methyl-1,4,8,11-tetraazacyclotetradecane), an unstable complex containing teta in the folded configuration is initially formed and slowly converts to a planar red complex.[14]

In a kinetic study by Kaden[15] of the formation of Ni(cyclam)$^{2+}$, no intermediates were reported. The rate of formation was second order, first order in nickel ion and first order in cyclam. In order for an intermediate such as *cis*-Ni(cyclam)$(H_2O)_2{}^{2+}$ to be undetected, the rate of isomerization of the folded complex to the planar form would have to be more rapid than the rate of formation. Although slow, the isomerization rates observed here are indeed faster than the rates of formation measured by Kaden. Thus it is possible that the formation of Ni(cyclam)$^{2+}$ proceeds through the proposed folded intermediate. In order for the intermediate to accumulate in detectable amount during the formation reaction, much higher concentrations of metal ion and of ligand would be necessary.

It is also expected that acid dissociation of Ni(cyclam)$^{2+}$ proceeds through a succession of folded intermediates, of which *cis*-Ni(cyclam)$(H_2O)_2{}^{2+}$ is the first. Linear polydentate ligands generally dissociate via a stepwise unwrapping mechanism; although this mechanism is not available for complexes of macrocyclic ligands, a comparable mechanism would begin with the folding of the planar macrocycle. It is unlikely that the folded isomer could be detected in the acid dissociation of Ni(cyclam)$^{2+}$, an extremely slow process.[16]

Registry No. *cis*-Ni(cyclam)(en)$(ClO_4)_2$, 78638-51-4; *cis*-Ni(cyclam)Br_2, 78684-34-1; Ni(cyclam)$(ClO_4)_2$, 15220-72-1; *cis*-Ni(cyclam)$(H_2O)_2{}^{2+}$, 78684-35-2.

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(4-Aminopyridine)pentaammineruthenium(II) and -(III)

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The investigations of binuclear bis(pentaammineruthenium) complexes bridged by ligands of the 4,4′-dipyridyl type revealed that the properties of the 4,4′-dipyridylamine analogue were in certain respects distinctly different from those of the other complexes in the series.[1] These differences included a greater instability toward aquation for the fully reduced complex and the appearance of a new electronic transition in the visible region of the spectrum for the fully oxidized complex.

This study was undertaken to gain further insight into these differences. Absorption characteristics of (4-aminopyridine)pentaammineruthenium(II) and -(III) and the aquation kinetics of the reduced form as a function of the acidity of the medium used are reported here.

Experimental Section

Materials. 4-Aminopyridine was purchased from Aldrich, ammonium hexafluorophosphate from Ozark-Mahoning, and hexaammineruthenium chloride from Matthey-Bishop, all used without further purification. Europium(III) oxide was obtained from Research Chemicals and reduced to Eu(II) in acidic medium with use of zinc amalgam.

Table I. Absorption Maxima in the UV-Visible Spectra of (4-Aminopyridine)pentaammineruthenium(II) and -(III)[a]

Ru(II)		Ru(III)	
λ, nm	log ε	λ, nm	log ε
239	3.95	253	4.05
359	3.78	321	3.68
388	sh[b]	505	3.51

[a] Obtained in pH pH 8 phosphate buffer. Ru(II) complex prepared by reduction of the Ru(III) complex with Eu^{2+}. [b] sh = shoulder.

Argon (99.995%) and chlorine gases were purchased from Liquid Carbonic. The argon was freed of oxygen by passing it through a scrubbing tower charged with 0.25 M chromium(II) in 0.5 M perchloric acid over zinc amalgam. The chlorine was used as supplied.

House line distilled water was purified by redistillation from alkaline permanganate in an all-glass still.

