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Cyanopyridine Complexes of Pentaammineruthenium(II)[1]

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The nitrile-coordinated pentaammineruthenium(II) complexes of 2-, 3-, and 4-cyanopyridine are described. In each case, coordination of the nitrile results in a negative shift in the carbon–nitrogen triple bond stretching frequency (ν(CN)). Protonation of the pyridine nitrogen results in an even greater decrease in ν(CN) from the free-ligand value (where the free ligand is the cyanopyridinium salt). Using spectral techniques, the protonation constants of the nitrile-coordinated pentaammine(cyanopyridine)ruthenium(II) complexes were determined. Each of these complexes is *more basic* than the corresponding uncoordinated cyanopyridine having pK_a's 0.80, 1.75, and 2.72 for coordinated 2-, 3-, and 4-cyanopyridine, respectively, compared to −0.26, 1.45, and 1.90 for the respective free cyanopyridines.

Introduction

The ligand properties of 2-, 3-, and 4-cyanopyridines (cp) have been the subject of several recent investigations.[2-7] This interest stems primarily from the existence of two potential coordination sites, the nitrile nitrogen and the pyridine nitrogen, on each ligand. The presence of two sites raises the possibility of linkage isomerism and provides the opportunity for comparison of coordination bond strengths between a particular metal ion and the nitrile or pyridine function of the same ligand. This comparison of course is valid only when the complexes are sufficiently labile to establish thermodynamic equilibria. An additional feature of these ligands which has not received previous attention is the effect of coordination on either reactions or ligand properties of the functional group remote from the coordination site. We have been concerned with the ligand properties of organonitriles coordinated to various ruthenium(II) and -(III)–ammine complex fragments.[8,9] As an extension of this interest, we report here the nitrile-coordinated 2-, 3-, and 4-cyanopyridine complexes of pentaammineruthenium(II) and some data relating to their ability to protonate at the pyridine nitrogen.

Experimental Section

Reagents.—The nitriles 2-, 3-, and 4-cyanopyridine were purchased from the Aldrich Chemical Co. and purified by recrystallization from ethanol. Sodium tetraphenylborate was purchased from K & K Laboratories, Inc. Chloropentaammineruthenium(III)dichloride, $[Ru(NH_3)_5Cl]Cl_2$, was prepared by the method of Allen, *et al.*,[10] from ruthenium trichloride (Engelhard Industries). Perdeuteriochloropentaammineruthenium(III) chloride, $[Ru(ND_3)_5Cl]Cl_2$, was prepared by serial recrystallization of $[Ru(NH_3)_5Cl]Cl_2$ from D_2O (99.8% D, Stohler Isotope Chemicals).[11]

Syntheses.—Pentaammine(cyanopyridine)ruthenium(II) salts were prepared from $[Ru(NH_3)_5Cl]Cl_2$ by a procedure slightly modified from that used to prepare the analogous benzonitrile complex.[8,9] The method used for 4-cyanopyridine (below) was applicable to the 2- and 3-cyanopyridine complexes. Syntheses starting with $[Ru(ND_3)_5Cl]Cl_2$ were carried out entirely in D_2O solvent.

$[Ru(NH_3)_5(4\text{-cp})][ClO_4]_2$.—$[Ru(NH_3)_5Cl]Cl_2$ (0.1 g) was digested in 2 ml of silver trifluoroacetate solution (made by dissolving Ag_2O (0.06 g) in sufficient aqueous trifluoroacetic acid). The resulting mixture was filtered to remove the resulting silver chloride, and 4-cyanopyridine (0.3 g), trifluoroacetic acid (sufficient to give $[H^+] \approx 0.5$ *M*), and granular zinc amalgam (0.5 g) were added. The mixture was stirred for 30 min at room temperature and then filtered. Saturated sodium perchlorate solution was added to the dark red filtrate solution and a red-orange solid precipitated. Recrystallization from hot water gave the red-orange crystalline solid $[Ru(NH_3)_5(4\text{-cp})][ClO_4]_2$ (0.11 g, 65% yield). *Anal.* Calcd for $C_6N_{19}O_8N_7Cl_2Ru$: C, 14.73; H, 3.92; N, 20.04. Found: C, 14.21; H, 3.71; N, 20.67.

