Kinetic Effects in Outer Sphere Ion Clusters: Interactions of $[Ru(NH_3)_5H_2O]^{3+}$ with $[Ru(CN)_6]^{4-}$, $[Fe(CN)_6]^{4-}$, $[Os(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$

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A study of the kinetics of substitution in $[Ru(NH_3)_5H_2O]^{3+}$ by the nucleophiles $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{4-}$, $[Os(CN)_6]^{4-}$, and $[Co(CN)_6]^{3-}$ in the absence of indifferent electrolyte shows that k for substitution (in every case first order in cation concentration) increases as the ratio of the concentration of the nucleophile to the aquo ion increases, and then it abruptly becomes independent of this ratio. When the reaction medium is 1.5×10^{-2} M H^+ (chosen to eliminate catalysis by the formation of $[Ru(NH_3)_5H_2O]^{2+}$ when $[Fe(CN)_6]^{4-}$ is the nucleophile), the critical values of R are ca. 4 for $[M(CN)_6]^{4-}$, but 8 for $[Co(CN)_6]^{3-}$. In a reaction medium adjusted to pH = 3.1, the $[M(CN)_6]^{4-}$ species are less fully protonated. Again, approximately constant values of k are reached as R increases, but now at higher values of R. Short of these values of R, maxima in k are observed, which, as in the case of earlier studies of oscillator strength of the intervalence absorption bands, are attributed to structural changes, the anions rearranging from positions on the apices of the cation octahedron, to the faces. A study of catalysis of substitution by extrinsic $[Ru(NH_3)_5H_2O]^{2+}$ and, in the case of $[Fe(CN)_6]^{4-}$, intrinsic Ru(II) reveals some unusual kinetic effects which also have their origin in ion clustering.

Introduction

In an earlier paper we reported[1] that the rate constants for the collapse of the ion pairs formed by $[Ru(NH_3)_5H_2O]^{3+}$ and the nucleophiles $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$, i.e., k ($s^{-1} \times 10^4$) at 20 °C measured as 2.8, 1.5, 1.1, and 1.4, respectively, are very close to that reported for water exchange between the cation and solvent,[2] i.e., 1.2×10^{-4} s^{-1} at the same temperature. Later work with the same cation and the nucleophiles $[Fe(CN)_6]^{4-}$ and $[Ru(CN)_6]^{4-}$ revealed that the rates of substitution in 1.5×10^{-2} M HO_3SCF_3 increase as the ratio R (≡[anion]/[cation]) increases at constant cation concentration until $R = 4$ is reached, when there is an abrupt decrease in the slope of the plot of k against R. These changes were taken as evidence of ion clustering, $R = 4$ indicating that four anions cluster about the cation, a conclusion that is supported by measurements of the oscillator strength of the intervalence bands for the clusters as a function of R.[3]

Only a few of the kinetic data on substitution were shown in the earlier publication. In this paper we complete the report on the kinetic studies we have done on rates of substitution in clusters containing ions of high charge. The substitution reactions are subject to catalysis by $[Ru(NH_3)_5H_2O]^{2+}$. The data we have obtained in an experimental study of the effect of clustering on the reaction kinetics when measured amounts of $[Ru(NH_3)_5H_2O]^{2+}$ are added are also reported.

Burewicz and Haim[4] in their study of the substitution kinetics for the $[Ru(NH_3)_5H_2O]^{3+}/[Fe(CN)_6]^{4-}$ system did not encounter the sharp "breaks" as the concentration of the nucleophile is raised, which we report. We ascribe the difference mainly to the circumstance that background electrolyte was used by them to maintain the ionic strength at 0.10 M. To maximize the effects of interionic attraction, we avoided background electrolytes as much as possible. Because of the high charges on the reactants, reducing the ionic strength greatly increases the association constants.[1] The maximum electrolyte concentration, in addition to that comprised by the agents themselves, in an experiment was at the 1.5×10^{-2} M level. The concentration of the reactant cation in their experiments was lower by a factor of 4, and the pH was maintained at a value between 4.6 and 4.9. Because of deprotonation of the cation, this reduces its charge and again moderates the effect of interionic attraction. Most of our experiments were carried out at pH 4.0 or lower.

Experimental Section

General Procedures. $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ was prepared as described in the literature.[5] The rate constant[5] for the aquation of $[Ru(NH_3)_5(CF_3SO_3)]^{2+}$ is 1.9×10^{-2} s^{-1}; in all experiments the ruthenium solutions were kept for 20 min before the nucleophiles were added.

$[Ru(NH_3)_5H_2O]^{2+}$ was prepared by reduction of a solution of $[Ru(NH_3)_5H_2O]^{3+}$ with H_2 over a platinum gauze. The solutions for the study of the catalytic reactions were kept under hydrogen to avoid formation of the dinitrogen−ruthenium(II) complex in the controlled atmosphere box (CAB).

$K_4Os(CN)_6$ was prepared from K_4OsCl_6 as described in the literature.[6] Sodium hexacyanoferrate(II) decahydrate (Strem), potassium ferrocyanide trihydrate (Baker), potassium ferricyanide (Sigma), potassium hexacyanoruthenate (II) trihydrate (Aldrich), and potassium hexacyanocobaltate were used as received.

$[Ru(en)_3]Cl_2$ (Alfa) was kept under argon and oxidized by silver trifluoromethanesulfonate (Aldrich). About 2% of $[Ru(en)_2(diimine)]^{2+}$, a common impurity, was always present in our $[Ru(en)_3]^{3+}$ samples.

Unless otherwise specified, the temperature for all of the kinetic measurements was 27.0 °C, the reaction medium was water, and the materials used to prepare the reaction mixtures for the uncatalyzed reactions with ferrocyanide were kept in the CAB, under an atmosphere of N_2, and thus were deoxygenated to the level obtainable by the equipment ($O_2 \leq 5$ ppm).

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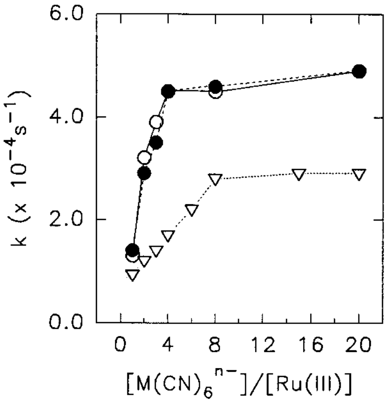

Figure 1. Rate constants for the collapse to inner sphere products of the outer sphere complexes of $[Ru(NH_3)_5H_2O]^{3+}$, with the nucleophiles (●) $[Fe(CN)_6]^{4-}$ (in the presence of 1.0×10^{-4} M $[Fe(CN)_6]^{3-}$ for $R > 8$); (○) $[Ru(CN)_6]^{4-}$; and (▽) $[Co(CN)_6]^{3-}$. $[[Ru(NH_3)_5H_2O]^{3+}] = 2.5 \times 10^{-4}$ M. Reaction medium $[CF_3SO_3H] = 1.5 \times 10^{-2}$ M, $t = 27$ °C.

