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Synthesis and Properties of Some Tetraammineruthenium(II) Complexes of Bidentate Ligands, cis-$Ru(NH_3)_4(X-Y)^{2+}$

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Abstract: Reported are the syntheses and spectral characterizations of a series of ruthenium(II) complex ions of the type $Ru^{II}(NH_3)_4(X-Y)$, where X-Y is a bidentate ortho-substituted pyridine such as 2-aminomethylpyridine, 2-pyridinalimine, 2-pyridinecarboxaldehyde, or bipyridine. The 2-pyridinalimine complex is formed by facile and quantitative air oxidation of the 2-aminomethylpyridine complex, while the 2-pyridinecarboxaldehyde complex is formed by reaction of the free ligand with either $Ru(NH_3)_5H_2O^{2+}$ or cis-$Ru(NH_3)_4(H_2O)_2^{2+}$ in aqueous solution. In aqueous solution the aldehyde complex exists entirely in the nonhydrated carbonyl form in contrast to the free ligand which is largely hydrated under similar conditions. The $Ru(NH_3)_4(2-pyridinecarboxaldehyde)^{2+}$ complex does react reversibly with aqueous hydroxide to give the aldehyde hydrate anion, and the equilibrium constants for this reaction and the analogous reaction of aqueous hydroxide with $Ru(NH_3)_5(4-pyridinecarboxaldehyde)^{2+}$ have been evaluated. In addition, the reduction potentials for the Ru(III)/Ru(II) couples for a number of these complexes are reported. These data are interpreted in terms of the special stability of unsaturated metallocyclic complexes formed between Ru(II) and a π-unsaturated bidentate ligand.

Recent research in these laboratories has focused on the reactions and properties of monodentate ligands coordinated in the pentaammine and tetraammine complexes of the group VIII metal ions: ruthenium(II), ruthenium(III), and rhodium(III).[2-5] This work has established the metal-to-ligand back-bonding which characterizes Ru(II) complexes of monodentate, π-unsaturated organic ligands, as well as other differences in the abilities of the various ions to affect the electronic character of coordinated ligands. In the course of studying ligand substitution rates of related complexes,[6] it was discovered that the ruthernium(II) 2-aminomethylpyridine complex, A, undergoes facile air oxidation in aqueous solution to a product proposed to be the ruthenium(II) imino species B (eq 1). This reaction is analo-

$$(NH_3)_4Ru \overset{air}{\underset{in\ H_2O}{\longrightarrow}} (NH_3)_4Ru \qquad (1)$$

A   B
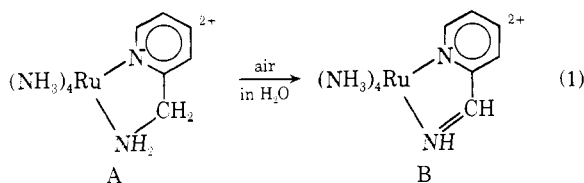
gous to air oxidation reported for $Ru(en)_3^{2+}$ to form the α-diamine complex C (eq 2).[7,8] Complexes such as B and C

$$Ru(en)_3^{2+} \overset{air}{\underset{in\ H_2O}{\longrightarrow}} (en)_2Ru \qquad (2)$$

C
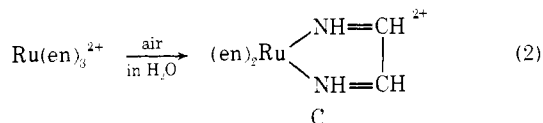
where the π-unsaturated bidentate ligand forms a cyclic configuration including the metal potentially have substantially different metal-ligand interactions than do complexes of monodentate ligands. Here we report the synthesis and properties of several complexes of ortho-substituted pyridine ligands (including B) which can form such unsaturated

metallo ring systems with the goal of comparing these to the analogous monodentate pyridine complexes. In a subsequent paper we shall report on kinetics studies regarding certain reactions relating to the formation of these complexes.

Experimental Section

Materials. Chloropentaammineruthenium(III) dichloride,[9] $[Ru(NH_3)_5Cl]Cl_2$, and cis-dichlorotetraammineruthenium(III) chloride,[10] cis-$[Ru(NH_3)_4Cl_2]Cl$, were prepared according to literature procedures. Organic ligands used in syntheses of complexes were purchased from Aldrich and were purified by vacuum distillation. Water used in these studies was redistilled from alkaline permanganate. Argon used to entrain air from reaction solutions was deoxygenated by passing through chromous solution in gas scrubbing bottles. Standard sodium hydroxide solutions were prepared from commercial solution concentrates (Dilut-It).

Syntheses. Tetraammine(2-aminomethylpyridine)ruthenium(II) Tetrafluoroborate, $[Ru(NH_3)_4(2-NH_2CH_2C_5H_4N)][BF_4]_2$. A deaerated solution (3.0 ml) of cis-$Ru(NH_3)_4(H_2O)_2^{2+}$, generated[11] by Zn(Hg) reduction of aqueous cis-$[Ru(NH_3)_4Cl_2]Cl$ (0.20 g, 7.2 × 10^{-4} mol) was added to a fivefold molar excess of deaerated 2-aminomethylpyridine (~0.2 g), and the reaction was allowed to proceed under an argon atmosphere for 30 min. Subsequently, the reaction mixture was filtered, and upon addition of 2 ml of saturated aqueous NaBF$_4$, a yellow precipitate, $[Ru(NH_3)_4(NH_2CH_2C_5H_4N)][BF_4]_2$, formed. The solid was separated by filtration and washed with 2 ml each of cold ethanol–H$_2$O (2:1 v/v), ethanol, ethanol-ether (1:1 v/v), and ether. Recrystallization was from hot water under deaerated conditions to prevent air oxidation of the ruthenium(II) complex. The recrystallized solid was washed with ice-cold deaerated water (1 ml) then 2 ml each of cold ethanol-H$_2$O (2:1 v/v), ethanol, ethanol-ether (1:1 v/v), and ether. The yellow crystals were dried under a vacuum at room temperature, yield 0.130 g, 80%. *Anal.* Calcd for $C_6H_{20}N_6B_2F_8Ru$: C, 15.87; H, 4.47; N, 18.64; Ru, 22.41. Found: C, 15.65; H, 4.53; N, 18.74; Ru, 21.90.