The protonated salt $[Ru(NH_3)_5(4\text{-cpH})][ClO_4]_3$ was prepared by dissolving pentaammine(4-cyanopyridine)ruthenium(II) perchlorate in warm water, adding sufficient trifluoroacetic acid to give $[H^+] \cong 4$ *M*, and then adding sodium perchlorate to precipitate the dark purple protonated salt in nearly quantitative yield.

The cyanopyridinium tetraphenylborate salts were prepared by dissolving the appropriate cyanopyridine in 2 *M* aqueous hydrochloric acid and then adding saturated sodium tetraphenylborate solution. The resulting white precipitate was thoroughly washed with dilute HCl and dried overnight in a vacuum desiccator. The resulting white salts were odorless.

Spectra.—All uv–visible spectra were recorded on a Cary 14 spectrophotometer. Spectra were obtained, at 25°, of dilute solutions in redistilled water. Solutions for extinction coefficient measurements were prepared by gravimetric procedures followed by quantitative serial dilutions to give appropriate concentrations. Extinction coefficients were determined from duplicate solutions and found reproducible within ±3%.

Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 225 recording spectrophotometer. Frequencies of absorption maxima were determined by direct reading of the spectrometer frequency scale during a slow scan or by measuring from calibrated paper used with the spectrometer in an expanded-scale mode. With sharp peaks, these values were reproducible to within ± 1 cm^{-1}.

pH Measurements.—pH measurements were made with a Radiometer pH meter, Model 26, at 25° using commercial standard buffer solutions (pH 4.0 and 7.0) as the reference points.

Results

The reduction of $Ru(NH_3)_5Cl^{2+}$ in pH 6 aqueous solution and in the presence of a large excess of 4-

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[1] Taken in part from the M.A. dissertation of R. E. C. Presented in part at the 158th National Meeting of the American Chemical Society, New York, Sept 1969.

[2] R. A. Walton, *J. Inorg. Nucl. Chem.*, **28**, 2229 (1966).

[3] L. El-Sayed and R. O. Ragsdale, *J. Inorg. Nucl. Chem.*, **30**, 651 (1968).

[4] I. Piljac and R. T. Iwamoto, *Inorg. Chim. Acta*, **3**, 49 (1969).

[5] F. Farha, Jr., and R. T. Iwamoto, *Inorg. Chem.*, **4**, 844 (1965).

[6] P. T. T. Wong and D. G. Brewer, *Can. J. Chem.*, **46**, 131 (1968).

[7] J. Nelson and S. M. Nelson, *J. Chem. Soc., A*, 1597 (1969).

[8] P. C. Ford and R. E. Clarke, *Chem. Commun.*, 1109 (1968).

[9] R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970).

[10] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Am. Chem. Soc.*, **89**, 5595 (1967).

[11] A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337 (1967).

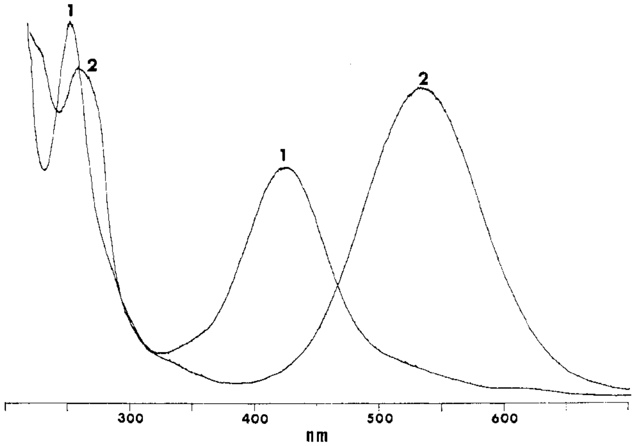


Figure 1.—Uv-visible spectra: pentaammine(4-cyanopyridine)ruthenium(II), $Ru(NH_3)_5(4\text{-cp})^{2+}$ (1); its protonated analog, $Ru(NH_3)_5(4\text{-cpH})^{3+}$ (2).