The kinetic measurements were made outside the CAB, but, as demonstrated by experiments with other O_2-sensitive solutions, leakage of O_2 into the cell is not a significant factor even for slow reactions.

Instrumentation. UV–vis spectra and kinetic measurements were recorded with a Hewlett-Packard 8452 A spectrophotometer with a thermostated cell holder. An mgw Lauda RC 20 Brinkmann circulating water bath was used to maintain the temperature in the cell holder. All kinetic measurements were performed in spectrophotometric cells with greased glass stoppers.

Results

Substitution in $[Ru(NH_3)_5H_2O]^{3+}$ by Hexacyano Complexes. In Figure 1 the first-order rate constants, k, for the formation of inner sphere products in the reactions of $[Ru(NH_3)_5H_2O]^{3+}$ with the nucleophiles $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{4-}$, and $[Co(CN)_6]^{3-}$ are shown as a function of R, the ratio of the concentration of the anion to that of the cation. The concentration of the cation in each case was 2.5×10^{-4} M, and the temperature 27 °C. The rates remain strictly first order in each experiment to at least 90% completion, in line with the high values of association constants at low ionic strength. Comparisons between the nucleophiles are complicated by the fact that $[Fe(CN)_6]^{4-}$ is a strong enough reducing agent to lead to electron transfer catalysis of substitution by $[Ru(NH_3)_5H_2O]^{2+}$.[4] To suppress this additional path, the experiments with this nucleophile were carried out in 1.5×10^{-2} M HO_3SCF_3 as the reaction medium. The affinity of $[Fe(CN)_6]^{4-}$ for protons is moderately high[7] (K_a for $[HFe(CN)_6]^{3-}$ is 1.6×10^{-4} at an ionic strength of 1.5×10^{-2} M) while $[HFe(CN)_6]^{2-}$ is a strong acid, effects which weaken the reducing power of the couple; $[HCo(CN)_6]^{2-}$ is completely dissociated at 1.5×10^{-2} M H^+.

A striking feature of the results is that, for the nucleophiles in acidic solution, the rate constants, k, increase with R until 4 is reached, at which point there is a "break", the slope of the profile beyond $R = 4$ being much reduced. In the case of $[Co(CN)_6]^{3-}$, the initial slope of the profile is lower, and the break occurs at $R = 8$, rather than $R = 4$. Another significant result is that the plateau values do vary with the conditions, and it is to be noted that the highest reached (4.6×10^{-4} s^{-1}) exceeds the rate of exchange of H_2O between $[Ru(NH_3)_5H_2O]^{3+}$ and the solvent, which at 27 °C is 2.9×10^{-4} s^{-1}.[2]

The break at $R = 4$ for the negative ions implies that clusters with at least four anions about each cation form in these solutions. Because, below $R = 4$, k is sensitive to this ratio, the fact that first-order behavior persists over a substantial range in the concentration of the cluster shows that the driving force for amassing each additional anion is quite high. Of course, at high values of R first-order behavior in an experiment has no special significance because the change in concentration of the reagent in excess is small.

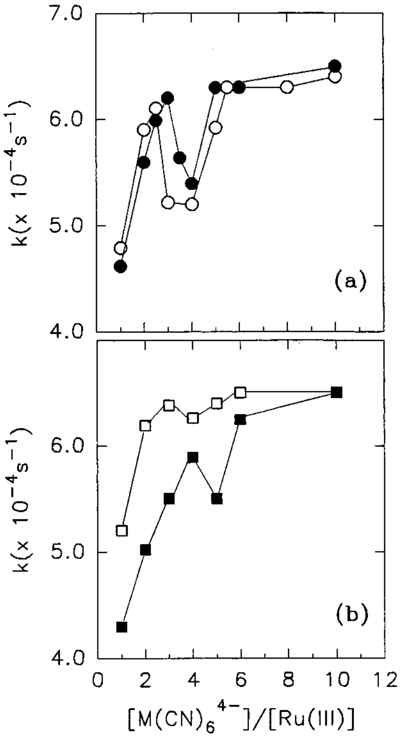

Figure 2. Rate constants for the collapse of the outer sphere complexes of $[Ru(NH_3)_5H_2O]^{3+}$ with the nucleophiles (a) (○) $[Ru(CN)_6]^{4-}$; (●) $[Os(CN)_6]^{4-}$, pH 3.1. (b) $[Ru(CN)_6]^{4-}$, pH 3.6 with (■) and without (□) LiO_3SCF_3 present at 1.5×10^{-2} M. $[[Ru(NH_3)_5H_2O]^{3+}] = 2.5 \times 10^{-4}$ M, pH adjusted with HO_3SCF_3, $t = 27$ °C.

Experiments with tetranegative nucleophiles similar to those shown in Figure 1 were also carried out at higher pH, 3.1 and 3.6, but excluding $[Fe(CN)_6]^{4-}$ because of the possible interference of catalysis by $[Ru(NH_3)_5H_2O]^{2+}$, and are summarized in Figure 2. The pH was adjusted by titration with a solution of HO_3SCF_3. Apart from the pH, the conditions were the same as those in the experiments at higher acid concentration. Values of pK_a for $[HRu(CN)_6]^{3-}$ and $[HOs(CN)_6]^{3-}$ have not been reported, but titrations we performed result in at least approximate measures. These experiments were carried out at 24 °C with $K_4Ru(CN)_6$ and $K_4Os(CN)_6$ each at 2.0×10^{-3} M, and they led to pK_a values of 3.2 and 3.3, respectively. Because, for ions of high charge, values of equilibrium constants can be very sensitive to the composition of the environments, titrations were performed with both $Na_4Fe(CN)_6$, the salt used in the experiments, and $K_4Fe(CN)_6$, which showed that substituting K^+ for Na^+ lowers the pK_a by 0.09 unit. The formal ionic strength of the solutions at midtitration is 1.2×10^{-2} M. The value of pK_a for $[HFe(CN)_6]^{3-}$ reported by Jordan et al.[7] for the same ionic strength maintained by KCl at 25 °C is 3.8. The difference from our value for $K_4Fe(CN)_6$, 3.4, can be attributed to association of the countercation with $[Fe(CN)_6]^{4-}$, which will tend to enhance the acidity of $[HFe(CN)_6]^{3-}$. Our measurements nevertheless suffice to show that the proton affinities of $[Ru(CN)_6]^{4-}$ and $[Os(CN)_6]^{4-}$ are significantly less than that of $[Fe(CN)_6]^{4-}$.

