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Comparison of the rates of substitution in $[Ru(NH_3)_5H_2O]^{3+}$ and $[Os(NH_3)_5H_2O]^{3+}$ by hexacyano complexes: substitution coupled to electron transfer

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Abstract

A comparison of the rates of substitution (in water solutions, 20 °C) in $[Ru(NH_3)_5H_2O]^{3+}$ and $[Os(NH_3)_5H_2O]^{3+}$ by $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$ and $Co(CN)_6^{3-}$ shows that the reaction of $[Os(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6^{3-}$ is unique. Substitution in this and in the other cases takes place, as has been shown by others in earlier work, by rapid formation of ion pairs, followed by collapse of the ion pairs to inner-sphere products. For most of the systems the slight differences in the first-order rates governing inner-sphere formation can be accounted for by the tetranegative ions being more nucleophilic than the trinegative, and rates for Os(III) being somewhat slower than for Ru(III). Substitution in the special case takes place 1.5×10^3 times more rapidly than it does with $Co(CN)_6^{3-}$ as entering group. The singularity of the Os(III)·Fe(III) system is ascribed to substitution coupled to $1e^-$ oxidation of Os(III) by Fe(III). A similar effect with $[Ru(NH_3)_5H_2O]^{3+}$ is minor because of the greater difficulty of $1e^-$ oxidation (a distinction which is borne out by comparison of the energies of the charge transfer spectra). In all cases but those involving $Co(CN)_6^{3-}$, strong absorption in the visible of charge transfer character is observed. In the systems with $Fe(CN)_6^{3-}$ as nucleophile, interesting complications appear. On reacting with $[Ru(NH_3)_5H_2O]^{3+}$, $Fe(CN)_6^{3-}$ produces two products by parallel paths. We conclude that the product showing absorption at higher energy, S_h, is $[Ru^{III}(NH_3)_5\cdot Fe^{III}(CN)_6]$ while that at lower energy, S_l, is $[Ru^{IV}\cdot Fe^{II}(CN)_6]$. The former is unstable with respect to the latter, and transforms to it in a process much slower than substitution. On reacting with $[Os(NH_3)_5H_2O]^{3+}$, $Fe(CN)_6^{3-}$ leads initially to two products by parallel paths: S_l, which we conclude is $[Os^{III}(NH_3)_5\cdot Fe^{III}(CN)_6]$ and the major product, S_i (i for 'intermediate'), which is $[Os^{IV}\cdot Fe^{II}(CN)_6]$. In this system S_l, [Os(III)·Fe(III)], is unstable to S_i, [Os(IV)·Fe(II)] which eventually dispropionates to S_h and [Os(III)·Fe(II)]. In following the reactions spectrophotometrically induction periods are observed in all of the reactions involving substitution (and/or redox change) with Os(III), except for the formation of S_i, the appearance of which is first order without complications. The induction periods in all cases are greatly reduced when the solutions are acidified. Our working hypothesis, to be tested in further work, is that the induction periods are caused by linkage isomerization of the bridging CN^-.

Keywords: Kinetics and mechanism; Electron transfer; Ruthenium complexes; Osmium complexes; Ammine complexes

1. Introduction[1]

A number of papers has been published on the properties of complexes formed between pentaammines of metal ions in the +3 oxidation state and $Fe(CN)_6^{4-}$, where the stability of the ion pair complexes, the rates of collapse to inner-sphere forms, the absorption spectra (metal to metal charge transfer), and the photochemical behavior [1–9] are among the points of interest. As far as we know, nothing has been published on the properties of the analogous systems when $Fe(CN)_6^{4-}$ is replaced by $Fe(CN)_6^{3-}$.

In the course of studying the reaction of $[Osen_2H]^{3+}$ [10] with $Fe(CN)_6^{4-}$, we noted that with $Fe(CN)_6^{3-}$ as nucleophile a complex is formed which also gives rise to a colored species. The properties of the absorption band in the visible, which adventitiously has a maximum very near to that observed for $Fe(CN)_6^{4-}$ as nucleophile, suggests that it arises from metal to metal charge transfer, which was interpreted as involving $Fe(CN)_6^{3-}$ as electron acceptor. Qualitative experiments showed

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[1] An inner-sphere complex will be denoted by $[Ru^{III}(NH_3)_5\cdot Fe^{II}(CN)_6]^-$, or in short hand notation by Ru(III)·Fe(II), and an outer-sphere complex by $[Ru(NH_3)_5H_2O]^{3+}\cdot[Fe(CN)_6]^{4-}$ or [Ru(III)]·[Fe(II)].

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that highly colored species are also produced in the reactions of $Fe(CN)_6^{3-}$ with $[Os(NH_3)_5H_2O]^{3+}$ and $[Ru(NH_3)_5H_2O]^{3+}$ and the results of a more systematic study of a number of pentaammine systems forms the subject of the present communication, in which we mainly focus on the rates of substitution. Complete characterization of the products of the reactions with $Fe(CN)_6^{3-}$ awaits the results of further investigation and of structural studies on crystals separated from the reaction solutions; suitable crystals have not yet been obtained.