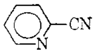
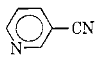
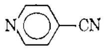
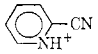
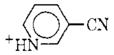
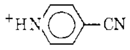
cyanopyridine gives a product mixture displaying two strong visible-range absorptions, the major band occurring at 425 nm and a much less intense band at 500 nm. The same reaction carried out in strongly acidic solution (pH 1–0) leads to the formation of a single ruthenium complex (λ_{max} 425 nm in neutral solution) isolable as a variety of salts and having a $Ru(NH_3)_5^{2+}$ to 4-cp elemental composition ratio of 1:1. Since the pH of the latter synthesis was sufficiently low to protonate essentially all the free cyanopyridine (at the pyridine base site) and since stable $Ru(NH_3)_5^{2+}$ organonitrile complexes are rapidly formed under these conditions,[8,9] the expected product is the nitrile-coordinated pentaammine(4-cyanopyridine)ruthenium(II) complex ion. This conclusion is reinforced by the observation that the 425-nm band of the latter synthesis product is reversibly shifted to 532 nm on making the spectrum medium acidic, a spectral pH dependence which is predictable for the nitrile-coordinated isomer, as it would have the pyridine base site available for reversible protonation (see below).

Another linkage isomer can be envisioned involving $Ru(NH_3)_5^{2+}$ coordination to the pyridine nitrogen. Pentaammineruthenium(II) complexes of an extensive series of substituted pyridines have been reported,[12] and each pyridine complex displays a strong, substituent-sensitive, visible-range metal-to-ligand charge transfer (CT) band. In consideration of the electron-withdrawing nature of the 4-cyano group, an absorption at 425 nm is 50–100 nm lower than the value expected for the pyridine-coordinated isomer. On the other hand, the 500-nm band observed in the spectrum of the product of the pH 6 synthesis would fall into this range. Selective recrystallization of the pH 6 reaction products gave a small sample of a material still displaying both the 425- and 500-nm bands but with the 500-nm absorption the much more intense. The latter band proved to be insensitive to the pH of the spectral medium.

The products of $Ru(NH_3)_5Cl^{2+}$ reduction in the presence of excess 2- or 3-cyanopyridine appear to be exclusively the nitrile-coordinated isomers independent of whether the reaction was carried out under acidic or neutral conditions. The products from the respective syntheses displayed pH-dependent visible spectra (below).

TABLE I

AQUEOUS SOLUTION UV–VISIBLE ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS FOR PENTAAMMINERUTHENIUM(II)–CYANOPYRIDINE COMPLEX IONS[a] $Ru^{II}(NH_3)_5L$

L	λ_{max} in nm (log ϵ)
	408 (3.82), 256 (4.09), 222 (3.96)
	401 (3.75), 336 sh (3.58), 255 (4.07), 219 (3.87)
	425 (3.73), 253 (3.95)
	505 (3.91), 271 (4.14)
	460 (3.67), 327 sh (3.48), 261 (4.10), 218 (3.83)
	532 (3.91), 260 (3.93)

[a] Unprotonated complexes in dilute aqueous solution (pH ~5); protonated complexes in 1 *M* hydrochloric acid solution except the 2-cpH$^+$ complex whose spectrum was determined in 2 *M* HCl.

The three nitrile-coordinated pentaammineruthenium(II) cyanopyridine complex ions are substitution inert and relatively insensitive to air oxidation in aqueous solution or the solid state.

