for protonated pyridine (Table I) implying that this transition is essentially localized in the aromatic ligand and is presumably analogous to the π^* ← π absorption seen in the free ligand. Similar bands occur in the spectrum of pentaamminepyridineruthenium(III); on the other hand, transitions in this region for hexaammineruthenium(II) and the hexaammineruthenium(III) are of much lower intensity (Table I).

The absorption bands for pyridine, when it is free, when it is protonated, and when it is bound to ruthenium(III), are close in energy while the analogous band for the pyridine bound to ruthenium(II) is shifted to higher energy.

(3) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 151 (1957).
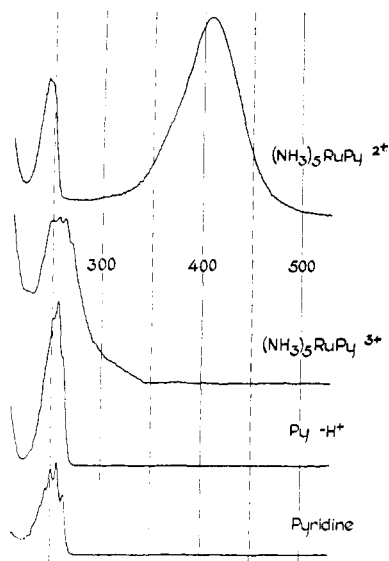
Figure 1. Absorption spectra of pyridine complexes in water (spectra in mμ).

Figure 2. Absorption spectrum of $(NH_3)_5Ru(p\text{-formylpyridine})^{2+}$ in different solvents.

Ruthenium(II) Complexes of Substituted Pyridines.

The effect of substituents on the position of the visible absorption band of compounds of the type $(NH_3)_5Ru$-(py-X)(ClO$_4$)$_2$ (where py-X is a *meta*- or *para*-substituted pyridine) is summarized in Table II. Clearly, the position of the band is extremely sensitive to the nature of the substitution, especially to those substituents in the *para* position. The trend is such that electron-withdrawing groups (as estimated by the Hammett σ-substituent function) in both the *para* and the *meta* series lower the energy of the transition. However, *para* substituents which have possible π interaction with the aromatic ring have the greater effect in lowering the transition energy.

Table II. Effect of Substituents on the Spectrum of $(NH_3)_5Ru^{II}py\text{-}X$

Substituent	σ^a	λ_{max}, mμ (log ϵ_{max})	$\nu \times 10^4$, cm^{-1}
p-CH$_3$	-0.17	398	2.51
H	0.00	407 (3.89)^b	2.45
p-CH$_2$OH	...	412	2.43
p-CH(OH)$_2$	...	420	2.38
p-CO$_2^-$	0.00	457	2.19
p-CONH$_2$	0.27^c	479 (4.02)	2.09
p-CO$_2$CH$_3$	0.39	497 (4.10)	2.01
p-CO$_2$H	0.405	497	2.01
p-CHO	$\sim$0.5^d	545 (3.97)	1.83
m-CH$_3$	-0.069	404	2.48
H	0.00	407 (3.87)	2.45
m-CO$_2$CH$_3$	0.32	417 (3.77)	2.39
m-I	0.35	426	2.35
m-Cl	0.37	426	2.35
m-Br	0.39	427	2.34
m-CONH$_2$	0.28^c	427 (3.78)	2.34

^{a} J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 87. ^{b} A rather high experimental error ($\sim\pm 10\%$) must be associated with these reported extinction coefficients. The compounds are sensitive to air, light, and solution impurities, making the determination of an accurate extinction coefficient difficult. As a result, only the value for the $(NH_3)_5Ru$-(py)$^{2+}$ ion was determined with high reproducibility (see Experimental Section). ^{c} H. H. Jaffé, *J. Am. Chem. Soc.*, **77**, 4441 (1955). ^{d} Estimated from value for CH$_3$CO, in the *para* position.
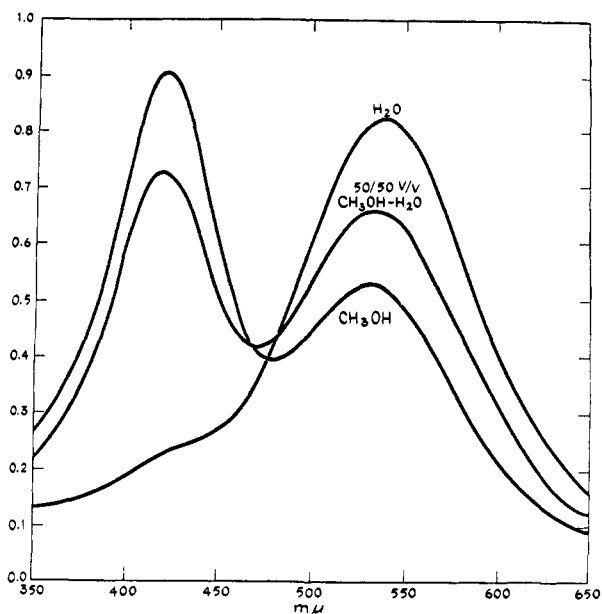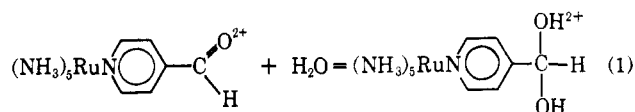
The dramatic difference in their effect on the spectra of these complexes between functional groups which can interact with the π orbitals of the complexed pyridine ring and those which cannot interact provides a probe into the chemistry of the p-formylpyridyl complex (Figure 2). In water the spectrum has two resolvable peaks in the visible range, one at 545 mμ and the other at 420 mμ. In 50% aqueous methanol the absorption at 420 mμ is accentuated at the expense of the lower energy transition, and in absolute methanol the trend is continued further. These data undoubtedly reflect an equilibrium between the aldehyde species and some other derivative of it, presumably the aldehyde hydrate in water (eq 1) and the acetal or hemiacetal form in methanol.

