Charge Delocalization in Pentaammineruthenium(II) Complexes. I. Spectral Properties, Basicities, and Charge Densities by Nuclear Magnetic Resonance Spectroscopy

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Abstract: The monomeric pentaammineruthenium(II) complexes $(NH_3)_5RuL^{2+}$, with L = pyridine, pyrazine, 4-phenylpyridine, 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethylene, and the dimeric complexes $[(NH_3)_5Ru]_2L'^{4+}$, with L′ = pyrazine, 4,4′-bipyridine, and 1,2-bis(4-pyridyl)ethylene, have been synthesized and characterized. The visible absorption spectra of the complexes were studied to determine the relationship of the charge-transfer energies to electronic properties of the ligand and a reasonable molecular orbital scheme for the complexes was developed. The basicities of the pyrazine, 4,4′-bipyridine, and 1,2-bis(4-pyridyl)ethylene complexes were determined at 25° and an ionic strength of 0.05. The ligand pK's are: for 4,4′-bipyridine, pK_1 = 3.2 and pK_2 = 4.9; for 1,2-bis(4-pyridyl)ethylene, pK_1 = 4.4 and pK_2 = 5.9. The ruthenium complexes $(NH_3)_5RuL^{2+}$ had pK's of 2.6 for pyrazine, 4.4 for 4,4′-bipyridine, and 5.0 for 1,2-bis(4-pyridyl)ethylene. Nuclear magnetic resonance spectra of the series of complexes are reported, showing a net positive charge on the ligands due to complexation. This study points to an interpretation of the increased ligand basicity for complexed pyrazine as the Ru(II) allowing for easier delocalization of the protonated species as compared to the alternative explanation based on an increase in electron density of the free nitrogen *via* dπ–pπ back bonding.

This paper is the first of two papers discussing the chemistry of pentaammineruthenium complexes. The ruthenium ion provides a system with a varied chemistry that we have investigated and herein report.

The preparation of the pentaammineruthenium(II) complexes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)-ethylene apparently represent the first preparation of monomeric complexes of these ligands with transition metal ions. Both 4,4′-bipyridine[3–6] and 1,2-bis(4-pyridyl)ethylene[7–10] characteristically form polymeric species. The aquopentaammineruthenium(II) ion has only one labile position, however, and forms monomeric complexes when an excess of the ligand is used. The dimeric complexes with a pentaammineruthenium(II) group bonded to each of the nitrogen atoms can be prepared by using a 2:1 mole ratio of the aquopentaammineruthenium(II) ion to the ligand.

The visible absorption spectra of the monomeric complexes were obtained and the energies of the various bands (ligand–ligand and charge-transfer) were correlated with the ligand properties of observed polarographic half-wave potentials and calculated molecular orbital energies. These data are summarized by a reasonable molecular orbital scheme for this ruthenium system.

The nuclear magnetic resonance spectra of this series of complexes were determined and the results interpreted. A careful consideration of the change in chemical shifts of the ligands on complexation demonstrates that the ligands obtain a net positive charge on complexation and that the so-called "back bonding" into the ligand system does not appear to increase the electron density of the unprotonated complexes. These results also are employed to aid in the interpretation of ligand basicity studies and visible absorption spectra studies.

The basicities of the pentaammineruthenium(II) heterocyclic complexes, $(NH_3)_5RuL_2{}^+$, where L is pyrazine, 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethylene, were determined by spectrophotometric titrations. The basicities of the latter two ligands were determined *via* potentiometric titration. All the measurements were carried out at 25° and an ionic strength of 0.05. The ligand pK's are for 4,4′-bipyridine, pK_1 = 3.2 and pK_2 = 4.9; and for 1,2-bis(4-pyridyl)ethylene, pK_1 = 4.4 and pK_2 = 5.9. The ruthenium complexes $(NH_3)_5RuL^{2+}$ had pK's of 2.6 for pyrazine, 4.4 for 4,4′-bipyridine, and 5.0 for 1,2-bis(4-pyridyl)ethylene. The large increase in the ligand basicity of pyrazine on complexation, as previously noted by Taube and coworkers, is not obtained in the case of the ligands 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene. This study points toward an interpretation of the increased ligand basicity for complexed pyrazine as the Ru(II) ion allowing for a easier delocalization of the protonated species as compared to the alternative interpretation of an increase in electron density of the free nitrogen *via* dπ–pπ back bonding.

Experimental Section

Purification of Reagents. 4,4′-Bipyridine·2HCl (Aldrich) was dissolved in distilled water (about 10 ml/g of compound) and filtered by suction through a medium porosity fritted glass Büchner funnel. An equal volume of 4 *M* NaOH was then added, immediately precipitating the free base. The 4,4′-bipyridine was then recrystallized from hot (80°) distilled water (about 20 ml/g) until the crystals were very white. Generally, four or five recrystallizations were necessary to obtain the fine needle-shaped crystals (mp 69.8–71.3°). If the anhydrous compound was required, the recrystallized 4,4′-bipyridine was sublimed under reduced pressure using a 100° oil bath and a standard cold finger sublimation apparatus (mp 109.7–110.1°). The colorless, well-developed crystals which formed at

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the surface of the melt had a melting point of 149.5–150.2°. These crystals were of the space group $P2_1/C$ with two molecules per unit cell, showing that the molecules are planar in this crystal form.

1,2-Bis(4-pyridyl)ethylene (Aldrich) was purified by recrystallization from hot (80°) distilled water (about 25 ml/g) until very white needle-shaped crystals were obtained (mp 149.9–151.0°). Again, this required four or five recrystallizations. The sublimed compound had a melting point of 150.5–151.3°.

4-Phenylpyridine formed an orange oil when mixed with hot water. The boiling hot water was decanted from the oil and allowed to cool, giving white glossy platelet-shaped crystals (mp 73.0–73.6°), after several recrystallizations. This product was then sublimed as above but at a temperature of about 65° to give a compound with a melting point of 73.2–73.7°.

Argon, nitrogen, and helium were purified by passing the gas through a series of Drechsel bottles in which the first contained a solution of 1 *M* $Cr(ClO_4)_2$ in 1 *M* $HClO_4$ over amalgamated zinc, the second contained concentrated sulfuric acid, and the third served as a trap.

Preparation of Reagents. $[(NH_3)_5Ru^{III}Cl]Cl_2 \cdot {}^2/_3H_2O$ was prepared by two methods. The simpler method, which provided the better opportunity to obtain the product without the dichlorotetraammine complexes (both the cis and trans forms are orange) as impurities, was that of Vogt, *et al.*[11] $(NH_3)_6Ru^{III}Cl_3$ (Matthey-Bishop) (10 g) was dissolved in 250 ml of 6 *M* HCl and refluxed overnight producing a bright yellow precipitate. The product was recrystallized from hot 2 *M* HCl twice, washed with methanol, and dried, giving a yield of 75%.

In the less expensive method, after Allen, *et al.*,[12] 2.5 g of $RuCl_{3-4} \cdot 1\text{–}3H_2O$ (Alfa Inorganics) was dissolved in 30 ml of H_2O to which 29.6 ml of hydrazine hydrate (85%, Aldrich) was then carefully added, with stirring, through a reflux condenser. The brown mixture was refluxed overnight, producing a purple solution. After filtering 40 ml of 9 *M* HCl was added to the reaction mixture. Bright yellow crystals developed after 2 hr of refluxing. The product was purified by dissolving it in 1 *M* HCl and filtering into concentrated HCl to produce a bright yellow precipitate, washing with methanol, and drying in a vacuum dessicator. After two recrystallizations, the yield was 55%. Anal. Calcd for $[Ru^{II}(NH_3)_5Cl]Cl_2 \cdot {}^2/_3H_2O$: H, 5.38; N, 23.10; Cl, 34.65. Found: H, 5.24; N, 22.47; Cl, 34.84.

Amalgamated zinc was prepared by cleaning mossy zinc with 1 *M* $HClO_4$, mixing the zinc with a 2 *M* $HClO_4$ solution containing 2% as much mercuric chloride as zinc, and washing with 1 *M* $HClO_4$. The amalgamated zinc was stored under 1 *M* $HClO_4$.

Preparation of the Complexes. The complexes were synthesized by the general method of combining aquopentaammineruthenium(II) with the ligand in aqueous solution, in analogy to the method of Taube, *et al.*,[13,14] with modifications according to the properties of the particular ligand.

4,4′-Bipyridine, 1,2-bis(4-pyridyl)ethylene, and 4-phenylpyridine are nearly insoluble in cold water but dissolve quite readily in hot water. Hence, the complexes of these ligands were prepared by heating the solution containing the ligand and adding the aquopentaammineruthenium(II) ion solution slowly to prevent precipitation of the ligand. The 4,4′-bipyridine and 4-phenylpyridine complexes could be synthesized by suspending the ligand and $[(NH_3)_5Ru^{II}Cl]Cl_2$ over amalgamated zinc in H_2O which was continually flushed with purified argon or helium.[15] The 1,2-bis(4-pyridyl)ethylene complex, however, could not be prepared by allowing the ligand to be in contact with the amalgamated zinc. In this case, the ethylenic double bond was reduced, producing the 1,2-bis(4-pyridyl)ethane complex. In order to prevent formation of the dipentaammineruthenium(II) complexes of ligands with two available nitrogen atoms and to increase the rate of complex formation, an excess of ligand was used in all cases. In a typical preparation, 0.303 g (1 mM) of $[(NH_3)_5Ru^{III}Cl]Cl_2 \cdot {}^2/_3H_2O$ was suspended in 20 ml of deaerated, argon-saturated H_2O and was added to 10 g of amalgamated zinc which was covered by 15 ml of deaerated H_2O. In another section of the apparatus, 4 mM of the ligand was suspended in 20 ml of deaerated H_2O and heated to 80° with a hot H_2O bath. After about 15 min, the suspension of $[(NH_3)_5Ru^{III}Cl]Cl_2 \cdot {}^2/_3H_2O$ turned into a clear yellow solution, indicating the formation of $[(NH_3)_5Ru^{II}(H_2O)]^{2+}$. This solution was filtered through a medium porosity frit into the solution of the ligand, causing an immediate coloration (orange for the 4,4′-bipyridine and 4-phenylpyridine complexes and rose for the 1,2-bis(4-pyridyl)ethylene complex). The color increased in intensity for about 10 min, after which no further change was visually perceptible. The reaction was allowed to proceed for 30 min with continuous argon flushing. The reaction was tested for completion by comparing the visible absorption spectra several times during the course of the reaction.

The solution was then evaporated on a Rotavap equipped with a nitrogen inlet. The dried product was then handled in a nitrogen filled glovebox. It was first dissolved in 300 ml of hot, deaerated nitrogen saturated absolute ethanol, cooled to room temperature, and precipitated with 1 l. of deaerated anhydrous ethyl ether. A noticeable bathochromic shift occurs in ethereal solution for the 4,4′-bipyridine and the 1,2-bis(4-pyridyl)ethylene complex, making the suspensions bluish. The 4-phenylpyridine complex does not show such a pronounced color change. The product was collected by suction filtration and dried in a vacuum dessicator over Drierite.

The pyrazine complex was prepared by the same method as the 4,4′-bipyridine complex, but at room temperature.

The pyridine complex was prepared by combining 0.5 mM of $[(NH_3)_5Ru^{III}Cl]Cl_2 \cdot {}^2/_3H_2O$ and 0.5 mM of the ligand over 2 g of amalgamated zinc in 4 ml of deaerated D_2O and flushing with argon for 30 min. The solution was identified by its visible and ultraviolet absorption spectrum.[13]

The dipentaammineruthenium(II) complexes of pyrazine, 4,4′-bipyridine, and 1,2-bis(4-pyridyl)ethylene were prepared by adding 0.5 mM of aquopentaammineruthenium(II) in about 25 ml of H_2O or D_2O, which had been prepared from $[(NH_3)_5Ru^{III}Cl]Cl_2$ over amalgamated zinc, to a solution of 1.0 mM of the ligand in about 20 ml of H_2O or D_2O. In the cases of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene, the reaction solutions were maintained at 75° in order to dissolve the ligands. The progress of the reaction was followed spectrophotometrically, requiring about 8 hr for completion. The complexes were used in solution.

Analysis

Analysis of elemental composition was performed by Micro-Tech Laboratories of Skokie, Ill., and Chemalytics of Tempe, Ariz. The complexes were found to have reasonable carbon to nitrogen ratios, but low determinations for carbon, nitrogen, and hydrogen. Chloride determinations and neutron activation analysis results showed that $ZnCl_2$ was present in the samples. The presence of a small amount of $ZnCl_2$ should not interfere with the measurements made on the complexes and, hence, was grudgingly tolerated. Other methods, such as precipitation with a large counter ion, such as perchlorate, gave much worse results and were discarded.