Ruthenium Complexes. The hexaammineruthenium chloride was converted to chloropentaammineruthenium(III) chloride by following the literature procedure.[2]

(4-Aminopyridine)pentaammineruthenium(III) Hexafluorophosphate. A 100-mg sample of finely powdered $[Ru(NH_3)_5Cl]Cl_2$ was suspended in 5 mL of water and purged with argon before reducing over zinc amalgam for 1 h. Excess 4-aminopyridine was added and allowed to react for 15 min before oxidizing the product by bubbling chlorine gas through the solution. A crude sample was precipitated by adding the solution to 150 mL of rapidly stirred acetone. The solid was collected and redissolved in 10 mL of water, and solid NH_4PF_6 was added to bring $[PF_6^-]$ to about 5 M. The resulting solution was stored in the refrigerator overnight, producing purple crystals, which were filtered, washed with ethanol and ether, and dried in a vacuum desiccator; yield 85 mg (35%). Anal. Calcd for $[Ru(NH_3)_5(4\text{-}NH_2py)](PF_6)_3$: C, 8.39; H, 2.96; N, 13.71. Found: C, 8.30; H, 3.26; N, 13.79.[3]

Instrumentation. Electronic Spectra. Spectra in the ultraviolet and visible regions were recorded with use of matched quartz cells in a Beckman Model 5270 spectrophotometer.

Electrochemistry. Electrochemical measurements were made on a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer system. Formal potentials ($E_{1/2}$) were measured by cyclic voltammetry using a carbon-paste electrode. Carbon paste was purchased from Bio-Rad, Inc., packed into the cavity of a Teflon plug fitted with a copper wire to form a lead, and held in a glass tube. Potentials were measured against a saturated calomel electrode (SCE, Beckman Model 39190) at 20 °C and are uncorrected for junction potentials. They were corrected to the hydrogen scale by adding 0.244 V. The voltammetric measurements were made in a standard H-cell with the test solution compartment separated from the reference electrode compartment by a fine-porosity glass frit. A platinum wire was used as an auxiliary electrode.

Temperature Control. Constant temperatures (±0.2 °C) were maintained with a Haake Model FK2 constant-temperature bath connected to a thermostated cell holder in the spectrophotometer. The temperature of the cell was monitored with a Digitic Model 5810 digital thermometer.

Kinetics. The rate of aquation of (4-aminopyridine)pentaammineruthenium(II) to produce the corresponding aquopentaammine ion was followed spectrophotometrically by monitoring the disappearance of the visible transition of the ruthenium(II) complex associated with coordination of 4-aminopyridine.

A solution of the corresponding ruthenium(III) complex was prepared in the appropriate concentration of hydrochloric acid (ionic strength adjusted to 2 M with NaCl), placed in a spectrophotometer cell, degassed, and allowed to equilibrate thermally in the spectrophotometer. Ruthenium(III) was reduced to ruthenium(II) by syringing a stoichiometric amount of europous ion into the cell. The absorbance was then monitored at a fixed wavelength as a function of time. The data were plotted as log $(A_t - A_\infty)$ vs. time where A_t and A_∞ represent the absorbances at time t and at completion of the reaction, respectively. These plots were linear over at least 4 half-lives,

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(2) Vogt, L.; Katz, J.; Wiberly, S. *Inorg. Chem.* **1965**, *4*, 1157.
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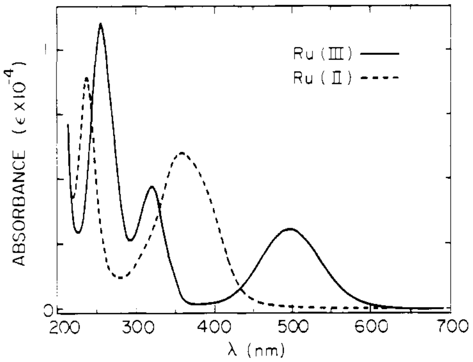

Figure 1. UV–visible spectra of $[Ru(NH_3)_5(4\text{-}NH_2py)]^{3+,2+}$ (in pH 8 phosphate buffer).

Table II. Variation of Position of Ligand-to-Metal Transition with Environment for (4-Aminopyridine)pentaammineruthenium(III)

salt[a]	λ_{max}, nm	salt[a]	λ_{max}, nm
KF	499	H(TFMS)[c]	521
Na_2SO_4[b]	504	NH_4PF_6	529
NaCl	514	$NaClO_4$	529

[a] Concentration of salt is 5 M except where otherwise indicated. [b] Saturated solution. [c] 3.4 M trifluoromethanesulfonic acid.

yielding values for the pseudo-first-order rate constant (k_{obsd}) as the slopes of the plots.