Electronic Spectra.—The uv-visible spectra of nitrile-coordinated pentaammine(4-cyanopyridine)ruthenium(II), $Ru(NH_3)_5(4\text{-cp})^{2+}$, and the protonated ion, $Ru(NH_3)_5(4\text{-cpH})^{3+}$, are shown in Figure 1. Absorption maxima and corresponding extinction coefficients for the 2-, 3-, and 4-cyanopyridine complexes and their protonated analogs are summarized in Table I. In each case, the intense visible range band is shifted to higher wavelength by protonation. We have previously reported the electronic spectra of a series of pentaammine(substituted benzonitrile)ruthenium(II) ions and assigned the substituent-sensitive visible range band to a metal-to-ligand charge transfer (CT).[9] The similarity of the cyanopyridine to benzonitrile as well as the red shift on protonating the coordinated cyanopyridine (hence, increasing the electronegativity of the aromatic ring) suggests the validity of the same assignment for the cyanopyridine complex visible bands. The uv-range absorptions are probably π–π^* bands characteristic of the ligand aromatic ring and are paralleled by similar absorptions in the free-ligand spectra.[13]

pK_a Measurements.—The electronic spectral difference between the base form of the cyanopyridine complexes (B) and the protonated analogs (BH$^+$) (Figure 1) provides an excellent probe for measurement of protonation constants. The method is similar to that used previously to measure the pK_a for the pentaammineruthenium(II)–pyrazine complex.[12] A classically shaped titration curve (Figure 2) is obtained from

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[12] P. Ford, De F. P. Rudd, R. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).

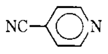
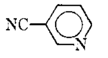
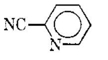
[13] S. F. Mason, *J. Chem. Soc.*, 1247 (1959).

a plot of pH *vs.* the logarithm of the ratio of the absorption at the wavelength of the BH^+ maximum to the absorption at the wavelength of the B maximum ($\log (A_{532nm}/A_{425nm})$ for the 4-cyanopyridine complex). The pK_a, the pH where $[BH^+] = [B]$, is defined by that pH where the curve equals the log of the extinction coefficient ratio of $\epsilon(B) + \epsilon(BH^+)$ at the λ_{max} of BH^+ divided by $\epsilon(B) + \epsilon(BH^+)$ at the λ_{max} of B ($\log [(\epsilon(B)_{532} + \epsilon(BH^+)_{532})/(\epsilon(B)_{425} + \epsilon(BH^+)_{425})]$ for the 4-cyanopyridine complex). The pK_a's so determined are summarized in Table II. Comparison of these values to those reported for the free ligands indicates that in each example the coordinated ligand is *more basic* than the corresponding free ligand.

TABLE II

pK_a VALUES FOR CYANOPYRIDINE COMPLEXES[a]

$Ru(NH_3)_5(cp)^{2+} + H^+ \rightleftharpoons Ru(NH_3)_5(cpH)^{3+}$

cp	pK_a (complex)	pK_a (free ligand)[b]	ΔpK_a
	2.72 ± 0.12	1.90	0.82
	1.75 ± 0.05	1.36	0.39
	0.80 ± 0.10	−0.26	1.06

[a] At 25°. [b] Reference 13.