$$(NH_3)_5RuN\!\!\bigcirc\!\!-C\overset{O}{\underset{H}{\diagdown}}{}^{2+} + H_2O = (NH_3)_5RuN\!\!\bigcirc\!\!-\overset{OH}{\underset{OH}{\overset{|}{C}}}{}^{2+}\!\!-H \quad (1)$$
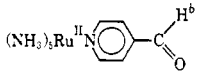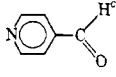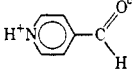
Analysis of the spectrum in water using the approximations for band shape described in the Discussion section (below) indicate that the hydrate form is 17% of the total complex concentration at 37°, giving an equilibrium constant of $K_1 = 0.20$. This method of obtaining the equilibrium constant is not ideal and was adopted only because the nmr method, which, as described in the following, works well for the uncomplexed pyridine, fails for the pyridine–ruthenium complexes. The reason for the failure to observe a signal is not known with certainty; we are inclined to ascribe it to line broadening by traces of Ru(III). It is of interest to consider the effect of metal ion coordination on the magnitude of this type of ligand equilibrium constant, and thus the ratios of the hydrated to carbonyl form of the free p-formylpyridine and of the protonated p-formylpyridine were determined in this case using the nuclear magnetic resonance spectra in D$_2$O. For free p-formylpyridine, the spectrum included the expected aromatic protons at 7.50–8.90 ppm[4] with an assumed

(4) δ parts per million from tetramethylsilane taken as zero.

integration of four protons as well as two other resonances at 6.13 and 10.08 ppm., respectively. The total integration of each of these two equals one-fourth of the total aromatic protons, indicating that these two reflect the free aldehyde–aldehyde hydrate equilibrium, the lower field resonance being that of the carbon-bound aldehyde hydrogen.[5] The spectrum of the protonated p-formylpyridine is very similar. Hydrate equilibrium constants for the free p-formylpyridine, the protonated p-formylpyridine, and the pentaammineruthenium(II) complex of the p-formylpyridine at 37° are summarized in Table III. The data show that coordination to the ruthenium(II) center favors the carbonyl over the hydrate form of the ligand.

Table III. Hydration of p-Formylpyridine

Compound	% hydrate	K^a = [hydrate]/[aldehyde]
(NH₃)₅Ru^II N⟨⟩—C(H^b)=O	17	0.20
N⟨⟩—C(H^c)=O	46	0.84
H⁺N⟨⟩—C(O^c)–H	48	0.88

ᵃ In D_2O, 37°. ᵇ From analysis of electronic spectrum. ᶜ From analysis of nmr data.

Solvent Effect on the Visible Range Spectrum of (NH₃)₅Ru(py)(ClO₄)₂. The absorption band appearing at 407 mμ in the spectrum of aqueous pentaamminepyridineruthenium(II) perchlorate solutions proved to be very sensitive to environmental characteristics such as the nature of different solvents. The position of this band for solutions of pentaamminepyridineruthenium(II) perchlorate in different media is reported in Table IV.

Table IV. Effect of Solvent on the Spectrum of (NH₃)₅Ru^IIpy(ClO₄)₂

Solvent	Dielectric constant	λ_max, mμ
Water	78.5	407
Acetonitrile	37.5	408
Methanol	32.6	415
Ethanol	24.3	417
Acetone	20.7	417
Formamide	109.0	424
DMF	37.0	436
DMSO	47.0	447

Attempts to correlate the shifts of the band maxima from its position in water with known solvent parameters such as dielectric constant as well as with the empirical relationship derived by Kosower (Z values)[6] proved unsuccessful. A significant observation is that added potassium chloride affected the spectrum of the complex in dimethylformamide solution, shifting the λ_max of the visible absorption to higher wavelengths.

(5) R. H. Bible, "Interpretation of NMR Spectra, an Empirical Approach," Plenum Press, New York, N. Y., 1965, p 16.
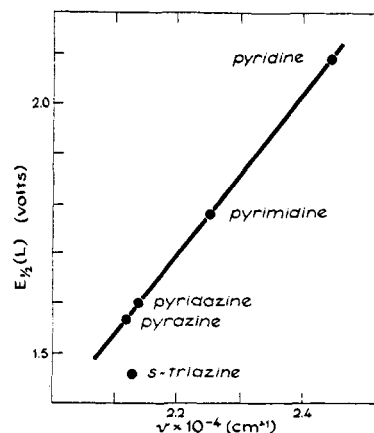(6) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

Figure 3. Correlation between polarographic $E_{1/2}$ (free ligand) and visible absorption band frequency for the pentaammineruthenium(II) azine complexes.

However, similar shifts were not observed in aqueous solution. These observations suggest that the solvent effects may be intimately connected with ion pairing.