At higher pH again "saturation" effects are observed (Figure 2) in plots of k for substitution as a function of R, but now they occur at higher values of R, ca. 6. Even more striking are the

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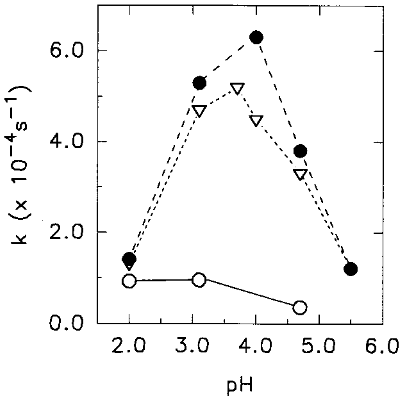

Figure 3. Effect of pH on the rate constants for the collapse of the ion pairs between $[Ru(NH_3)_5H_2O]^{3+}$ and the nucleophiles (●) $[Fe(CN)_6]^{4-}$; (▽) $[Ru(CN)_6]^{4-}$; and (○) $[Co(CN)_6]^{3-}$, to the inner sphere products. $[[Ru(NH_3)_5H_2O]^{3+}] = [[M(CN)_6]^{n-}] = 2.5 \times 10^{-4}$ M, $t = 27$ °C. Buffers used: pH 4.0−4.7, $NaC_2H_3O_2 + HC_2H_3O_2$ (3.0×10^{-3} M); pH 5.5, $KHC_8H_4O_4$ + NaOH (3.0×10^{-3} M); pH = 3.1 and 3.6 adjusted with HO_3SCF_3.

patterns observed short of reaching the plateau values of *k*, sharp maxima being registered at $R = 2-3$ at pH = 3.1 where the nucleophiles are mainly present as $[HM(CN)_6]^{3-}$. At pH 3.6, the concentration of $[HRu(CN)_6]^{3-}$ is much reduced and the contrast in the profile is also much reduced. The structure observed at low values of *R* resembles qualitatively that reported[3] for oscillator strengths of the intervalence bands as a function of *R* and will be referred to again in the Discussion section. It should be noted that the value of *k* extracted from the published data[4] on the $[Ru(NH_3)_5H_2O]^{3+}/[Fe(CN)_6]^{4-}$ system for solutions (1.4−1.44) × 10^{-3} M in $Na_4Fe(CN)_6$, and containing also 2.5×10^{-4} M $K_3Fe(CN)_6$, is 6.9×10^{-4} s^{-1} at 25 °C, which can be compared to 6.5×10^{-4} s^{-1} at 27 °C (see Figure 2b) for $[Ru(NH_3)_5H_2O]^{3+}/[Ru(CN)_6]^{4-}$ in the range 1.5 × 10^{-3} to 2.0×10^{-3} M $K_4Ru(CN)_6$.

Catalysis by $[Fe(CN)_6]^{3-}$ under certain concentration conditions was reported in the earlier work on $[Fe(CN)_6]^{4-}$ as nucleophile,[4] an effect we have investigated under our conditions. To avoid catalysis by Ru(II) these experiments were done at 1.5×10^{-2} M H^+; other conditions, $[[Ru(NH_3)_5H_2O]^{3+}] = [[Fe(CN)_6]^{4-}] = 2.5 \times 10^{-4}$ M, 27 °C. In one reaction mixture, $[Co(CN)_6]^{3-}$ was present at 1.0×10^{-3} M, and in another, $[Fe(CN)_6]^{3-}$, at the same concentration. In the former experiment, both $[Ru(NH_3)_5Fe(CN)_6]^-$ and $[Ru(NH_3)_5Co(CN)_6]$ were formed; the specific rate for the completion of substitution is 3.0×10^{-4} s^{-1}. In the second, the only product was $[Ru(NH_3)_5Fe(CN)_6]^-$, and the rate of consumption of $[Ru(NH_3)_5H_2O]^{3+}$ was identical to that quoted above. The rate for the ion pair $[Ru(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{4-}$ itself, i.e., absent the trinegative nucleophiles, is 1.4×10^{-4} s^{-1}. In the experiment with $[Co(CN)_6]^{3-}$ added, the rate constant for the formation of $[Ru(NH_3)_5Fe(CN)_6]^-$ is 1.3×10^{-4} s^{-1}, and for the alternative product, 1.7×10^{-4} s^{-1}. Only a single product is formed when $[Fe(CN)_6]^{3-}$ is present because reaction 1, the equilibrium state of which reflects the higher affinity of $[Fe(CN)_6]^{4-}$ for $[Ru(NH_3)_5]^{3+}$ than for $[Ru(NH_3)_5H_2O]^{2+}$, is rapid.

$$[Ru(NH_3)_5Fe(CN)_6] + [Fe(CN)_6]^{4-} = [Ru(NH_3)_5Fe(CN)_6]^- + [Fe(CN)_6]^{3-} \quad (1)$$

In Figure 3 is shown the effect of pH on *k* for the ion pairs between $[Ru(NH_3)_5H_2O]^{3+}$ and the nucleophiles $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{4-}$, and $[Co(CN)_6]^{3-}$. For $[Co(CN)_6]^{3-}$, which does not associate with H^+ in the acidity range under investigation, the only effect of acid is a decrease in rate, from 0.93 s^{-1} in the acid range to 0.36 s^{-1} at pH 4.7. This decrease is attributable to partial conversion of the aqua cation to the hydroxo. The decrease in rate by a factor of 2.6 is smaller than the factor of 5 expected if $pK_a = 4.1$ for $[Ru(NH_3)_5H_2O]^{3+}$ prevailed in the experiments. Because the interaction of a 3− ion with a 3+ cation is greater than it is with a 2+, the protic form of the cation is stabilized in the ion pair, pK_a being raised by outer sphere association. With $[Ru(CN)_6]^{4-}$ as nucleophile, the increase in *k* from 1.3×10^{-4} s^{-1} at 1.5×10^{-2} M H^+ to 5.2×10^{-4} s^{-1} at pH 3.7 is ascribed to the deprotonation of $[HRu(CN)_6]^{3-}$. The decrease beyond pH = 3.7 is attributable, as in the case of $[Co(CN)_6]^{3-}$, to conversion of the cation to the hydroxo form, but the effect of electrostatic stabilization of the aqua form in the ion pair is even more marked than it is for the trinegative ion. The decrease in rate is only a factor of 1.6, far from the factor of 5 expected lacking this interaction.

