redistilled, giving a yield of 5%. Spectral data are as follows. ^{19}F NMR: ϕ −61.5, −58.8. ^{1}H NMR: δ_A 9.62 and $\delta_{A'}$ 9.52 (aldehydic proton of the isomers), $\delta_{B,B'}$ 4.7–5.6 (broad multiplet), $\delta_{C,C'}$ 3.5–4.5 (broad multiplet; δ_B:δ_C integration gives a 1:2 ratio. Infrared (gas phase): 2970 m, 1740 s, 1280 vs, 1240 vs, 1175 vs, 930 m, 735 s cm^{-1}.

(p) Reaction of CF_3OCl with $CH_3C(O)CH{=}CH_2$ (**10**) gave the product $CH_3C(O)CHClCH_2OCF_3$ (**10a**), which was isolated in a trap at −40 °C (55%). Spectral data are as follows. ^{19}F NMR: ϕ −60.58. ^{1}H NMR: δ_{CH_3} 2.37 (s), δ_{CH} 4.68 (t), δ_{CH_2} 4.32 (d); J_{CH-CH_2} = 4.1. Hz. Infrared (gas phase): 1735 s, 1360 m, 1280 vs, 1240 vs, 1220 vs, 1170 vs, 1030 m cm^{-1}. MS (17 eV) (mass (fragment), relative intensity) 190 (M^+), 45; 155 ($M^+ - Cl$), 10; 112 ($M^+ - CH_3C(O)Cl$), 100; 105 ($M^+ - OCF_3$), 18; 43 ($CH_3C(O)^+$), 100.

(q) Reaction of CF_3OCl with $CH_3OC(O)CH{=}CH_2$ (**11**) gave $CH_3OC(O)CHClCH_2OCF_3$ (**11a**), which was collected in a trap at −35 °C (65%). Spectral data are as follows. ^{19}F NMR: ϕ −60.6 (s). ^{1}H NMR: δ_{OCH_3} 2.38 (s), 2.8–to 3.4 (broad multiplet; protons on α- and β-carbons). Infrared (gas phase): 2980 w, 1770 vs, 1430 w, 1340 s, 1290 vs, 1280 vs, 1250 s, 1200 s, 1180 vs, 1080 m, 850 w cm^{-1}. MS (17 eV) (mass (fragment), relative intensity): 206 (M^+), 3; 175 ($M^+ - OCH_3$), 80; 170 ($M^+ - HCl$), 100; 162.5 ($M^+ - CO_2$), 90; 121 ($M^+ - OCF_3$), 20.

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Kinetics and Mechanism of the Substitution Reactions of the Pentacyanoaquoruthenate(II) Ion with Nitrogen Heterocycles in Aqueous Media

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The kinetics of the substitution reactions of the $Ru(CN)_5OH_2^{3-}$ ion with a series of nitrogen heterocycle ligands were studied in aqueous media. The rate constants for the formation of $Ru(CN)_5L^{(3-n)-}$ are sensitive to the charge on the incoming ligand L^{n+}. The kinetic and activation parameters are consistent with an ion-pair dissociative mechanism, with a rate constant of 10 ± 5 s^{-1} (25.0 °C, μ = 0.10 M) for water exchange on $Ru(CN)_5OH_2^{3-}$. This value is 30 times lower than that for $Fe(CN)_5OH_2^{3-}$ but larger than that for cationic complexes such as $Ru(OH_2)_6^{2+}$ or $Ru(NH_3)_5OH_2^{2+}$. The differences in substitution lability are discussed in terms of electronic effects on the $M-OH_2$ bond interactions. At higher acidities (pH <5) the substitution rates for $Ru(CN)_5OH_2^{3-}$ decrease substantially as the protonation of a cyanide ligand yields a more substitution-inert $(HNC)Ru(CN)_4OH_2^{2-}$ ion (pK_a = 2.24 ± 0.10).