Azine Complexes. To investigate the possibility that the spectral features of these complexes might show some dependence on the energy of the unoccupied molecular orbitals of the free ligands, a series of pentaammineruthenium(II) complexes of aromatic nitrogen heterocycles was prepared. The heterocycles used in this series were pyridine, pyrazine, pyridazine, pyrimidine, and s-triazine; for these, the polarographic half-wave potentials of the one-electron reductions in dimethylformamide have been measured.[7] It is evident from the data summarized in Table V that a strong interdependence exists between the transition energy of the visible range band for each of these complexes and the half-wave reduction potential of the corresponding free ligand. This relationship is dramatically illustrated by the linear plot of the band frequency vs. the free-ligand half-wave reduction potential in Figure 3.

Table V. Correlation of $E_{1/2}$ (Free Ligand) to Low-Energy Band of (NH₃)₅Ru^IIL^{2+ a}

Ligand	$E_{1/2}$ (L), v^b	λ_max, mμ (log ε_max)	Frequency, cm⁻¹ × 10⁴
Pyridine	2.09	407 (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	4.71 (3.70)	2.13
Pyrazine (H⁺)		529 (4.08)	1.89
Pyridazine (H⁺)		556 (3.96)	1.83
Pyrimidine (H⁺)		∼463	∼2.16

ᵃ L is one of the azines (perchlorate salts in H_2O). ᵇ Reference 6.

In strong acid solution, it is possible to protonate reversibly the pyrazine and the pyridazine–pentaammineruthenium(II) complexes. The protonation equilibria can be observed spectrally by the large bathochromic shifts of the visible range bands as well as smaller changes in the rest of the spectrum from the nonpro-

(7) K. B. Wiberg and T. Lewis, private communication. Polarographic reduction potentials reported in Table V were measured in reference to a mercury pool anode. Wiberg and Lewis have revised their value for pyridine to $E_{1/2}$ = 2.01 v.
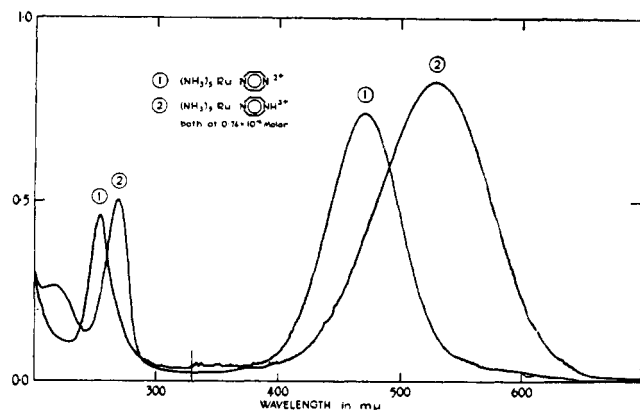
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Figure 4. Absorption spectra of the pentaamminepyrazineruthenium(II) ion and its protonated analog.

Figure 5. pK_a measurement for the protonation equilibrium of the pentaamminepyrazineruthenium(II) complex.

tonated species to the protonated species (Figure 4, Table V). These spectral differences between the free base and the conjugate acid can be used to determine the acidity constants of the complexes. A plot of solution pH vs. the ratio of absorption at the wavelengths of the respective maxima for the pyrazine equilibrium demonstrates the characteristic shape of a weak base titration curve (Figure 5). This curve gives a pK_a value for the equilibrium (eq 2) of 2.5 ± 0.1. Comparison of this

$$(NH_3)_5RuN\bigcirc N^{+2} + H^+ = (NH_3)_5RuN\bigcirc NH^{3+} \quad (2)$$
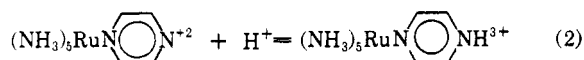
to the reported value for the free ligand, $pK_a = 0.6$,[8] indicates that the complexed pyrazine is nearly two orders of magnitude *more basic than the free ligand.*

The pyridazine complex being much less basic could not be subjected to quite the same analysis as the pyrazine complex equilibrium; however, dissolving this compound in solutions of varying acidity gave different ratios of protonated to nonprotonated complex dependent on the acid concentration with half-protonation occurring in 0.93 M hydrochloric acid solution. If changes in activity coefficients are neglected, this result gives a pK_a value of 0.03 ± 0.05. In contrast to the pyrazine and pyridazine complexes, the pyridine complex showed no distinctive spectral change on dissolving in strong acid solutions up to 6 M in perchloric acid. The pyrimidine complex did show a small and reversible change in its spectrum in hydrochloric acid solution with half-protonation of the complex in solution estimated as occurring at approximately 1 M acid. However, in these strongly acidic solutions, the complex underwent rapid and irreversible decomposition to unknown products.

Attempts to prepare and isolate the pentaammineruthenium(III) complex of pyrazine, $(NH_3)_5Ru(C_4H_4N_2)^{+3}$, by a method similar to that described in the Experimental Section for the Ru(III)–pyridine compound proved unsuccessful due to the sensitivity of the desired compound to the synthetic conditions. However, oxidation of the pentaamminepyrazineruthenium(II) complex by titration with cerium(IV) perchlorate solution gave a faintly yellow solution having spectral