Typical analysis results were: calculated for $RuC_{12}N_7H_{25}Cl_2$ (1,2-bis(4-pyridyl)ethylenepentaammineruthenium(II)) $C/N = 1.47$, found 1.51; calculated for $RuC_{10}N_7H_{23}Cl_2$ (4,4′-bipyridinepentaammineruthenium(II)) $C/N = 1.23$, found 1.25. The percentage of $ZnCl_2 \cdot xH_2O$ ranged from less than 1% to nearly 4%.

Acid Dissociation Constants of 1,2-Bis(4-pyridyl)ethylene. A 5×10^{-3} *M* solution of 1,2-bis(4-pyridyl)ethylene was prepared by suspending 0.0140 g of

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(15) The use of nitrogen as the "inert gas" has previously been reported for the synthesis of several pentaammineruthenium(II) complexes;[13] however, it has been shown that this leads to the formation of the nitrogenopentaammineruthenium(II) ion from the reaction of the aquopentaammineruthenium(II) ion from the reaction of the aquopentaamineruthenium(II) ion with molecular nitrogen [D. E. Harrison and H. Taube, *ibid.*, **89**, 5706 (1967)] and to the formation of μ-nitrogenobis(pentaammineruthenium(II)) from the reaction of the nitrogenopentaammineruthenium(II) ion and the aquopentaammineruthenium(II) ion [D. E. Harrison, E. Weissberger, and H. Taube, *Science*, 159, 320 (1968)].

the purified ligand in 400 ml of H_2O in a 500-ml volumetric flask, warming gently until the ligand had dissolved, cooling slowly to 25°, filling the flask to 500 ml, and mixing gently but thoroughly. No precipitation was evident during the titration. The HCl solution used for the titration was standardized by titration against a standardized NaOH solution. The ionic strength of all solutions was adjusted with KCl (Mallinkrodt, analytical reagent grade). The pH measurements were made with a Beckman expandomatic pH meter equipped with a combination glass calomel electrode. All measurements were made at 25°.

Acid Dissociation Constants of the Complexes. The measurements for the complexes were made on aliquots of a solution whose concentration was determined from the extinction of the solution at the wavelength of maximum absorbance of the unprotonated complex. Each aliquot was acidified by the addition of 0.050 *M* HCl or made alkaline by the addition of 0.050 *M* NaOH. The absorbances at the wavelength of maximum absorbance of the unprotonated complex and the protonated complex were then quickly measured using a thermostated compartment (at 25°) and the pH was then measured. Previous to the recording of the visible absorbances, the solutions were handled in a nitrogen filled glovebox and were sealed before removal. The ionic strength of the solutions of the complexes were maintained at 0.050 *M* with KCl.

Solution Preparation for Nmr Spectra. Solutions of the pentaammineruthenium(II) complexes of 4,4′-bipyridine, 4-phenylpyridine, and 1,2-bis(4-pyridyl)-ethylene were prepared by dissolving dried samples of the chloride salt of each complex in deaerated, helium saturated D_2O (Stohler Chemical Co., 99.8% D) and filtered through glass wool into an nmr tube. The resulting solutions were about 0.01 *M* in complex and required the use of a computer averaging unit for proper resolution of the nuclear magnetic resonance spectrum. The solutions were handled in a nitrogen atmosphere glovebox and were sealed before removal. 3-(Trimethylsilyl)propanesulfonic acid (DSS) (sodium salt, "Uvasol," E. Merck and Co.) was used as an internal standard.

Solutions of the pentaammineruthenium(II) complexes of pyridine and pyridine-*2-d*[16] were prepared by synthesizing the complexes in D_2O, placing the reaction apparatus in the glovebox, filtering into an nmr tube, and sealing the tube. These solutions were about 0.25 *M* in complex and could be employed without the use of the computer averaging unit.

Pyridine-*2-d* was synthesized by the method of R. A. Abramovitch, D. J. Kroeger, and D. Staskin from 2-pyridyllithium and D_2O. The 2-pyridyllithium was synthesized from freshly prepared *n*-butyllithium[17] and freshly vacuum distilled 2-bromopyridine (Reilly Tar Co.).

Nuclear Magnetic Resonance Spectra. The nuclear magnetic resonance spectra were recorded on a Varian A-60A or a Varian HA-100 nmr spectrometer equipped with a C-1024 time averaging computer. The frequency differences between the lock signal and the end points of the frequency field swept by the C-1024 time averaging unit were calibrated by averaging values obtained from a Hewlett-Packard V-4315 frequency counter for ten successive 100-sec sweeps (about 2–3 cps for the field widths used). The accuracy of the field width is about 1 cps and those of the individual peaks are on the order of 0.1 cps. The number of sweeps for each spectrum is noted with the spectrum.

The probe temperatures of the nmr spectrometers were 37 ± 1° for the HA-100 and 40 ± 1° for the A-60A.

Spectra of the ligands were taken in D_2O in order to minimize solvent effect differences between the ligands and the complexes. Supersaturated solutions of about 0.1 *M* were used to obtain the spectra of 4,4′-bipyridine, 4-phenylpyridine, and 1,2-bis(4-pyridyl)ethylene.

Correlation of Charge-Transfer Energies to Ligand Orbital Energies. A characteristic feature of the visible absorption spectra of the pentaammineruthenium(II) complexes of aromatic nitrogen heterocycles and the cyanopyridines is an intense absorption band with an extinction coefficient of approximately 10^4 M^{-1} cm^{-1} which follows the expected trend in energy shift with the nature of the substituent pyridine ligands corresponding to a metal-to-ligand charge transfer.[13] The more easily the ligand is reduced, as indicated by the magnitude of the Hammett ρ value for the substituent, the lower is the energy of the charge-transfer absorption. In these complexes, the situation is favorable for metal-to-ligand charge transfer due to facile oxidation of the Ru^{II} ion when it is not stabilized by several π electron-withdrawing groups (*e.g.*, for the couple $[Ru^{II}(NH_3)_6]^{2+}/[Ru^{III}(NH_3)_6]^{3+}$, the standard reduction potential is 0.103 V[18] and for the couple $[Ru^{II}(NH_3)_5(H_2)]^{2+}/[Ru^{III}(NH_3)_5(H_2O)]^{3+}$, the reduction potential = 0.16 V,[18] but for the couple $[Ru^{II}(2,2'\text{-bipyridine})_3]^{2+}/[Ru^{III}(2,2'\text{-bipyridine})_3]^{3+}$ the reduction potential = 1.347 V[19]) and to the relatively low reduction potentials of the nitrogen heterocycles used as ligands.[20] The absorption of these complexes in the ultraviolet region is generally very close in energy to the transitions of the free ligand and would seem, therefore, to arise from transitions between molecular orbitals which are essentially localized on the ligand.

Both the charge transfer and the ultraviolet spectra of pentaammineruthenium(II) complexes of aromatic nitrogen heterocycles which have a second nitrogen atom available for bonding undergo significant bathochromic shifts in acidic solution. This property was investigated to determine the dependence of the charge-transfer energy on the energy of the lowest unoccupied π antibonding molecular orbital. This property is compatible with the assignment of the transition in the visible absorption spectrum as a metal-to-ligand charge transfer since the association of the positively charged species should make the reduction of the ligand easier and, therefore, lower the charge-transfer energy. The protonation of the ligand would not be expected to affect the energy of the 4d orbitals of the ruthenium ion to nearly as large a degree.

The energy of the metal-to-ligand charge transfer should depend directly on the difference in energy of the "essentially ruthenium" molecular orbital from the unoccupied "essentially ligand" π antibonding molecu-

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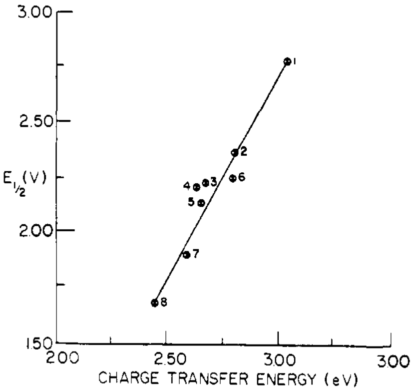

Figure 1. A plot of the polarographic half-wave potentials of some aromatic nitrogen heterocycles *vs.* the charge-transfer energy of the corresponding pentaammineruthenium(II) complex. See Table II for numbering scheme.

lar orbital to which it is promoted. If the energy of the ruthenium 4d orbitals is affected to very nearly the same degree by σ interaction with each of the ligands, the charge-transfer energy difference for complexes of different ligands will depend on the difference in energy of the π antibonding orbitals to which the electron is promoted and the difference is the amount of interaction of the π antibonding orbitals of the ligands and the ruthenium 4d t_{2g} orbitals which are of the proper symmetry to interact with them. If this is the case, the correlation expected between the charge-transfer energy and the molecular orbital energy might be shown by comparing the charge-transfer energy with the molecular orbitals energies determined by polarographic half-wave potentials, molecular orbital calculations, and ultraviolet absorption spectra.

Table I. Visible and Ultraviolet Absorption Spectra of Pentaammineruthenium(II) Complexes

Complex	—λ_{max}, nm (log ϵ_{max})—	
$(NH_3)_6Ru^{2+}$ [a]	400 (1.48)	275 (2.80)
$(NH_3)_5Ru(pyridine)^{2+}$ [b]	407 (3.89)	244 (3.66)
$(NH_3)_5Ru(pyrazine)^{2+}$ [b]	472 (4.03)	253 (3.65)
$(NH_3)_5Ru(4\text{-phenylpyridine})^{2+}$	446 (4.01)	289 (4.27)
$(NH_3)_5Ru(4,4'\text{-bipyridine})^{2+}$	478 (4.10)	348 (4.23)
$(NH_3)_5Ru(1,2\text{-bis(4-pyridyl)-ethylene})^{2+}$	508 (4.09)	382 (4.48)
$((NH_3)_5Ru)_2(pyrazine)^{4+}$ [c]	547 (4.47)	255 (4.08)
$((NH_3)_5Ru)_2(4,4'\text{-bipyridine})^{4+}$	542 (4.50)	250 (4.41)
$((NH_3)_5Ru)_2(1,2\text{-bis(4-pyridyl)-ethylene})^{4+}$	536 (4.54)	300 (4.48)

[a] T. Meyer, Ph.D. Dissertation, Stanford University, 1966, p 30. [b] P. Ford, De. F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968). [c] C. Creutz and H. Taube, *ibid.*, **91**, 3988 (1969).

The visible and ultraviolet absorption spectra of the pentaammineruthenium(II) complexes of 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethylene, 4-phenylpyridine, and the dipentaammineruthenium(II) complexes of 4,4'-bipyridine show an intense absorption in the visible region analogous to those of pentaammineruthenium(II) complexes of other aromatic nitrogen heterocycles which Taube, *et al.*, assigned to a metal-to-ligand charge transfer[13] and another intense absorption in the ultraviolet region which is very close in energy to the transitions of the ligands themselves. From the data which are summarized in Table I, it is evident that the charge-transfer energy varies significantly from one ligand to another. It was suggested by Taube, *et al.*, that a correlation exists between the polarographic half-wave potentials of the free ligands and the visible absorption band frequency of the pentaammineruthenium(II) azine complexes.[13] Such a dependence is indeed evident from the linear plot of the band frequency *vs.* the polarographic half-wave potentials shown in Figure 1 and the data in Table II.

Table II. Correlation between Charge-Transfer Energies of $(NH_3)_5Ru^{II}L^{2+}$ and the Polarographic $E_{1/2}$ of the Free Ligand

Ligand	λ_{max}, nm	ν, eV	$E_{1/2}$, V[a]
1. Pyridine	407[b]	3.04	2.76
2. Pyrimidine	445[b]	2.79	2.35
3. Pyridazine	467[b]	2.65	2.22
4. Pyrazine	472[b]	2.63	2.17
5. *sym*-Triazine	471[b]	2.64	2.10
6. 4-Phenylpyridine	446	2.79	2.24
7. 4,4'-Bipyridine	478	2.59	1.91
8. 1,2-Bis(4-pyridyl)ethylene	508	2.44	1.69

[a] B. J. Tabner and J. R. Jandler, *J. Chem. Soc. A*, 381 (1968). [b] P. Ford, De. F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1966).