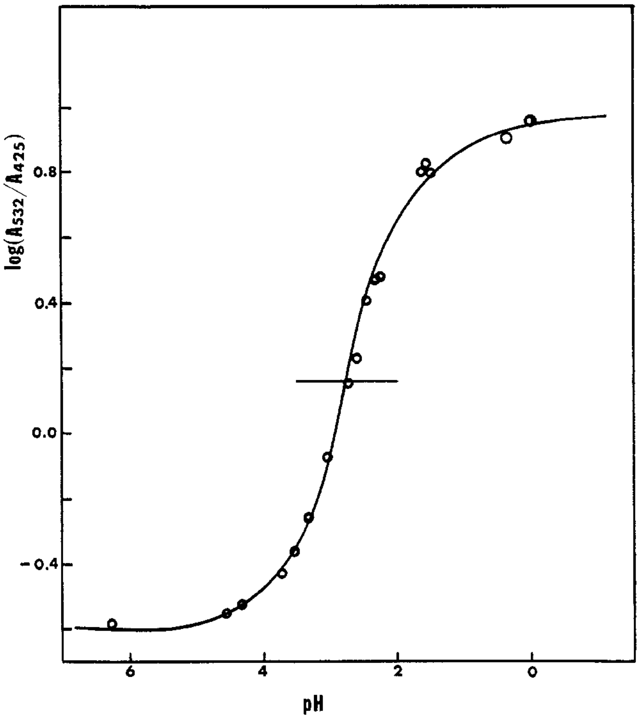
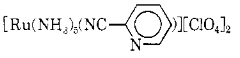
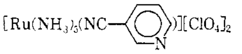
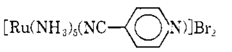
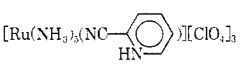
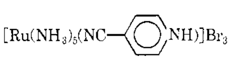
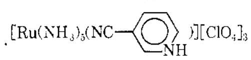


Figure 2.—Spectrophotometric titration curve used to determine the protonation equilibrium constant of pentaammine(4-cyanopyridine)ruthenium(II) in aqueous solution (25°): $Ru(NH_3)_5(4\text{-}cp)^{2+}$ (B) + $H^+ \rightleftharpoons Ru(NH_3)_5(4\text{-}cpH)^{3+}$ (BH^+). The horizontal line represents the value: $\log [(\epsilon(B)_{532} + \epsilon(BH^+)_{532})/(\epsilon(B)_{425} + \epsilon(BH^+)_{425})] = 0.16$.

Infrared Spectra.—A distinctive feature of the infrared spectra of the pentaammineruthenium(II)–cyanopyridine complexes is the absorption assigned to the carbon–nitrogen triple-bond stretch. In each case the C≡N stretching vibration (ν(CN)) occurs at lower frequency than that recorded for the free ligand (Table III). The ν(CN) decreases, while not usual for coordinated nitriles, parallel similar decreases reported[8,9] for pentaammineruthenium(II) complexes of benzonitrile and acetonitrile. The series of pentaammineruthenium–substituted-benzonitrile complexes, analogs of the coordinated cyanopyridines, display ν(CN) decreases ranging from −23 to −59 cm^{-1} with electron-withdrawing substituents giving the more negative shifts. The pyridyl group is more electron withdrawing than an unsubstituted phenyl group;[14] consequently, the ν(CN) decreases observed for the $Ru(NH_3)_5(cp)^{2+}$ salts, larger than that of $[Ru(NH_3)_5(C_6H_5CN)]Br_2$ (−37 cm^{-1}), are consistent with this pattern. These C≡N frequency decreases have been attributed to the unusually strong π-back-donor ability of the $Ru(NH_3)_5^{2+}$ moiety.[8,9]

TABLE III

ν(CN) (cm^{-1}) FOR PENTAAMMINERUTHENIUM(II)–CYANOPYRIDINE COMPLEXES[a]

	Complex	Free ligand	$\Delta\nu$(CN)[c]
	2179 s	2235 s	−56
	2181 s	2232 s	−51
	2179 s	2243 s	−64
	2153 s	2233 m–w[b]	−80
	2150 s	2243 m[b]	−93
	. . .	2243 m[b]	. . .

[a] KBr pellets. [b] $B(C_6H_5)_4^-$ salts. [c] $\Delta\nu(CN) = \nu(CN)_{complex} - \nu(CN)_{free\ ligand}$.

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[14] This conclusion is based on a comparison of the dissociation constant (K_D) of the carboxylic acids RCO_2H (R = phenyl or 2-, 3-, or 4-pyridyl) where K_D represents the reaction: $RCO_2H = RCO_2^- + H^+$. These constants are $10^{-4.12}$, $10^{-3.75}$, and $10^{-3.44}$ for the 2-, 3-, and 4-pyridinecarboxylic acids,[15] respectively, and $10^{-4.2}$ for benzoic acid.[16]

(15) K. Schofield, "Hetero-Aromatic Nitrogen Compounds, Pyroles and Pyridine," Plenum Press, New York, N. Y., 1967, p 148.