(8) R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds," Interscience Publishers, Inc., New York, N. Y., 1960, p 299. Attempts to confirm this value in these laboratories both by potentiometric titration and by spectrophotometric techniques gave a pK_a of 0.8 ± 0.2 for the free pyrazine.
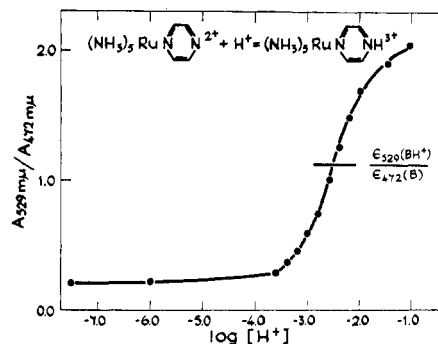
bands at 270, 255 (Ce(III)), and 238 mμ. Reduction of an aliquot of this solution with Cr(II) gave back the original Ru(II) complex. Cerium(IV) titration in this manner has been demonstrated in these laboratories to oxidize pentaamminepyridineruthenium(II) to pentaamminepyridineruthenium(III), so it can be reasoned by analogy that the result of the oxidation of the pentaamminepyrazineruthenium(II) is the corresponding Ru(III) complex in solution with an approximately equimolar quantity of Ce(III). Adjustment of the pH by adding constant volume aliquots of the Ru(III) solution to constant volumes of solutions of different acid concentrations resulted in little change in the spectra of the resulting solutions from pH 4.5 up to 1.0 M perchloric acid. However, in higher concentrations of perchloric acid, protonation of the pyrazine complex occurred as indicated by the bathochromic shift of the absorption band at 270 to 288 mμ. Half-protonation of the complex occurs at approximately 6 M perchloric acid. These results are summarized in Table VI.

Table VI. pK_a Measurements at 25°

Compound	$[H^+]_{1/2}$,[a] M	$-Log [H^+]_{1/2}$
$(NH_3)_5RuN\bigcirc N^{2+}$	0.0032[b]	2.5 ± 0.1
$(NH_3)_5RuN\bigcirc_N^{2+}$	0.93[c]	0.03 ± 0.05
$(NH_3)_5RuN\bigcirc_N^{2+}$	~1.0[c]	0.00
$(NH_3)_5RuN\bigcirc N^{3+}$	~6[b]	−0.8
Free ligands		
$N\bigcirc N$		2.33[d]
$N\bigcirc_N$		1.3[e]
$N\bigcirc N$		0.6[f]

[a] $[H^+]_{1/2}$ = acid concentration at [B] = [BH$^+$]. [b] HClO$_4$. [c] HCl. [d] Reference 8, p 286. [e] Reference 8, p 289. [f] Reference 8, p 299.

Experimental Section

Spectra. Ultraviolet and visible range spectra were measured using either a Cary 14 or a Cary 15 recording spectrophotometer. Unless otherwise noted, spectra were recorded with the cell com-

partment thermostated at 25°. Nuclear magnetic resonance spectra were obtained using a Varian A-60 spectrometer. The probe temperature for the nmr measurements was approximately 37°.

pH Measurements. pH measurements were made with a Beckmen Model G pH meter at 25° using a commercial standard buffer solution (pH 4.0) as the reference point.

Synthesis. The majority of the pentaammineruthenium(II) complexes of the substituted pyridines and related nitrogen aromatic heterocycles were prepared by method 1 described below. However, the complexes of pyridazine, pyrimidine, and s-triazine were synthesized by the milder procedure (method 2).

[(NH₃)₅Ru(py)](ClO₄)₂. Method 1. Chloropentaammineruthenium(III) dichloride was prepared by the method of Vogt, Katz, and Wiberley.[9] A 12.3-g portion of hexaammineruthenium-(III) trichloride (0.040 M) (Johnson, Matthey and Co., Ltd.) gave a yield of 11.0 g (94%) of chloropentaammineruthenium(III) dichloride after 4 hr refluxing in 200 ml of 6 M hydrochloric acid and recrystallization from 0.1 M hydrochloric acid. A 0.20-g portion of the chloropentaammineruthenium(III) dichloride (6.8 × 10⁻⁴ M) was digested with 4-ml of a solution of silver trifluoroacetate (prepared from 0.150 g of silver(I) oxide and just enough trifluoroacetic acid to dissolve it) to give after filtration a solution of chloropentaammineruthenium(III) trifluoroacetate. The ruthenium(III) complex was then reduced by reaction with zinc amalgam in the presence of a 30-fold excess (about 1 g) of pyridine. After approximately 20-min reaction time, saturated sodium perchlorate solution was added to the brilliant yellow reaction mixture to precipitate the yellow solid pentaamminepyridineruthenium(II) perchlorate (0.25 g, 80% yield), [(NH₃)₅Ru(py)](ClO₄)₂. The perchlorate salt[10] could be recrystallized from methanol–water mixtures with some loss in yield. Elemental analysis confirmed the suggested composition. *Anal.* Calcd for C₅H₂₀N₆Cl₂O₈Ru: C, 12.9; H, 4.3; N, 18.1; Cl, 15.3. Found: C, 12.9; H, 3.9; N, 17.9; Cl, 15.0.

[(NH₃)₅Ru(s-triazine)](ClO₄)₂. Method 2. A 0.10-g portion of chloropentaammineruthenium(III) dichloride (0.00034 M) was digested with 2 ml of silver trifluoroacetate solution (prepared from 0.075 g of Ag₂O) to give after filtration a solution of chloropentaammineruthenium(III) trifluoroacetate. Enough bicarbonate solution was added to neutralize the excess acid to approximately pH 5. Reduction of the ruthenium(III) by reaction with solid amalgamated zinc was accomplished under a purified nitrogen atmosphere. The resulting yellow pentaammineruthenium(II) solution was then transferred without exposure to air to a N₂-filled flask containing 0.100 g of s-triazine (0.012 M) (Aldrich). A deep red color was immediately apparent. After an approximately 10-min reaction time, saturated sodium perchlorate solution was added and the resulting red-orange precipitate collected on a sintered glass funnel. After recrystallization of this material twice from acetone–water mixtures, 0.07 g of [(NH₃)₅Ru(s-triazine)](ClO₄)₂ was obtained (44% yield). Elemental analysis confirmed the suggested composition. *Anal.* Calcd for C₃H₁₈N₈Cl₂O₈Ru: C, 7.72; H, 3.89; N, 24.04; Cl, 15.20. Found: C, 7.96; H, 3.82; N, 23.98; Cl, 15.11.