To relate the band frequency to the energy of the π antibonding orbital to which the electron is promoted, it is necessary to relate the half-wave potential to the energy of this orbital. Maccoll[21] suggested that the polarographic reduction half-wave potential is directly related to the electron affinity of the molecule. The relationship may be expressed as

$$E_{1/2} = EA + F_{\text{solv}} - K$$

where $E_{1/2}$ is the polarographic half-wave potential, EA is the electron affinity of the neutral molecule, F_{solv} is the difference in free energy of solvation of the neutral and the mononegative ion, and K is a constant.[22] This result is based on the assumption that the process being observed in the polarographic reduction is a reversible, one-electron transfer to form a mononegative ion. The prediction of a linear relationship between electron affinities and half-wave potentials for a series of compounds assumes that entropy changes among the species being compared may be neglected.

If the half-wave potential is proportional to the energy of the lowest unoccupied molecular orbital, it is assumed that (1) the electron which is transferred to the neutral molecule in the polarographic reduction occupies the lowest unoccupied molecular orbital, (2) the change in the reduction potential is equal to the change in heat content, and (3) the change in heat content is equal to the energy required to place an electron from outside the molecule into the lowest available molecular orbital. The relationship between changes in electron affinity and the energy of the lowest unoccupied molecular orbital is predicted by simple Hückel molecular orbital theory and has been found empirically to be[20,22–27]

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$$\Delta EA = 0.5\Delta(\alpha + b\beta)$$

where α is the coulomb integral, β is the resonance integral, and b is a constant. This value for the correlation between the polarographic half-wave potential and the energy of the lowest unoccupied π antibonding molecular orbital calculated by Hückel LCAO molecular orbital methods was obtained for several series of conjugated hydrocarbons[22–27] and for nitrogen heterocycles.[20] The compounds in each series were expected to have similar solvation properties in the solvent used for the polarographic measurements.

When molecular orbital overlap is taken into consideration, the empirical value for the proportionality constant becomes 0.54–0.56.[23] Values in this range were obtained for hydrocarbons using an SCF–MO formulation for the calculations[28] and for azines[29] using the CNDO/2 calculations developed by Pople, Santry, and Segal. (These calculations were performed for this study without the knowledge that they were also being performed by Wiberg and Lewis. All results tabulated herein are the results obtained in this laboratory.)

In order to compare the charge-transfer energies of the pentaammineruthenium(II) complexes with the lowest unoccupied π antibonding molecular orbital of the ligand, CNDO/2 calculations were employed.[30] The correlation results in a least-squares slope of 0.56 (see Table III).

Table III. Correlation of Polarographic $E_{1/2}$ and CNDO/2 Lowest π^* Energies of Aromatic Nitrogen Heterocycles

	$E_{1/2}$, V[a]	CNDO/2 lowest π^*, eV
1. Pyridine	2.76	3.54
2. Pyrimidine	2.35	3.22
3. Pyrazine	2.17	3.02
4. 4-Phenylpyridine	2.24	2.49
5. 4,4′-Bipyridine	1.91	2.18
6. 1,2-Bis(4-pyridyl)ethylene	1.69	1.28

[a] B. J. Tabner and J. R. Yandler, *J. Chem Soc. A*, 381 (1968).

The correlation of $E_{1/2}$ *vs.* the charge-transfer energies of the pentaammineruthenium(II) complexes of the ligands studied (Figure 1) results in a significantly different slope (2.0) from that of $E_{1/2}$ *vs.* CNDO/2 orbital energies (0.56). The energy of the charge-transfer band decreases much more slowly than would be predicted from the decrease in the energy of the unoccupied π antibonding molecular orbital of the ligand. This difference between the expected trend of the charge-transfer energies and those observed is due to the fact that the lowest unoccupied π ligand orbital becomes lower in energy as it approaches the ruthenium orbitals; as this energy difference becomes smaller there is a stronger interaction between the ligand π^* orbitals and the ruthenium $d\pi$ orbitals. This interaction will increase the charge-transfer energy from what it would be if the orbitals were noninteracting. Table IV shows a comparison of the charge-transfer energies calculated on the basis of the differences in the energy of the lowest unoccupied molecular orbital of the ligands, assuming that the σ bonding of each of the ligands affects the ruthenium t_{2g} 4d orbitals in the same manner.

Table IV. Comparison of Charge-Transfer Energies Calculated from Changes in π^* Energies and Experimental Values[a]

	E_{CT}	ΔE_{π^*}[b]	$E_{CT(calcd)}$[c]	ΔE_{CT}
1. Pyridine	3.04		2.89[d]	0.15[d]
2. Pyrimidine	2.79	0.73	2.31	0.48
3. Pyridazine	2.65	0.96	2.08	0.57
4. Pyrazine	2.63	1.05	1.99	0.64
5. *sym*-Triazine	2.64	1.17	1.87	0.77
6. 4-Phenylpyridine	2.79	0.93	2.11	0.68
7. 4,4′-Bipyridine	2.59	1.52	1.52	1.07
8. 1,2-Bis(4-pyridyl)-ethylene	2.44	1.91	1.13	1.31

[a] All values in electron volts. [b] Difference in energy of the lowest π^* MO from that of pyridine calculated by $\Delta E_{1/2} = 0.56\ \Delta E_{\pi^*}$. [c] Assuming that energy differences of the $Ru^{II}d^2_{xy}$, d^2_{xz}, and d^2_{yz} orbitals arise only from d-π^* interaction. [d] Estimated graphically.

A molecular orbital scheme which is compatible with these results is shown in Figure 2. Only those molecular orbitals of low enough energy to interact significantly with the ruthenium $4d_{xy}$, $4d_{xz}$, and $4d_{yz}$ orbitals are shown. The interaction of the $A_2(d_{x^2-y^2})$ with the $A_2(\pi^*)$ or $A''(\pi^*)$ orbital is not shown to simplify the figure. Splitting is assumed to result in symmetric displacement about the average energy of the interacting molecular orbitals. The differences in energy among the d_{xy}, d_{xz}, and d_{yz} orbitals without π interaction should be very small. For the $d_{x^2-y^2}$ and d_{z^2} orbitals, the difference in energy without π interaction is approximately $^2/_3\delta\sigma$ where $\delta\sigma$ is the difference in the bonding energy between the ligand which perturbs the octahedral symmetry (the aromatic nitrogen heterocycle) and the ligand (NH_3) which occupies the other five coordinate positions in the distorted octahedral complex under consideration.[31] The difference in σ bonding between NH_3 and the aromatic nitrogen heterocycles is probably not very great and differences in the value for the various heterocycles should be very small. Of the six possible transitions between the perturbed ruthenium d_{xy}, d_{xz}, and d_{yz} orbitals and the two lowest π antibonding orbitals, only one, the $B_2(\pi^*) \leftarrow B_1(d_{xz})$ transition in the pyridine complex and the $B_1(\pi^*) \leftarrow B_2(d_{yz})$ transition in the pyrazine, 4-phenylpyridine, and 4,4′-bipyridine complexes, is symmetry forbidden. In the 1,2-bis(4-pyridyl)ethylene complex, all four transitions are symmetry allowed. Transfer to the $A_2(\pi^*)$ orbital of the ligands is unlikely since this orbital has a node in the para position and the charge-transfer band of substituted pyridines has been shown to be very sensitive to the nature of the substituent in the para position. The similarity of the widths of the charge-transfer absorptions at half-height (pyridine = 4300 cm^{-1}, pyrazine = 3200 cm^{-1}, 4-phenylpyridine = 4450 cm^{-1}, 4,4′-bipyridine = 3850 cm^{-1}, and 1,2-bis(4-pyridyl)ethylene = 4150 cm^{-1}) when compared to the

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(25) A. T. Watsen and F. A. Matsen, *J. Chem. Phys.*, **18**, 1305 (1950).

(26) G. J. Hoijtink and J. Van Schooten, *Recl. Trav. Chim. Pays-Bas*, 71, 1089 (1952); 72, 691, 903 (1953).

(27) I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954).

(28) M. J. S. Dewar, J. A. Hashmall, and N. Trinajastic, *J. Amer. Chem. Soc.*, **92**, 5555 (1970).

(29) K. B. Wiberg and T. P. Lewis, *ibid.*, **92**, 7154 (1971).

(30) The CNDO/2 program of George Segal was supplied by the Quantum Chemistry Program Exchange at Indiana University. It employs the procedure outlined in (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, **43**, S1376 (1965); (c) *ibid.*, **44**, 3289 (1966).

(31) D. S. McClure, "Advances in the Chemistry of Coordination Compounds," Macmillan, New York, N. Y., 1961, p 498.

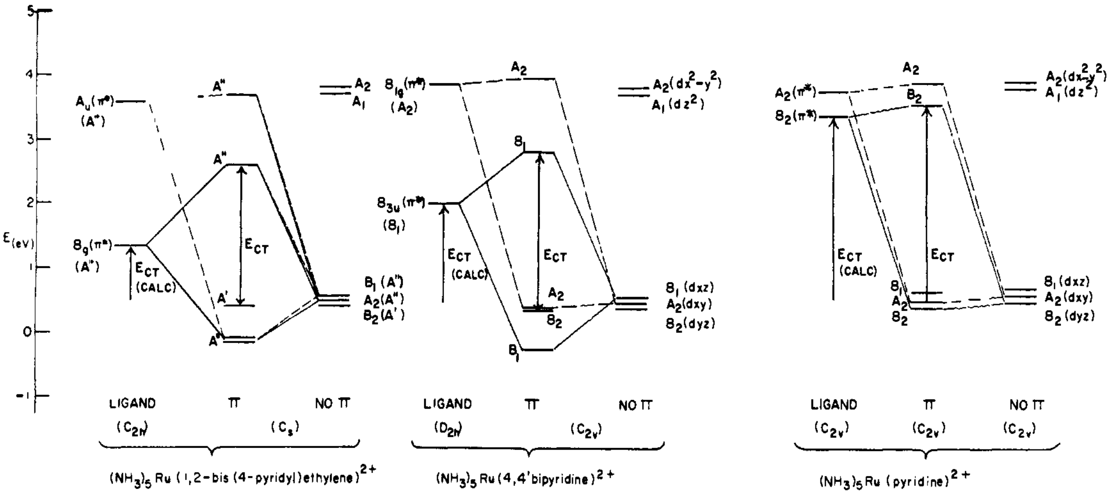


Figure 2. A molecular orbital scheme for the pentaammineruthenium(II) complexes of pyridine, 4,4′-bipyridine, and 1,2-bis(4-pyridyl)-ethylene. The similar schemes for the pyrazine and 4-phenylpyridine complexes follow the linear energy relationship (*vide infra*) and are omitted for clarity.

large difference in the energies of the lowest two unoccupied molecular orbitals of the ligands also indicates that transitions only occur to the lower unoccupied orbital, as suggested by Taube, *et al.*[13]

Protonation of those complexes which have a second nitrogen atom available for bonding results in a lowering of the energy of both the visible and ultraviolet absorption bands (Table V). CNDO/2 calculations of monoprotonated pyrazine and 4,4′-bipyridine indicate that the difference in energy between the highest occupied π molecular orbital and the lowest unoccupied π antibonding orbital is indeed less for the protonated species than for the free ligand. The ultraviolet absorption in the complex, of course, measures the transition between essentially ligand molecular orbitals which have interacted with the ruthenium d orbitals.

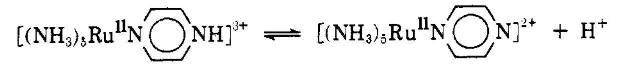
Table V. Visible and Ultraviolet Absorption Changes of $(NH_3)_5Ru^{II}L^{2+}$ Complexes Due to Protonation

Ligand	Visible absorption			Ultraviolet absorption		
	λ_{max}, nm (log ϵ_{max})	E, eV	ΔE, eV	λ_{max}, nm (log ϵ_{max})	E, eV	ΔE, eV
Pyrazine	472 (3.99)	2.63		253 (3.65)	4.90	
Pyrazine (H+)	529 (4.08)	2.34		270 (3.70)	4.59	
			−0.29			−0.31
4,4′-Bipyridine	478 (4.10)	2.59		248 (4.23)	5.00	
4,4′-Bipyridine (H+)	563 (4.14)	2.20		260 (4.27)	4.77	
			−0.29			−0.23
1,2-Bis(4-pyridyl)ethylene	508 (4.09)	2.44		283 (4.48)	4.35	
1,2-Bis(4-pyridyl)ethylene (H+)	578 (4.14)	2.14		310 (4.53)	4.00	
			−0.30			−0.35

Since all of the π antibonding molecular orbitals have lower energy due to protonation, the entire ultraviolet band is shifted significantly. The charge-transfer band of the protonated complexes is affected to nearly the same degree of the ultraviolet absorption, as expected from the molecular orbital scheme invoked for the unprotonated complexes. A transition from $A_2(d_{xz})$ orbital which is essentially unperturbed by π interaction to the lowered $B_1(\pi^*)$ orbital for pyrazine and 4,4′-bipyridine complexes and the analogous $A''(\pi^*) \leftarrow A(d_{yz})$ transition for the 1,2-bis(4-pyridyl)-ethylene complex should be lower in energy than the charge-transfer bands in the unprotonated complexes if the occupied orbitals of the ligand and the ruthenium ion are not lowered to as great an extent as the unoccupied π antibonding orbitals, as indicated by the results of the CNDO/2 calculations.