Results

Cyclic voltammetry shows a reversible redox wave at +0.15 V vs. NHE (scan rate = 100 mV/s) which does not change materially in the range pH ~2–10.

The spectra of the two oxidation states of the (4-aminopyridine)pentaammineruthenium complex are shown in Figure 1 and the salient features summarized in Table I. The spectrum of the ruthenium(III) is unaltered even when the medium is 6 M HCl, indicating that the protonated form is a strong acid indeed. However, a solution of this complex prepared in concentrated sulfuric acid gave a spectrum which lacked the absorption band at λ ~500 nm but which reappeared upon dilution with water. This transition was found to be remarkably sensitive to the concentration and identity of the anion in solution. The position of λ_{max} for the visible transition is reported in Table II for a variety of solution conditions.

The rutheniun(II) species shows a strong absorption at 360 nm. The spectrum is insensitive to pH until the solutions become rather acidic. In acid the absorption characteristic of the complex fades rather rapidly, precluding determining the pK_a of $[(NH_3)_5Ru(4\text{-}NH_3py[]^{3+}$ in a straightforward way spectrophotometrically. As will appear, a value of pK_a can be obtained by studying the rate of aquation as a function of acidity. The kinetics of the decomposition of the ruthenium(II) complex formed by reducing Ru(III) were determined by following the loss of absorbance at 460 nm. The initial absorbance was observed to increase with increasing $[H^+]$; [HCl] was varied at constant ionic strength (2 M, NaCl) at 25.0 ± 0.2 °C. Pseudo-first-order rate behavior was observed at all acid concentrations. The observed rate constants, k_{obsd}, were found to be independent of the concentration of europous ion used to produce the reduced complex. They are summarized in Table III. Cyclic voltammetry of the reaction mixture after completion of the reaction indicated that aquopentaammineruthenium(II) is the ruthenium product.

Discussion

The absence of an observable pK_a in the range of pH ~1–10 for the (4-aminopyridine)pentaammineruthenium(III) complex is consistent with ligation of 4-aminopyridine through the heterocyclic nitrogen. On the basis of the properties of the (pyrazine)pentaammineruthenium(III) complex where the pK_a of the pyrazinium ion is found to decrease by 1.4 pK_a units[5] when Ru(III) is coordinated, we expect that if the 4-aminopyridine were coordinated through the amine nitrogen, the pK_a of the free pyridine would then be expected to fall between a value of 9.1 observed for the free ligand[6] and ~7.7. A lower limit of 7.7 is reasonable since the effect of the ruthenium(III) is expected to be larger in the pyrazinium complex because the proton is closer to the metal in that molecule.

Table III. Aquation Rate of (4-Aminopyridine)pentaammineruthenium(II)[a]

$[H^+]$, M	$10^2 k_{obsd}$, s^{-1}	trials	$[H^+]$, M	$10^2 k_{obsd}$, s^{-1}	trials
2.0	4.49 ± 0.05	3	0.2	3.43 ± 0.02	3
1.5	4.39 ± 0.02	2	0.1	2.81 ± 0.01	3
1.0	4.25 ± 0.04	3	0.05	2.12 ± 0.08	2
0.5	3.97 ± 0.07	4[b]			

[a] $T = 25.0 \pm 0.1$ °C. $I = 2.0$ M, adjusted with NaCl. [Ru] ~ 3×10^{-4} M. Reaction monitored spectrophotometrically at λ = 460 nm. Reaction initiated by reducing the Ru(III) complex with Eu^{2+}. [b] In a second run conducted with a twofold excess of Eu^{2+}, $k_{obsd} = 3.97 \times 10^{-2}\ s^{-1}$.

The appearance of an intense absorption extending into the visible region of the spectrum of the ruthenium(II) complex similar to those observed for other complexes with pyridine-like ligands[5] supports the assignment of structure, the transition being assigned to metal-to-ligand charge transfer. Studies conducted on the pentacyanoferrate(II) complex of 4-aminopyridine also indicate coordination through the pyridine nitrogen.[7]

The $\pi^* \leftarrow d\pi$ transition observed in the spectrum of the ruthenium(II) complex occurs at higher energy than for other analogous pyridine complexes.[5] The shift to shorter wavelength, as well as the decrease in the reduction potential, reflects the weaker π-acceptor ability of the 4-aminopyridine ligand. This is believed to result from a coupling of the lone-pair electrons on the amine nitrogen and the π* levels of the pyridine ring, which destabilizes the latter orbitals, increasing the energy gap between the metal dπ and ligand π* orbitals. The increased energy gap also results in a weaker interaction between the metal and ligand levels, resulting in a smaller extinction coefficient for the 4-aminopyridine complex compared to those of other pyridine complexes.