(16) "Handbook of Chemistry and Physics," 40th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1958, p 1744.

TABLE IV

INFRARED SPECTRAL DATA[a] FOR 4-CYANOPYRIDINE (4-cp) SPECIES

Species	ν(C≡N)	In-plane ring deformations			
4-cp	2243 s	1592 s	1541 ms	1495 m	1414 s
(4-cpH)Cl	2242 m	1628 s	1590 s	1490 s	1430 w
$[Ru(NH_3)_5(4\text{-cp})]Br_2$	2179 s	1602 s		1485 m	1421 m
$[Ru(NH_3)_5(4\text{-cp})][ClO_4]_2$	2178 s	1583 s	1532 w	1480 mw	1406 m
$[Ru(NH_3)_5(4\text{-cpH})]Br_3$	2150 s	1617 s	1577 m	1490 m	1475 sh, m

[a] In cm^{-1}.

Addition of excess anion (X^-) to an acidic solution of either the 2- or 4-cyanopyridine complex of $Ru(NH_3)_5^{2+}$ precipitates the cyanopyridiniumpentaammineruthenium(II) salt, $[Ru(NH_3)_5(cpH)]X_3$. The procedure was unsuccessful for the isolation of the corresponding 3-cyanopyridinium complex. The protonated free ligands, the 2-, 3-, and 4-cyanopyridinium tetraphenylborate salts, were also prepared. The ir spectrum of each salt shows that ν(CN) is less intense and occurs at slightly higher frequency than the corresponding band in the spectrum of the free cyanopyridine (Table III). In contrast, protonation of either the 2-cyanopyridine or the 4-cyanopyridine complex of $Ru(NH_3)_5^{2+}$ leads to a decrease in the C≡N stretching frequency from the values observed for the nitrile-coordinated cyanopyridine complexes (Table III). This additional lowering of ν(CN) can again be attributed to electronic factors, a pyridinium group clearly being more electronegative than a pyridyl group.

The positions of the C–C and C–N vibrations characteristic of the aromatic ring have previously been used to assign the coordination site of cyanopyridine–metal complexes.[2–5] In general it has been observed that the four principal in-plane ring deformations arising from the C–C and C–N stretching modes and occurring in the 1400–1600-cm^{-1} region are shifted to higher frequency on coordination of the pyridine nitrogen.[17] The ir absorption bands in this region are summarized in Table IV for the various 4-cyanopyridine species. As expected, protonation leads to a blue shift in the various bands of the free 4-cyanopyridine. This effect is the most unambigously demonstrated in the shift of the highest energy absorption from 1592 to 1628 cm^{-1}. For $[Ru(NH_3)_5(4\text{-cp})]Br_2$, this band shows up as a strong and very sharp absorption at 1602 cm^{-1} superimposed on the medium-strong and broader NH_3 degenerate deformation at approximately 1630 cm^{-1}. The identity and position of these bands were confirmed by synthesizing the deuterated ammonia complexes $[Ru(ND_3)_5(4\text{-cp})]Br_2$ and $[Ru(ND_3)_5(4\text{-cpH})]Br_3$. The 10-$cm^{-1}$ blue shift of the 1592-cm^{-1} band for $[Ru(NH_3)_5(4\text{-cp})]Br_2$ is comparable in magnitude to blue shifts previously used to assign the coordination site as the pyridine nitrogen.[5] The additional blue shift to 1617 cm^{-1} on formation of $[Ru(NH_3)_5(4\text{-cpH})]Br_3$ is consistent with the effect of protonation on the free-ligand spectra. In contrast to the bromide salt, the perchlorate salt $[Ru(NH_3)_5(4\text{-cp})][ClO_4]_2$ shows a small red shift for each of the four in-plane ring deformations, the highest energy band occurring at 1583 cm^{-1}. The differences unquestionably arise from solid-state effects as both salts display identical electronic spectra and acid–base behavior. The existence of such differences, however, illustrates the danger inherent in attempts to interpret relatively minor shifts of bands in solid-state ir spectra of complex salts. Despite this warning, one might speculate that the unusual blue shifts in these pyridine bands of the nitrile-coordinated $[Ru(NH_3)_5(4\text{-cp})]Br_2$ are the result of hydrogen bonding in the crystal between the pyridine nitrogen and either an ammonia of another Ru(II) complex ion or a water of hydration.