2. Experimental

$[Os(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ [11] and $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$ [12] were prepared as described in the literature. Sodium hexacyanoferrate(II) decahydrate (Strem), potassium ferricyanide (Sigma), potassium hexacyanoruthenate(II) trihydrate (Aldrich) and potassium hexacyanocobaltate were used as received.

The rate constant for the aquation of $[Os(NH_3)_5(CF_3SO_3)]^{3+}$ is 8.8×10^{-4} s^{-1} at 25 °C [11]; solutions containing $[Os(NH_3)_5(CF_3SO_3)]^{3+}$ were prepared 2 h before mixing with the nucleophiles.

2.1. Instrumentation

UV–Vis spectra were recorded with a Hewlett-Packard 8452 A spectrophotometer and NIR spectra with a Beckman spectrophotometer UV 5270. For the kinetic studies we used a thermostated cell holder. A mgw Lauda RC 20 Brinkmann circulating water bath was used to maintain the temperature in the cell holder. NMR spectra were obtained on a Varian XL-400 spectrometer. IR spectra were obtained on a Perkin-Elmer 1600 FTIR spectrophotometer.

3. Results

While our primary interest was in the chemistry of the systems with $Fe(CN)_6^{3-}$ as substituent the results take on much greater significance when they are compared with those obtained with non-oxidizing nucleophiles, and we have dealt also with $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, $Co(CN)_6^{3-}$ as entering groups acting on $[Os(NH_3)_5H_2O]^{3+}$ and $[Ru(NH_3)_5H_2O]^{3+}$.

Unless otherwise specified, the reagents were each mixed at the 1.0×10^{-3} M concentration level. In the absence of added electrolyte, for the $[Ru(NH_3)_5H_2O]^{3+}$ systems, the rates of inner-sphere complex formation at equal concentrations of reagents, with one exception, adhere to first-order behavior at least through three half-lives, as expected for ion pair formation. The exception occurs for one of the products of the reaction with $Fe(CN)_6^{3-}$, where an induction period is observed, which disappears on acidification. For $[Os(NH_3)_5H_2O]^{3+}$ most of the observations under the same conditions are complicated by induction periods, but all the systems, except the one with $Fe(CN)_6^{4-}$, show first-order behavior after this stage to concentrations well below 1.0×10^{-3} M. That ion pair formation is complete at low concentrations is not surprising in the light of observations reported [2] for the outer-sphere association of $[Ru(NH_3)_5Cl]^{2+}$ with $Fe(CN)_6^{4-}$ in which deviations from the Lambert-Beer's law do not appear until the concentration of the reactants added in 1:1 ratio fall below 1.5×10^{-4} M (this implies that K_{os} is of the order of 10^5 or greater). In the case of a 3+ ion associating with a 3− ion, the affinities are expected to be even higher. We found that acidifying the solutions in all cases mitigates the interference by the induction period, which appears in the reactions of $[Os(NH_3)_5H_2O]^{3+}$ with each of the nucleophiles, and thus most of the rate data were obtained for solutions 1.5×10^{-2} M in HO_3SCF_3. This has the advantage as well that the concentration of the acid, which affects the rates in many of the systems, remains substantially constant throughout the course of the reaction. Increasing the concentration of the electrolyte decreases the value of K_{os} and limits the concentration of acid which can be used without introducing kinetic complications. Thus Gaswick and Malinak [13] have determined the value of K_{os} in the reaction of $[Cr(NH_3)_5H_2O]^{3+}$ with $Co(CN)_6^{3-}$ at an ionic strength of 1 M $LiClO_4$ as 15 ± 4 M^{-1}. In our systems for the 3+/3− cases, even in the acidified solutions, we found good first-order behavior for the collapse of the ion pairs to the inner-sphere complexes to concentrations well below 1.0×10^{-4} M.

3.1. Reactions of $[Ru(NH_3)_5H_2O]^{3+}$ with hexacyano complexes

The kinetic data on the conversion of the outer-sphere complexes to the inner-sphere forms are summarized in Table 1. The reaction of $[Ru(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6^{3-}$ differs from the others in that two products appear which are formed by parallel reaction paths. Because in the other three cases, the reactions proceed without apparent complications, they will be dealt with first.