[(NH₃)₅Ru(py)]₂(S₂O₆)₃. A 0.030-g sample of Ag₂O (0.00013 M) was dissolved in 1 ml of water plus a minimum of trifluoroacetic acid. In this solution was digested a 0.117-g portion of solid pentaamminepyridineruthenium(II) perchlorate (0.00025 M). The solution was then filtered to remove the resulting metallic silver. Addition of several milliliters of saturated sodium dithionate solution gave the solid [(NH₃)₅Ru(py)]₂(S₂O₆)₃ (0.077 g, 60% yield) which was collected by filtration and washed with cold ethanol. *Anal.* Calcd for C₁₀H₄₀N₁₂O₁₈S₆Ru: C, 11.82; H, 3.96; N, 16.60; S, 19.00. Found: C, 11.6; H, 4.4; N, 15.80; S, 18.83. The elemental analysis is equally consistent with the dihydrate of the salt [(NH₃)₅Ru(py)]₂(S₂O₆)₃·2H₂O, for which the calculated ratios are: C, 11.43; H, 4.19; N, 16.04; S, 18.23.

Extinction Coefficient of the Pentaamminepyridineruthenium(II) Visible Absorption Band. A 100-ml solution containing a 5.00-mg portion of (NH₃)₅RuCl₃ (1.71 × 10⁻⁵ M) and approximately 2.5 ml of doubly distilled pyridine (reagent grade) was deoxygenated in an aluminum-foil-covered glass vessel by entraining with purified nitrogen. To this solution was added chromous perchlorate solution (0.023 M) in 20% excess of the amount needed to reduce the ruthenium(III) to ruthenium(II). Upon addition of the chromous

solution, the ruthenium(III) pyridine mixture turned yellow, indicating rapid formation of the (NH₃)₅Ru(py)²⁺ ion. After 5 min, a portion of the solution was transferred to a deoxygenated aluminum-foil-covered silica cell (1-cm path length), which was then sealed. All the mixing and transferring procedures were carried out in an all-glass apparatus under a purified nitrogen atmosphere to exclude air and covered with aluminum foil to reduce exposure to light. The spectrum of the product solution was recorded on a Cary 14 spectrophotometer within 10 min of chromous addition. From the value of the initial absorbance, the extinction coefficient at 408 mμ was calculated to be (7.78 ± 0.06) × 10³ M⁻¹ cm⁻¹. A 2% increase in absorbance was observed after storing the solution in the dark for 12 hr. Much greater optical density increases were observed when the solution was exposed to light for extended periods.

Discussion

Spectrum of (NH₃)₅Ru(py)²⁺. Several pieces of evidence presented above strongly indicate that the broad visible absorption bands observed in the spectra of the pentaammineruthenium(II) complexes of pyridine and of the other aromatic nitrogen heterocycles are metal-to-ligand charge-transfer absorption. These would be analogous to the assignment made for spectra of the iridium(III)–pyridine complexes.[3] Electron-withdrawing substituents on the pyridine ring result in substantial bathochromic shifts in the band maximum while electron-donating substituents result in hypsochromic shifts. Clearly the direction of these effects is consistent with the expected behavior of an electron transfer from the ruthenium(II) center into an unoccupied orbital (presumably the lowest lying π-antibonding orbital) of the pyridine. The same type of behavior would also be expected if a d–d transition internal to the ruthenium(II) center were in question, but the intensity of the observed absorption in this, an octahedral complex, argues against this interpretation. Furthermore, the behavior of the visible band in different solvents is strong evidence in support of the charge-transfer assignment. A metal-to-ligand electron transfer leads to a separation of charge in the excited state, and the energy required for this type of transition should be especially sensitive to the environment of the complex ion. In contrast, a d–d transition in a nonlabile complex should show little dependence on its external environment.

The spectra of the azine complexes provide an especially interesting probe into the nature of this absorption band. Wiberg and Lewis[7] have calculated the energies of the molecular orbitals of pyridine, pyrazine, pyrimidine, pyridazine, and s-triazine using the SCF-MO–LCAO method. They report that the polarographic half-wave potential of the one-electron reduction at a dropping mercury electrode in anhydrous dimethylformamide demonstrates a linear relationship with the calculated energy of the lowest unoccupied molecular orbital of the aromatic nitrogen heterocycle. The linear plot of the polarographic potential for the free ligand *vs.* the energy of the charge-transfer transition in Figure 3 for pyridine and the three diazines is perhaps fortuitous; however, dependence between the energy of the unoccupied orbitals and of the charge transfer is certainly expected. The linearity of the relationship implies that the effects of coordination on the unoccupied molecular orbitals of the ligand and on the ruthenium(II) d orbitals for the series must be constant, cancelled out, or insignificant.