Tetraammine(2-pyridinealdehyde)ruthenium(II) Tetrafluoroborate, [Ru(NH₃)₄(2-CHOC₅H₄N)][BF₄]. This compound was prepared in deaerated solution from the reaction of *cis*-Ru(NH₃)₄(H₂O)₂²⁺ and 2-pyridinealdehyde in a manner analogous to the syntheses described above. The recrystallized compound forms blue needles, yield 53%. *Anal.* Calcd for C₆H₁₇ON₅B₂F₈Ru: C, 15.98; H, 3.77; N, 15.52; Ru, 22.45. Found: C, 15.80; H, 3.55; N, 15.69; Ru, 22.72. (*Warning:* The perchlorate salt of this complex detonates with little provocation.)

Tetraammine(bipyridine)ruthenium(II) Tetrafluoroborate, [Ru(NH₃)₄(bipy)][BF₄]₂. This compound was prepared from *cis*-Ru(NH₃)₄(H₂O)₂²⁺ and bipyridine in the manner described above, yield (of recrystallized compound) 35%. *Anal.* Calcd for C₁₀N₆H₂₀B₂F₈Ru · H₂O: C, 23.20; H, 4.25; N, 16.25; Ru, 19.95. Found: C, 22.95; H, 3.94; N, 14.42; Ru, 20.10.

Tetraammine(2-pyridinalimine)ruthenium(II) Tetrafluoroborate, [Ru(NH₃)₄(2-HN:CHC₅H₄N)][BF₄]₂. This compound was prepared by direct oxidation with O₂ of a saturated aqueous solution (2 ml) of the 2-aminomethylpyridine complex, [Ru(NH₃)₄(2-NH₂CH₂C₅H₄N)]²⁺(BF₄)₂ (0.95 g, 2.1 × 10⁻³ mol). The product was precipitated as the BF₄⁻ salt and was recrystallized from warm water. Due to the high solubility of [Ru(NH₃)₄(2-HN:CHC₅H₄N)][BF₄]₂, the yield after recrystallization was very low (0.12 g) 13%. *Anal.* Calcd for C₆H₁₈N₆B₂F₈Ru · H₂O: C, 15.42; H, 4.29; N, 18.00; Ru, 21.70. Found: C, 15.43; H, 4.06; N, 18.35; Ru, 21.74.

Ruthenium analyses were performed using the method of Larson and Ross.[4]

Spectra. Visible ultraviolet spectra were recorded on a Cary 14 spectrophotometer. All spectra were taken at room temperature as dilute solutions in deaerated redistilled water. Solutions for extinction coefficients were prepared gravimetrically followed by quantitative serial dilutions to give appropriate concentrations. In all cases, the extinction coefficient values were determined from duplicate solutions and found to be reproducible within 3%. Proton magnetic resonance spectra were obtained on a Varian HA-100 high-resolution spectrometer operating in a frequency sweep mode. A Varian Associates C-1024 time averaging computer was used to improve the signal-to-noise ratio of dilute samples. The internal standard was acetonitrile (2%) and the solvent was D₂O. Chemical shift values relative to TMS were determined by assigning the δ value 2.00 ppm to acetonitrile. Infrared spectra were obtained with a Perkin-Elmer Model 225 spectrophotometer. Spectra of solid complexes were taken as KBr pellets and of organic ligands as neat liquids between NaCl plates. Raman spectra of complexes were obtained on a Cary 82 laser Raman spectrophotometer using a high speed powder sample spinner (Cary accessory) to prevent photolytic decomposition by the laser beam.
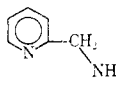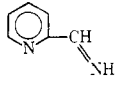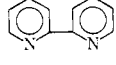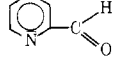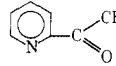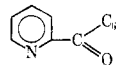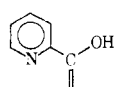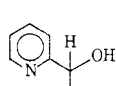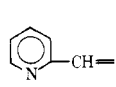
Electrochemical Measurements. Reduction potentials of the Ru(NH₃)₄(X-Y)³⁺/²⁺ couples were measured by cyclic voltammetry on a PAR Model 174 polarographic analyzer and data were recorded on a Houston Instrument, Model 2000 XY recorder. The electrochemical cell used was a conventional thr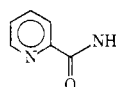ee-electrode type: platinum ball (attached to a fine Pt wire sealed in glass) working electrode, platinum wire auxilary electrode, and a saturated calomel reference electrode. Potentials reported are estimated to include ±10 mV overall uncertainty. The aqueous solutions were ~10⁻³ M in Ru(II) complex, 0.1 M p-toluenesulfonic acid, and 0.1 M sodium p-toluenesulfonate giving a pH of 1.3 and ionic strength ~0.20. Solutions were deaerated by entraining with purified argon prior to the electrochemical measurements. Scan rates were 100–500 mV/sec.

Equilibrium Measurements. Equilibrium constants at 25° for the reversible reactions of aqueous sodium hydroxide with tetraammine(pyridine-2-carboxaldehyde)ruthenium(II) and with pentaammine(pyridine-4-carboxaldehyde)ruthenium(II) were determined spectrophotometrically in deaerated solution. Solutions were prepared (in the serum-capped 1-cm optical cells) by syringe techniques. Various base concentrations were examined, and solution ionic strength was maintained at 1 M with NaCl. Because of the slow secondary reaction which occurs in the alkaline solutions (*vide infra*), spectra of these solutions were obtained immediately after preparation. p*K*ₐ values for the tetraammineruthenium(II) complexes of 2-pyridinecarboxylate and 2-pyridinecarboxamide were measured spectrophotometrically in a similar manner.