Introduction

In the past dozen years the chemistry of substituted pentacyanoferrate(II) complexes, $Fe(CN)_5L^{3-}$, has been the subject of numerous kinetic and spectroscopic investigations.[1-10] It has been demonstrated that the complexation reactions of $Fe(CN)_5OH_2^{3-}$ with a variety of ligands L and the dissociation reactions of $Fe(CN)_5L^{3-}$, in the presence of excess L′, follow a dissociative mechanism of ligand substitution. In addition an extensive correlation has been established between the spectroscopic properties of $Fe(CN)_5L^{3-}$ and $Ru(NH_3)_5L^{2+}$ complexes, both low-spin d^6 systems.

Although the synthesis of the analogous $Ru(CN)_5OH_2^{3-}$ ion was first reported some time ago,[11] it is only recently that this species has been utilized in the preparation of substituted pentacyanoruthenate(II) complexes with aromatic nitrogen heterocyles.[12] Unlike the $Fe(CN)_5OH_2^{3-}$ ion, the kinetics and mechanism of substitution reactions of $Ru(CN)_5OH_2^{3-}$ have yet to be reported. While the $Ru(OH_2)_6^{2+}$ ion is much more inert to substitution[13] than the $Fe(OH_2)_6^{2+}$ ion,[14] resulting from a difference in their spin configurations, the rates of substitution for the low-spin $Ru(CN)_5OH_2^{3-}$ and $Fe(CN)_5OH_2^{3-}$ complexes are expected to be of similar magnitude.

Table I. UV–Visible Band Maxima and Molar Absorptivity Coefficients for Substituted Pentacyanoruthenate(II) Complexes, $Ru(CN)_5L^{(3-n)-}$, in Aqueous Solution

ligand	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}
H_2O	308	1.64
pyridine	317	5.02
isonicotinate	351	5.00
4,4′-bipyridine	368	8.80
pyrazine	370	5.04
1-(4-pyridyl)pyridinium	393	5.04
2,3-pyrazinedicarboxylate	418	2.52
N-methylpyrazinium	522	6.84

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In this paper we report the results of a kinetic study of the complexation reactions of the $Ru(CN)_5OH_2^{3-}$ ion with a series of nitrogen heterocycle ligands: pyridine, pyrazine, imidazole, and derivatives thereof. This work provides an estimate for the rate of dissociation of the coordinated water ligand from $Ru(CN)_5OH_2^{3-}$. A comparison is made with the corresponding value for $Fe(CN)_5OH_2^{3-}$ as well as with rate constants reported for other octahedral ruthenium(II) complexes containing coordinated water ligands. Additional kinetic measurements were performed at low pH, providing information concerning the acid dissociation constant and substitution reactivity of a protonated pentacyanoaquoruthenate(II) species.

Experimental Section

Materials. Imidazole, 2,3-pyridinedicarboxylic acid, isonicotinic acid, 1-(4-pyridyl)pyridine chloride hydrochloride, pyrazine (Gold Label), and 4,4′-bipyridine hydrate from Aldrich and dimethyl sulfoxide and pyridine from Fisher were used as supplied. *N*-Methylpyrazinium iodide was prepared by the methylation of pyrazine by methyl iodide (Fisher) in chloroform.[1,15] The pentacyanoaquoruthenate(II) ion, $Ru(CN)_5OH_2^{3-}$, was prepared by mixing equimolar concentrations of $Ru(CN)_6^{4-}$ (from $K_4Ru(CN)_6{\cdot}3H_2O$, Alfa) and bromine in aqueous solution, in the presence of a 10-fold excess of sodium bromide. The solutions were saturated with nitrogen gas and used promptly. Low concentrations ($<2 \times 10^{-5}$ M) were used to minimize dimerization processes. Solutions of the substituted pentacyano(ligand)ruthenate(II) complexes were prepared by the addition of a 10-fold excess of the appropriate ligand to the nitrogen-saturated solutions of the $Ru(CN)_5OH_2^{3-}$ ion.