Changes of Ligand Basicity on Complexation

One of the interesting properties of pentaammineruthenium(II) complexes of aromatic nitrogen heterocycles is the enhancement of the basicity of pyrazine by two orders of magnitude on complexation.[13] This indicates that there is either an increase in the electron density of the nitrogen atom which becomes protonated caused by back bonding from the ruthenium ion to the ligand, *or* that the pentaammineruthenium(II)–N bond is more effective in delocalizing the positive charge of the protonated complex than the nitrogen atom of the free ligand. Either of these effects will make the dissociation of the protonated complex



less favorable than the analogous dissociation of the protonated ligand.

The basicities of azines are not solely dependent on the electron density of the nitrogen atom, as shown by comparison of electron densities and p*K* values in Table VI. This comparison shows, for example, that pyridine is a stronger base than pyrimidine, even

Table VI. Comparison of Excess Electron Densities and Basicities of Nitrogen Heterocycles

	Excess electron density on nitrogen[a]		
	NQR	CNDO/2	$\mathrm{p}K_a$[b]
Pyridine	1.00[c]	1.00	5.23[g]
Pyrimidine	1.10[d]	1.15	1.30[g]
Pyridazine	0.36[d]	0.07	2.33[g]
Pyrazine	0.92[d]	0.73	0.6[g]
4-Phenylpyridine		1.02	5.55[h]
4,4′-Bipyridine	0.99[e]	0.99	4.82[i]
1,2-Bis(4-pyridyl)ethylene		1.17[f]	5.7[j]

[a] Relative to the electron density for pyridine. Both NQR and CNDO/2 results are better for relative values than absolute ones. NQR is more reliable than CNDO/2. [b] For compounds with two nitrogens available for protonation, the p*K* for the dissociation of the monoprotonated species is given. [c] E. A. C. Lucken, *Trans. Faraday Soc.*, **57**, 729 (1961). [d] E. Schampp and P. J. Bray, *J. Chem. Phys.*, **46**, 1186 (1967). [e] H. Negita, M. Hayashi, T. Hirakawa, and H. Kawata, *Bull. Chem. Soc. Jap.*, **43**, 2262 (1970). [f] David G. Whitten, private communication. [g] A. Albert and J. Phillips, *J. Chem. Soc.*, 1294 (1956). [h] D. Feakin, S. N. Nagi, R. A. Shaw, and P. Watson, *ibid.*, *A*, 10, (1968). [i] T. R. Mustrave and Matson, *Inorg. Chem.*, **7**, 1433 (1968). [j] From K_2 *vs.* $\sqrt{\mu}$ extrapolated to $\mu = 0$.

though the pyrimidine nitrogen has a greater electron density than the pyridine nitrogen. Evidently, the azine basicity depends on other factors, such as the capacity of the ring to delocalize the positive charge introduced by the proton. The C–H group delocalizes positive charge better than the nitrogen atom, making pyridine a better base than pyrimidine.

A study of the effect of the pentaammineruthenium(II) moiety on other aromatic nitrogen heterocycles with terminal nitrogen atoms available for protonation was undertaken to investigate the nature of the interaction which leads to the increased basicity of the pyrazine complex.

The p*K*'s of the pentaammineruthenium(II) complexes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene were conveniently measured by plotting the absorbance at the wavelength of maximum absorbance of the protonated complex divided by the absorbance at the wavelength of maximum absorbance of the free complex *vs.* pH. By using the change in the combined absorbances rather than the change in each quantity separately, errors in the measurements of the concentration of the samples were avoided.

The p*K*'s of 4,4′-bipyridine were previously determined by P. Krumholz[32] and were much improved by T. R. Musgrave and C. E. Mattson.[3] Some improvement in the determination of its $\mathrm{p}K_1$ value was made by avoiding an approximation made in their study. A rather simple computer calculation was used to calculate the least-squares plot used to determine $\mathrm{p}K_2$ and to calculate the $\mathrm{p}K_1$ value. The $\mathrm{p}K_1$ and $\mathrm{p}K_2$ values of 1,2-bis(4-pyridyl)ethylene were determined by potentiometric titration.

The acid dissociation constants were defined as

$$K_1 = \frac{[\mathrm{H^+}][\mathrm{HB^+}]}{[\mathrm{H_2B^{2+}}]} \quad K_2 = \frac{[\mathrm{H^+}][\mathrm{B}]}{[\mathrm{HB^+}]}$$

where B is the free 4,4′-bipyridine, $\mathrm{HB^+}$ is the monoprotonated species, and $\mathrm{H_2B^{2+}}$ is the diprotonated species. The total concentration of all species of 4,4′-bipyridine during the titration is given by

$$C_\mathrm{B} = [\mathrm{B}] + [\mathrm{HB^+}] + [\mathrm{H_2B^{2+}}]$$

The total concentration of hydrogen ion added is given by

$$C_\mathrm{H} = [\mathrm{H^+}] + [\mathrm{HB^+}] + 2[\mathrm{H_2B^{2+}}]$$

By measuring the pH and volume of acid added and by knowing the amount of base in the solution and the concentration of the acid added, these quantities are easily determined. A fraction, *a*, representing the average number of hydrogen ions bound per 4,4′-bipyridine was defined as

$$a = \frac{C_\mathrm{H} - [\mathrm{H^+}]}{C_\mathrm{B}} = \frac{[\mathrm{HB^+}] + [2\mathrm{H_2B^{2+}}]}{[\mathrm{B}] + [\mathrm{HB^+}] + [\mathrm{H_2B^{2+}}]}$$

It was assumed that when $a = 0.5$, the quantity $\mathrm{H_2B^{2+}}$ was negligible and the expression for *a* could be simplified to

$$a = 1/((K_2/[\mathrm{H^+}]) + 1) \qquad (1)$$

leading to the equation

$$a/(1 - a) = (1/K_2)[\mathrm{H^+}]$$

Plotting $a/(1 - a)$ *vs.* $\mathrm{H^+}$ should give a straight line with a slope of $(1/K_2)$ and an intercept of zero. This approximation is shown to be reasonable by using Musgrave and Mattson's data to estimate the difference between the "real" K_2 and the approximated expression. For $\mu = 0.05$, $K_2 = 1.4 \times 10^{-5}$, $K_1 = 6.5 \times 10^{-4}$, and $[\mathrm{H^+}] = 5 \times 10^{-6}\ M$

$$[\mathrm{HB^+}]/[\mathrm{H_2B^{2+}}] = K_1/[\mathrm{H^+}] = 130$$

i.e., there is less than 1% as much of the diprotonated species as the monoprotonated species when $a = 0.5$. By using the approximate value for K_2, the difference between the real K_2 and the approximate K_2 can be approximated. Using the same values as above, for a real K_2 value of 1.4×10^{-5}, the approximate value is

$$K_2 = [\mathrm{H^+}]\left(\frac{1-a}{a}\right) = [\mathrm{H^+}]\frac{[\mathrm{B}] - [\mathrm{H_2B^{2+}}]}{[\mathrm{HB^+}] + 2[\mathrm{H_2B^{2+}}]} = 1.38 \times 10^{-5}$$

The difference then is 1.4%. This difference is within experimental error.

In order to calculate K_1, Musgrave and Mattson stated that B was negligible when $a > 1.0$. In that case, *a* could be rearranged to give

$$(a - 1)/(2 - a) = (1/K_1)[\mathrm{H^+}]$$

giving linear plots of the left side of the expression against $\mathrm{H^+}$ with a slope of $1/K_1$. To test the approximation, the data above with $\mathrm{H^+} = 5 \times 10^{-4}$ (to be in the range in which $a = 1.0$) gives the following for a real K_1 of 6.5×10^{-4}

$$\text{approximate } K_1 = [\mathrm{H^+}]\left(\frac{2-a}{a-1}\right) = [\mathrm{H^+}]\frac{2[\mathrm{B}] + [\mathrm{HB^+}]}{[\mathrm{H_2B^{2+}}] - [\mathrm{B}]}$$

$$\frac{[\mathrm{HB^+}]}{[\mathrm{H_2B^{2+}}]} = \frac{K_1}{[\mathrm{H^+}]} = 1.3$$

$$[\mathrm{B}] = K_2\frac{[\mathrm{HB^+}]}{[\mathrm{H^+}]} = 2.8 \times 10^{-2}[\mathrm{HB^+}]$$

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[32] P. Krumholz, *J. Amer. Chem. Soc.*, 74, 3847 (1951).

Table VII. pK_1 and pK_2 Values of 1,2-Bis(4-pyridyl)ethylene

μ	pK_2	p$K_2 \pm \bar{s}$	pK_1	p$K_1 \pm \bar{s}$
0.0250	5.86 ± 0.00		4.39 ± 0.05	
		5.84 ± 0.02		4.45 ± 0.05
	5.83 ± 0.00		4.50 ± 0.03	
0.0500	5.93 ± 0.01		4.45 ± 0.03	
	5.84 ± 0.01	5.89 ± 0.03	4.45 ± 0.03	4.45 ± 0.03
	5.88 ± 0.00		4.45 ± 0.03	
	5.91 ± 0.01			
0.1000	5.90 ± 0.00		4.55 ± 0.03	
	5.94 ± 0.01	5.92 ± 0.02	4.49 ± 0.03	4.49 ± 0.04
	5.92 ± 0.00		4.44 ± 0.04	

i.e., [B] is about 3% of the magnitude of the other species even where $a = 1.65$

approximate K_1 =

$$[\mathrm{H}^+]\frac{0.0560[\mathrm{HB}^+] + [\mathrm{HB}^+]}{\dfrac{[\mathrm{HB}^+]}{1.3} - 2.8 \times 10^{-2}[\mathrm{HB}^+]} = 7.11 \times 10^{-4}$$

giving a 9.2% difference between the real value and the approximated value. This demonstrates that even though these plots are linear (see Figure 1 and 2) the resulting K's can be improved by calculating K_1 without using the approximation.

From the definitions of C_B and C_H, we arrive at

$$[\mathrm{HB}^+] = 2C_\mathrm{B} - 2[\mathrm{B}] - C_\mathrm{H} + [\mathrm{H}^+]$$

by substituting the expression for [B] from the definition of K_2

$$[\mathrm{HB}^+] = 2C_\mathrm{B} - \frac{2K_2 + [\mathrm{HB}^+]}{[\mathrm{H}^+]} - C_\mathrm{H} + [\mathrm{H}^+] = (2C_\mathrm{B} - C_\mathrm{H}[\mathrm{H}^+])([\mathrm{H}^+]/(2K_2 + [\mathrm{H}^+]))$$

and

$$[\mathrm{H_2B}^{2+}] = C_\mathrm{B} - [\mathrm{B}] - [\mathrm{HB}^+] = \frac{K_2 + [\mathrm{HB}^+]}{[\mathrm{H}^+]} - [\mathrm{HB}^+] = C_\mathrm{B} - [\mathrm{HB}^+]\left(1 + \frac{K_2}{[\mathrm{H}^+]}\right)$$

using the expression for [HB+] from above

$$[\mathrm{H_2B}^{2+}] = C_\mathrm{B} - (2C_\mathrm{B} - C_\mathrm{H} + [\mathrm{H}^+])([\mathrm{H}^+]/(2K_2 + [\mathrm{H}^+]))\left(\frac{[\mathrm{H}^+] + K_2}{[\mathrm{H}^+]}\right) = C_\mathrm{B} - (2C_\mathrm{B} - C_\mathrm{H} + [\mathrm{H}^+])\left(\frac{K_2 + [\mathrm{H}^+]}{2K_2 + [\mathrm{H}^+]}\right)$$

Now

$$K_1 = \frac{[\mathrm{H}^+][\mathrm{HB}^+]}{[\mathrm{H_2B}^{2+}]} = \frac{[\mathrm{H}^+]^2(2C_\mathrm{B} - C_\mathrm{H} + [\mathrm{H}^+])\left(\dfrac{1}{2K_2 + [\mathrm{H}^+]}\right)}{C_\mathrm{B} - (2C_\mathrm{B} - C_\mathrm{H} + [\mathrm{H}^+])\left(\dfrac{K_2 + [\mathrm{H}^+]}{2K_2 + [\mathrm{H}^+]}\right)}$$

$$K_1 = \frac{[\mathrm{H}^+]\{2C_\mathrm{B} - C_\mathrm{H} + [\mathrm{H}]\}}{K_2C_\mathrm{H} + [\mathrm{H}^+]C_\mathrm{H} - [\mathrm{H}^+]C_\mathrm{B} - K_2[\mathrm{H}^+] - [\mathrm{H}^+]^2} \quad (2)$$

A computer program was used to evaluate K_1 using the least-squares value of K_2 as obtained from eq 1.[33]

The results of the values of the pK_1 and pK_2 of 1,2-bis(4-pyridyl)ethylene are provided in Table VII. The value of the pK_2, the negative of the logarithm of the equilibrium constants for the dissociation of the monoprotonated ligand, is found to be close to that of pyridine (pK_a = 5.23)[34] as expected from their structural similarity. The excess electron density at the nitrogen is possibly somewhat greater (by CNDO/2 calculations)[35] for the 1,2-bis(4-pyridyl)ethylene than for pyridine and it would be expected to have greater charge delocalization ability due to its extended conjugated system, both leading to an increase in its basicity and, hence, a higher pK value. The pK_1 value for the 1,2-bis(4-pyridyl)ethylene is expected to be lower than the pK_2 value both from a statistical consideration (the bound proton may leave from either equivalent nitrogen of the diprotonated species and has only one site available for its return, while in the equilibrium of the dissociation of the monoprotonated species, the proton leaves from one site and may return to either of the two equivalent sites) and from the electrical considerations in the equilibrium of the diprotonated species, the proton leaves a dipositive species or approaches a monopositive species, a much less favorable situation than in the equilibrium of the monoprotonated species in which the leaving proton dissociates from a monopositive species and the incoming proton approaches a neutral free base.