In two cases comparisons with the literature data are possible. The value we record for $Fe(CN)_6^{4-}$, 2.8×10^{-4} s^{-1} at 20 °C (without added $Fe(CN)_6^{3-}$), is

Table 1
Rate constants (s^{-1}) for the conversion of the outer-sphere complexes made by $[Ru(NH_3)_5H_2O]^{3+}$ to the inner-sphere forms

Nucleophile	Medium	k (20 °C) (s^{-1})
$Fe(CN)_6{}^{4-}$	(H_2O)	2.8×10^{-4}
	($[H^+]=1.5\times10^{-2}$ M	1.1×10^{-4}
$Co(CN)_6{}^{3-}$	(H_2O)	1.1×10^{-4}
	($[H^+]=1.5\times10^{-2}$ M	5.9×10^{-5}
$Ru(CN)_6{}^{4-}$	(H_2O)	1.5×10^{-4}
	($[H^+]=1.5\times10^{-2}$ M	6.4×10^{-5}
$Fe(CN)_6{}^{3-}$	(H_2O)	1.4×10^{-4} [a]
	($[H^+]=1.5\times10^{-2}$ M	5.9×10^{-5} [b]

[a] At 810 nm (where only S_l is absorbing), $k=1.1\times10^{-4}$ s^{-1} (based on last 50% reaction); at 540 nm (maximum for S_h), $k=1.4\times10^{-4}$ s^{-1}.

[b] At 810 nm, $k=5.8\times10^{-5}$ s^{-1}; at 540 nm, $k=5.9\times10^{-5}$ s^{-1}.

Table 2
Properties of the inner-sphere complexes (metal to metal charge transfer)

	$[H^+]=$ 1.5×10^{-2} M		H_2O	
	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})
$[Ru^{III}(NH_3)_5\cdot Fe^{II}(CN)_6]^-$	848	1.9×10^3	980	3.0×10^3
$[Ru^{III}(NH_3)_5\cdot Ru^{II}(CN)_6]^-$	648	2.1×10^3	676	2.7×10^3
$[Ru^{III}(NH_3)_5\cdot Co^{III}(CN)_6]$	358	6.4×10^2	370	6.7×10^2
$[Ru^{III}(NH_3)_5\cdot Fe^{III}(CN)_6]$	540		540	0.9×10^3
$[Ru^{IV}\cdot Fe^{II}(CN)_6]$	855		935	3.5×10^3

in good agreement with that reported by Burewicz and Haim [8], $6.9(\pm0.7)\times10^{-4}$ s^{-1} at 25 °C. We observed no effect in the presence of air and added $Fe(CN)_6{}^{3-}$. The actual values for our experiments in the absence and presence of air are 2.81×10^{-4} and 2.74×10^{-4} s^{-1}, respectively, which agree with that obtained with 1.0×10^{-4} M of added $Fe(CN)_6{}^{3-}$ (2.80×10^{-4} s^{-1}). The differences in behavior compared to those observed in Ref. [8] can perhaps be ascribed to the lower value of pH in our experiments: 3.4 as compared to 4.0 and above. For $Ru(CN)_6{}^{4-}$ as an entering group a value of 0.7 s^{-1} (22 °C) has been reported [14] for the transformation of the ion pair to the inner-sphere complex. It is difficult to reconcile such a high rate constant with the much lower values obtained in two different laboratories for the analogous reaction of $Fe(CN)_6{}^{4-}$, which for the purpose of substitution is expected to be very similar to that to $Ru(CN)_6{}^{4-}$.

The properties of the inner-sphere product complexes for the simpler systems are summarized in the first three entries of Table 2. The maximum for the absorption of $[Ru^{III}(NH_3)_5\cdot Fe^{II}(CN)_6]^-$ which we observe, 980 nm ($\epsilon_{max}=3.0\times10^3$ M^{-1} cm^{-1}), agrees with that reported earlier by Burewicz and Haim [8] (980 nm, $\epsilon_{max}=3.0\times10^3$ M^{-1} cm^{-1}). For $[Ru^{III}(NH_3)_5\cdot Ru^{II}(CN)_6]^-$ we found $\lambda_{max}=676$ nm ($\epsilon_{max}=2.7\times10^3$ M^{-1} cm^{-1}); Vogler and Kisslinger [2] report 680 nm ($\epsilon_{max}=2.8\times10^3$ M^{-1} cm^{-1}). No literature values for the product of the reaction with $Co^{III}(CN)_6{}^{3-}$ exist, nor have previous workers dealt with the effect of acid on the absorption characteristics.

In the reaction of $[Ru(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6{}^{3-}$, initially only $Fe(CN)_6{}^{3-}$ contributes significantly to the color of the solution which is light yellow at the concentrations we used. With the progress of time, the solution turns red, with maxima appearing at 540 and 935 nm. These correspond to separate species which we designate as S_h and S_l (for high and low energy, respectively) which are formed by parallel reaction paths. For parallel reactions, regardless of which species is being monitored, the value of k_{obs} must be the same, and in each case would measure (k_h+k_l). Eventually, the concentration of S_h passes through a maximum (trace b, Fig. 1) after which S_l continues to grow at the expense of S_h. In this reaction phase substitution has been completed, and we follow the first-order transformation of S_h to S_l. This reaction is very slow: $k_{obs}\simeq1.6\times10^{-6}$ s^{-1} at 25 °C. The extinction coefficient for S_l is calculated from the measurement of the optical density of the final solution, that for S_h from the relative changes in the course of the $S_h\rightarrow S_l$ conversion. The absorption (Fig. 1) at 420 nm is attributable to $Fe(CN)_6{}^{3-}$ ($\epsilon=1050$ M^{-1} cm^{-1}) and the band disappears on completion of the S_h to S_l transformation.