Kinetic Measurements. Kinetic measurements were made by using both stopped-flow and conventional mixing techniques. Slower reactions, along with product spectra, were measured in a quartz "split" cell (Hellma, 2 × 4.37 mm) on a Perkin-Elmer 552 spectrophotometer, modified with a cell block thermostated by means of an external water bath. The more rapid reactions were studied on a TDI Model IIA (Cantech Scientific) stopped-flow apparatus. The transmittance data was collected by a TDI Model 1024C transient recorder and processed on an interfaced Sinclair ZX81 microcomputer. The complexation reactions were followed by monitoring at the λ_{max} for the $Ru(CN)_5L^{(3-n)-}$ complex (Table I). Pseudo-first-order conditions of excess ligand concentrations were employed, and plots of ln $(A_\infty - A_t)$ against time were generally linear for 3 or more half-lives. The reported rate constants represent an average of four to six replicate runs. The pH the reaction mixture was controlled with phthalate, phosphate, and borate buffers and the appropriate amounts of HCl at low pH. The solution acidities were measured after the completion of the reaction by using a Fisher Accumet 825 pH meter. All solutions were maintained at an ionic strength of 0.10 M with added sodium chloride.

Results

The pentacyanoaquoruthenate(II) ion, $Ru(CN)_5OH_2^{3-}$, may be generated in solution by the rapid aquation of the $Ru(CN)_6^{4-}$ ion in the presence of bromine.[11,16]

$$Ru(CN)_6^{4-} + Br_2 \xrightarrow{H_2O} Ru(CN)_5OH_2^{3-} + Br^- + BrCN \quad (1)$$

The pale yellow $Ru(CN)_5OH_2^{3-}$ ion has an absorption maximum at 308 nm with $\epsilon = 1640 \pm 50$ M^{-1} cm^{-1}. At higher concentrations ($>10^{-4}$ M) the $Ru(CN)_5OH_2^{3-}$ ion is observed to undergo a slow dimerization reaction ($k_d \sim 10^{-2}$ M^{-1} s^{-1} at pH 7, 25.0 °C), presumably to yield a cyanide-bridged $Ru_2(CN)_{10}^{6-}$ ion,[18] as observed with the pentacyanoiron(II) system.[19]

The addition of an excess of a ligand such as pyridine or pyrazine to a dilute solution of the $Ru(CN)_5OH_2^{3-}$ ion results in a shift in λ_{max} in the UV–visible spectrum, ascribed to the formation of a substituted pentacyanoruthenate(II) species, $Ru(CN)_5L^{3-}$. The values of λ_{max} and ϵ for a series of these complexes, where L is pyridine, pyrazine, or a derivative thereof, are listed in Table I. These absorptions have been assigned[12] as the metal-to-ligand charge-transfer transitions and correlate linearly with the MLCT energies of the corresponding $Fe(CN)_5L^{3-}$ and $Ru(NH_3)_5L^{2+}$ species, also low-spin d^6 systems.