Results

The Imine Complex. Reaction of 2-aminomethylpyridine with *cis*-Ru(NH₃)₄(H₂O)₂²⁺ in deaerated solution results in the formation[6b] of *cis*-Ru(NH₃)₄(2-NH₂CH₂C₅H₄N)²⁺. The electronic spectrum of this complex ion (Table I) is closely analogous, as expected, to that of the

Table I. Electronic Spectra[a] of the Complexes *cis*-Ru(NH₃)₄(X–Y)²⁺

Ligand X–Y	λ_max[b] (ε × 10⁻³)			
[pyridine-CH₂-NH₂]	414 (6.3),		248 (5.8)	
[pyridine-CH=NH]	520 (6.1),	378 (4.4),	267 (7.5)	
[pyridine-pyridine (bipy)]	523 (3.5),	367 (5.7),	294 (32.0) 286 (21.4) 244 (10.0)	
[pyridine-CH=O (aldehyde)]	635 (5.5),	380 (4.0),	273 (9.3)	
[pyridine-C(CH₃)=O]	622 (5.4),	386 (4.3),	273 (9.8)	
[pyridine-C(C₆H₅)=O]	653 (6.9),	383 (4.0),	292 (16.0)	
[pyridine-C(NH₂)=O]	544[c] (4.2), 490[d] (4.0)	397[c] (4.4) 398[d] (3.9)	262[c] (12.1) 262[d] (10.6)	222[c] (10.5)
[pyridine-C(OH)=O]	540[e] (1) 499[f] (2)	386[e] (1) 396[f] (3)	254[e] (6) 257[f] (12)	217[f] (6)
[pyridine-CH(OH)(O⁻)][g]	426 (6.8)	250 (6.1)		
[pyridine-CH=NOH]	515 (3.6)	376 (5.8)	270 (11.0) 238 (12.0)	

[a] In dilute aqueous solution, 25°. [b] In nanometers. [c] [HCl] = 0.29 M. [d] [NaOH] = 0.19 M. [e] [HCl] = 1.20 M. [f] [NaOH] = 0.40 M. [g] [NaOH] = 0.25 M.

pentaammine ion Ru(NH₃)₅py²⁺ with visible region dominated by a strong metal-to-ligand charge transfer band at 414 nm (*vs.* 408 for Ru(NH₃)₅py²⁺),[12] and the uv region dominated by a π–π* internal ligand transition at 248 nm (*vs.* 244 nm) (Figure 1). However, reaction with air or pure oxygen in neutral or slightly acidic aqueous solution leads to markedly different pathways for the two complexes. Clean oxidation of Ru(II) to Ru(III) (eq 3) is the observed

$$\text{Ru(NH}_3)_5\text{py}^{2+} \xrightarrow{\text{O}_2} \text{Ru(NH}_3)_5\text{py}^{3+} \qquad (3)$$
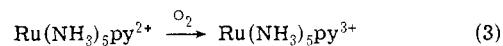
pathway for Ru(NH₃)₅py²⁺ to give a solution which is virtually colorless. In contrast oxidation of the 2-aminomethylpyridine complex produces a deep red solution which we attribute to formation of the 2-iminomethylpyridine complex B (eq 1), a product of ligand, not metal, oxidation. The ultimate fate of the oxygen in the redox reaction was not determined; however, O₂ oxidations of aqueous Ru(NH₃)₆²⁺ and

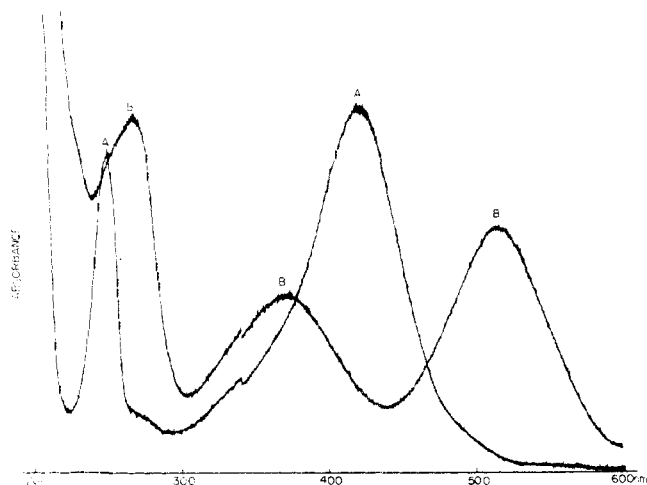**Figure 1.** (A) Electronic spectrum of $Ru(NH_3)_4(2\text{-}NH_2CH_2C_5H_4N)^{2+}$ (1.16×10^{-4} M) in aqueous solution. (B) Electronic spectrum of $Ru(NH_3)_4(2\text{-}HN:CHC_5H_4N)^{2+}$ (1.16×10^{-4} M) in aqueous solution.

$Ru(en)_3^{2+}$ to the Ru(III) analogs have been shown to produce hydrogen peroxide quantitatively.[13]

The identity of the imine complex is assigned on the following bases. First, oxidation of the 2-aminomethyl complex produces a major change in the electronic spectrum, principally disappearance of the charge transfer band at 414 nm accompanied by appearance of comparably intense absorption bands at 520 and 378 nm. Isolation of solid product gives a material with identical spectral properties as the redox solution (Table I), yet with an elemental analysis having the same 6:6:1 N:C:Ru composition as the starting material. The pmr spectra of both materials show multiplets for the pyridine protons (7.7–8.4 and 7.1–8.8 ppm, respectively, Table II). The principal pmr spectral differences are that A displays a singlet at 3.93 ppm which can be assigned to the ortho-methylene group while B has a singlet at 9.08 ppm which can be assigned to the methyne group. A similar low field resonance has been reported for the methyne hydrogens (8.8 ppm) of the α-diimine complex C.[8]

The apparent cleanness of the O_2 oxidation of A to B is illustrated by two results. First, extinction coefficients determined for an aqueous solution of B produced directly by oxidation of A are within experimental uncertainty of those determined from the isolated and recrystallized product. Second, the pmr spectrum of a degassed solution made up from solid product and D_2O was found comparable in intensity and sharpness to the spectrum of the degassed D_2O solution of the 2-pyridinalimine complex generated in vitro by O_2 oxidation of the 2-aminomethylpyridine complex. Failure to see broadening implies the absence of significant concentrations of paramagnetic ruthenium(III) impurities, especially those capable of rapid electron exchange with B.