The plots of the absorbance at the wavelength of the maximum absorbance of the protonated complex divided by the absorbance at the wavelength of maximum absorbance of the charge-transfer band of the free complex against pH for the pentaammineruthenium(II) complexes of 4,4′-bipyridine are shown in Figure 3. The horizontal line on Figure 3 represents the point in the titration when the concentration of the protonated complex is equal to the concentration of the unprotonated complex, which is the point at which the pH = pK_a.[36] The value will obviously depend upon the degree to which the charge-transfer bands of the protonated and unprotonated species overlap one another at the two wavelengths being compared in the ratio. In the determination of the pK_a of the pyrazinepentaammineruthenium(II) complex, Taube, *et al.*, used the value of $\epsilon(\mathrm{BH})_{\lambda_{\max}\mathrm{BH}^+}/$

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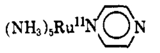
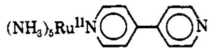
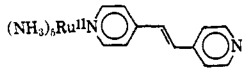
(33) For computer program and data see the thesis of David K. Lavallee, The University of Chicago, 1971.

(34) A. Albert and J. Phillips, *J. Chem. Soc.*, 1294 (1956).

(35) Provided by David G. Whitten of the University of North Carolina, from a paper of George Segal supplied through the Quantum Chemistry Exchange Program at Indiana University.

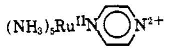
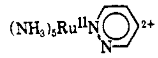
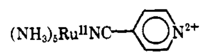
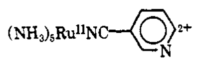
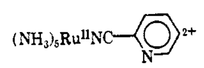
(36) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, 9, 495 (1970).

Table VIII. pK Values of Para Diazo Heterocycles and Corresponding Pentaammineruthenium(II) Complexes[a]

	pK_2 of ligand	pK_1 of ligand	pK of complex	pK^* of complex[b]
	0.6 ± 0.2[c]	−5.8 ± 0.1[d]	2.6 ± 0.1	7.4 ± 0.1
	4.9 ± 0.1[e]	3.2 ± 0.2[f]	4.4 ± 0.1	11.1 ± 0.1
	5.9 ± 0.1	4.4 ± 0.1	5.0 ± 0.1	10.1 ± 0.1

[a] Values for an ionic strength of 0.050. [b] Using $pK^* = pK_{(gs)} + 2.86(\nu_1 - \nu_2)/2.3RT$. [c] A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 2240 (1948). [d] A. S. Chia and R. F. Trimble, Jr., *J. Phys. Chem.*, **65**, 863 (1961). [e] T. R. Musgrave and C. E. Mattson, *Inorg. Chem.*, **7**, 1433 (1968). [f] The recalculated value, using the data in ref *e*.

Table IX. pK_a Values of Some $(NH_3)_5Ru^{II}L^{2+}$ Complexes[a]

Complex	pK_a of complex[b]	pK_a of ligand[c]	ΔpK_a
	2.5 ± 0.1[d]	0.65[e]	1.85
	0.03 ± 0.05[d]	2.33[f]	−2.03
	0.00[d]	1.3[f]	−1.3
	2.72 ± 0.12[g]	1.90[h]	0.82
	1.75 ± 0.05[g]	1.36[h]	0.39
	0.80 ± 0.10[g]	−0.26[h]	1.06

[a] At 25°, μ unspecified. [b] $pK_a = -\log [H^+]_{1/2}$ where $[H^+]_{1/2}$ = acid concentration at which B = BH$^+$. [c] If there are two pK_a's for a ligand, the value is for the dissociation of the monoprotonated species. [d] P. Ford, De. F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968). [e] A. Chia and R. F. Trimble, Jr., *J. Phys. Chem.*, **65**, 863 (1961). [f] A. Albert and J. Phillips, *J. Chem. Soc.*, 1294 (1956). [g] R. E. Clarke and P. Ford, *Inorg. Chem.*, **9**, 495 (1970). [h] S. F. Mason, *J. Chem. Soc.*, 1247 (1959).

$\epsilon(B)_{\lambda\ \max B}$ rather than

$$\frac{\epsilon(BH)_{\lambda\ \max BH^+} + \epsilon(B)_{\lambda\ \max BH^+}}{\epsilon(BH)_{\lambda\ \max B^+} + \epsilon(B)_{\lambda\ \max B}}$$

to determine the value of the pH at which the two species had the same concentration. This was incorrect, but the value obtained is nearly the same as the properly determined one. The main reason for the redetermination of the pK_a of the pyrazine complex in this study was to maintain the same ionic strength for all measurements.

The results of the determination of the pK_a's of the pyrazine, 4,4′-bipyridine, and 1,2-bis(4-pyridyl)ethylene complexes of pentaammineruthenium(II) at an ionic strength of 0.050 M are shown in Table VIII. See Figure 4 for an example of the determination of pK by spectrophotometric titration. The pK_a values of other azine pentaammineruthenium(II) complexes determined by other workers using this method are shown in Table IX.

The results summarized in Table VIII indicate that the great enhancement in the basicity of pyrazine on complexation to form the pentaammineruthenium(II) complexes is not found for the other ligands. The pK values of the other complexes lie between the pK_2 and pK_1 values of the ligand, indicating that the major effect of the complexation of these ligands is the polarization of the electron density by the Ru(II) ion. The high pK^* values of all the complex studies indicates large charge delocalization in the charge-transfer excited state, as expected.

The differences in the ability of the complexes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene to delocalize the positive charge of the proton relative to the free ligands should be much less than the corresponding difference for the pyrazine complex, by the following reasoning. The pyridine group (in 4,4′-bipyridine) and the vinylpyridine group [in 1,2-bis(4-pyridyl)-ethylene] are both very good for charge delocalization. The extra contribution to charge delocalization from the pentaammineruthenium(II) moiety is a relatively small perturbation. In the case of pyrazine, however, the group to which the pentaammineruthenium(II) moiety is bonded (a nitrogen atom) is a very poor

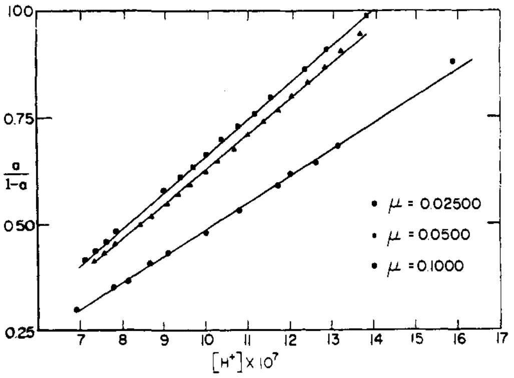


Figure 3. A plot of $[a/(1 - a)]$ *vs.* $[H^+]$ to give the value of K_2 of 1,2-bis(4-pyridyl)ethylene.

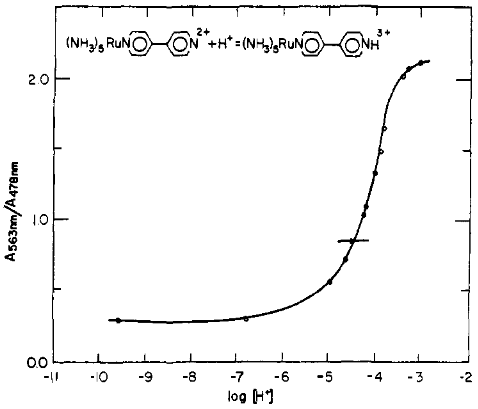


Figure 4. A plot of $A_{563\ \text{nm}}/A_{478\ \text{nm}}$ *vs.* log [H$^+$] for the 4,4′-bipyridinepentaammineruthenium(II) ion.

delocalizing agent for positive charge. The contribution of the pentaammineruthenium(II) group in increasing the stability of the protonated complex is very significant in this case.

The information on the basicities of these pentaammineruthenium(II) complexes indicates that charge delocalization capability afforded by the pentaammineruthenium(II) moiety's dπ–pπ back bonding is responsible for the increased basicity of the pyrazinepentaammineruthenium(II). This back bonding is a local effect induced by the added proton, not a remote increase in electron density in the unprotonated complex.

The changes in the basicity of the ligands shown in Table IX on complexation are consistent with either the delocalization of charge by dπ–pπ back bonding or by an increase in electron density at distant positions due to the back bonding. From the possible resonance forms, the significance of either of these effects is expected to be greater at the ortho and para positions than at the meta position. The low value for the pK_a of the pyridazine complex is probably due to steric interference.

The important conclusion of this study is that the increase in basicity observed in the ruthenium–pyrazine complex is the result of the delocalization of charge in the protonated form more than the increase in the electron density of the nitrogen due to the ruthenium dπ–pπ back bonding in the unprotonated form. The para N on pyrazine is a very inefficient delocalizer of the charge upon protonation as seen by its very low basicity compared to pyridine (pK_a = 0.6 for pyrazine compared to pK_a = 5.23 for pyridine). The other complexes studied have ligands in which the atom para to the protonated nitrogen is a carbon or stubstituted carbon atom. Since these systems already have a good charge delocalizer, the perturbation of the ruthenium ion is very small and we do not observe the very large and anomalous effect seen in the pyrazine case.

Chemical Shift and π Electron Density Changes of Ligands upon Complexation

Changes in the chemical shift of the ligand protons are used in this study to differentiate between the ability of the Ru(II) ion in pentaammineruthenium(II) complexes of aromatic nitrogen heterocycles to increase basicity of certain ligands by either charge delocalization in the ground state leading to an increase in the electron density of the uncomplexed nitrogen atom or the delocalization of the additional positive charge of the protonated form of the complex.

Many studies of the relationship of π electron density to proton chemical shifts have been carried out for hydrocarbon molecules and ions,[37–41] substituted benzenes,[42–48] and for nitrogen heterocycles.[49–54] For simple aromatic systems,[37–40] the proton chemical shifts have been shown to be linearly proportional to the excess π electron density on the carbon atom to which it is bonded. For substituted aromatic systems, however, several other effects must be considered, since changes in the nature of several types of current which are set up in a molecule due to an external magnetic field (*i.e.*, the magnetic field employed in the nmr experiment) affect the chemical shift of the nuclei and these currents in turn are affected by the electric and magnetic properties of the substituent. The significance of the three general types of current which are set up in a molecule due to an external field have been discussed in depth by Richards, *et al.*,[37] Dailey, *et al.*,[45,46] and Speisecke and Schneider.[49] These three general types of current are (1) the current around atoms, (2) the current within bonds, and (3) the current induced to flow from atom to atom around an aromatic ring. In this discussion, the pentaammineruthenium(II) moiety will be considered the substituent on the aromatic nitrogen heterocycle. The various effects of the magnetic and electric properties of the substituent on the various types of current induced by the external magnetic field and the effect of these currents on the proton chemical shifts of the heterocycle will be investigated. Not all of these effects will turn out to be significant for this study, but since oversimplification has often been the rule rather than the exception in the application of chemical shift changes to electron density changes, each known effect should be eliminated only after its insignificance in a particular situation has been demonstrated.