Because most other pyridine complexes of Ru(III) do not show absorption in the visible region, the transition at 505 nm for the aminopyridine complex must involve the amine group. It is assigned as a ligand-to-metal charge-transfer transition originating in the HOMO of the ligand containing the lone-pair electrons of the amine nitrogen. As is to be expected, this absorption disappears when the medium is made acidic enough to protonate the amine lone pair of electrons. The HOMO of the ring then resembles that of other pyridine complexes and the spectrum is also similar. The dependence of λ_{max} for this transition on the character of the anion in solution is likely due to the differing abilities of the counterions to stabilize the partial positive charge centered on the amine nitrogen when the lone-pair electrons delocalize into the pyridine ring. Stabilizing the positive charge will increase the mixing of the amine π levels with the ring π levels, stabilizing the former and shifting the transition to higher energy. The apparent order of stabilization is $ClO_4^- \sim PF_6^- < Cl^- < F^-$. $(CF_3SO_3^-$

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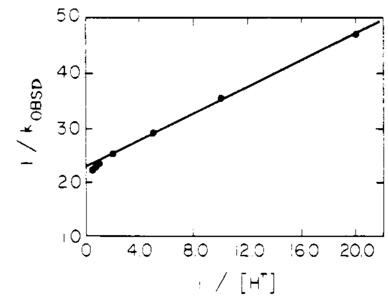


Figure 2. Plot of $1/k_{\mathrm{obsd}}$ vs. $1/[\mathrm{H}^+]$ for the aquation of $\mathrm{Ru^{II}(NH_3)_5(4\text{-}NH_2py)}$ (T = 25.0 °C, I = 2.0 M (NaCl)).

and $\mathrm{SO_4}^{2-}$ cannot be ordered because the concentrations were different in these cases.)

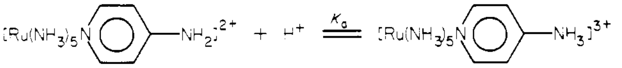
Turning now to the kinetics of aquation of the Ru(II) complex, $1/k_1K_a$ note that a plot of $1/k_{\mathrm{obsd}}$ vs. $1/[\mathrm{H}^+]$ yields a straight line for most of the proton concentration range covered, as shown in Figure 2. This behavior is consistent with a rate law of the form

$$-\frac{d[\mathrm{RuL}]}{dt} = \frac{k_1K_a[\mathrm{H}^+][\mathrm{RuL}]}{1 + K_a[\mathrm{H}^+]}$$

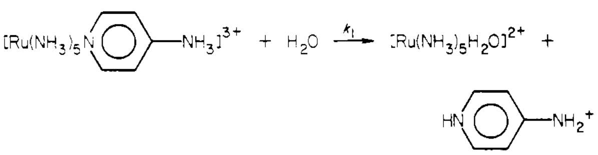
where [RuL] represents the total concentration of (4-aminopyridine)pentaammineruthenium(II) and the observed rate constant is given by

$$k_{\mathrm{obsd}} = \frac{k_1K_a[\mathrm{H}^+]}{1 + K_a[\mathrm{H}^+]}$$

K_a and k_1 are defined by reactions 1 and 2. At high concentrations of H^+, k_{obsd} reduces to k_1, resulting in the observed rate saturation. The deviations from the plot observed at high $[\mathrm{H}^+]$ can be ascribed to an additional path involving the reaction of the protonated complex with an additional proton.



(1)



(2)

The plot of $1/k_{\mathrm{obsd}}$ vs. $1/[\mathrm{H}^+]$ will have a slope of $1/k_1K_a$ and an intercept of $1/k_1$. The value thus determined for k_1 is 4.4×10^{-2} s^{-1} and for K_a, 24. When the intensity of the initial absorbance as determined from the kinetic runs (see below) is plotted against $[\mathrm{H}^+]$, the value of K_a obtained, though not precise, is consistent with that recorded above.