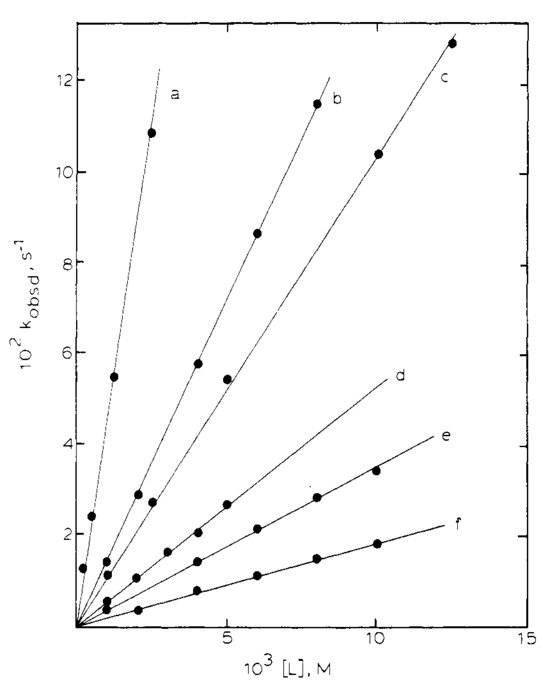

Figure 1. Dependences of k_{obsd} on ligand concentrations for the substitution reactions of $Ru(CN)_5OH_2^{3-}$ (25 °C, $\mu = 0.10$ M). Ligands: (a) *N*-methylpyrazinium; (b) 4,4′-bipyridine; (c) pyrazine; (d) pyridine; (e) isonicotinate; (f) 2,3-pyrazinedicarboxylate.

Table II. Rate and Activation Parameters for the Substitution Reactions of $Ru(CN)_5OH_2^{3-}$ in Aqueous Media

ligand	k_2,[a] M^{-1} s^{-1}	$\Delta H^\ddagger$,[b] kcal mol^{-1}	$\Delta S^\ddagger$,[c] cal K^{-1} mol^{-1}
N-methylpyrazinium	47.0	17.3	7.1
1-(4-pyridyl)pyridinium	44.4	17.0	6.1
4,4′-bipyridine	14.4	17.2	4.3
pyrazine	10.9	17.2	4.0
pyridine	5.4	17.9	4.8
imidazole	5.1	17.0	1.6
isonicotinate	3.5	17.5	2.6
2,3-pyrazinedicarboxylate	1.8	16.7	−1.2

[a] pH 7–9; $\mu = 0.10$ M (NaCl). [b] Uncertainty is ±0.5 kcal mol^{-1}. [c] Uncertainty is ±2.0 cal K^{-1} mol^{-1}.

Kinetic Studies. The kinetics of the substitution reactions of $Ru(CN)_5OH_2^{3-}$ with a series of nitrogen heterocyclic ligands L^{n+} were investigated by using conventional mixing and stopped-flow techniques.

$$Ru(CN)_5OH_2^{3-} + L^{n+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ru(CN)_5L^{(3-n)-} + H_2O \quad (2)$$

The reactions were studied in a pH range of 7–9 and at an ionic strength of 0.10 M (NaCl). The formation of the $Ru(CN)_5L^{(3-n)-}$ ion was monitored at its λ_{max} (Table I) and, under pseudo-first-order conditions of excess ligand concentrations, followed the rate expression in eq 3, where $k_{obsd} = k_2[L^{n+}] + k_{-2}$. Plots of k_{obsd}

$$d[Ru(CN)_5L^{(3-n)-}]/dt = k_{obsd}[Ru(CN)_5OH_2^{3-}] \quad (3)$$

against ligand concentration, as shown in Figure 1, were linear for each ligand under study. The lack of an intercept suggests that the reverse process in eq 2 is very slow. This has been confirmed by studies[20] of the substitution reactions of $Ru(CN)_5L^{(3-n)-}$ in the presence of an excess of L′, which demonstrated that k_{-2} ((2–10) × 10^{-5} s^{-1}) is negligible when compared with k_{obsd}