The experiments to be described bear on the nature of the two species. Ethanol was added to the reaction solution after completion of the substitution but before conversion to S_l is complete. This resulted in the precipitation of a green solid leaving behind a red solution, the spectrum of which is shown in Fig. 2(a). The IR spectrum of this solid was taken in a KBr disc. It shows the C≡N stretch at 2046.2 cm^{-1}, to be compared to 2033 for $K_4Fe(CN)_6$ and 2122 for $K_3Fe(CN)_6$. The green solid dissolves in water, and shows only the maximum at 935 nm. The formation of Fe(II) mandates that S_l be an Ru(IV)·Fe(II) species. This conclusion is supported by measurements of the magnetic susceptibility of the reaction mixture as a function of time. The measurements were done at the 3.0×10^{-3} M concentration level, using an adaptation of the Evans' method [15]. The magnetic moment (20 °C) for the 1:1 Ru(III)·Fe(III) combination initially was 4.27 BM, close to the sum of the Ru(III) and Fe(III) moments, 4.35 BM. Well after the substitution was complete (19 h) 3.21 BM was recorded. The magnetic moment continued to decrease and after 43 h, reached 2.71 BM. Beyond this time, precipitation began.

That $Fe(CN)_6{}^{3-}$ can oxidize a ruthenium ammine from the 3+ to the 4+ state in acidic solution is at

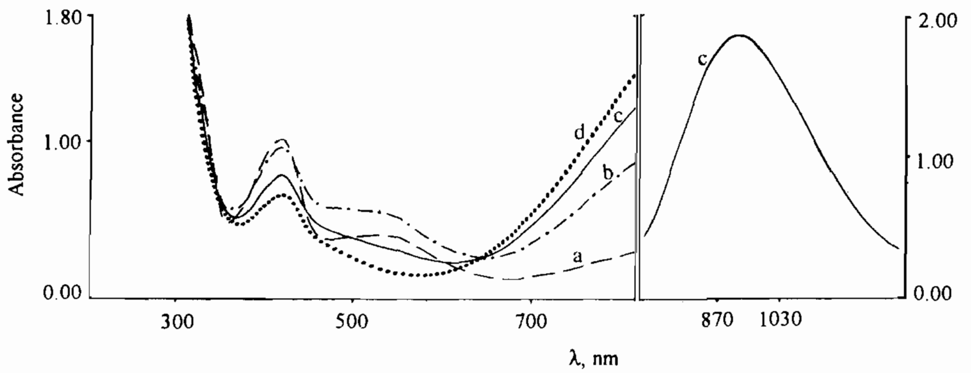

Fig. 1. Spectra of the Ru(III)–Fe(III) system in unacidified solution. $[[Ru(NH_3)_5H_2O]^{3+}]=[Fe(CN)_6^{3-}]=9.3\times10^{-4}$ M in water; (a) 4 h after mixing, (b) the completion of substitution, (c) 48 h after mixing, (d) 120 h after mixing, reaction still incomplete.

first notice a surprising outcome. The conclusion however is unambiguous, and we must look for factors which stabilize the 4+ state. Ru(IV) will be strongly electron-withdrawing so that ammonias can be deprotonated even in acidic solution. How many ammonias are involved is not known and it is for this reason that in Table 2 the composition of the species Ru(IV)·Fe(II) is not fully specified. A factor such as a 'flip' of the bridging CN^-, might also contribute but this remains to be established.

Addition of ascorbic acid to the red solution after precipitation of S_l yields the spectrum of $[Ru^{III}(NH_3)_5\cdot Fe^{II}(CN)_6]^-$ (see Table 2 and Fig. 2). Apparently Fe(III) but not Ru(III) is reduced and we infer that S_h is to be formulated as $[Ru^{III}(NH_3)_5\cdot Fe^{III}(CN)_6]$.