We took the substantially higher rate of substitution in the ion pair $[Ru(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{4-}$ compared to $[Ru(NH_3)_5H_2O]^{3+},[Ru(CN)_6]^{4-}$ as measured at pH = 4.0, where protonation of the anions is minor, as resulting from catalysis by $[Ru(NH_3)_5H_2O]^{2+}$ formed in equilibrium with $[Ru(NH_3)_5H_2O]^{3+}$ and $[Fe(CN)_6]^{4-}$, and we undertook a study of the effect of $[Fe(CN)_6]^{3-}$ on the rate of reaction. In the ion pair ($R = 1$), the addition of $[Fe(CN)_6]^{3-}$ at 1.0×10^{-5} M barely affects the rate (6.3×10^{-4} s^{-1} absent $[Fe(CN)_6]^{3-}$ compared to 6.2×10^{-4} s^{-1}). When the concentration of $[Fe(CN)_6]^{3-}$ is increased to 2.5×10^{-4} M, *k* for substitution is 5.5×10^{-4} s^{-1}, and when the concentration of $[Fe(CN)_6]^{3-}$ is further increased, *k* now increases. In contrast to the insensitivity of *k* at $R = 1$ to the small concentration of $[Fe(CN)_6]^{3-}$, at $R = 10$, where in the absence of the oxidant *k* is 5.7×10^{-3} s^{-1}, $[Fe(CN)_6]^{3-}$ present at 1.0×10^{-5} M decreases the rate to 1.4×10^{-3} s^{-1}, but still short of the value for $[Ru(CN)_6]^{4-}$, 6.4×10^{-4} s^{-1}, where catalysis by intrinsic Ru(II) is not a factor. A rather high sensitivity of the rate of substitution to $[Fe(CN)_6]^{3-}$ at 1.0×10^{-5} M is registered also when $R = 5$. In 1.5×10^{-2} M H^+, the rates for $[Fe(CN)_6]^{4-}$ and $[Ru(CN)_6]^{4-}$ in the ion pairs are almost identical, and in this medium over the whole range of *R*, $[Fe(CN)_6]^{3-}$ has no effect on the rate except at very high *R* (>8), where a slight enhancement of the rate is observed, which is eliminated by addition of $[Fe(CN)_6]^{3-}$. Figure 3 shows that at pH = 5.5, where $[Ru(NH_3)_5H_2O]^{3+}$ is almost completely converted to the hydroxy form, the rates of substitution for $[Fe(CN)_6]^{4-}$ and $[Ru(CN)_6]^{4-}$ are, within experimental error, identical. Catalysis by $[Ru(NH_3)_5H_2O]^{2+}$ is expected to be minor here because Ru(III) is stabilized relative to Ru(II) by OH^-.

In the experiments in which $[Fe(CN)_6]^{3-}$ is associated with the reactant cluster, departures from first-order kinetics appear as the reaction progresses. For these experiments, initial rates were obtained by the Guggenheim method.

Catalysis by Extrinsic $[Ru(NH_3)_5H_2O]^{2+}$. Experiments in which $[Ru(NH_3)_5H_2O]^{2+}$ was deliberately added to catalyze substitution by the nucleophiles were performed at 22.0 ± 0.5 °C in acetate buffer at pH 4.7 (3.0×10^{-3} M) with a single exception at pH = 3.1, adjusted by HO_3SCF_3. The concentration of Ru(III) was 2.5×10^{-4} M; that of the catalyst, unless otherwise stated, was 2.5×10^{-5} M; and unless otherwise stated, the concentration of the nucleophile was equal to the concentration of the ruthenium cations.

In Figure 4 are shown the experimental traces for (a) $[Fe(CN)_6]^{4-}$ equal to the sum, 2.75×10^{-4} M, of the concentrations of Ru(III) and the catalyst; (b) $[Ru(CN)_6]^{4-}$

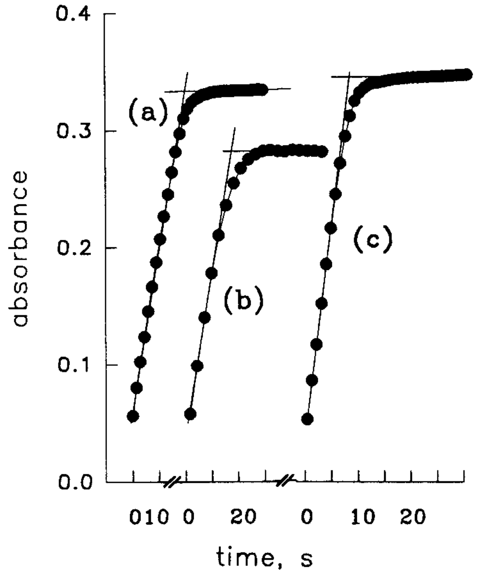

Figure 4. Absorbance vs time traces for the substitution on $[Ru(NH_3)_5H_2O]^{3+}$ catalyzed by $[Ru(NH_3)_5H_2O]^{2+}$, temperature 22.0 ± 0.5 °C; pH 4.7 (acetate buffer 3.0×10^{-3} M). $[[Ru(NH_3)_5H_2O]^{3+}] = 2.5 \times 10^{-4}$ M: (a) $[[Fe(CN)_6]^{4-}] = ([[Ru(NH_3)_5H_2O]^{3+}] + [[Ru(NH_3)_5H_2O]^{2+}]) = 2.75 \times 10^{-4}$ M; (b) $[Ru(CN)_6]^{4-}$ replacing $[Fe(CN)_6]^{4-}$ in trace a; and (c) $[[Ru(NH_3)_5H_2O]^{2+}] = 5.0 \times 10^{-5}$, $[[Fe(CN)_6]^{4-}] = 3.3 \times 10^{-4}$ M.

replacing $[Fe(CN)_6]^{4-}$ in trace a; (c) $[Ru(NH_3)_5H_2O]^{2+}$ at 5.0×10^{-5}, $[[Fe(CN)_6]^{4-}]$ at 3.3×10^{-4} M. In each case, throughout most of the reaction, the rate is zero order in the reactant ion pair $[Ru(NH_3)_5H_2O]^{3+}$,$[Fe(CN)_6]^{4-}$, in the case of trace a to ca. 90%, trace b to noticeably less than for trace a (the trace for $[Os(CN)_6]^{4-}$ as nucleophile is not shown, but it is almost identical to that for $[Ru(CN)_6]^{4-}$); trace c to ca. 80% of the reaction. In the zero-order modes, the slope divided by the catalyst concentration for trace a is 0.41 s^{-1}; for trace b 0.38 s^{-1}, applicable also to $[Os(CN)_6]^{4-}$; for trace c 0.39 s^{-1}. An experiment similar to experiment a was performed at pH 3.1 and gave the same result (0.41 s^{-1}) for the zero-order mode.

Having noted the effects on the rate of increasing the concentration of the nucleophile relative to that of $[Ru(NH_3)_5H_2O]^{3+}$, an analogous series of experiments was performed also for the reaction catalyzed by $[Ru(NH_3)_5H_2O]^{2+}$. The results obtained are shown in Supporting Information Figure 1; over the range of R covered, 1−8, the rate constant for substitution increases 3.8-fold from 0.39 s^{-1}. In this case, involving a 2+ ion rather than a 3+ in the substitution reactions, the sharp breaks are not observed.