The effect of the current flowing around the hydrogen atom on the proton chemical shift will depend upon both the electron population of the hydrogen 1s orbital and any distortion of the current flow due to a strong electric field[55,56] of a substituent in the neighborhood

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of the hydrogen atom or due to the magnetic anisotropy of the substituent.[57–64] The chief effect of the electric field of a substituent on intramolecular current has been explained in terms of the polarization of the C–H bond,[56] rather than the effect on the current around the hydrogen atom itself. This effect will be discussed later. The effect of the magnetic anisotropy can act directly on the proton's current distribution. The paramagnetic anisotropy of a transition metal ion possessing incompletely filled d levels with the electrons in a low spin configuration (*e.g.*, low spin Ru(II) with six 4d electrons occupying the three t_{2g} orbitals in the ground state) arises from the mixing of the electronic ground state with low lying excited states in which there are unpaired electrons.[65,66] The significance of the term "low lying" depends upon the observation being made. As long as the matrix elements of the magnetic field operator between the ground state and the excited state(s) result in an observable effect, the excited state(s) is (are) said to be low lying. The effect of the paramagnetic anisotropy of a transition metal ion on the proton chemical shift of protons on ligand molecules was shown to be observable for transition metal ions whose excitation energies are of the same order of magnitude as that of the excitation energy of Ru(II) in pentaammineruthniume(II) complexes of aromatic nitrogen heterocycles.[58–64] Hence, it must be considered in the analysis of the effects which result in chemical shift changes for protons in these complexes compared to the proton chemical shifts in the free ligands. Recently, the effect of the magnetic susceptibility of Ni(II) and Pd(II) on nearby protons of alkenylaryl ligands has been shown to be the major contributor to proton chemical shift changes of these protons on complexation.[36]

The dependence of the shielding of protons on the magnetic anisotropy of substituents has been analyzed by use of a point–dipole approximation[67] in which the chemical shift is related to the anisotropy, $\Delta\chi$, by

$$\Delta\sigma = (\Delta\chi/3R^3)(1 - 3\cos^2\theta)$$

where $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$, and R and θ define the position of the proton under consideration relative to that of the magnetic point dipole. Although consistent assignments have been difficult in the case of diamagnetic substituents such as halogen and cyano groups,[48] the assignments for transition metal ions showing temperature independent paramagnetism have been demonstrated to be reasonable, at least on a qualitative basis.[64] Calculations based on the point–dipole approximation cannot be reasonably employed for the case of the pentaammineruthenium(II) complexes studied when the size of the Ru(II) ion (about 2 Å in diameter) and the proximity of the ion to the ortho protons of the aromatic nitrogen heterocycles used as ligands (about 3.0 Å) are taken into consideration. Hence, calculations of the $\chi_{\parallel}$ and $\chi_{\perp}$ parameters for the ortho protons were not attempted. The effect on the more distant protons might be better investigated by the point–dipole approximation. Since the dependence diminishes as a function of $1/R^3$, however, a very small effect would be expected at the meta position relative to the ortho position, and a still smaller relative effect at the para position. Indeed, the only paramagnetic (upfield) shifts found for the pentaammineruthenium(II) complexes studied are those which are confidently assigned to the protons ortho to the substituent, the pentaammineruthenium(II) moiety.

The effect on the proton chemical shift of the current flowing about the carbon atom has been estimated by replacing the currents with point magnetic dipoles. The chemical shift of the proton is then found to be proportional to the diamagnetic anisotropy constants of the atoms.[57,68]

Paramagnetic current[57,69] flows in the C–H bond as a result of the contribution of the excited state resulting from the promotion of an electron from the C–H σ bonding orbital to a σ antibonding orbital. This difference in the contribution of this effect to the proton chemical shift is probably very small both before and after complexation of the ligand and the magnitude of this effect probably differs very little from one carbon atom to another on the aromatic rings. The C–H bond current may also affect the proton chemical shift if it is distorted by a nearby electric field. The effect of an electric field on the proton shielding has been expressed by Buckingham[56] as

$$\Delta\sigma_E = -2 \times 10^{-12}E_z - 10^{-18}E^2$$

where z is taken to be along the C–H bond. $\Delta\sigma_E$ has been approximated as the product of the substituent dipole moment and a geometric factor determined by the position of the proton with respect to the dipole,[70] but the results proved inconsistent with experimental data. Although accurate calculations are not possible at the present time for lack of sufficient information about the magnitudes and positions of the electric dipoles of substituents, the nature of the function for the dependence of proton chemical shift on an electric field as a through-space function, rapidly decreasing with distance, would suggest that protons ortho to the substituent (the pentaammineruthenium(II) group) would be affected by its electric field to a much greater extent than the other protons on the aromatic nitrogen heterocycle.

The third type of current brought about by an external magnetic field is the so-called "ring current."[69,71–75] If the aromatic rings studied are of about

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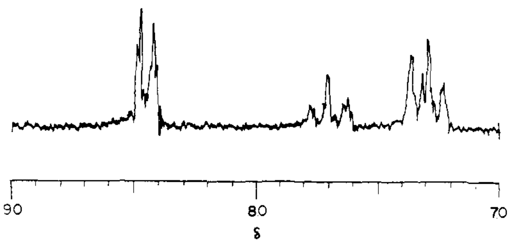

Figure 5. The nuclear magnetic resonance absorption spectrum of pyridine pentaammineruthenium(II) single sweep on an HA-100 spectrometer.

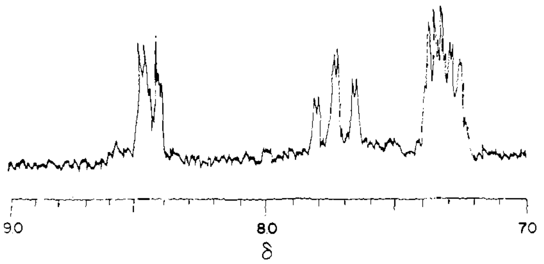

Figure 6. The nuclear magnetic resonance absorption spectrum of pyridine-*2-d*-pentaammineruthenium(II) single sweep on an HA-100 spectrometer.

the same size, the changes in ring current will be due principally to the magnitude of the "rotating current." If the total change in π electron density is small, the contribution due to this effect will also be small (approximately 1.2 ppm per electron[69]) and should be distributed over the entire ring rather evenly. For six-membered rings, the current-corrected chemical shift, σ_1, is found to be about 0.95 of the value of the observed proton chemical shift.[75] Since the compensation for the ring current effect is of such a small relative magnitude, it will only change the conclusions about changes in the electron density at carbon atoms whose protons undergo small chemical shift changes relative to the proton chemical shifts of the other protons on the aromatic ring.

An extremely important effect which results in changes in (1) the current flow about the hydrogen atom due to a change in the electron density of the 1s orbital, (2) the C–H bond current flow due to an alteration in the diamagnetic anisotropy of the carbon atom, (3) the paramagnetic current of the C–H bond, and (4) in the ring current is the change in the electron density at the carbon atom. These changes should be approximately proportional to the change in the π electron density of the carbon atoms. It has been shown[47–50] that the shift of an aromatic hydrogen atom is related to the change in π electron density at the carbon atom to which it is bonded by the expression

$$\delta(\sigma) = aq$$

where $\delta(\sigma)$ is the change in the chemical shift, a is a constant for a particular aromatic ring, and q is change in the charge at the carbon atom due to the substituent. Therefore addition of positive charge at carbon atoms leads to a downfield shift. The largest contribution to the constant, a, has been proposed[47] to arise from the increase in the electron density on a hydrogen atom caused by the polarization of the C–H bond by the change in the π electron density at the carbon atom. The value of a is about 9.2 $\delta(\sigma)$/unit charge. Note that the effect of charge is about ten times greater than the ring current or other effects in causing chemical shifts.

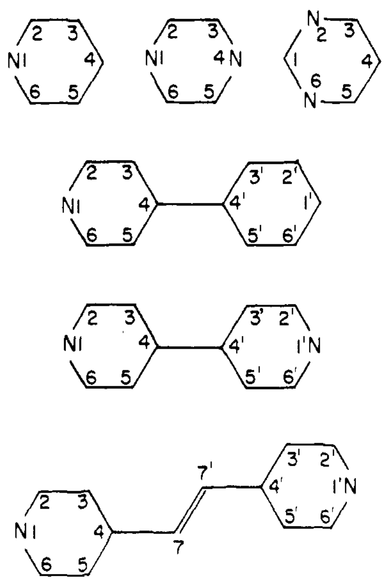

Figure 7. The numbering scheme for the aromatic nitrogen heterocycles.

The proportionality of the change in the proton chemical shift to the change in electron density at the carbon atom to which it is bonded has been justified in a very straightforward manner by Fraenkel, *et al.*[37]

Studies of the comparison of molecular orbital calculations and experimental chemical shifts[37,48,49] have shown that proton chemical shifts of para position protons correlate excellently with calculated π electron densities, while shifts at the ortho and meta positions do not appear to be simply dependent on the π electron density changes. In the discussion of effects responsible for the proton chemical shift, changes of ligands on complexation to form pentaammineruthenium(II) complexes and changes in proton chemical shifts at the para position are assumed to be an accurate measure of π electron density changes, while changes in the ortho and meta positions are discussed only qualitatively.

In order to assign the chemical shifts of the ring protons in pyridinepentaammineruthenium(II), the pyridine-*2-d* complex was also prepared and studied. From the nmr spectra of the pyridinepentaammineruthenium(II) complex (Figure 5) and pyridine-*2-d*-pentaammineruthenium(II) (Figure 6), the chemical shift of δ 8.45 is assigned as $H_{2,6}$ (see Figure 7 for the numbering scheme used for the ligands) because the relative intensity of the absorption at this position is twice as large for the pyridine complex, with two equivalent protons ortho to the pentaammineruthenium(II) group, as compared to the pyridine-*2-d* complex with only one proton in the ortho position. The relative integrated intensities of the nmr absorption spectra of the pentaammineruthenium(II) complexes of pyridine, pyridine-*2-d*, 4,4′-bipyridine, and 1,2-bis(4-pyridyl)ethylene are compiled in Table X. The intensities were measured with a polar planimeter rather

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Table X. Integrated Intensities for Nmr Spectra of $[(NH_3)_5Ru^{II}L]^{2+}$ Complexes

Ligand	Chemical shift position in δ (rel intensity)[a]		
Pyridine	8.45 (1.47)	7.75 (1.00)	7.3 (2.03)
Pyridine-*2-d*	8.45 (0.73)	7.75 (1.00)	7.3 (1.99)
Pyrazine	8.67 (2.00)	8.13 (1.38)	
4,4′-Bipyridine	8.90 (3.41)	7.88 (2.00)	7.69 (1.98)
1,2-Bis(4-pyridyl)-ethylene	8.56 (2.00)	8.25 (1.36)	7.66, 7.57, 7.51, and 7.48 (5.94)[b]

[a] Based on the absorption at one position being made equivalent to the number of protons assigned to that absorption (see text) and of the other areas made relative to the area chosen as reference. [b] The separation of these absorptions would be unreliable and would not affect the conclusions based on this table.

than the nmr spectrometer itself because the integration of the averaged spectra stored in the C-1024 unit operated in the frequency sweep mode is not possible with the HA-100 nmr spectrometer which was used. The shifts of δ 7.75 and 7.3 are assigned to the H_4 and $H_{3,5}$ atoms, respectively, due to the approximately 1:2 ratio of their relative intensities. The shift at δ 7.75 also shows the perturbed triplet structure which is expected for a para position proton whose most significant coupling results from interaction with the two neighboring meta protons.

It should be noted that the intensity of the $H_{2,6}$ proton(s) in these two complexes is not an integral multiple of the intensities of the H_4 and $H_{3,5}$ protons but is significantly less: about 0.7 of the intensity expected for one proton based on the intensity of the H_4 proton being equivalent to that of one proton. This feature of the nmr spectrum is proposed to be due to the spin–spin interaction of the ortho protons with the nuclei of the isotopes of Ru with a nuclear spin of $^5/_2$. From the natural abundance of the isotopes of ruthenium (Table XI), isotopes of Ru with $I = {}^5/_2$ constitute 29.8% of the element. Spin–spin interaction between $H_{2,6}$ atoms and these isotopes should cause a sextuplet structure shifted symmetrically from the position of the absorption for molecules containing the $I = 0$ nuclei, leaving 70.2% of the intensity at this position. The sextuplet would be expected to be broadened by quadrapole relaxation (since the spin of the Ru is greater than $^1/_2$) and, hence, would not be observable. Spin–spin interactions between protons and other nuclei (*e.g.*, ^{205}Tl, $I = {}^1/_2$;[76] ^{199}Hg, $I = {}^1/_2$;[77] and ^{19}F, $I = {}^1/_2$[78,79]) have been observed for several compounds. The spin–spin coupling constants generally attenuate rapidly as the distance between the interacting nuclei (*i.e.*, the number of covalent bonds) increases.[80] In the pentaammineruthenium(II) complexes studied, only the ortho protons, which are three covalent bonds removed from the ruthenium ion, appear to be significantly affected by proton–ruthenium spin–spin coupling.