It will be noted from the data in Table 2 that the band energies for some of the species are sensitive to change in acidity from pH 3.5 to 4, the range characteristic of the solutions without added acid, to 1.5×10^{-2} M HSO_3CF_3. This change shifts the band maximum for Ru(III)·Fe(II) from 980 to 848 nm. Free $HFe(CN)_6^{3-}$ at low ionic strength has a pK_a value of 4.6 but this will be somewhat decreased in the ion pair. In recent work [10] it was noted that when $Fe(CN)_6^{4-}$ forms an inner-sphere complex with $[Osen_2H(H_2O)_2]^{3+}$, here as well a hypsochromic effect is observed on acidification. Protonation of $Fe(CN)_6^{4-}$ is expected to shift the absorption band corresponding to electron loss from $Fe(CN)_6^{4-}$ to higher energy. A similar but less dramatic effect is observed for Ru(III)·Ru(II), but no effect for Ru(III)·Co(III), the latter result expected because of the low proton affinity of $Co(CN)_6^{3-}$ in water solution. No change in λ_{max} on acidification for Ru(III)·Fe(III) is expected because $HFe(CN)_6^{2-}$ is a strong acid. In Ru(IV)·Fe(II), the increase in the energy of the maximum on acidification is much smaller than it is for Ru(III)·Fe(II). This suggests that not only the state of protonation of $Fe(CN)_6^{4-}$ but also that of Ru(IV) is affected, in the acid range covered.

The data of Table 1 show that the rates of substitution are decreased on addition of acid, though the effects are small. In the reaction of $[Ru(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6^{3-}$, not only the rate of the reaction but also the product distribution is affected by the acidity. While without added acid, at the stage where substitution is complete, S_h/S_l is 2.3, at 1.5×10^{-2} M H^+ the ratio is 12.

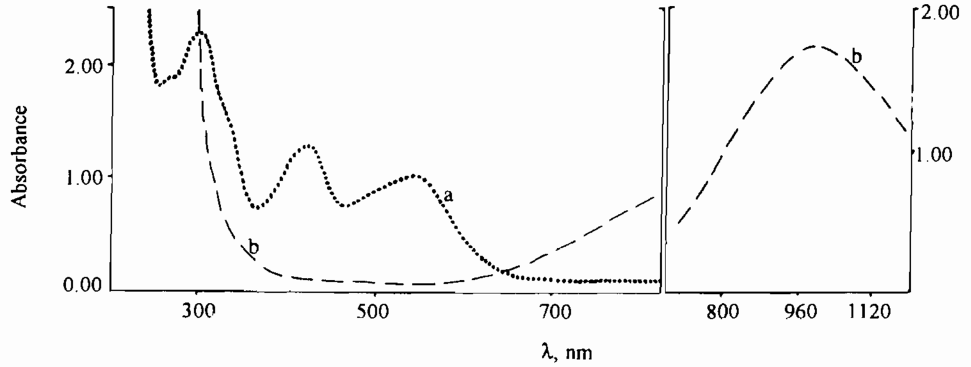

Fig. 2. Reduction of Ru(III)·Fe(III) with ascorbic acid. Conditions as in Fig. 1. (a) Spectrum of the red solution after precipitation of S_l; (b) addition of excess ascorbic acid.

3.2. Reactions of $[Os(NH_3)_5H_2O]^{3+}$ with hexacyano complexes

The results of measuring the rates of transformation of ion pairs to inner-sphere complexes for $[Os(NH_3)_5H_2O]^{3+}$ are summarized in Table 3. As has been mentioned all of these systems are complicated by induction periods when the reaction medium is water. In every case this complication is much reduced in 1.5×10^{-2} M HO_3SCF_3. With this change, the reactions of $Co(CN)_6^{3-}$ and $Ru(CN)_6^{4-}$ show good first-order behavior to at least 90% completion. This however is not the case for $Fe(CN)_6^{4-}$ as entering nucleophile, where the induction period extends to ~20% reaction, and the determination of the absorbance of the solution at completion is rendered impossible by the formation of a precipitate before reaction is complete. A determination of the absorption of the product was made by allowing the reaction to proceed to completion in a non-acidified solution, then acidifying. That this procedure is justified is indicated by the fact that the absorption maximum for the solution acidified after substitution, is the same as that when acid is present initially, and the absorbance is measured after the end of the induction period. However, the uncertainty in the value of specific rate for the $Fe(CN)_6^{4-}$ reaction may be as high as a factor of 2.

The large discrepancy between the rate constants determined for $Ru(CN)_6^{4-}$ and $Fe(CN)_6^{4-}$ made us suspicious that the former reaction system was subject to catalysis by an oxidant, it having been noted that $Fe(CN)_6^{3-}$ substitutes much more rapidly than $Co(CN)_6^{3-}$. We found that the addition of $Fe(CN)_6^{4-}$ (1.0×10^{-4} M) to the $[Os(NH_3)_5H_2O]^{3+}$–$Ru(CN)_6^{4-}$ reaction mixture reduces the rate constant for substitution by $Ru(CN)_6^{4-}$ by a factor of almost 10, a result which suggests that the sample of $Ru(CN)_6^{4-}$ is contaminated by $Ru(CN)_6^{3-}$ (see Section 4). The effect of $Fe(CN)_6^{4-}$ has reached saturation value at the concentration stipulated, and we feel that the intrinsic rate constant for substitution by $Ru(CN)_6^{4-}$ at 20 °C is 3.0×10^{-5} s^{-1}, as entered in Table 3.