Experiment b was repeated but with $[Co(CN)_6]^{3-}$ replacing $[Ru(CN)_6]^{4-}$. In contrast to the behavior of $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{4-}$, and $[Os(CN)_6]^{4-}$ as nucleophiles, a first-order collapse of the $[Ru(NH_3)_5H_2O]^{3+}$,$[Co(CN)_6]^{3-}$ ion pair to the inner sphere product was observed with a small deviation at the early stages of the reaction. The specific rate was measured as 3.0×10^2 M^{-1} s^{-1}.

Spectrophotometry. Ion pairs have played an important role in kinetic studies, the results of which have important features in common with those obtained in the studies of the properties of the IT bands. Improved values for the spectrophotometric properties of the ion pairs are summarized in Table 1. The values of H_{12} were calculated making use of the equation $H_{12} = 2.06 \times 10^{-2} (\epsilon_{max}\nu_{max}\Delta\nu_{1/2})^{1/2}/d$, where ν_{max} is the band energy maximum, $\Delta\nu_{1/2}$ is the band width at half-height, and d is the distance in Å.[8]

Table 1. Properties of the Ion Pairs in Neutral Solutions

ion pair	E_{max} ($cm^{-1} \times 10^{-1}$)	H_{12} (cm^{-1})[a]
$[Ru(NH_3)_5H_2O]^{3+}$,$[Fe(CN)_6]^{4-}$	1390	101
$[Ru(NH_3)_5H_2O]^{3+}$,$[Os(CN)_6]^{4-}$	1695	150
$[Ru(NH_3)_5H_2O]^{3+}$,$[Ru(CN)_6]^{4-}$	1860	127

[a] d = 8.3 Å for $[Ru(NH_3)_5H_2O]^{3+}$,$[Fe(CN)_6]^{4-}$ and 8.5 Å for $[Ru(NH_3)_5H_2O]^{3+}$,$[Os(CN)_6]^{4-}$ and $[Ru(NH_3)_5H_2O]^{3+}$,$[Ru(CN)_6]^{4-}$.[6b]

On protonation, the absorption bands, as expected, shift to higher energies: in 1.5×10^{-2} M H^+ the values of ΔE ($cm^{-1} \times 10^{-1}$) for $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{4-}$, and $[Os(CN)_6]^{4-}$ are 370, 210, and 197, respectively, and areas decrease by ca. 45%.

Some preliminary experiments have also been carried out with the $[Ru(en)_3]^{3+}$, $[Ru(CN)_6]^{4-}$ system. At the 2.0×10^{-4} M level in each reagent, ion pair formation is substantially complete. The area (ϵ cm^{-1}) of the IT band is 44 compared to 175 for that observed for $[Ru(NH_3)_6]^{3+}$,$[Ru(CN)_6]^{4-}$, and the maximum is shifted to lower energy by 2.8×10^3 cm^{-1}.

Discussion

A striking result of the studies on the kinetics of substitution in these systems in which the cation and the entering anion each carry a high charge is the evidence of saturation effects as the value of R increases, the rate constant increasing until a critical value of R is reached, after which further changes are small. In an earlier publication[3] we ascribed these effects, there reported only in part, to outer sphere ion clustering, this conclusion being supported by measurements of the oscillator strengths of the intervalence transitions (light-induced electron transfer from the nucleophile to $[Ru(NH_3)_5H_2O]^{3+}$), which show them to reach plateau values rather sharply as R increases. For all of the cases we studied, which include $[Ru(NH_3)_6]^{3+}$ as cation, the critical value of R is 8.[3] In the kinetic studies, the critical values of R depend on the solution composition and, with a single exception, are lower than 8 (with $[Co(CN)_6]^{3-}$ the critical value is 8). At R less than the critical value, deviations from a monotonic increase are observed in all cases for anion clustering about the cation. However, for the inverse case, there is a monotonic increase in oscillator strength with R, but now the plateau value of R is 6 rather than 8. On the basis of these results, we concluded that, in the ion pair, the anion is attached to the cation by hydrogen bonds, an arrangement which persists for cation about anion, until each CN^- of $[M(CN)_6]^{4-}$ is occupied. In the case of anion about cation we postulated that, though the structure at small values of R is based on hydrogen bonding, as R increases it becomes unstable and the anions now fit into the faces of the octahedron, giving rise to departures from monotonic behavior, with relatively stable binding terminating at 8. As mentioned in ref 3, clusters of such high order are presumably stabilized by the incorporation of monovalent cations.

The departures from a monotonic response of oscillator strength on increasing R are rather modest and, except for their reproducibility, might be dismissed as lacking significance. When the concentration of acid leads to less protonation of the nucleophiles (pH = 3.1), the departures in the kinetic data from monotonic response are very striking (Figure 2) and can be taken to confirm in a general way the conclusions reached on the basis of the spectrophotometric data, namely, that structural changes occur as the anion accumulates about the cation (it must be kept in mind that, at pH 3.1, the anion in associating with a tripositive ion may lose the proton). That such structural change

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will affect the rates of substitution is expected. Just why saturation effects are observed, i.e., plateau values of *k* are reached, remains to be considered. In the earlier publication[3] the tentative suggestion was made that, were an intermediate of reduced coordination number formed, the critical value of *R* at which the plateau in *k* is reached could correspond to the composition of the ion cluster at which the intermediate is completely scavenged by the accumulated nucleophile. But a complete explanation must account for the change in the limiting rate of changing the nucleophile; the plateau values for the nucleophiles are, for $[Co(CN)_6]^{3-}$, 2.9×10^{-4} s $^{-1}$; for $[M(CN)_6]^{4-}$ in 1.5×10^{-2} M H^+, 4.5×10^{-4} s^{-1}; for $[M(CN)_6]^{4-}$ at low acid, 6.5×10^{-4} s^{-1}. Moreover, as has already been mentioned, the plateau values of *k* can exceed the rate of water exchange, 2.9×10^{-4} s^{-1}, in the absence of strong nucleophiles, which, if the formation of an intermediate is postulated, requires that its rate of formation be enhanced by changes in the environment.