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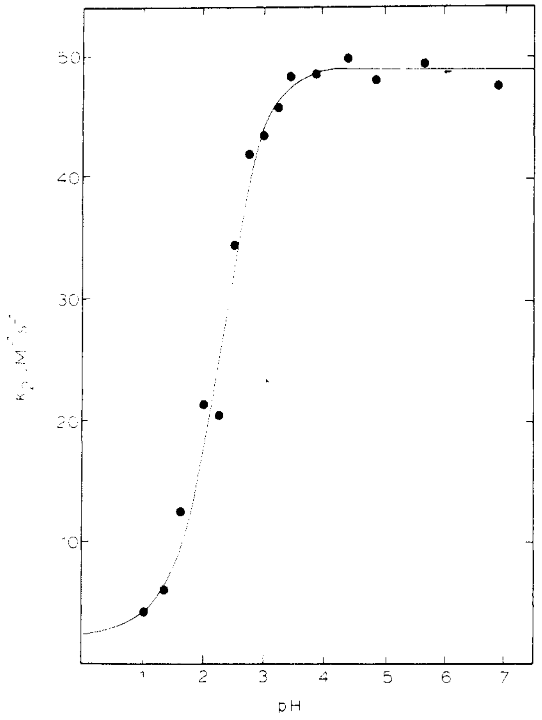

Figure 2. Dependence of k_2 on pH for the substitution reaction of $Ru(CN)_5OH_2^{3-}$ with the *N*-methylpyrazinium cation (25 °C, $\mu = 0.10$ M).

in these reactions. Slower secondary reactions were sometimes observed, and these are attributed to substitution processes involving small quantities of dimeric species. Interferences from this source were minimized by the use of low concentrations of freshly prepared $Ru(CN)_5OH_2^{3-}$ solutions.

The rate and activation parameters for the $Ru(CN)_5OH_2^{3-}$ substitution reactions are collected in Table II. The rate constant k_2 is observed to increase with an algebraic increase in the charge on the ligand, from the dianionic through the cationic species. The entropies of activation ($\Delta S^{\ddagger} = -1$ to $+7$ cal K^{-1} mol^{-1}) also increase in the same manner, while the enthalpy values are reasonably constant, at $\Delta H^{\ddagger} = 17.0 \pm 0.7$ kcal mol^{-1}. When compared with the corresponding parameters for the substitution reactions of the $Fe(CN)_5OH_2^{3-}$ ion with the same ligands,[1,7] k_2 is 30–50 times lower and $\Delta H^{\ddagger}$ is about 2 kcal mol^{-1} higher ($\Delta S^{\ddagger}$ is approximately the same) for the $Ru(CN)_5OH_2^{3-}$ ion substitutions.

As the acidity of the reaction medium is increased below pH 5 the substitution reactions of the $Ru(CN)_5OH_2^{3-}$ become markedly slower. This pH dependence, also observed for the $Fe(CN)_5OH_2^{3-}$ ion,[21] results from the protonation of a coordinated cyanide ligand. The kinetics of $Ru(CN)_5OH_2^{3-}$ substitution were investigated in the pH range 1–5 by using the *N*-methylpyrazinium cation ($Mepyz^+$) as the incoming ligand, as the pK_a of its conjugate acid is reported to be <0.[1] The reaction scheme for this system is given in eq 4–6. A spectrophotometric titration of the reaction

$$(HNC)Ru(CN)_4OH_2^{2-} \overset{K_a}{\rightleftharpoons} Ru(CN)_5OH_2^{3-} + H^+ \qquad (4)$$

$$(HNC)Ru(CN)_4OH_2^{2-} + Mepyz^+ \xrightarrow{k_a} Ru(CN)_5Mepyz^{2-} + H_3O^+ \qquad (5)$$

$$Ru(CN)_5OH_2^{3-} + Mepyz^+ \xrightarrow{k_b} Ru(CN)_5Mepyz^{2-} + H_2O \qquad (6)$$

product with acid suggests that protonation of the $Ru(CN)_5Mepyz^{2-}$ ion does not occur above pH 1. The variation in the observed rate constant with pH is illustrated in Figure 2. The specific rate constants k_a and k_b, along with the acid dissociation constant K_a, were determined by a least-squares fit of the data to the expression for k_2 in eq 7. The values of k_a and k_b (25.0