Table 3
Rate constants (s^{-1}) for the conversion of the outer-sphere complexes of $[Os(NH_3)_5H_2O]^{3+}$ to the inner-sphere forms (in 1.5×10^{-2} M HO_3SCF_3, except in the last case, where the medium was unacidified)

Nucleophile	k (20 °C) (s^{-1})
$Fe(CN)_6^{4-}$	$\sim1.0\times10^{-5}$
$Co(CN)_6^{3-}$	2.1×10^{-6}
$Ru(CN)_6^{4-}$	2.6×10^{-4} 3.0×10^{-5}
$Fe(CN)_6^{3-}$	3.2×10^{-3} [a] 1.5×10^{-2} [b]

[a] At 810 nm (close to the max. for S_l), $k=3.7\times10^{-3}$ s^{-1}; at 614 nm (max. for S_i), $k=3.2\times10^{-3}$ s^{-1}.

[b] At 810 nm, $k=1.5\times10^{-2}$ s^{-1} (based on last 40% of the reaction); at 614 nm $k=1.5\times10^{-2}$ s^{-1}.

As in substitution by $Fe(CN)_6^{3-}$ on $[Ru(NH_3)_5H_2O]^{3+}$, more than one product results from the replacement of water in $[Os(NH_3)_5H_2O]^{3+}$ by $Fe(CN)_6^{3-}$. In this case, three species must be dealt with: one, S_l, with $\lambda_{max}=826$ nm, a species, S_i, with λ_{max} in the range 580–614 nm (acidity dependent), and a third, S_h, with a maximum at ~420 nm (l, i, h for low, intermediate and high energy).

As to S_l and S_i: in unacidified solutions, in following the progress of the reaction at 826 nm, where S_l has a maximum, a pronounced induction period is observed, while the growth of absorbance for S_i ($\lambda_{max}=614$ nm) shows good first-order behavior (see Fig. 3). The rate constants entered in Table 3 for the non-acidified solutions are based on observations for S_i. In acidic solution, the induction period for S_l disappears. The half-life for reaction as measured by following S_l or S_i agree, as must be the case for parallel reaction paths: this remains true even for additional products formed by parallel paths.

As in the case of the $[Ru(NH_3)_5H_2O]^{3+}\cdot[Fe(CN)_6]^{3+}$ system, after completion of the substitution phase, another sets in: on reaching a maximum S_l then decreases while S_i shows an increase. The specific rate for the decline of S_l is 1.4×10^{-5} s^{-1} at 20 °C, to be compared to 1.5×10^{-2} s^{-1} for substitution. The successive reaction stages are illustrated in Fig. 4.

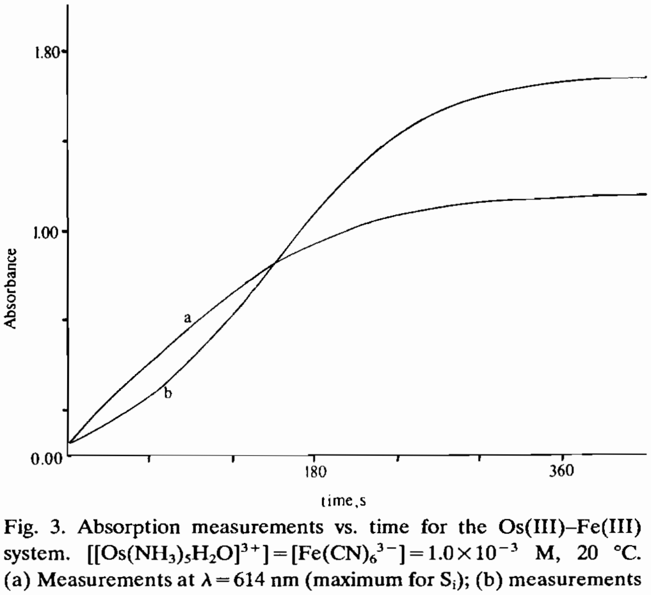

Fig. 3. Absorption measurements vs. time for the Os(III)–Fe(III) system. $[[Os(NH_3)_5H_2O]^{3+}]=[Fe(CN)_6^{3-}]=1.0\times10^{-3}$ M, 20 °C. (a) Measurements at $\lambda=614$ nm (maximum for S_i); (b) measurements at $\lambda=810$ nm (close to the maximum for S_l).

The data on the properties of the inner-sphere complexes obtained for substitution on $[Os(NH_3)_5H_2O]^{3+}$ are summarized in Table 4. The maxima for the absorption of $[Os^{III}(NH_3)_5 \cdot Fe^{II}(CN)_6]^-$ and $[Os^{III}(NH_3)_5 \cdot Ru^{II}(CN)_6]^-$ which we observe, 628 ($\epsilon = 1.6 \times 10^3$ M^{-1} cm^{-1}) and 494 ($\epsilon = 1.8 \times 10^3$ M^{-1} cm^{-1}) nm agree with that reported by Vogler et al. [1] (628 ($\epsilon = 1640$ M^{-1} cm^{-1}) and 490 ($\epsilon = 1840$ M^{-1} cm^{-1}) nm).