The idea that replacement of H_2O from the coordination spheres of πd^5 and πd^6 cations requires substantial stretching of the metal$-H_2O$ bond seems to be generally accepted. It can be expected then that the accompanying charge separation will be stabilized by electrolytes, thus lowering the free energy of activation. Such effects were documented in a study[9] of the dynamics of the interaction of $[Co(NH_3)_5H_2O]^{3+}$ with $SO_4{}^{2-}$ which showed that, at 0.014 M $SO_4{}^{2-}$, the outer sphere association to ion pairs is complete. At this concentration of $SO_4{}^{2-}$ and above, the reaction is represented by

$$[Co(NH_3)_5H_2O]^{3+},[SO_4]^{2-} = [Co(NH_3)_5\ SO_4]^{+} + H_2O$$

and the equilibrium constant (ca. 0.8) governing the reaction is found to be almost independent of the sulfate concentration up to 2.6 M (in fact, the fraction of Co(III) present in the inner sphere form *decreases* slightly as the concentration of $SO_4{}^{2-}$ increases). Over this concentration range, the half-time to reach equilibrium decreases by a factor of approximately 4. In view of the constancy of K_{eq}, this is an unequivocal demonstration of rather large electrolyte effects on the rates of substitution, forward and reverse. That the rate of replacement of water would be enhanced by raising the concentration of $SO_4{}^{2-}$ is hardly surprising. That the rate of release of $SO_4{}^{2-}$ from the inner sphere would be increased correspondingly by $SO_4{}^{2-}$, as it must be because K_{eq} hardly changes, is not at first sight expected. But, viewed as an electrolyte effect, it becomes reasonable. Effects of this kind seem sufficient to provide a qualitative explanation of major features of the results we are reporting, without the need to invoke the formation of an intermediate of reduced coordination number. Because the cyano complexes have higher charges than does $SO_4{}^{2-}$, saturation effects for them are expected to be more sharply defined. The saturation effects in the spectrophotometric data, by our interpretation, arise when the eight equivalent sites presented by the faces of an octahedron are occupied. The saturation effects observed in the kinetic studies are not the same as in the former case, because now only one site on the octahedron is involved. Saturation can be taken to occur when positions for the nucleophile near enough to the leaving group to influence its rate of departure are fully occupied, and they may well number fewer than 8. Full occupancy of the eight sites will be a ceiling value of *R* also for substitution, a situation which apparently applies when $[Co(CN)_6]^{3-}$ is the nucleophile in 1.5×10^{-2} M H^+.

The activation for substitution by electrostatic effects is expected to be particularly prominent for an acceptor center of high charge, such as is featured in these studies, as well as in most of the earlier work with traditional coordination complexes, and to be less pronounced in substitution in organic molecules. Acknowledging the assistance of the incoming group in removal of water from the coordination sphere blurs the distinction between classical S_N1 vs S_N2 formulations of activation for substitution. How do we distinguish between an entering group assisting in the removal of the leaving group and taking its place, and assisting in its removal but forming an intermediate of reduced coordination number? Even were an intermediate formed, the diagnostic strategy, which depends on the limiting rate at high nucleophile concentration being independent of the nature of the nucleophile, would lose much of its power.

Though electrolyte effects offer a qualitative explanation of the saturation effects observed in our studies, this does not mean that competition for an intermediate does not play a role. Measurements of the rate of exchange of H_2O between the cation and solvent could be very useful in providing further insight into the mechanisms of substitution in these systems. The single experiment[10] carried out on the rate of the exchange of water for $[Co(NH_3)_5H_2O]^{3+}$ in the presence of sulfate (0.33 M, high enough to accelerate the approach to equilibrium on substitution by a factor of ca. 2) shows that the rate of water exchange is diminished only by ca. 10% as compared to the exchange in the absence of $SO_4{}^{2-}$. Water exchange results in the $[Co(NH_3)_5H_2O]^{3+}/SO_4{}^{2-}$ system are difficult to interpret because the reverse of reaction 2 provides a path for water exchange. This complication is absent for nucleophiles such as $[Fe(CN)_6]^{4-}$ or $[Co(CN)_6]^{3-}$ which form very stable inner sphere products.

A number of features of the data presented in Figures 1 and 2 remain to be commented on. The almost quantitative agreement of the data for $[Fe(CN)_6]^{4-}$ and $[Ru(CN)_6]^{4-}$ shown in Figure 1 must mean that the states of protonation of the nucleophiles in the cluster are the same, despite the difference in proton affinities of the free ions. The outer sphere association with the cation will decrease proton affinities, and it is likely therefore that in the cluster they are present as the ion dipoles $HM(CN)_6{}^{3-}$. That protonation does change the nature of the interaction is expected, but just why the changes take the form they do is by no means clear. An obvious difference between the data of Figure 2 (pH = 3.1 or 3.6) and those of Figure1 (1.5×10^{-2} M H^+) is that the sharp maxima which appear before the plateau value of *k* is reached, and which presumably are the manifestation in the kinetics of the structural changes postulated on the basis of values of oscillator strength as a function of *R*, are absent in Figure 1, perhaps only because plateau values of *k* are reached at lower values of *R*.

The effect of protonation of $[M(CN)_6]^{4-}$ on the rate of substitution is most directly revealed by comparing the rate constants for the collapse of the ion pair with $[Ru(CN)_6]^{4-}$ as nucleophile in 1.5×10^{-2} M HO_3SCF_3 with that in LiO_3SCF_3 at the same concentration pH adjusted to 3.6. The values are 1.4×10^{-4} s^{-1} and 4.3×10^{-4} s^{-1}. Presumably, most of the difference is attributable to protonation rather than to the nature of the monovalent cation, H_3O^+ vs Li^+. This conjecture is supported by the observation that the rate at pH = 3.6 in the absence of LiO_3SCF_3 is 5.2×10^{-4} s^{-1}. The difference from 4.3×10^{-4} s^{-1}, LiO_3SCF_3 present, can be attributed to Li^+ playing the same role as H^+, but to a much lesser degree.

Full deprotonation, absent additional electrolyte, has a very marked effect on the *k* vs *R* profile. The structure preceding the plateau values of *k* is now almost absent, and the maximum

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(10) Rutenberg, A. C.; Taube, H. *J. Chem. Phys.* **1952**, *20*, 825.

value of k is almost reached at $R = 2$ (top trace, Figure 2b). This may be associated with a tendency for the tetranegative nucleophiles to congregate near the leaving group, hydrogen bonding to H_2O being stronger than it is with NH_3.

$[Fe(CN)_6]^{4-}$ as Nucleophile: Catalysis by $[Fe(CN)_6]^{3-}$. The experiments on catalysis of substitution by $[Fe(CN)_6]^{3-}$ in the $[Ru(NH_3)_5H_2O]^{3+}/[Fe(CN)_6]^{4-}$ system were carried out in acidic solution so that the effect would not be complicated by catalysis by $[Ru(NH_3)_5H_2O]^{2+}$. Catalysis is expected because an additional path is introduced, and the product of the substitution reaction rapidly produces the final product by electron transfer:

$$[Ru(NH_3)_5Fe(CN)_6] + [Fe(CN)_6]^{4-} = [Ru(NH_3)_5Fe(CN)_6]^{-} + [Fe(CN)_6]^{3-}$$

It is to be noted that the effects exerted by $[Fe(CN)_6]^{3-}$ and $[Co(CN)_6]^{3-}$ on the rates of consumption of $[Ru(NH_3)_5H_2O]^{3+}$ in the reaction solution containing $[Fe(CN)_6]^{4-}$ are identical. As is the case for $[Fe(CN)_6]^{4-}$ vs $[Ru(CN)_6]^{4-}$, the activation effects for the trinegative ions are similar.