$$k_2 = \frac{k_a[H^+] + k_bK_a}{[H^+] + K_a} \qquad (7)$$

°C, $\mu = 0.10$ M) were found to be 2 ± 1 M^{-1} s^{-1} and 49 ± 3 M^{-1} s^{-1}, respectively, with $K_a = (5.75 \pm 1.40) \times 10^{-3}$ M ($pK_a = 2.24 \pm 0.10$). The pK_a value for $(HNC)Ru(CN)_4OH_2^{2-}$ is slightly lower than the corresponding constant reported for $(HNC)Fe(CN)_4OH_2^{2-}$, $pK_a = 2.63 \pm 0.12$ (25.0 °C, $\mu = 0.10$ M),[21] measured by a similar procedure. Above pH 5 there is no dependence of k_2 on pH, which may be attributed to a deprotonation of the coordinated water on the $Ru(CN)_5OH_2^{3-}$ ion.

Discussion

The variations in the substitution rate constants in Table II indicate that the rate of complexation of $Ru(CN)_5OH_2^{3-}$ is dependent on the charge on the entering ligand while generally insensitive to the nature of the ligand within a given charge type. This kinetic behavior is consistent with an ion-pair dissociative mechanism as depicted in eq 8–10. The rate-determining loss

$$[Ru(CN)_5OH_2]^{3-} + L^{n+} \overset{K_{os}}{\rightleftharpoons} [Ru(CN)_5OH_2,L]^{(3-n)-} \qquad (8)$$

$$[Ru(CN)_5OH_2,L]^{(3-n)} \xrightarrow{k_{-H_2O}} [Ru(CN)_5,L]^{(3-n)-} + H_2O \qquad (9)$$

$$[Ru(CN)_5,L]^{(3-n)-} \xrightarrow{\text{fast}} [Ru(CN)_5L]^{(3-n)-} \qquad (10)$$

of the coordinated water molecule (eq 9) is preceeded by an outer-sphere ion-pair association (eq 8), for which K_{os} is dependent on the size and charge of L^{n+} and on the ionic strength of the reaction medium. The rate expression for the observed formation rate constant consistent with the above mechanism is given in eq 11. If $K_{os}[L] << 1$ and k_{-10} is negligible, then the expression

$$k_{obsd} = \frac{k_{-H_2O}K_{os}[L]}{1 + K_{os}[L]} \qquad (11)$$

for k_{obsd} will reduce to the form $k_{obsd} = k_{-H_2O}K_{os}[L]$. Saturation of k_{obsd} at high ligand concentrations was not observed, even for the *N*-methylpyrazinium and 1-(4-pyridyl)pyridine cations. Kinetic studies of the dissociation kinetics of $Ru(CN)_5L^{(3-n)-}$ complexes using high L′ concentrations indicate that for the ligands under study k_{-10} would be in the range $(2-10) \times 10^{-5}$ s^{-1},[20] and negligible when compared to $k_{-H_2O}K_{os}[L]$. The values of the association constant K_{os} may be calculated by using the Eigen–Fuoss expression[22]

$$K_{os} = (4\pi N\sigma^3/3000)\exp(-w(\sigma)/RT) \qquad (12)$$

where

$$w(\sigma) = \frac{z_1z_2e^2}{D_s\sigma(1 + \beta\sigma\mu^{1/2})} \qquad (13)$$

In these expressions σ is the sum of the radii of the reactants, z_1 and z_2 are the charges on the reactants, D_s is the solvent dielectric constant and $\beta = (8\pi Ne^2/1000D_skT)^{1/2}$. The values of σ were estimated by using 4.6 Å as the radius of the $Ru(CN)_5OH_2^{3-}$ ion and by using ligand radii ranging from 2.3 to 3.3 Å. The calculated K_{os} constants range from ~0.05 M^{-1} for the 2,3-pyrazinedicarboxylate dianion to ~5.5 M^{-1} for the 1-(4-pyridyl)pyridine cation, with $K_{os} \sim 1$ M^{-1} for the neutral species such as pyridine or pyrazine. The variations in K_{os} with the charge and size of the ligand parallel, for the most part, the variations in the observed substitution rate constants.