The entries in Table 4 about the nature of S_i and S_l anticipate conclusions which were reached on the basis of evidence now to be introduced. Addition of HO_3SCF_3 to the reaction mixture after the full development of the peak at 826 nm and before the transformation of S_l to S_i has progressed far, causes the following changes in the band maximum for S_i: no acid, 614 nm; 2.5×10^{-3} M, 590 nm; 1.5×10^{-2} M, 580 nm; 0.10 M, 552 nm. No change in λ_{max} for S_l is observed even at 1 M H^+.

The addition of ethanol to the reaction mixture causes the precipitation of a blue solid. The IR spectrum of this solid was taken in a KBr disc and shows a broad absorption with a maximum at 2045 cm^{-1} which is assigned to the C≡N stretch, and is close to that of $K_4Fe(CN)_6$ (2033 cm^{-1}), well removed from that of $K_3Fe(CN)_6$ (2122 cm^{-1}). The solution of the blue solid in water has an absorption maximum at 614 nm, a shoulder at 430 nm and a peak at 320 nm, where $Fe(CN)_6{}^{4-}$ is known to absorb. We conclude on the basis of these observations that S_i is an Os(IV)·Fe(II) species, but acknowledge that the state of protonation of the ammonias is not known. This assignment is consistent with the observation that the addition of acid shifts the absorption to higher energies, as observed in other cases in which $Fe(CN)_6{}^{4-}$ participates in a charge transfer transition.

We now describe the procedure for determining the extinction coefficients of the individual species where we rely on interconversions and the results of redox reactions involving them. To determine that for S_l, a solution containing $[Os(NH_3)_5H_2O]^{3+}$ and $Fe(CN)_6{}^{3-}$, each at 5.6×10^{-4} M, was prepared and left until substitution was complete. Before a significant decrease in S_l had set in, $Fe(CN)_6{}^{4-}$ was added (5.6×10^{-4} M). This resulted in the immediate disappearance of S_l and an increase in the S_i region of the spectrum (see Fig. 5). From the fact that λ_{max} for S_l does not change with acidity, we infer that it is to be formulated as Os(III)·Fe(III). This is consistent with the rapid disappearance of Os(III)·Fe(III) on the addition of $Fe(CN)_6{}^{4-}$. Coordination of $Fe(CN)_6{}^{3-}$ to Os(III) raises the $Fe(CN)_6{}^{3-/4-}$ redox potential, so that $Fe(CN)_6{}^{4-}$ readily reduces Os(III)·Fe(III) to Os(III)·Fe(II). The extinction coefficient of Os(III)·Fe(II) being known, the amount formed can be calculated and this fixes the concentration of Os(III)·Fe(III) before the addition of $Fe(CN)_6{}^{4-}$. From the total absorbance of S_l before the addition of $Fe(CN)_6{}^{4-}$, ϵ for S_l at 826 nm is calculated as 6.4×10^3 M^{-1} cm^{-1}. Since S_i absorbs in the same region of the spectrum as Os(III)·Fe(III), it is important to the success of the experiment that $Fe(CN)_6{}^{4-}$ does not affect S_i.

We now turn to the procedure for determining the extinction coefficients for S_i and S_h. A solution containing equal concentrations (5.0×10^{-4} M) of $[Os(NH_3)_5H_2O]^{3+}$ and $Fe(CN)_6{}^{4-}$ in water was prepared. On the completion of the formation of $[Os^{III}(NH_3)_5 \cdot Fe^{II}(CN)_6]^-$, (see trace a, Fig. 6). a three-fold excess of $Fe(CN)_6{}^{3-}$ was added. This produces an increase in absorption in the region where $Fe(CN)_6{}^{3-}$ also has a maximum, and a decrease in absorbance in the S_i region of the spectrum (this almost coincides with that of Os(III)·Fe(II) but S_l is not produced. The trace at the completion of this reaction phase, about 1 h later, is identified as trace b in Fig. 6. There is a slight shift in the band maximum in the 600 nm region of the spectrum consistent with the formation of S_i (Os(IV)·Fe(II)) from Os(III)·Fe(II). Because association of $Fe(CN)_6{}^{4-}$ with a cation disfavors its oxidation by free $Fe(CN)_6{}^{3-}$ the net oxidation takes Os(III) to