The material recrystallized from the pH 6 synthesis of the 4-cyanopyrdine complex and having the pH-insensitive visible band at ~500 nm (above) displayed two infrared absorptions in the nitrile region. One at 2178 cm^{-1} (ClO_4^- salt) can be attributed to the nitrile-coordinated isomer. The other nitrile band at 2232 cm^{-1} presumably is characteristic of the material responsible for the 500-nm visible-region band. As small negative shifts in ν(CN) have been observed for other cyanopyridine complexes assigned the pyridine-coordinated structure,[2] this value would be reasonable for the nitrile stretch of the pyridine-coordinated linkage isomer, $[Ru(NH_3)_5(4\text{-cp})][ClO_4]_2$, suggested above. The 1400–1600-cm^{-1} region of the ir spectrum was too complicated to assign, but it also would not be inconsistent with a mixture of the two linkage isomers.

Another potential reaction product which could have visible and ir spectra similar to those attributed to the second product would be the diruthenium(II) species $[\{Ru(NH_3)_5\}_2(4\text{-cp})][ClO_4]_4$ coordinated at both the nitrile and pyridine sites. The regular synthesis technique involves generation of the reactive Ru(II) species in a solution containing a large cyanopyridine molar excess (see Experimental Section), conditions expected to favor the monoruthenium species. When the reaction was run under conditions expected to favor the diruthenium product (2:1 Ru to 4-cp molar ratio), the product contained a major new species displaying a nitrile band at 2172 cm^{-1} (ClO_4^- salt) and a uv–visible spectrum different from either of the previously described complexes. On this basis, we have concluded that the minor product of the pH 6 preparation is not the diruthenium complex, and that among the expected products, the pyridine-coordinated isomer is the most consistent with the limited spectral data described.

Discussion

The synthesis of the pentaammineruthenium(II)–cyanopyridine complexes from $Ru(NH_3)_5Cl^{2+}$ involves

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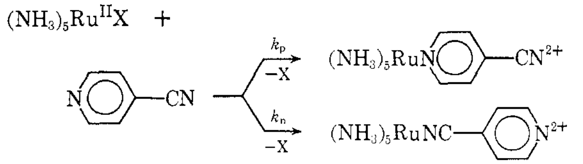
[17] N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1130 (1960).

two principal steps: (a) reduction of the Ru(III) to Ru(II) with the resultant labilization of the sixth coordination postion and (b) rapid reaction of cyanopyridine with $Ru^{II}(NH_3)_5X$ ($X = Cl^-$ or H_2O). The formation of the nitrile-coordinated $Ru(NH_3)_5(cp)^{2+}$ as the nearly exclusive product in each case, even at a solution pH substantially above the cyanopyridine pK_a, must reflect kinetic control of the reaction products. This conclusion stems from the observation that $Ru(NH_3)_5^{2+}$ complexes of neither pyridines[18] nor organonitriles[9] are sufficiently labile to establish a thermodynamic equilibrium during the synthesis procedure. Consequently, the rate constant (k_n) for formation of the nitrile-coordinated species must be substantially larger than the rate constant (k_p) for formation of the pyrdine-coordinated linkage isomer (*e.g.*, eq 1). One might speculate that part of these rate differences lies in transition-state steric interactions for the two reactions. Examination of space-filling models demonstrates that the pyridine-coordinated 2-cyanopyridine complex would be subject to substantial crowding between the nitrile group and the *cis* ammonias, and furthermore that the pyridine-coordinated 3- and 4-cyanopyridines would display some constraint between the *ortho* hydrogens and the *cis* ammonias. The models also illustrate the relatively uncrowded nature of the nitrile-coordinated isomers. Another feature which may affect the respective transition-state energies is the hydrogen bonding between the pyridine nitrogen and water which should give a more ordered solvent structure at that site. Hydrogen bonding to the nitrile should be less significant owing to its relative weakness as a Brønsted base.[19]