(9) L. Vogt, T. Katz, and S. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).
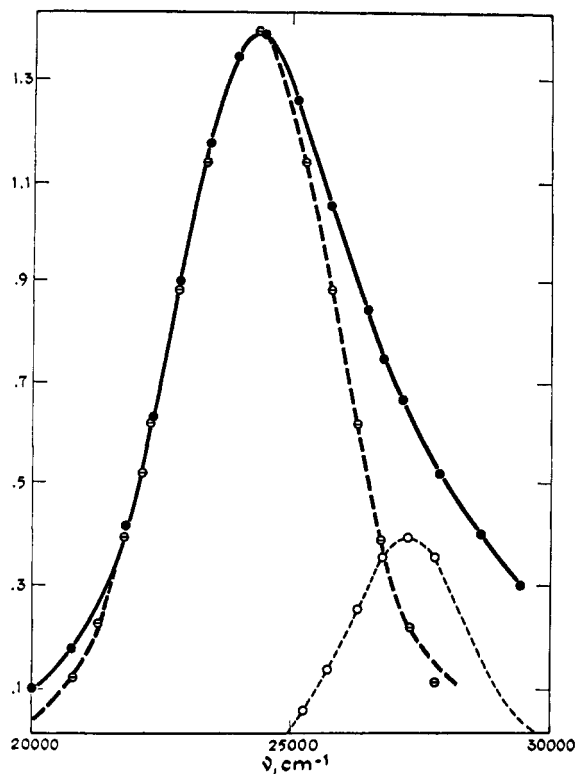(10) *Caution:* these perchlorate salts have proved to be explosive.

Figure 6. Gaussian analysis of the charge-transfer absorption band of $(NH_3)_5Ru(4\text{-pyridylcarbinol})^{2+}$. Solid line represents actual band; dashed lines represent mathematically resolved bands.

The absorption band at 244 mμ observed for the pentaamminepyridineruthenium(II) ion in aqueous solution probably reflects a transition between molecular orbitals essentially localized in the pyridine ligand.[11] The energy of the transition as well as its intensity are closely analogous to those for the free pyridine, protonated pyridine, and pentaamminepyridineruthenium(III). The $\sim$100-Å hypsochromic shift of the absorption maximum of the ruthenium(II)–pyridine complex ion from those of the other three may reflect some special interaction between the ruthenium(II) d orbitals and either the lowest lying antibonding or highest bonding molecular orbitals in the pyridine moiety, as will be discussed.

Protonation Equilibrium Constant for $(NH_3)_5Ru(pyrazine)^{2+}$. The one clear piece of evidence suggesting substantial ground-state interaction of the ruthenium(II) d orbitals with the π molecular orbitals of the aromatic heterocyclic ligand comes from the pK_a measurement for the pentaamminepyrazineruthenium(II) complex ion. The doubly charged cation (pK_a = 2.5 ± 0.1) is nearly two orders of magnitude *more basic* than the uncoordinated ligand. Since the protonation is accompanied by a large bathochromic shift (570 Å) of the charge-transfer band, the uncoordinated nitrogen base site of the bound ligand must be the active base. If protonation occurred at the filled d orbitals of the metal center, the result would be to raise, not lower, the energy of metal-to-ligand charge transfer. The electrostatic effect of coordination of the pyrazine to the positively charged pentaammineruthenium(II) center would be

(11) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p 191.

expected to make the remaining nitrogen less basic than the free ligand. In support of this conclusion, the pK_a of the pentaamminepyrazineruthenium(III) complex ion, $(NH_3)_5Ru(pyrazine)^{3+}$, is at least 1.5 orders of magnitude less basic than uncoordinated pyrazine[12] (Table VI). The inescapable conclusion is that the ruthenium(II) center participates in some special interaction with the ligand that more than compensates for the expected electrostatic effect. Such an interaction must be back-donation of electron density from the filled t_{2g} orbitals into the unoccupied π antibonding orbitals of the ligand. This kind of interaction will be much reduced for Ru(III) because the increased positive charge increases the energy required to remove d-electron density from the metal ion. The low basicity of the pyridazine complex (pK_a = 0.03) compared to the free ligand (pK_a = 2.33) can be explained in the light of the probable steric effect as well as the much greater electrostatic induction from the adjacent pentaammineruthenium(II). More significant is the lower basicity of the pentaamminepyrimidineruthenium(II) ion (pK_a = $\sim$0.0) compared to the free ligand (pK_a = 1.3). This can be explained on the basis that the symmetry of the ligand orbital which interacts with the t_{2g} orbitals is such that the coefficient at the *meta* position is very small, and the dominating contribution from metal coordination at that site is electrostatic.

It is possible to calculate the pK_a of the excited states of each of these complexes from the effect of protonation on the spectrum. The bathochromic shift of the visible absorption bands of the pyrazine, pyrimidine, and pyridazine complexes (Table V) is convincing evidence that the transition is indeed a metal-to-ligand charge transfer. The pK_a's of the charge-transfer excited state can be calculated from

$$pK_a^* = pK_a(gs) + \frac{2.86(\nu_1 - \nu_2)}{2.3RT} \qquad (3)$$

where pK_a^* is the charge-transfer excited state pK_a, pK_a(gs) is the ground state pK_a, ν_1 is the frequency in wavenumbers of the charge-transfer absorption maxima of the unprotonated form, and ν_2 is the frequency of the corresponding transition in the protonated form. In each case the pK_a^* of the pentaammineruthenium(II) complex of the diazines (pyrazine, 7.3; pyrimidine, $\sim$1.9, and pyridazine, 6.5) is substantially greater than pK_a(gs) (Table VI), suggesting that ligand electron density is significantly increased in the excited state.
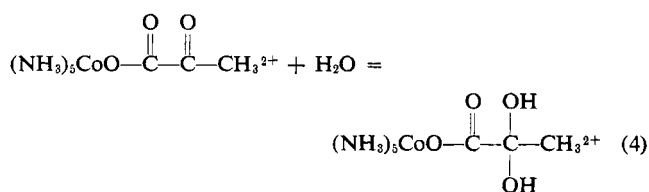
Band Shape of the Charge-Transfer Absorption. In the discussion above, the assumption has been made that the charge-transfer absorption maximum represents a single transition. However, the band is asymmetric and does not follow the Gaussian distribution curve.[13] Analysis of the band shape using the Gaussian formula (Figure 6) allows one to resolve at least one additional maximum in nearly every case, but not cleanly, and this additional band may well not be real. Charge-transfer absorptions are normally asymmetric. Briegleb[14] states that charge-transfer absorp-