The rate of substitution is apparently also influenced by the number of coordination sites on the ligand and by their proximity to the charges on the ligand. The former effect has previously been suggested to explain the larger than expected rates of substitution of the $Fe(CN)_5OH_2^{3-}$ ion by cystine,[10] histidine,[7] cyanopyridines,[6] and ethylenediamine,[23] ligands with two or more

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Table III. Water Substitution Rate Constants for Iron(II) and Ruthenium(II) Complexes at 25 °C

complex	k_{ex}, s^{-1}	ref
$Ru(H_2O)_6^{2+}$	1.4×10^{-2}	13
$Fe(H_2O)_6^{2+}$	4.4×10^{6}	14
$Ru(CN)_5OH_2^{3-}$	10	this work
$Fe(CN)_5OH_2^{3-}$	300	1
$Ru(edta)OH_2^{2-}$	15	24
$Ru(NH_3)_5OH_2^{2+}$	0.10	25
trans-$Ru(NH_3)_4(pyr)OH_2^{2+}$	2×10^{-2}	26
cis-$Ru(NH_3)_4(CO)OH_2^{2+}$	4×10^{-6}	26
$Ru(terpy)(bpy)OH_2^{2+}$	7×10^{-5}	26

possible coordination sites. In this study the same effect in seen in the trend in k_2, bipyridine > pyrazine > pyridine, and by the fact that k_2 values for 4,4′-bipyridine and the 2,3-pyrazinedicarboxylate dianion are somewhat larger than expected for their size and charge. The latter effect, the proximity of the charge to the coordination site, likely has a small influence on k_2 for the cationic and anionic ligands in this study. The slightly larger size of the 1-(4-pyridyl)pyridine cation, compared with the *N*-methylpyrazinium cation, is apparently negated by the larger separation distance of the charge from the donor atom. The values of K_{os} for the isonicotinate and 2,3-pyrazinedicarboxylate anions may have been underestimated, as the carboxylate groups bearing the negative charges are not all located near the N-donor atom.

Employing the calculated K_{os} values and taking the other minor effects into consideration, we estimated the water exchange rate constant, k_{-H_2O}, for the $Ru(CN)_5OH_2^{3-}$ ion to be 10 ± 5 s^{-1}. The exchange rate constant is approximately 30 times lower than the corresponding value estimated for the $Fe(CN)_5OH_2^{3-}$ ion (250–400 s^{-1})[10] and is consistent with the difference of about 2 kcal mol^{-1} observed in the enthalpies of activation associated with the respective substitution reactions. For both species the entropies of activation are similar and appear to depend on the charge on the incoming ligand (Table II). The outer-sphere ion-pair association is primarily controlled by entropic effects,[10] with ΔS_{os} (calculated from eq 12, assuming $\Delta H_{os} \sim 0$) decreasing by 2–3 cal K^{-1} mol^{-1} with each decrease in the unit charge on L^{n+}. The consistency in this trend in ΔS^{*} (Table II) lends support to an ion-pair dissociative mechanism.