(1)

The argument suggesting kinetic control of the cyanopyridine reaction products is further supported by preliminary rate studies on these systems.[20] The reaction of 4-cyanopyridine with $Ru(NH_3)_5H_2O^{2+}$ which gives >90% of the nitrile-coordinated isomer is about twice as rapid as the corresponding reaction of pyridine with $Ru(NH_3)_5H_2O^{2+}$ under analogous conditions. Furthermore, substituent-effect studies show that electron-withdrawing groups (as in 3-chloropyridine) make the pyridine less reactive. By inductive reasoning, we then draw the conclusion that the pyridine site of 4-cyanopyridine is substantially deactivated with respect to pyridine by the strongly electron-withdrawing 4-cyano group. Since pyridine itself is less active than the nitrile of 4-cyanopyridine, this additional deactivation may be sufficient to explain the product distribution.

Protonation Equilibrium Constants.—The enhancement of the cyanopyridine basicity (Table II) on nitrile coordination to $Ru(NH_3)^{5+}$ has precedent. The pyrazine complex, $Ru(NH_3)_5(pyrazine)^{2+}$ ($pK_a = 2.5$), has been shown to be nearly two orders of magnitude more basic than free pyrazine ($pK_a = 0.6$).[12] The $Ru(NH_3)_5^{2+}$ complexes of pyrimidine and pyridazine, however, display pK_a's less than those of the free ligands in the manner expected for coordination of the second-ring nitrogen to a positive metal ion. In this context, the most striking feature of the cyanopyridine species is that pyridine basicity is enhanced in all three cases whether the $Ru(NH_3)_5^{2+}$-coordinated nitrile is in the 2, 3, or 4 position with respect to the ring nitrogen. Furthermore, the enhancement alternates in magnitude around the aromatic ring, being largest for $Ru(NH_3)_5(2\text{-cp})^{2+}$ ($\Delta pK_a = 1.06$), smallest for $Ru(NH_3)_5(3\text{-cp})^{2+}$ ($\Delta pK_a = 0.39$), and again larger for $Ru(NH_3)_5(4\text{-cp})^{2+}$ ($\Delta pK_a = 0.80$). Such a pattern of alternation about the aromatic ring is typical of a π-resonance substituent effect on the reactivity and/or properties of the ring position. A purely inductive or field effect would be expected to have a sequentially decreasing importance as one proceeds to the more distant ring positions.[21] Consequently, the pattern of basicity enhancement for the cyanopyridine complexes confirms the earlier conclusions relating to the pK_a of the pyrazine complex.[12] Namely, the unusually strong π back-donation of electron density from the low-spin d^6 $Ru(NH_3)_5^{2+}$ moiety into the unsaturated ligand is sufficient to overwhelm the opposing electrostatic influence expected from coordination to a dipositive metal ion. This metal-to-ligand π-back-bonding is apparently also responsible for the $\nu(CN)$ decreases observed for the $Ru(NH_3)_5^{2+}$ coordinated nitrile of the cyanopyridines and of the previously reported[8,9] benzonitrile and acetonitrile complexes.

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[18] P. C. Ford, J. R. Kuempel, and H. Taube, *Inorg. Chem.*, **7**, 1976 (1968).

[19] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 278 (1963).

[20] R. J. Allen and P. C. Ford, work in progress.

[21] K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, New York, N. Y., 1964, pp 278–291.