The ir and Raman spectra of B (as its BF_4^- salt) show a number of bands in the region between 1600 and 1400 cm^{-1} as is characteristic of pyridine type species. Comparison of the spectra of the amino and imino complexes shows that the only transition in this region unique to the imino complex is a strong infrared absorption at 1507 cm^{-1}. This band was not seen in the Raman experiment. This frequency would be consistent with that expected for the stretching band of the imino group's conjugated nitrogen double bond.

Both the 2-aminomethylpyridineruthenium(II) complex ion A and the imino analog B can be oxidized by the addition of 1 equiv of ceric ion in acidic aqueous solution. The resulting solutions in each case are virtually colorless with the oxidation product of A showing a single λ_{max} at 256 nm

Table II. Pmr Spectra of Free and Coordinated Ligands[a]

| Species	Chemical shifts observed[b] Aromatic protons	Other ligand protons
pyridine–CH₂–NH₂	7.0–8.4 m	3.78 s (–CH₂–)
(NH₃)₄Ru–pyridine–CH₂–NH₂	7.7–8.4 m	3.93 s (–CH₂–)
(NH₃)₄Ru–pyridine–CH=NH	7.1–8.8 m	9.08 s (=CH–)
pyridine–CH=O	7.4–8.7 m	5.89 s (–CH-(OD)₂), 9.81 s (–CHO)[c]
(NH₃)₄Ru–pyridine–CH=O	7.7–9.1 m	10.40 s (–CHO)
(NH₃)₄Ru–pyridine–CHO + OD	7.2–8.5 m	4.65 s $\left(\!-\overset{\displaystyle O}{\underset{\displaystyle OD}{C}}\!-\!H\right)$
(NH₃)₄Ru–pyridine–CH=O + OD⁻	6.9–8.9 m	4.15 s $\left(\!-\overset{\displaystyle O}{\underset{\displaystyle OD}{C}}\!-\!H\right)$

[a] Spectra obtained on a Varian HA-100 in D_2O solution with 2% CH_3CN as internal standard, $T \sim 37°$. [b] In ppm downfield from TMS. [c] This compound exists as mixture of aldehyde and aldehyde hydrate in aqueous solution at spectra temperature. [d] [NaOD] = 0.1 N.

(ϵ 6.8×10^3 M^{-1} cm^{-1}) while that of B shows three peaks at 273 (sh) (ϵ 6.6×10^3), 263 (sh) (ϵ 14.7×10^3), and 258 nm (ϵ 17.1×10^3 M^{-1} cm^{-1}). The positions and intensities of these bands are consistent with assignment as π–π^* internal ligand transitions. These spectra are similar to that reported[12] for $Ru(NH_3)_5py^{3+}$, thus suggesting that the oxidation gives merely the Ru(III) analogs of A and B. Consistent with this conclusion is the fact that adding amalgamated zinc to the oxidation solutions regenerated the original Ru(II) complexes in a nearly quantitative yield for both cases. Addition of a second equivalent of Ce(IV) to the oxidized A solution results in the slow, but nearly quantitative, formation of B. In addition, the following qualitative observations can be made regarding the solution chemistry of the Ru(III) analogs of A and B. Neutralization of the oxidized A solution by adding sodium bicarbonate leads to the formation of the Ru(II) imine complex B. In the presence of air, this reaction is roughly quantitative while in deaerated solution a yield approximating only 50% was observed. In 0.3 M H_2SO_4 solution the Ru(III) imine complex slowly reverts spontaneously to the Ru(II) species B.

The Aldehyde Complex. In an attempt to synthesize B by an independent route, 2-pyridinecarboxaldehyde was allowed to react with $Ru(NH_3)_5H_2O^{2+}$ in deaerated aqueous solution. The result was not the red imine complex but a deep blue complex, D, which could be isolated as a solid BF_4^- salt. This blue species was originally thought to be pentaammine(2-pyridinecarboxaldehyde)ruthenium(II),

the product of simple H_2O displacement. However, reaction of the aldehyde ligand with cis-$Ru(NH_3)_4(H_2O)_2^{2+}$ produces a complex ion with identical electronic, infrared, and nmr characteristics to those of D. The recrystallized BF_4^- salt of this complex gives an elemental analysis conforming to the formulation[13] [$Ru(NH_3)_4$(2-pyridinecarboxalde-hyde)][BF_4]$_2$. Thus, one can conclude that reaction of $Ru(NH_3)_5H_2O^{2+}$ results in the relatively facile displacement of one-coordinated ammonia. Under similar synthetic conditions with monodentate pyridine ligands including 4-pyridinecarboxaldehyde, there has been no evidence for ammonia displacement from pentaammineruthenium(II) complexes[12] although at elevated temperatures aqueous $Ru(NH_3)_5py^{2+}$ has been reported[11] to react with pyridine to give cis- and trans-$Ru(NH_3)_4py_2^{2+}$.