Table XI. Natural Abundance of Ru Isotopes

Isotope	% abundance	I[a]
^{96}Ru	5.68	0
^{98}Ru	2.22	0
^{99}Ru	12.81	$^5/_2$
^{100}Ru	12.70	0
^{101}Ru	16.98	$^5/_2$
^{102}Ru	31.34	0
^{104}Ru	18.27	0

[a] J. H. E. Griffiths, J. Owen, and I. M. Ward, *Proc. Roy. Soc., Ser. A*, **65**, 951 (1952).

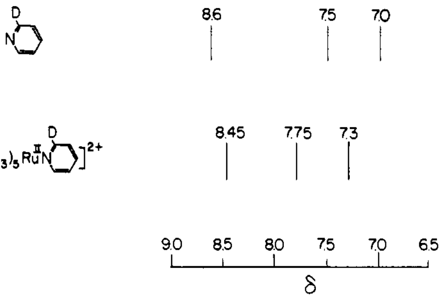

Figure 8. A proton chemical shift chart for pyridine-*2-d* and pyridine-*2-d*-pentaamminerurthenium(II). The same chart applies for pyridine and pyridinepentaammineruthenium(II).

When the resonance positions of the pyridine-*2-d* complex are compared to the absorption positions of a dilute solution of pyridine-*2-d* in D_2O (compiled in Figure 8), it is evident that the proton chemical shift of the H_2 proton is moved upfield on complexation, while the other shifts move downfield. The upfield, or paramagnetic, shift of the H_2 chemical shift could be caused by (1) an increase in the π electron density on C_2, (2) the effect of the paramagnetic anisotropy of the Ru(II) ion on distortion of the H_2 1s orbital spatial electron distribution, and/or (3) the effect of the electric field of the Ru(II) ion on the electron distribution. From the trend of the chemical shift changes of all the other ring protons on complexation, a downfield or diamagnetic shift, a π electron deficiency on the ring is indicated. On this basis, it does not seem plausible to propose that the paramagnetic shift change for H_2 arises from a π electron density increase for C_2. The effect of the paramagnetic anisotropy of transition metal ions exhibiting temperature independent paramagnetism has been demonstrated in Ni^{II} and Pd^{II} complexes for protons in close proximity to the metal ions[64] and is a very plausible explanation of the paramagnetic shift for H^2. The paramagnetic anisotropy of the transition metal ion may produce either a paramagnetic or diamagnetic shift, depending on the geometry of the possible orientations of the C–H bond to the spin direction of the metal ion while it is aligned to the field.[64] Since the paramagnetic shift is not due to π electron charge increase on C_2 and since the effect of the electric field of the Ru(II) ion is predicted to be deshielding or diamagnetic by Buckingham's equation, the paramagnetic effect attributable to the temperature independent paramagnetic anisotropy of the Ru(II)

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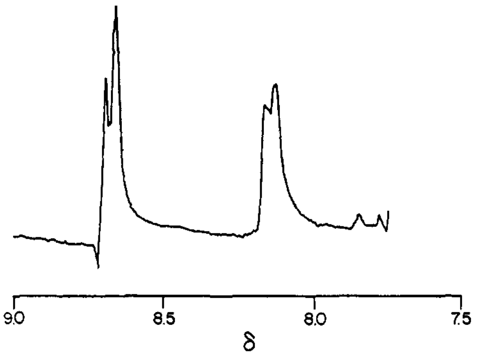


Figure 9. The nuclear magnetic resonance absorption spectrum of pyrazinepentaammineruthenium(II) 500 averaged spectra on an HA-100 spectrometer.

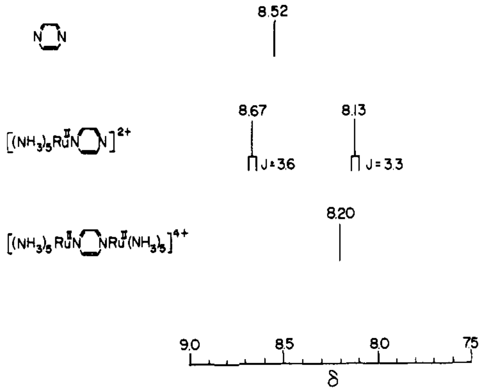
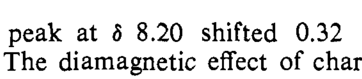


Figure 10. A proton chemical shift chart for pyrazinepentaammineruthenium(II) and μ-pyrazine-bis(pentaammineruthenium(II)).

ion must be greater than these other effects to cause a net upfield change.

The nmr spectrum of pyridinepentaammineruthenium(II) shows the same chemical shifts as the pyridine-2-*d*-pentaammineruthenium(II) complex. The relative intensity of the absorption at δ 8.45 is doubled, as previously mentioned.

The nmr spectrum of the pyrazinepentaammineruthenium(II) complex (Figure 9) shows an absorption at δ 8.13 which arises from an upfield (paramagnetic) shift of δ 0.39 from the absorption of a dilute solution of pyrazine in D_2O and an absorption at δ 8.67, a downfield shift of δ 0.15 from the free ligand value. The intensity of the upfield peak in the nmr spectrum of the complex is about 0.7 of the intensity of the downfield peak, indicating that the upfield peak is the $H_{2,6}$ absorption, less intense due to the ruthenium–proton coupling for the ruthenium isotopes of $^5/_2$ nuclear spin. The spectrum of the complex



$[(NH_3)_5Ru^{II}NC_4H_4NRu^{II}(NH_3)_5]^{4+}$

is a single peak at δ 8.20 shifted 0.32 upfield from pyrazine. The diamagnetic effect of charge deficiency is undoubtedly greater in the "dimeric" complex than in the "monomeric" complex, causing a less paramagnetic net effect on the chemical shift of the pyrazine protons which are ortho to the pentaammineruthenium(II) "substituent." A chart comparing the absorptions of the pyrazinepentaammineruthenium(II) and μ-pyrazine-bis(pentaammineruthenium(II)) complexes with pyrazine in D_2O is shown in Figure 10. The coupling constants in this chart and other similar charts in this study are given in cycles per second.

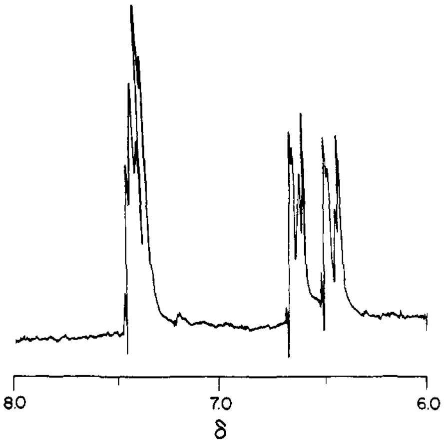


Figure 11. The nuclear magnetic resonance absorption spectrum of 4,4′-bipyridinepentaammineruthenium(II) 300 averaged spectra on an HA-100 spectrometer.

The $H_{2,6}$ nmr absorptions of 4-phenylpyridine are assigned to the absorptions which are farthest downfield. This is consistent with studies of substituted pyridines[81,82] in which the nitrogen atom is shown to cause a diamagnetic shift of protons ortho to its position relative to similar compounds with carbon in place of nitrogen. The $H_{3,5}$ peaks of the free ligand were identified by comparing the coupling patterns in the 60-Mc and 100-Mc nmr spectra. The peaks assigned to the $H_{3,5}$ atoms are those indicated on the figures by the coupling brackets. It was hoped that a well-resolved spectrum of the 4-phenylpyridinepentaammineruthenium(II) complex would show the coupling pattern, allowing the identification of the $H_{3,5}$ peaks. For both the free ligand and the complex, the $H_{3,5}$ and $H_{2,6}$ peaks have the same coupling pattern with $J_{23} = J_{32} \approx 5$ cps and $J_{25} = J_{52} \approx 1.5$ cps. The $H_{3,5}$ peaks, however, were not identifiable in the nmr spectrum of the complex. The $H_{2,6}$ peaks were shifted upfield by δ 0.10 on complexation. The resolution of the remaining peaks was poor, indicating a slight general diamagnetic shift.

The nmr spectrum of a supersaturated solution of 4,4′-bipyridine (about 0.1 *M*) consists of two doublets with coupling constants of about 4.6 cps which are further split into superimposed doublets with a coupling constant of 1.8 cps. The downfield (δ 8.55) set of "doubled doublets" are assigned as the absorptions of the $H_{2,6}$ and $H_{2',6'}$ atoms and the upfield (δ 7.60) absorptions are assigned to the $H_{3,5}$ and $H_{3',5'}$ atoms. The coupling constants were accurately determined by reducing the frequency range swept in the spectrum to 100 cps on the Varian A-60A spectrometer.

The nmr spectrum of the 4,4′-bipyridinepentaammineruthenium(II) complex (Figure 11) shows a complex absorption at δ 8.90 with an intensity corresponding to 3.4 protons relative to the peaks at δ 7.88 and 7.69 for which the intensities are made equivalent to two protons. The peaks centered at δ 8.90 are assigned

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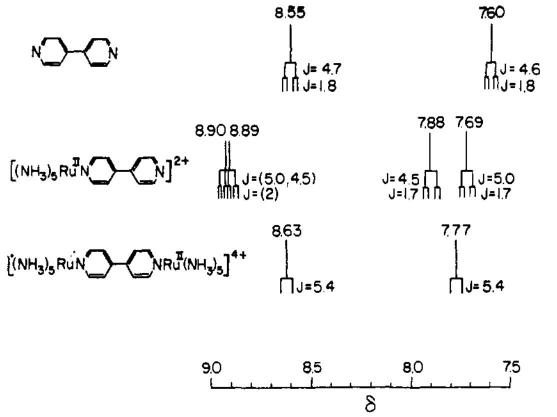

Figure 12. A proton chemical shift chart for 4,4′-bipyridinepentaammineruthenium(II) and μ-4,4′-bipyridine-bis(pentaammineruthenium(II)).

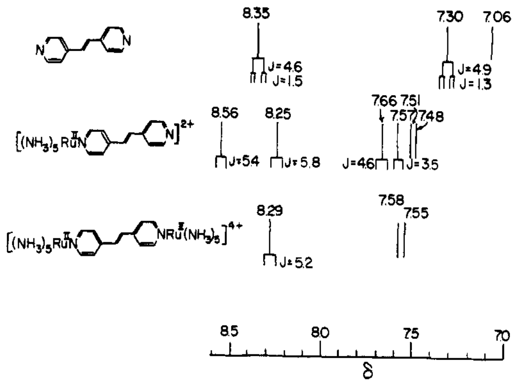

Figure 13. A proton chemical shift chart for 1,2-bis(4-pyridyl)ethylenepentaammineruthenium(II) and μ-1,2-bis(4-pyridyl)ethylene-bis(pentaammineruthenium(II)).

to overlapping peaks due to $H_{2,6}$ and $H_{2',6'}$, since the relative intensity of the $H_{2,6}$ should be reduced to 1.4 protons due to the spin–spin coupling of the protons to ^{99}Ru and ^{101}Ru and, as mentioned above, the protons which are ortho to a nitrogen atom generally absorb further downfield than the other ring protons. The peaks centered at δ 7.88 are assigned to $H_{3,5}$ on the basis of the similarity in chemical shift change (δ −0.28) on complexation to the change in chemical shift of $H_{3,5}$ in pyridine (δ −0.30) and to a change of δ −0.28 in 1,2-bis(4-pyridyl)ethylene on complexation. The only protons which are common to all three complexes are the $H_{2,6}$, which are assigned by the spin–spin coupling, and the $H_{3,5}$.

The nmr spectrum of the μ-4,4′-bipyridine-bis(pentaammineruthenium(II)) complex consists of a doublet at δ 8.63 which is assigned to $H_{2,6}$ and $H_{2',6'}$ and a doublet at δ 7.77 which is assigned to $H_{3,5}$ and $H_{3',5'}$ (Figure 12).

It should be noted that the 4,4′-bipyridine case is the only one studied in which all of the chemical shift changes on complexation with pentaammineruthenium(II) are diamagnetic (downfield). The reason for a diamagnetic change for the $H_{2,6}$ atoms in this case but not for pyridine and 1,2-bis(4-pyridyl)ethylene is not immediately evident.