(12) In fact, the effective acidity of perchloric acid solutions as concentrated as that required for half-protonation of pentaamminepyrazineruthenium(III) is substantially greater than the molarity (6 *M*): R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 81.

(13) C. Sandorfy, "Electronic Spectra and Quantum Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, p 104.

tions are usually unsymmetrical with the band at half-height being approximately 40% broader (in wavenumbers) on the high-energy side than on the low-energy side. The pentaammineruthenium(II) complexes of the aromatic heterocycles show asymmetry on the high-energy side ranging from 80% broader for the pyridine complex to 10% for the pyrazine complex. Consequently, while more than one transition may occur in the charge-transfer region, there is no unequivocal evidence supporting this possibility.

Aldehyde Hydration Equilibria. The low hydrate formation constant for the pentaammine(p-formyl-pyridine)ruthenium(II) ion ($K = 0.20$ in D_2O at 37°) compared to hydrate–aldehyde equilibrium constants for free p-formylpyridine ($K = 0.84$) and its protonated analog ($K = 0.88$) is further indication of a π interaction between the ruthenium(II) d orbitals and the aromatic ring. A purely electrostatic inductive effect on the equilibrium by metal ion coordination should be no greater than that of protonation. This fact was demonstrated in a study by Price[15] in measuring the consequence of coordination to pentaamminecobalt(III) on pyruvate hydrate formation.

$$(NH_3)_5CoO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3{}^{2+} + H_2O =$$

$$(NH_3)_5CoO-\overset{O}{\overset{\|}{C}}-\overset{OH}{\underset{OH}{\overset{|}{C}}}-CH_3{}^{2+} \quad (4)$$

The coordinated ligand ($K_4 = 0.38$ at 25° in D_2O) proved to be more hydrated than the pyruvate anion ($K' = 0.089$) but less so than pyruvic acid ($K'' = 1.03$). The Co(III) center, because of the increased positive charge, would not be expected to have significant back-bonding properties, and thus its influence should be purely electrostatic, and it is observed to be less than that of a proton. Presumably, coordination stabilizes the carbonyl form of the aldehyde over the hydrate form in the pentaammine(p-formylpyridine)ruthenium(II) ion because the carbonyl group but not the hydrate form can accept the electron density donated to the conjugated system by Ru(II).

A Molecular-Orbital Description of $(NH_3)_5Ru(py)^{2+}$. A simplified molecular-orbital description of the pentaamminepyridineruthenium(II) ion appears in Figure 7. At the left, the free pyridine π orbitals are represented, and on the right is a crystal field approximation for the ruthenium(II) 4d orbitals in an octahedral field of six ammonias. Perturbation of O_h symmetry to C_{2v} by substituting a pyridine for one of the ammonias (excluding any special π interaction) splits the d orbitals in the manner shown in column 3. Mixing of the $B_2(\pi^*)$ and the $B_2(d_{yz})$ as well as $A_2(\pi^*)$, $A_2(d_{xy})$, and $A_2(d_{x^2-y^2})$ orbitals and leaving the other orbitals essentially unchanged gives the order in column 2. The A_2–A_2 interaction is undoubtedly small because of the separation which reduces overlap between the d orbitals in the xy plane of the metal ion and the $A_2(\pi^*)$ orbital of the ligand. Consequently, the primary contribution to "back-bonding" must be the B_2–B_2 interaction mixing the lowest unoccupied ligand orbital with the d_{yz} orbital

(14) G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, p 46.

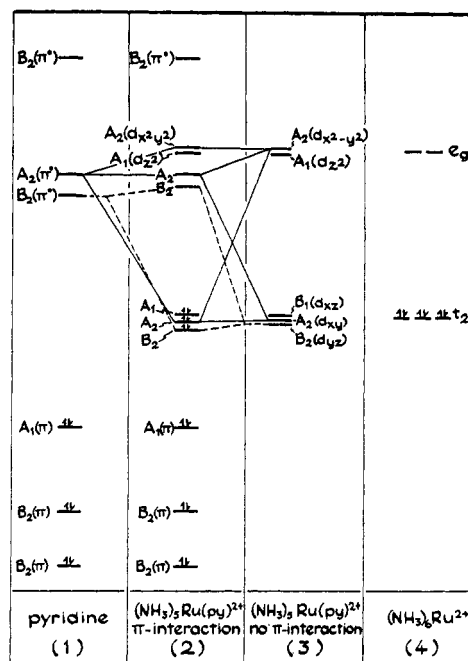(15) H. Price, Ph.D. Dissertation, Stanford University, 1966, p 21.

Figure 7. An orbital description of $(NH_3)_5Ru(py)^{2+}$.

to give two new molecular orbitals, one bonding but still primarily of metal d character and one antibonding but still primarily of ligand π^* character.