The elemental composition of D suggests the chelate structure

$$(NH_3)_4Ru \begin{array}{c} \\ \end{array}^{2+}$$

D
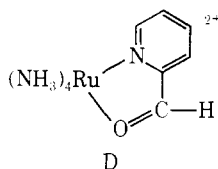
This conclusion is supported by the spectral properties. The nmr spectrum clearly shows the aldehyde proton (Table II) as a sharp singlet shifted downfield 0.6 ppm from the free ligand value. A downfield shift is consistent with coordination to the cationic center. The electronic spectrum (Table I) shows two broad and relatively intense absorption bands in the visible–near-uv region plus a $\pi-\pi^*$ internal ligand transition in the uv (273 nm). This pattern is quite similar to that observed for the chelate imino complex B, although the lowest energy absorption band appears at a lower energy for D (635 nm) than for B (520 nm). Finally, neither the ir nor Raman spectra of the BF_4^- salt of D show a carbon-oxygen double bond stretching band in the region expected for a free carbonyl (the free ligand shows a strong ν_{CO} band at 1716 cm^{-1} in both the ir and Raman spectra). Comparison of the ir and Raman spectra of the free ligand, and of the BF_4^- salts of B and D yields only one band in the region between 1750 and 1400 cm^{-1} unique to D. This band is a strong Raman transition at 1520 cm^{-1}; however, the failure to see this band in the ir spectrum casts some doubt as to whether it is the ν_{CO} band of the coordinated aldehyde.

The aldehyde complex ion D reacts rapidly with added sodium hydroxide in deaerated aqueous solution. The result is the disappearance of the blue color and the formation of a yellow solution with a broad and intense charge transfer band at 426 nm and a $\pi-\pi^*$ ligand transition at 250 nm (Figure 2). Addition of acid sufficient to neutralize the reaction solution leads to the quantitative re-formation of D thus showing the reaction with base is reversible. However, if the reaction solution is allowed to remain basic indefinitely, over a period of hours the solution slowly turns red, eventually giving a spectrum (λ_{max} at 525, 400, and 256 nm) similar, but not identical, to that of B. The spectral similarities suggest structural similarities, thus it might be proposed that the slow secondary reaction involves condensation of the aldehyde function with coordinated ammonia to form an imino species.

The reversible reaction with base to give the species with a λ_{max} at 426 nm also results in the disappearance of the aldehyde proton in the pmr spectrum and some broadening of the pyridine proton resonances. The pmr experiments were carried out in D_2O solution using NaOD as the added base and using the complex [$Ru(ND_3)_4$(pyridine-2-carbox-aldehyde)][BF_4]$_2$ prepared from perdeuterated [cis-
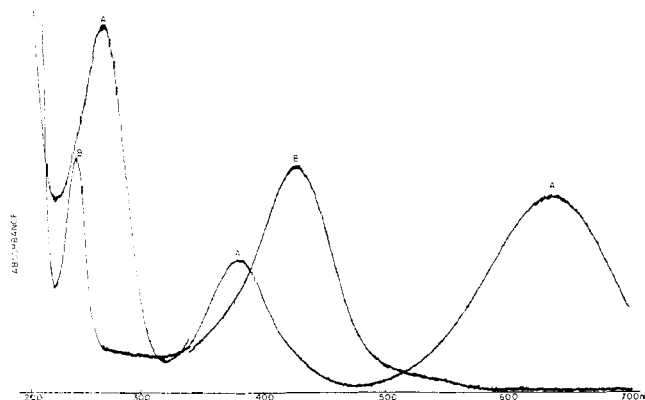

Figure 2. Electronic spectrum of $Ru(NH_3)_4$(2-$CHOC_5H_4N$)$^{2+}$ (1.03 $\times 10^{-4}$ M) in aqueous solution: (A) [H^+] = 0.5 M, (B) [OH^-] = 1.0 M.

$Ru(ND_3)_4Cl_2]Cl$. The disappearance of the aldehyde proton was accompanied by the appearance of a new resonance at δ 4.15 ppm. Addition of NaOD to a D_2O solution of the 2-pyridinecarboxaldehyde free ligand also leads to disappearance of the aldehyde proton with concurrent appearance of a new resonance at δ 4.65 ppm (Table II). In both cases, neutralization of the base with excess D_2SO_4 led to regeneration of the aldehyde species as evidenced by reappearance of the aldehyde proton resonances. These observations are interpreted in terms of an equilibrium addition of hydroxide ion to the carbonyl function.

$$(NH_3)_4Ru \begin{array}{c} \\ \end{array}^{2+} + OH^- \rightleftharpoons (NH_3)_4Ru \begin{array}{c} \\ \end{array}^+ \quad (4)$$
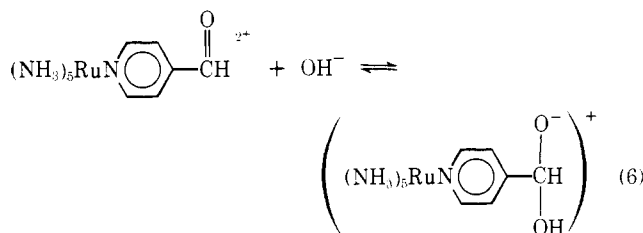
D E
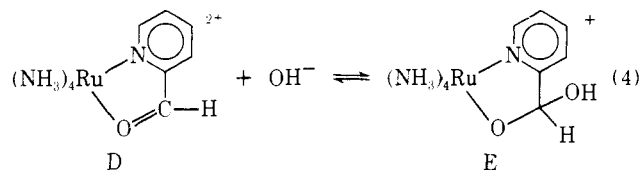
The formation constant of the coordinated aldehyde hydrate anion E can be evaluated from the electronic spectra of aqueous solutions of the aldehyde complex in various concentrations of base in deaerated solution. Deaeration was necessary as the aldehyde complex is exceedingly sensitive to air in alkaline solution and decomposes irreversibly to unknown products. A plot of log (absorbance 635/absorbance 426) vs. $-\log$ [OH^-] gives a typical weak acid titration curve. The equilibrium constant K_4 = [E]/[D][OH^-] is equal to [OH^-]$^{-1}$ at the concentration of base where[5b]

$$\log \left(\frac{Abs(635)}{Abs(426)} \right) = \log \left(\frac{\epsilon_D(635) + \epsilon_E(635)}{\epsilon_D(426) + \epsilon_E(426)} \right) \quad (5)$$

The value determined in this manner was $(1.4 \pm 0.1) \times 10^2$ M^{-1} in 1.0 M ionic strength solution (maintained with NaCl).