$[Fe(CN)_6]^{4-}$ as Nucleophile: Catalysis by Intrinsic $[Ru(NH_3)_5H_2O]^{2+}$. A comparison of the rate constants for substitution by $[Fe(CN)_6]^{4-}$ and $[Ru(CN)_6]^{4-}$ in the respective ion pairs as displayed in Figure 3 shows that catalysis by intrinsic Ru(II) in the former system reaches a maximum at pH ca. 4, corresponding to the reactant in the form $[Ru(NH_3)_5H_2O]^{3+}$,$[Fe(CN)_6]^{4-}$ reaching the maximum concentration. The difference between the two rate constants for substitution, 1.7×10^{-4} s^{-1}, provides a good measure of the contribution by the catalytic path in the $[Fe(CN)_6]^{4-}$ system. In the Results section, attention was directed to the fact that, at $R = 1$, the catalytic contribution is almost insensitive to the addition of $[Fe(CN)_6]^{3-}$ at the 1.0×10^{-5} M level, a concentration level so low that the catalytic effect is insignificant, while at $R = 10$, a 4-fold decrease in rate is observed. This difference, at first sight puzzling, finds a ready explanation when ion clustering is taken into account. When R is low, the inhibitor is incorporated into the cluster, e.g., for the ion pair, the reaction representing the formation of Ru(II) is

$$[Ru(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{4-},[Fe(CN)_6]^{3-} = [Ru(NH_3)_5H_2O]^{2+},[Fe(CN)_6]_2{}^{3-}$$

The effect of $[Fe(CN)_6]^{3-}$ under these conditions is purely stoichiometric: only those clusters containing $[Fe(CN)_6]^{3-}$ are affected, and the rate of substitution for them will not be reduced to 0. However, at high values of the ratio, $[Fe(CN)_6]^{3-}$ is excluded from the cluster by the anion of higher charge, $[Fe(CN)_6]^{4-}$, and the reaction in the limit of $R = 8$ and above is

$$[Fe(CN)_6]^{4-} + [Ru(NH_3)_5H_2O]^{3+},([Fe(CN)_6]^{4-})_8 = [Ru(NH_3)_5H_2O]^{2+},([Fe(CN)_6]^{4-})_8 + [Fe(CN)_6]^{3-}$$

By making use of the data for the experiments with $[Ru(NH_3)_5H_2O]^{2+}$ deliberately added, the catalytic contribution to the rate at $R = 10$ corresponds to an equilibrium concentration of Ru(II) of 2.3×10^{-6} M in the intrinsic system, which will also be the concentration of $[Fe(CN)_6]^{3-}$. The addition of $[Fe(CN)_6]^{3-}$ at the 1.0×10^{-5} M level is then expected to exert a strong effect on reducing the equilibrium concentration of Ru(II), as is observed.

Catalysis of Substitution by Extrinsic $[Ru(NH_3)_5H_2O]^{2+}$. Catalysis by $[Ru(NH_3)_5H_2O]^{2+}$ of substitution in $[Ru(NH_3)_5H_2O]^{3+}$,$[M(CN)_6]^{4-}$ features the remarkable result that the rate of a reaction over most of its course depends only on the concentration of the catalyst and is independent of the concentration of the reactant ion pair until it is almost depleted. The simple kinetic behavior is a result of ion clustering. The following mechanism accounts for the kinetic behavior:

$$[Ru(NH_3)_5H_2O]^{3+},[M(CN)_6]^{4-},[Ru(NH_3)_5H_2O]^{2+} \xrightarrow{k_1} [Ru(NH_3)_5H_2O]^{3+},[Ru(NH_3)_5M(CN)_6]^{2-} + H_2O \quad (2)$$

$$[Ru(NH_3)_5H_2O]^{3+},[Ru(NH_3)_5M(CN)_6]^{2-} \xrightarrow{k_2} [Ru(NH_3)_5H_2O]^{2+},[Ru(NH_3)_5M(CN)_6]^{-} \quad (3)$$

Reaction 2 involves intramolecular substitution by $[M(CN)_6]^{4-}$ on Ru(II). Electron transfer in reaction 3 regenerates $[Ru(NH_3)_5H_2O]^{2+}$, the products being favored because $[Ru(NH_3)_5]^{3+}$ compared to $[Ru(NH_3)_5]^{2+}$, in exerting a stronger field, will select the inner sphere attachment to $[M(CN)_6]^{4-}$. These steps are followed by the reassembly of $[Ru(NH_3)_5H_2O]^{3+}$,$[M(CN)_6]^{4-}$,$[Ru(NH_3)_5H_2O]^{2+}$ from the reactant ion pair and the products of reaction 3. Since reassembly involves only ion reassociation, it will take place at diffusion-controlled rates and will not be rate determining.

The mechanism, on applying the condition that at the steady state reactions 2 and 3 proceed at the same rate, leads to the rate law

$$d[[Ru(NH_3)_5M(CN)_6]^{-}]/dt = \frac{k_1k_2[Cat]}{k_1 + k_2}$$

where [Cat] represents the total [Ru(II)] in the system, i.e., the sum of $[[Ru(NH_3)_5H_2O]^{3+},[M(CN)_6]^{4-},[Ru(NH_3)_5H_2O]^{2+}]$ and $[[Ru(NH_3)_5H_2O]^{3+},[Ru(NH_3)_5M(CN)_6]^{2-}]$.

The experimental values $k_1k_2/(k_1 + k_2)$ for $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{4-}$, and $[Os(CN)_6]^{4-}$ at 22°C are 0.41 s^{-1}, 0.38 s^{-1}, and 0.38 s^{-1} respectively. Rates of intermolecular transfer between ruthenium amines of like charge are of the order of 1×10^3 M^{-1} s^{-1} and above, and when converted to first-order rates by estimating the work of bringing ions together, the values are in excess of 10^5 s^{-1}. It is therefore certain that the slow step in the reaction is substitution ($k_2 >> k_1$) so that $k_1k_2/(k_1 + k_2)$ reduces to k_1. The conclusion that the substitution on Ru(II) is rate determining is reinforced by the approximate agreement of the estimated value of the rate constant for the exchange of H_2O between $[Ru(NH_3)_5H_2O]^{2+}$ (2.7 s^{-1} at 25 °C [11]) and the experimental value of k_1 (0.4 ± 0.1 s^{-1}).