The 1,2-bis(4-pyridyl)ethylene ligand has an nmr spectrum which consists of a "doubled doublet" at δ 8.35 and one at δ 7.30 and a single spike at δ 7.06. From the relative intensities (4:4:2) and the coupling patterns, the peaks which are furthest downfield are assigned as the $H_{2,6}$ and $H_{2',6'}$ absorptions, those at at δ 7.30 are assigned as the $H_{3,5}$ and $H_{3',5'}$ absorptions and the single peak is the H_7 and $H_{7'}$ absorption. Again, the spectrum was taken of a supersaturated solution (about 0.1 *M*) and the sweep width was reduced to provide accurate coupling constants.

The nmr spectrum of the 1,2-bis(4-pyridyl)ethylene complex contains a doublet with a relative intensity of 3.3 protons assigned as the $H_{2,6}$ absorption, again, with a lessened intensity due to proton–ruthenium spin–spin coupling. This doublet is shifted δ 0.10 upfield from the corresponding absorption in the free ligand. Another doublet occurs downfield at δ 8.56. It is assigned as the $H_{2',6'}$ absorbance due to its downfield position, which is δ 0.19 from the corresponding resonance of the ligand. Doublets at δ 7.66 and 7.57 are assigned to $H_{3',5'}$ and $H_{3,5}$, respectively. This assignment is based on the similarity of the δ −0.27 change to changes found for pyridine and 4,4′-bipyridine on complexation. This assignment is weak and, fortunately, does not alter conclusions drawn in this study. The peaks at 7.51 and 7.48 are assigned to H_7 and $H_{7'}$ together, since there is no adequate means to specifically distinguish one from the other.

The nmr spectrum of μ-1,2-bis(4-pyridyl)ethylene-bis(pentaammineruthenium(II)) also contains a doublet due to the presence of some of the "monomeric" complex at δ 8.56. The peaks of the dipentaammineruthenium(II) complex show little change from those of the monomeric complex after the deletion of the doublet due to $H_{2',6'}$ in the spectrum of the monomer. A slight diamagnetic shift of the $H_{2,6}$ resonance on complexation of both ends of the ligand relative to the complexation of one end of the ligand occurs (Figure 13).

The chemical shift charts of these complexes will now be interpreted in terms of charge distributions in the complexed ligands.

As discussed above, meta shifts may not be a reliable measure of π electron density due to complications from the electric field and paramagnetic anisotropy of the substituent, but para positions proton chemical shift changes have been shown to be a reliable measure of π electron density changes for various substituents. As a consequence, π electron density changes on complexation have been computed only for the para position of pyridine and the para substituents of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene (Figure 14). The values were calculated using a value of $a = 9.5\delta$/per positive charge

$$\delta(\sigma) = aq$$

which was found for the pyridinium ion.[50]

The pattern of diamagnetic shifts for all para position protons (also true of the meta protons) and substituents shows that the overall effect of coordination of the ligand to the pentaammineruthenium(II) moiety is a polarization of electron density *toward* the Ru(II) ion. If coordination of the pyrazine resulted in an excess of electron density in the ground state as a result of dπ–pπ back bonding from the Ru(II), it would also be expected that the back bonding would cause an excess of electron density in the ground state for other complexes with low-energy charge-transfer transitions. This excess of electron density would be ex-

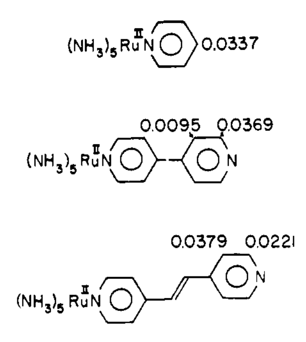

Figure 14. π electron density deficiencies from chemical shift changes of some aromatic nitrogen heterocycles.

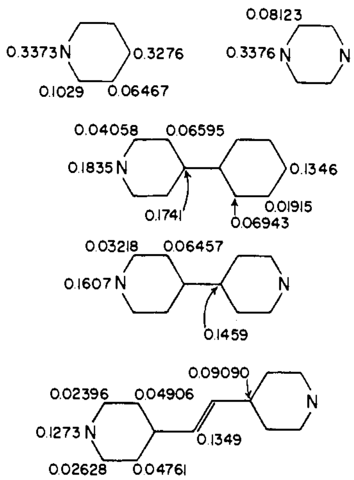

Figure 15. CNDO/2 populations of the lowest unoccupied molecular orbital of some aromatic nitrogen heterocycles.

pected to distribute itself about the molecule in proportion to the population probability of the molecular orbital to which it is promoted. CNDO/2 calculations[83] for the lowest unoccupied π molecular orbital of the free ligands result in significant populations at all positions (Figure 15). Thus, for all positions for which the proton chemical shift is a reliable measure of π electron density changes, the shifts should move upfield on complexation if there is a net electron transfer to the ligand by the Ru(II). On the other hand, polarization of electron density by protons results in a lowering of electron density at all positions for the pyridinium ion (experimental[50]), pyrazine (CNDO/2), and 4,4′-bipyridine (CNDO/2) as shown in Figure 16. Polarization of electron density by the metal ion, then, would cause shifts to move downfield, as observed. Note the calculated shifts of Figure 16 due to the H^+ are about 4 times those observed for the Ru(II).

From the results of the study of chemical shift changes of pyridine, pyridine-*2-d*, pyrazine, 4-phenylpyridine, 4,4′-bipyridine, and 1,2-bis(4-pyridyl)ethylene on complexation with pentaammineruthenium(II), an explanation of the enhancement in the basicity of pyrazine on the basis of an increase in the electron density of the uncomplexed nitrogen due to dπ–pπ back bonding from the Ru(II) ion to pyrazine is not reasonable. This conclusion was suggested by the study of the basicity changes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene on complexation. Rather, the enhancement is likely due to the greater ability of the nitrogen atom bound to the pentaammineruthenium(II) moiety than that of the free ligand to delocalize the positive charge added by the protonation of the other nitrogen.

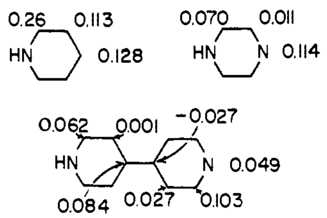

Figure 16. π electron deficiencies due to protonation of pyridine (experimental), pyrazine (calculated, CNDO/2), and 4,4′-bipyridine (calculated, CNDO/2) (relative to the electron densities of the free ligand).

Thus all the evidence in this study points to a polarization of electron density toward the ruthenium ion with a net positive charge of the ligand atoms when complexed to the ruthenium ion. Although the back bonding argument may be important in a localized way, *i.e.*, to the nitrogen atom attached to the ruthenium ion, its use in explaining basicities, for instance, in these pentaammineruthenium(II) complexes by increasing electron density at atoms a large distance from the ruthenium ion, is incorrect.

Conclusion

All pentaammineruthenium(II) complexes of aromatic nitrogen heterocycles studied to date exhibit an intense absorption in the visible region which has been demonstrated to be a metal-to-ligand charge transfer.[13] By comparing the energies of these charge-transfer absorptions with the energies of the lowest unoccupied π antibonding molecular orbital, it was found that a linear relationship existed which could be explained on the basis of a reasonable molecular orbital scheme. The relationship revealed that the interacting molecular orbitals of the ruthenium ion and the ligand interact most strongly (*i.e.*, causing a greater separation) as they approached each other in energy, as expected from basic quantum mechanics. Using the graphical relationship illustrated in Figure 1 it should be possible to predict the wavelength of maximum absorbance of the charge transfer of any pentaammineruthenium(II) complex of an aromatic nitrogen heterocycle knowing only the polarographic half-wave potential of the heterocycle.

A study comparing the basicities of the pentaammineruthenium(II) complexes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene with the ligands themselves revealed that the explanation of the increase in basicity of the cyanopyridines and pyrazine on complexation to form the pentaammineruthenium(II) complexes on the basis of an increase in the ground state electron density of noncomplexed nitrogen atoms in the heterocycles due to dπ–pπ back bonding from the ruthenium ion to the ligand did not satisfy the results for the 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene complexes. Localized dπ–pπ back bonding to the bound nitrogen could explain all the available data because this mechanism would allow charge delocalization of the positive charge introduced by the proton, making the cyanopy-

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(83) Using a CNDO/2 program of George Segal supplied through the Quantum Chemistry Program Institute at Indiana University.

ridine and pyrazine complexes better bases, but would be much less effective for the 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene complexes.

The net effect of the pentaammineruthenium(II) moiety on the electronic charge of the ligand was determined by a study of change in the chemical shifts of the protons of the ligands on complexation. It was found that the pentaammineruthenium(II) group polarized electron density toward itself, making the ligand slightly electron deficient. This was determined by the diamagnetic shifts found for all para protons and the protons on para substituents. The polarization was less than that of a proton, which is to be expected, since the polarization of charge is based on the charge to volume ratio of the polarizing agent. The charge to volume ratio is certainly much smaller for Ru(II) ion than for a proton. This result would predict that the basicities of the 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene complexes would be intermediate between the basicity of the free ligand and the monoprotonated ligand. This was found to be the case.

Acknowledgments. This work was supported generously by grants from the NIH and NSF.

Charge Delocalization in Pentaammineruthenium(II) Complexes. II. A Study of Dipentaammineruthenium(II) Complexes of Pyrazine, 4,4′-Bipyridine, and 1,2-Bis(4-pyridyl)ethylene[1]

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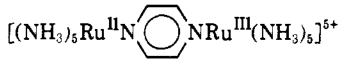
Received April 22, 1971

Abstract: The dipentaammineruthenium complexes with pyrazine, $(NH_3)_5Ru\text{–}NC_4H_4N\text{–}Ru(NH_3)_5{}^{4+}$, 4,4′-bipyridine, $(NH_3)_5Ru\text{–}(C_5H_4N)_2\text{–}Ru(NH_3)_5{}^{4+}$, and 1,2-bis(4-pyridyl)ethylene, $(NH_3)_5Ru\text{–}NC_5H_4C_2H_4C_5H_4N\text{–}Ru(NH_3)_5{}^{4+}$, were subjected to both chemical and electrochemical oxidations in order to study the "II–III" species. The 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene analogs of the previously characterized II–III type of complex with pyrazine could not be produced by either chemical oxidation or electrochemical oxidation. The characteristic near-ir band of the pyrazine II–III dimer does not exist for the other two ligands, and the cyclic voltammetry study indicated one two-electron change in the oxidation. Thus the properties of these latter systems can be described as mixtures of the II–II and III–III complexes, with no special stability to the II–III complex.

It has been reported[3] that μ-pyrazine-bis(pentaammineruthenium(II)) undergoes oxidation by silver ion to form



$$[(NH_3)_5Ru^{II}N\bigcirc NRu^{III}(NH_3)_5]^{5+}$$

which has a broad, intense absorption in the near-infrared. This absorption is attributed to the transition [2, 3] → [3, 2]*, *i.e.*, the Franck–Condon[4] barrier to electron transfer required for a transition between two centers with the same chemical composition but differing in environment due to their different charges. By use of the Marcus–Hush theory,[5–7] the rate of electron transfer may be approximated from the energy of the near-infrared absorption.

If this interpretation of the occurrence of the near-infrared absorption of the above complex is correct, it would be interesting to see how different bridging groups would affect the rate of electron transfer between the ruthenium centers. For this reason, the preparation of the "Ru(II)–Ru(III)" complexes of μ-4,4-bipyridinebis(pentaammineruthenium(II)) and μ-1,2-bis(4-pyridyl)ethylene-bis(pentaammineruthenium(II)) was attempted both by chemical and electrochemical means.

Experimental Section

Chemical Oxidation of the "Ru(II)–Ru(II)" Complexes. Oxidation of the μ-pyrazine-bis(pentaammineruthenium(II)) complex was accomplished in two well-defined steps by potentiometric titration with Ce(IV)[3]. Production of the Ru(II)–Ru(III) species was also achieved by oxidation with silver ion. Since only the Ru(II)–Ru(III) species was desired for the dipentaammineruthenium(II) complexes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene, and since these complexes proved to be sensitive to the highly acidic conditions used in ceric oxidations, the oxidations were attempted with silver ion.[1]

The addition of a stoichiometric amount of $AgNO_3$ to solutions of the dipentaammineruthenium(II) complexes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene was performed in a nitrogen-atmosphere glovebox. D_2O was used as the solvent so that near-infrared spectra could be taken. The solutions were filtered through glass wool to remove the black metallic silver formed during the oxidation.

Near-Infrared Spectra. A Cary-14 recording spectrometer was used to record near-infrared spectra from 700 to 2500 nm. The solutions were placed in deaerated, matched quartz cells. The cell compartment was maintained at 25°.

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