The pentaammineruthenium(II) complex of 4-pyridine-carboxaldehyde has previously been shown to undergo hydrate formation in water and acetal or hemiacetal formation in methanol.[14,15] Hydrate formation in water is small but detectable as a shoulder on the principal charge transfer absorption band of the aldehyde complex. In contrast, there is no indication in the electronic or pmr spectra of the 2-aldehyde complex D of the presence of any aldehyde hydrate in acidic solutions. The reaction of the 4-aldehyde complex with base has not been previously reported, although it was noted that the ratio of hydrate to aldehyde form of the complex was slightly pH dependent between pH 1.4 and 5.10.[15] However, we have noted that in deaerated solution the presence of base causes an acid reversible decrease in the absorption band attributed to the nonhydrated form of the al-

dehyde complex (λ_{max} 543 nm) with a corresponding increase in absorbance at a wavelength (λ_{max} 413 nm) (Figure 3) close to the absorption band (λ_{max} 420 nm) which has been attributed to the hydrated form. These observations can be rationalized in terms of the equilibrium

$$(NH_3)_5RuN\bigcirc-\overset{O}{\overset{\|}{C}}H + OH^- \rightleftharpoons$$

$$\left((NH_3)_5RuN\bigcirc-\overset{O^-}{\overset{|}{\underset{OH}{C}}}H\right)^+ \quad (6)$$

Using procedures analogous to those described for the 2-aldehyde complex, an equilibrium constant for eq 6, K_6, can be evaluated as equal to $15 \pm 2\ M^{-1}$.

Other Complexes of Bidentate Ligands. Reaction in deaerated aqueous solution between cis-Ru-$(NH_3)_4(H_2O)_2^{2+}$ and the bidentate pyridine ligands 2-pyridinealdoxime, 2,2'-bipyridine, 2-acetylpyridine, 2-benzoylpyridine, 2-pyridinecarboxamide, and 2-pyridinecarboxylic acid leads in each case to the formation of complex ions Ru$(NH_3)_4(X-Y)^{2+}$ isolable as the BF_4^- salts. The electronic spectra of these complexes are summarized in Table I. Reaction with hydroxide was examined for the latter four with the following results. Neither the 2-acetylpyridine nor the 2-benzoylpyridine complex showed detectable reaction with hydroxide up to 0.25 M concentration in deaerated solution. Thus addition processes analogous to eq 4 were not observed and given the systematic experimental uncertainties must have equilibrium constants less than 0.5 M^{-1} for these two complexes. In contrast, both the 2-pyridinecarboxylic acid and 2-pyridinecarboxamido complexes showed changes in electronic spectra between acidic and basic solution (Table I). Comparison of the spectral absorbances as a function of solution pH showed characteristic weak acid behavior for both complexes, and plots such as described for 2-aldehyde complex gave pK_a values of 0.7 for the 2-pyridinecarboxylic acid complex and 13 for the 2-pyridinecarboxamide complex.

Electrochemical Measurements. Reduction potentials determined for the Ru(III)/Ru(II) couples by cyclic voltammetry are summarized in Table III. Each of the cell potentials listed are for highly reversible voltammograms where the measured separation between the cathodic and anodic peaks (60–75 mV) is close to the theoretical Nernstian value of 59 mV. Attempts to measure the potentials for the aldehyde complexes, Ru$(NH_3)_4$(2-pyridinecarboxaldehyde)$^{2+}$ and Ru$(NH_3)_5$(4-pyridinecarboxaldehyde)$^{2+}$, led to irreversible behavior with peak separations of 395 and 150 mV, respectively, under the experimental conditions. The value reported here for the pyridine complex is very close to that reported by Lim, Barclay, and Anson[16] for the same complex under similar but not identical conditions. The 2-aminomethylpyridine complex, as expected, has a potential virtually identical with that of the pyridine complex. However, in contrast to observations with several ethylenediamine complexes,[8] the oxidative portion of the cycle did not show a second, irreversible ligand redox process at voltages higher than the oxidation to Ru(III) under the experimental conditions. The reduction potential of the pyridinalimine ruthenium(III) complex is substantially more positive than that of the aminomethylpyridine complex. Similarly, larger potentials are seen for the Ru$(NH_3)_4^{3+}$ complexes of bipyridine and 2-acetylpyridine.
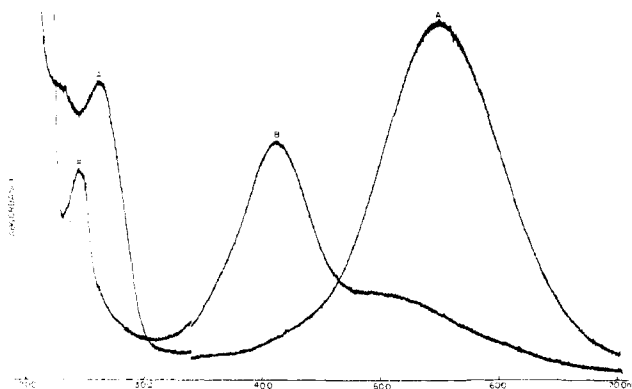
Figure 3. Electronic spectrum of Ru$(NH_3)_5$(4-CHOC$_5$H$_4$N)$^{2+}$ (0.82 $\times 10^{-4}\ M$) in aqueous solution: (A) [H$^+$] = 0.5 M, (B) [OH$^-$] = 1.0 M.