In the C_{2v} point group, all transitions except A_2–A_1 and B_2–B_1 are symmetry allowed; however, in the spectrum of the pentaamminepyridineruthenium(II) ion only two transitions are resolvable. One of these at 244 mμ is undoubtedly the equivalent of the $B_2(\pi^*) \leftarrow A_1(\pi)$ band observed at 253 mμ in the free ligand. The hypsochromic shift in its energy can be the result of the splitting due to the interaction of the B_2 orbitals.

Because of the sensitivity of the charge-transfer absorption to substituents in the *para* position of the pyridine ligand, the observed band must be a transition from either the $A_2(d_{xy})$ or $B_2(d_{yz})$ occupied orbitals into the $B_2(\pi^*)$ orbital (the $A_2(\pi^*)$ has a node through the *para* position). The complication arising here results from the fact that five transitions are symmetry allowed: $B_2(\pi^*) \leftarrow A_2(d_{xy})$, $B_2(\pi^*) \leftarrow B_2(d_{yz})$, $A_2(\pi^*) \leftarrow B_1(d_{xy})$, $A_2(\pi^*) \leftarrow A_2(d_{xy})$, and $A_2(\pi^*) \leftarrow B_2(d_{xz})$, while only one charge-transfer absorption is unequivocally identifiable. In the pyridine complex, $A_2(\pi^*)$ and $B_2(\pi^*)$ should have very similar energies in analogy to the orbital picture for the free ligand,[14] and the d_{xy}, d_{yz}, and d_{xz} orbitals are also not widely separated. Consequently, the reasonably broad charge-transfer band (width at half-height $= 4300$ cm^{-1}) could be a compilation of all five transitions. On the other hand, because of the much greater separation of the $A_2(\pi^*)$ and the $B_2(\pi^*)$ orbitals in free pyrazine,[16] the pentaamminepyrazineruthenium-(II) complex should demonstrate analogous separation of these orbitals. In this case one would expect significant broadening of the charge-transfer absorption or even resolution of the several allowed transitions. Since the width of the pyridine complex band is not substantially different from that of the pyrazine complex (width at half-height $= 3200$ cm^{-1}), it appears un-

(16) See Jaffé and Orchin, footnote b, Table I, p 366.

likely that transitions both to $A_2(\pi^*)$ and to $B_2(\pi^*)$ are included in the charge-transfer band. Because of the pattern of sensitivity to substituents, the acceptor orbital must be the $B_2(\pi^*)$. The two transitions $B_2(\pi^*) \leftarrow B_2(d_{yz})$ and $B_2(\pi^*) \leftarrow A_2(d_{xy})$ could both comprise the absorption band, as the splitting between the d orbitals is probably small and should be relatively insensitive to perturbations on the pyridine ring.

A Variable-Temperature Nuclear Magnetic Resonance Study of Complexes of Borane and Boron Trihalides with Acetone, Diethyl Ether, Dimethyl Ether, N,N-Dimethylformamide, Methanol, and Tetrahydrofuran

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Abstract: A proton and boron-11 chemical shift and coordination number study of complexes of diborane and the boron trihalides with dimethyl ether, diethyl ether, methanol, tetrahydrofuran, and, to a small extent, acetone and N,N-dimethylformamide has been completed. At low temperatures, separate proton resonance signals are observed for bulk solvent and solvent molecules complexed with the boron species. Coordination numbers were measured by the direct integration of the separate signals. The chemical shift separations for bulk and complexed solvent signals decreased in the order $BBr_3 > BCl_3 > BF_3 > BH_3$. An attempt is made to relate these separations to the coordinating abilities of the boron halides. The proton chemical shift data of the bases were correlated with some diborane ^{11}B and ^1H nuclear magnetic resonance results to obtain information concerning the species present in the ether–diborane solution.

Numerous attempts have been made to assess the relative strengths of donor–acceptor interactions in solution by nuclear magnetic resonance (nmr) chemical shift techniques. Although complexes of borane and the boron halides with a variety of Lewis bases have been the object of the most intensive study,[1-8] similar complexes of Ga(III)[9] and other ions[3,10] have been investigated by nmr methods. Using this technique, one relates the nmr signal displacements observed when the complexing species are mixed, often in another solvent, with the strength and the equilibrium of complex formation. However, at room temperature, only one set of resonance signals is usually observed for a particular ligand, since rapid exchange averages the signals arising from molecules in bulk medium and in the coordination shell of the complex. A study of the displacements of these averaged signals presents several disadvantages. The resonance positions of such signals are subject to all processes occurring in solution, including complex formation, ionic strength, temperature, and the nature of the solvent in which the complex is being studied. Further, systems which can be studied are limited to those that do not undergo reaction at room temperature. Such a limitation would have prevented the study of several of the boron halide complexes to be discussed here.

It has recently been demonstrated that in several systems involving complexes of Al(III) and other diamagnetic ions with N,N-dimethylformamide,[11,12] dimethyl sulfoxide,[13] and methanol[14,15] solvent exchange is slow enough to permit the observation of proton resonance signals for bulk solvent and molecules in the first coordination shell of the cation. In such systems, one obtains the most accurate value of the effect of complex formation on the chemical shift of a ligand proton. Integration of the separate resonance signals yields an unambiguous coordination number for the central ion.

We have applied this proton magnetic resonance technique to studies of complexes of borane and boron trihalides with several oxygen-containing organic bases, namely, dimethyl ether (Me_2O), diethyl ether (Et_2O), methanol (MeOH), tetrahydrofuran (THF), and, to a lesser extent, acetone and N,N-dimethylformamide (DMF). In addition, boron-11 room-temperature nmr

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