If the conclusion is accepted that substitution, by a wide margin, is rate determining, it follows that the generalized mechanism represented by reactions 2 and 3 followed by reassembly of the reactant ion triplet is overprescribed. At the steady state the catalyst is present largely as $[Ru(NH_3)_5H_2O]^{2+}$, that is, $[[Ru(NH_3)_5H_2O]^{2+}] >> [[Ru(NH_3)_5M(CN)_6]^{2-}]$ and the only requirement for observing zero order behavior in an experiment is that $[Ru(NH_3)_5H_2O]^{2+}$ remain fully associated with $[M(CN)_6]^{4-}$, i.e., the formulation $[M(CN)_6]^{4-},[Ru(NH_3)_5H_2O]^{2+} \rightarrow [Ru(NH_3)_5M(CN)_6]^{2-} + H_2O$ accounts for the kinetics over most of the reaction course in each experiment. However, it must be kept in mind that if the $[Ru(NH_3)_5H_2O]^{2+}$ is fully combined with $[M(CN)_6]^{4-}$, this will apply with even greater force to $[Ru(NH_3)_5H_2O]^{3+}$, so that the ion triplet (eq 2) is the proper representation of the state of the catalyst. Deviations from a zero-order course must appear in each experiment when the concentration of $[Ru(NH_3)_5H_2O]^{3+}$,$[M(CN)_6]^{4-}$ falls below that of the catalyst, leaving some of it idle. If the concentration of the catalyst is high enough so that the reactant ion pair remains in association with it, the reaction rate will now be first order in the ion triplet, and the rate constant will be identical to that determined by dividing the zero-order rate by the concentration of the catalyst: this condition is substantially met in experiment c in Figure 4, where the concentration of the catalyst is the highest. The first-order rate constant calculated from the residual 20% of the reaction is 0.35 s^{-1}, which is close to the average value 0.39 ± 0.01 s^{-1} calculated from the zero-order reaction phase. For experiment a in Figure 4, the rate constant for the residual reaction is 0.2 s^{-1}; the lower value is ascribable to incomplete complexation of the reactants at a lower catalyst concentration.

In contrast to the behavior just described, when $[Co(CN)_6]^{3-}$ is the nucleophile, a first-order conversion of the ion pair $[Ru(NH_3)_5H_2O]^{3+}$,$[Co(CN)_6]^{3-}$ to the inner sphere product is observed. Inspection of the mechanism advanced for the tetranegative ions suggests that a difference between the two systems lies in the reduced affinity of the anionic nucleophile for the dipositive catalyst. If we assume that conversion to an ion triplet under experimental conditions is incomplete, we have

$$[Ru(NH_3)_5H_2O]^{3+},[Co(CN)_6]^{3-} + [Ru(NH_3)_5H_2O]^{2+} = [Ru(NH_3)_5H_2O]^{3+},[Co(CN)_6]^{3-},[Ru(NH_3)_5H_2O]^{2+} \qquad K_{eq} \tag{4}$$

Electron transfer to regenerate $[Ru(NH_3)_5H_2O]^{2+}$ and reassembly

$$[Ru(NH_3)_5H_2O]^{3+},[Co(CN)_6]^{3-},[Ru(NH_3)_5H_2O]^{2+} \xrightarrow{k_1} [Ru(NH_3)_5H_2O]^{3+},[Ru(NH_3)_5Co(CN)_6]^{-} + H_2O \tag{5}$$

of the reactant ion pair is taken to be rapid also for this system, the only difference being that $[Ru(NH_3)_5Fe(CN)_6]^{2-}$ is replaced by $[Ru(NH_3)_5Co(CN)_6]^{-}$ in reaction 3. If conversion of the ion pair to the triplet is assumed to be minor, the rate law for the reaction becomes

$$d[[Ru(NH_3)_5Co(CN)_6]]/dt = k_1K_{eq}[[Ru(NH_3)_5H_2O]^{3+},[Co(CN)_6]^{3-}][Cat]$$

k_1K_{eq} being given by the experimental value of the rate constant, 3.0×10^2 M^{-1} s^{-1}. The rate constant for substitution in $[Ru(NH_3)_5H_2O]^{3+}$,$[Ru(CN)_6]^{4-}$ is 4.5 times that in $[Ru(NH_3)_5H_2O]^{3+}$,$[Co(CN)_6]^{3-}$. Because $[Ru(NH_3)_5H_2O]^{2+}$ has a lower charge than $[Ru(NH_3)_5H_2O]^{3+}$, a reduced contrast in rates is expected. We arbitrarily take the factor in this case to be 2, so that k_1, as estimated from substitution on $[Ru(NH_3)_5H_2O]^{2+}$ by $[M(CN)_6]^{4-}$, becomes 0.20 s^{-1}. With this value for k_1, K_{eq} is calculated as 1.5×10^3, which is high enough to result in substantial conversion of the reagents to the triplet form, leading to deviations from the rate law based on the assumption of minor formation. Such deviation is observed and was taken into account by evaluating k_1K_{eq} from the later, major reaction phase.

The study of catalysis of substitution by extrinsic $[Ru(NH_3)_5H_2O]^{2+}$ has provided a convenient means of assessing the effect on the rate of substitution of clustering by $[M(CN)_6]^{4-}$ about the cation for an acceptor center of reduced charge. Such assessment is particularly significant for $[Ru(NH_3)_5H_2O]^{2+}$, because, on the basis of experiments with neutral molecules as entering groups, which show that the second-order rate coefficients are almost constant irrespective of the nucleophile,[11] we have concluded that activation for substitution in this cation involves mainly bond breaking. The surprising outcome is that the rate of substitution by $[M(CN)_6]^{4-}$ in $[Ru(NH_3)_5H_2O]^{2+}$ is more sensitive to raising the concentration of the nucleophile than it is in the case of $[Ru(NH_3)_5H_2O]^{3+}$, the rate increasing by a factor of 3.8 in the former system, and by less than 2 in the latter, over the same range in concentration of the nucleophile. Though not understood, this appears to us to be an important result, perhaps pointing to a substantial difference in detailed mechanism for the two reactions.

Properties of Ion Pairs. In the earlier publication we reported that the electronic coupling for $[Ru(NH_3)_6]^{3+}$,$[Ru(CN)_6]^{4-}$ is greater than it is for the ion pair with $[Fe(CN)_6]^{4-}$ in place of $[Ru(CN)_6]^{4-}$, attributing the difference to a greater extension of the πd orbitals in the latter case. The summary in Table 1 shows that, in line with expectation, this trend continues to the last member of the triad. A shift of the maximum to lower energy, for the ion pair with $[Ru(en)_3]^{3+}$ as compared to that with $[Ru(NH_3)_6]^{3+}$, is expected because of the greater oxidizing potential of the former species (by 0.11 V).[12] The very large decrease in the electronic coupling—the ratio of the areas corrected for the position of the band is 4.7—when en replaces NH_3 on the metal ion is presumably attributable to hydrophobic hydrocarbons replacing H on the donor nitrogen.

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Supporting Information Available: A plot of substitution rate constants of the zero-order phase for the catalyzed reaction as a function of *R* (Figure 1) (1 page). Ordering information is given on any current masthead page.

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