Table III. Reduction Potentials of Complexes, Ru$(NH_3)_4(X-Y)^{3+/2+}$ as determined by Cyclic Voltammetry[a]

| Couple	E^f (mV) vs. nhe	Separation[b] (mV)
(NH$_3$)$_5$Rupy$^{3+/2+}$	300 305[c]	75 Not reported
(NH$_3$)$_4$Ru (2-aminomethylpyridine)$^{3+/2+}$	295	75
(NH$_3$)$_4$Ru (2-pyridinealdoxime)$^{3+/2+}$	565	65
(NH$_3$)$_4$Ru (bipyridine)$^{3+/2+}$	507	70
(NH$_3$)$_4$Ru (2-acetylpyridine)$^{3+/2+}$	552	70
(NH$_3$)$_6$Ru$^{3+/2+}$	51[c,d]	Not reported

[a] This work unless noted, scan rate 0.5 V/sec in aqueous solution containing 10^{-3} M complex, 0.1 M p-toluenesulfonic acid, and 0.1 M sodium p-toluenesulfonate. [b] Potential separation between cathodic and anodic peaks. [c] Reference 16, 0.1 F CF$_3$CO$_2$Na and 0.1 F CF$_3$CO$_2$H. [d] 0.1 F NaBF$_4$.

Discussion

Electronic Spectra. The visible region absorption bands observed for the complexes Ru$(NH_3)_4(X-Y)^{2+}$, where X–Y is an ortho-substituted bidentate pyridine ligand, can be qualitatively assigned as metal-to-ligand charge transfers (MLCT) on the basis of their intensities and of analogies to previously reported[5,14] Ru(II) ammine complexes of π unsaturated ligands. Similarly, the strong bands in the region ~250–270 nm can be qualitatively assigned to internal ligand π_L–π_L^* transitions commonly observed in this region for pyridine complexes. The 2-aminomethylpyridine complex (A) has, as expected, a spectrum closely analogous to that of Ru$(NH_3)_5$py^{2+} with only small λ_{max} shifts for the MLCT band (414 vs. 408 nm) and the π_L–π_L band (248 vs. 244 nm). The complex E (product of hydroxide reaction

with the aldehyde complex, eq 4), also shows an absorption spectrum rather closely analogous to that of $Ru(NH_3)_5py^{2+}$ (Table I). Since those complexes in which the coordinating pyridine ortho substituent is an unsaturated carbonyl or imine species show two visible charge transfer bands (see below), the observation of a single MLCT band for E supports the conclusion that E is indeed the product of hydroxide addition to the aldehyde carbonyl.

Single MLCT maxima are observed in the visible spectra of complexes where X–Y is a symmetrical bidentate α-ethylenediimine ligand. For example, $Ru(NH_3)_4$(ethylenediimine)$^{2+}$ (448 nm)[17] and $Ru(en)_2$(ethylenediimine)$^{2+}$ (448 nm)[8] show single maxima, although the breadth and somewhat unsymmetrical nature of these absorbances suggest the possible presence of more than one electronic transition in this spectral region. The unsymmetrical cases in which X–Y is a pyridine ortho substituted with a conjugating functional group, e.g.
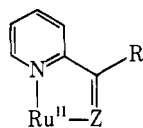
(where Z is either O or NH), each shows two absorption bands in the visible region (Table I). One of these occurs with λ_{max} ~380–400 nm and its position is relatively insensitive to the nature of Z and of the substituent R. The position of the longer wavelength band is more sensitive to R and Z. When R is CH_3–, H–, or C_6H_5– and Z is an oxygen, the maxima of this band occur at 622, 635, or 653 nm, respectively, an order paralleling the relative electron withdrawing character of the R substituent. When Z is NH and R is –H this band appears at higher energy (520 nm). These patterns of behavior suggest in a very qualitative sense that the longer wavelength band involves specifically the cyclic chromophore containing the metal ion


F
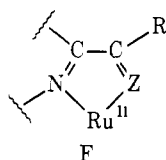
while the shorter wavelength band may involve a transition of the ruthenium–pyridine chromophore.

Formation of Complexes. Air oxidation of the 2-aminomethylpyridine complex A to the 2-pyridinalimine complex B (eq 1) is not surprising given the analogy of eq 2 to form a diimine ruthenium(II) species.[8] Similar reactions have been noted for iron(II) polydentate amine complex ions,[18] and for the latter case it was suggested that the ability of the iron to undergo reversible single electron oxidation to iron(III) was an important feature in ligand oxidation mechanism. In addition redox reactions of various amines coordinated to ruthenium have been noted previously.[19] In the present case, the stability of the Ru(II) diimine type chromophore, as demonstrated by the substantial reduction potential of the Ru(III) pyridinalimine complex, apparently provides a driving force for the formation of the Ru(II) complex as the final reaction product.

More surprising is the facile formation of the tetraammineruthenium(II) complex of 2-pyridinecarboxaldehyde by reaction of this ligand with $Ru(NH_3)_5H_2O^{2+}$. Rate studies currently in progress[20] show the reaction kinetics to be complicated for reaction of 2-pyridinecarboxaldehyde with either $Ru(NH_3)_5H_2O^{2+}$ or cis-$Ru(NH_3)_4(H_2O)_2^{2+}$ in deaerated aqueous solution. However, in 0.01 N free ligand

(25°, pH ~8), the formation half-life of D from Ru-$(NH_3)_5H_2O^{2+}$ (10^{-4} M) is approximately 20 min while formation of D from $Ru(NH_3)_4(H_2O)_2^{2+}$ under similar conditions occurs with a half-life of about 6 min. Under similar conditions the reaction of pyridine and $Ru(NH_3)_5H_2O^{2+}$ to give $Ru(NH_3)_5py^{2+}$ has a half-life of about 13 min[6a] with no observable labilization of coordinated NH_3 while the reaction of pyridine with cis-$Ru(NH_3)_4H_2O^{2+}$ to give $Ru(NH_3)_5py^{2+}$ occurs in two observable steps,[6b] the first having a $t_{1/2}$ of ~6 min, the second a $t_{1/2}$ of ~60 min. Clearly the labilization of one NH_3 from $Ru(NH_3)_5H_2O^{2+}$ on reaction with pyridine-2-carboxaldehyde does not represent the intrinsic lability of NH_3 coordinated to ruthenium(II) in ammine complexes of these nitrogen aromatic heterocycles but must represent a special property of this ligand as a nucleophilic for the Ru(II) center.