In the kinetic runs the initial absorbance at 460 nm was observed to increase in intensity with increasing acid concentration. Since measurement is being made on the long-wavelength side of the band, this shows that the absorption band is shifting to greater wavelengths with decreasing pH. When the amine group is protonated, the 4-aminopyridine becomes a better π acceptor, and since the π^* level lies above the $d\pi$, λ_{max} moves to longer wavelengths, as is observed for other pyridine-derived ligands on Ru(II).

While the proton dependence of the rate shows that an additional proton is contained in the activated complex, its location is not thereby specified. It seems likely that in the transition state the proton shifts from the amine group; note that the increased π-acceptor ability of 4-aminopyridine protonated at the amine nitrogen would result in a slower aquation rate. As has been suggested in other cases, the proton in the activated complex may become coordinated to a pair of $d\pi$ electrons directed at the face of the coordination octahedron. This would withdraw electron density from the metal–pyridine bond and facilitate aquation. If the proton were on a face adjacent to the 4-aminopyridine ligand, it would moreover be available to protonate the pyridine as it is being released.

The work shows that the lone-electron pair of the amine nitrogen of 4-aminopyridine interacts with the pyridine ring and significantly modifies its properties as a ligand. This coupling of the amine nitrogen electron pair with the aromatic rings is also responsible for the increased interaction between the metal centers in the binuclear complex bridged by 4,4′-dipyridylamine[1] as compared to dipyridylmethane as bridging group.

Acknowledgment. Support of this work by National Science Foundation Grant No. CHE79-08633 is gratefully acknowledged.

Registry No. $\mathrm{Ru^{II}(NH_3)_5(4\text{-}NH_2py)}$, 78064-39-8; $\mathrm{Ru^{III}(NH_3)_5(4\text{-}NH_2py)}$, 78064-35-4; $\mathrm{[Ru(NH_3)_5(4\text{-}NH_2py)](PF_6)_3}$, 78656-92-5.

Contribution No. 2863 from the Central Research and
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Methane Formation in the Reaction of Carbon Monoxide and Hydrogen in the Presence of Iridium and Osmium Clusters

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In a previous publication,[2] homogeneous solutions of $\mathrm{Ir_4(CO)_{12}}$ or $\mathrm{Os_3(CO)_{12}}$ in toluene were reported to catalyze the formation of methane from carbon monoxide and hydrogen. Also, the rate of methane formation was found to be significantly enhanced by the addition of phosphorus ligands, especially trimethyl phosphite. In this paper, we report the results of a more quantitative investigation. Less than stoichiometric amounts[3] of methane were formed by hydrogenation of carbon monoxide within a 5-day period. Isotopic labeling studies (^{13}C and ^{2}H) have established that the enhanced formation of methane in the presence of trimethyl phosphite arises from a trimethyl phosphite and hydrogen reaction catalyzed by the iridium and osmium complexes.

Experimental Details

Quantitative Determination of Methane Formation. Reaction tubes were opened at ambient temperature into an evacuated system of

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(1) (a) Central Research and Development Department, Du Pont. (b) University of California.

(2) M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976).

(3) (a) Widely different yields of methane in this reaction have been obtained by several experimenters (ELM research group). The values reported here are believed to be the most accurate ones. (b) On the basis of light scattering, there was no evidence of particles present in the solution phase. However, the wavelength was not varied to very short wavelengths, and it is possible that very small crystallites may have been present.

(4) In related experiments, it was found that a mixture of $\mathrm{[IrCl(C_8H_{14})_2]_2}$, trimethyl phosphite, and hydrogen produced methane ($\mathrm{CH_4{:}Ir_2}$ = 14:1) and that substitution of nitrogen for hydrogen also produced methane but in lower yield ($\mathrm{CH_4{:}Ir_2}$ = 5:1). Toluene solutions of $\mathrm{Co_4(CO)_{12}}$, $\mathrm{Co_2(CO)_8}$, and $\mathrm{Fe_3(CO)_{12}}$ also effected methane formation from trimethyl phosphite, CO, and $\mathrm{H_2}$, but the reaction systems were not homogeneous.