The difference in the rate constants for water exchange in the $Ru(CN)_5OH_2^{3-}$ and $Fe(CN)_5OH_2^{3-}$ ions is related to the relative strengths of their $M-OH_2$ bond. Both species have low-spin d^6 electronic configurations, and similar rates of water exchange might be expected. A slightly stronger $Ru-OH_2$ bond may result from a more favorable radial extension of the unoccupied $4d(e_g)$ orbitals toward the oxygen lone pairs on the coordinated water. A much larger difference in substitution lability is found when the water exchange rates of the $Ru(OH_2)_6^{2+}$ and $Fe(OH_2)_6^{2+}$ ions are compared (Table III). This difference may be attributed to a change in the spin configuration from a low-spin Ru(II) to a high-spin Fe(II) system. The water exchange rate constant for $Ru(CN)_5OH_2^{3-}$ may also be compared with values for other octahedral ruthenium(II) complexes containing coordinated water molecules (Table III). The anionic complexes $Ru(CN)_5OH_2^{3-}$ and $Ru(edta)OH_2^{2-}$ ($edta^{4-}$ = ethylenediaminetetraacetate) are at least 2 orders of magnitude more labile than cationic complexes such as $Ru(OH_2)_6^{2+}$ and $Ru(NH_3)_5OH_2^{2+}$. The labilization of the $Ru-OH_2$ bond is presumably a result of a reduction in the effective positive charge on the metal center. This in turn lowers the energy barrier for water dissociation by the interaction between the metal and the lone pairs on the oxygen atom. When spectator ligands, such as CO or 2,2′-bipyridine, are present in the cationic Ru(II) complexes the removal of electron density via π-back-donation to these ligands results in an increase in the effective positive charge on the metal. The lability of the coordinated water in these complexes is further reduced.

The water substitution rate constants for both $Fe(CN)_5OH_2^{3-}$ and $Ru(CN)_5OH_2^{3-}$ decrease substantially in acidic solution, as a coordinated cyanide ligand is protonated. Cyanide protonation would tend to draw some electron density away from the metal center, strengthening the $M-OH_2$ bond. The pK_a values for $(HNC)Ru(CN)_4OH_2^{2-}$, 2.24 ± 0.10 (μ = 0.10 M), and $(HNC)Fe(CN)_4OH_2^{2-}$, 2.63 ± 0.12 (μ = 0.10 M),[21] may be compared with values reported for hexacyano complexes: $(HNC)Ru(CN)_5^{3-}$, 2.53 (μ = 1.0 M);[27] $(HNC)Fe(CN)_5)^{3-}$, 3.16 ± 0.03 (μ = 0.10 M).[28] The basicity of the cyanide ligands is reduced by the replacement of one cyanide by a water molecule. This trend continues when two cyanides are replaced by a 2,2′-bipyridine ligand to form $(HNC)M(CN)_3bpy^{-}$: for M = Fe, $pK_a = 1.69 \pm 0.02$ (20.0 °C, μ = 0.089 M);[29] for M = Ru, $pK_a = 0.12 \pm 0.06$ (21 °C, ionic strength not held constant).[30] Taking into consideration the differences in ionic strength, the pK_a values for the respective Ru(II) and Fe(II) complexes are quite similar. A slightly lower pK_a for the Ru(II) species may reflect somewhat stronger metal–ligand interactions, consistent with the more inert $Ru-OH_2$ bond.

The kinetic and activation parameters in this study support an ion-pair dissociative mechanism for ligand substitution reactions of the $Ru(CN)_5OH_2^{3-}$ ion. The mechanistic criterion of an independence of k_L on the nature of the entering ligand has not been severely tested in this study, with the use of similar nitrogen heterocycle ligands. Preliminary investigations of the rate of substitutions by other nitrogen and sulfur donor ligands (k_2 = 12 M^{-1} s^{-1} and 13 M^{-1} s^{-1}, for dimethyl sulfoxide and cysteine, respectively), however, suggest that k_2 is fairly constant for a given charge type. Further studies, employing other organic and inorganic complexes as entering ligands, are in progress.

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Registry No. $Ru(CN)_5(H_2O)^{3-}$, 74009-27-1; pyridine, 110-86-1; isonicotinate, 55-22-1; 4,4′-bipyridine, 553-26-4; pyrazine, 290-37-9; 1-(4-pyridyl)pyridinium, 16077-77-3; 2,3-pyrazinedicarboxylate, 89-01-0; *N*-methylpyrazinium, 17066-96-5.

Supplementary Material Available: A table of kinetic data for the substitution reactions of $Ru(CN)_5OH_2^{3-}$ (3 pages). Ordering information is given on any current masthead page.

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