Reaction of Aldehyde Complexes with Base. Previous studies[14,15] of the complex ion $Ru(NH_3)_5$(4-pyridinecarboxaldehyde)$^{2+}$ have shown that hydrate formation (eq 7)


(7)
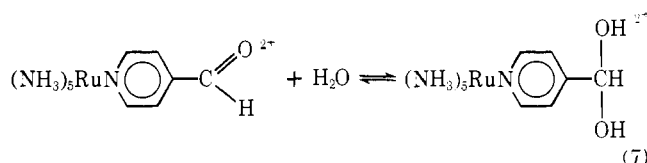
has a substantially smaller equilibrium constant for the complex than for the free ligand in neutral or acidic solution. This increased stability of the carbonyl form of the ligand when coordinated to Ru(II) has been attributed to the π back-bonding interaction between the $4d^6$ metal center and the unsaturated ligand. Similarly, while 2-pyridinecarboxaldehyde has been shown[21] to be more than 50% hydrated in neutral aqueous solution and completely hydrated in strongly acidic solution, there is no indication of hydrate formation in either the nmr or electronic spectra of the complex D. This suggests that opportunity for forming the Ru(II) metallocycle having the unsaturated configuration F (Z = oxygen) strongly favors the carbonyl form of the coordinated aldehyde over the hydrate form which results in the partially saturated metallocycle configuration G. The possi-

G
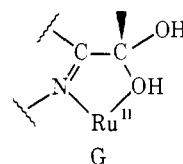
ble "aromatic" character of unsaturated metallocycles such as F has been previously discussed for iron(II) α-diimine complexes,[22] and the analogy to the Ru(II) diimine complexes is reinforced by the strongly positive reduction potential of the Ru(III) 2-acetylpyridine complex. The failure of reversible behavior in the cyclic voltammetry of $Ru(NH_3)_4$(2 - pyridinecarboxaldehyde)$^{2+}$ and $Ru(NH_3)_5$-(4 - pyridinecarboxaldehyde)$^{2+}$ is very likely due to the tendency of the Ru(III) species to form hydrates[15] in the time scale of the experiment.

Reaction of the aldehyde complexes with aqueous hydroxide produces a species in each case whose electronic spectra and pmr spectrum (in the case of the 2-pyridinecarboxaldehyde complex) are interpreted as indicating formation of the coordinated pyridine aldehydes in the hydrate anion form (eq 4 and 6). Equilibrium constants for the analogous reaction of the free ligands (eq 8) have been determined[23] as being 100 M^{-1} for 4-pyridinecarboxaldehyde and 25 M^{-1} for 2-pyridinecarboxaldehyde, respectively, at

$$\text{(pyridyl)}{-}CHO \;+\; OH^- \;\rightleftharpoons\; \text{(pyridyl)}{-}\overset{O^-}{\underset{H}{C}}{-}OH \qquad (8)$$
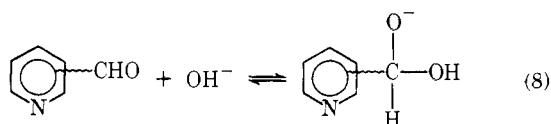
20°. Comparison of the equilibrium constants for the complexes to those for the respective free ligand show that coordination to $Ru(NH_3)_5^{2+}$ decreases the tendency for 4-pyridinecarboxaldehyde to form the aldehyde hydrate anion (K(complex)/K(free ligand) = 0.2). This effect is consistent with the behavior of this complex in neutral or acidic solution where the tendency to form the hydrate complex is decreased by at least a factor of 7 despite the fact that coordination of pyridine nitrogen to a cationic center normally enhances hydrate formation.[15,21] Since it has been argued[14,15] that the back-bonding interaction between the Ru^{II} center and the 4-pyridinecarboxaldehyde ligand is responsible for decreased tendency of the coordinated ligand to add H_2O to form the aldehyde hydrate, a similar argument can be applied to the decreased tendency of the complex to add OH^- to form the aldehyde hydrate anion.

A contrasting observation is that coordination to $Ru(NH_3)_4^{2+}$ enhances the tendency of 2-pyridinecarboxaldehyde to add OH^- to form the hydrate anion (K(complex)/K(free ligand) $\simeq$ 8.6). This behavior not only contrasts that of the 4-aldehyde in alkaline and neutral aqueous solution but also that of the 2-aldehyde complex D in neutral and acidic solution. Since in neutral solution formation of the hydrate is disfavored by coordination, the enhanced tendency to form the hydrate anion for the chelating 2-aldehyde complex must be the result of stabilizing the oxygen localized charge of the anion by coordination to the Ru(II) cation. Simply summarized, the electrostatic contribution resulting from the direct interaction of the cationic Ru(II) and anionic oxygen centers in this case must be more than sufficient to overcome the effect of any special stabilization due to the unsaturated metallocycle such as F.

A similar argument can be applied to rationalize the proton dissociation constants observed for $Ru(NH_3)_4(\text{2-pyridinecarboxylic acid})^{2+}$ and $Ru(NH_3)_4(\text{2-pyridinecarboxamide})^{2+}$. For the carboxylic acid, the reported[24] pK_a for the carboxylate function of the free ligand is 4.1 while the Ru(II) coordinated ligand is significantly more acidic (pK_a = 0.7). While the pK_a has not been reported for proton dissociation from the amide function of 2-pyridinecarboxamide, it is unlikely that the free ligand is substantially more acidic than acetamide (pK_a = 15.1)[25] or benzamide (pK_a uncertain, values of ~15 and greater than 19 have been reported).[25,26] Consequently, the acidity of the Ru(II) coordinated ligand (pK_a = 13) appears greater than that of the free ligand by several orders of magnitude. While these en-

hancements of the groups' acidities are not an unexpected consequence of their coordination to the positively charged metal, they are substantially less than the enhancements observed (for example) when acetamide is coordinated to centers such as $(NH_3)_5Ru^{3+}$ (pK_a = 2.0)[4] or $Co(NH_3)_5^{3+}$ (pK_a = 3.0).[27]

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