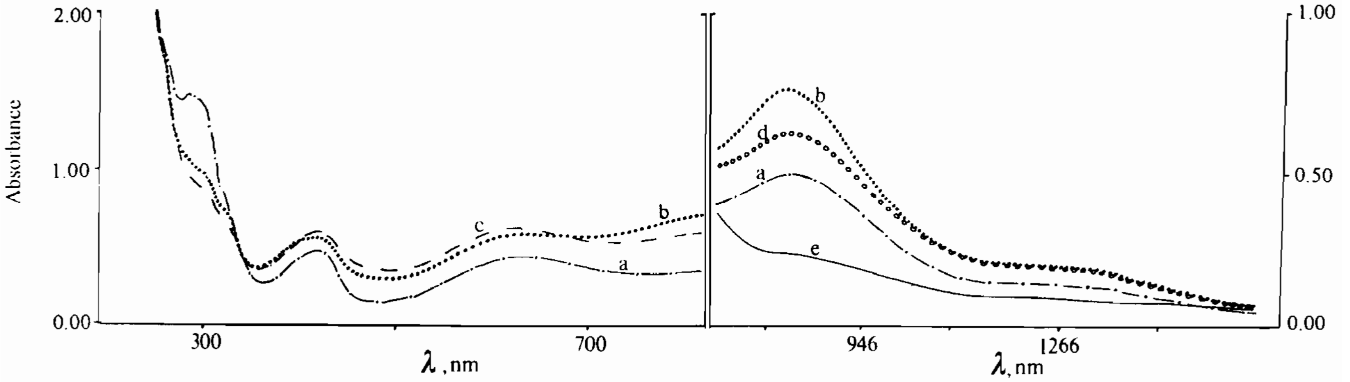

Fig. 4. Spectra of the Os(III)–Fe(III) system in unacidified solution. $[[Os(NH_3)_5H_2O]^{3+}] = [Fe(CN)_6{}^{3-}] = 1.0 \times 10^{-3}$ M in water; (a) 1 min after mixing, (b) the completion of substitution (~6 min later), (c) 30 min after mixing, (d) 1 h after mixing, (e) 22 h later.

Table 4
Spectrophotometric properties of the inner-sphere complexes of $[Os(NH_3)_5H_2O]^{3+}$, metal to metal charge transfer

	$[H^+]=1.5\times10^{-2}$ M		H_2O	
	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})
$[Os^{III}(NH_3)_5\cdot Fe^{II}(CN)_6]^-$	570	1.0×10^3	628	1.6×10^3
$[Os^{III}(NH_3)_5\cdot Ru^{II}(CN)_6]^-$	478	1.7×10^3	494	1.8×10^3
$[Os^{III}(NH_3)_5\cdot Co^{III}(CN)_6]$	306	1.3×10^3	312	1.4×10^3
$[Os^{III}(NH_3)_5\cdot Fe^{III}(CN)_6]$	826		826	6.4×10^3
$[Os^{IV}\cdot Fe^{II}(CN)_6]$	580		614	1.5×10^3

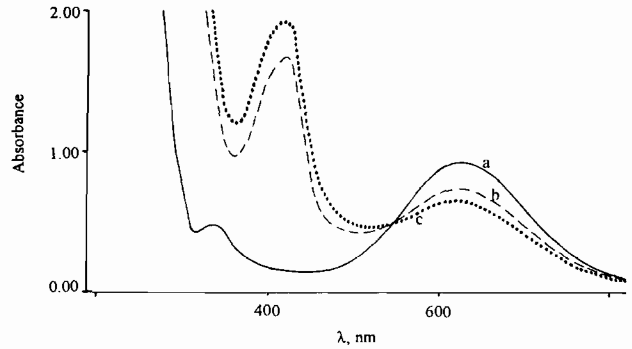

Fig. 5. Addition of Fe(II) to the Os(III)–Fe(III) system after completion of substitution. $[[Os(NH_3)_5H_2O]^{3+}]=[Fe(CN)_6{}^{3-}]=5.6\times10^{-4}$ M. (a) The completion of substitution; (b) addition of $Fe(CN)_6{}^{4-}$ with concentration equal to $Fe(CN)_6{}^{3-}$.

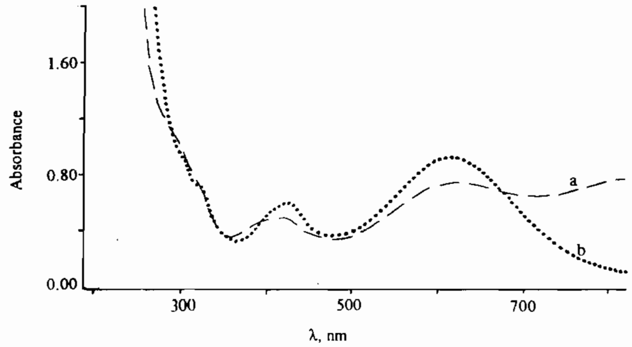

Fig. 6. Addition of Fe(III) to the Os(III)·Fe(II) solution. $[[Os(NH_3)_5H_2O]^{3+}]=[Fe(CN)_6{}^{4-}]=5\times10^{-4}$ in water. (a) The completion of substitution (formation of the inner-sphere complex Os(III)·Fe(III)); (b) addition of $Fe(CN)_6{}^{3-}$ with concentration 1.5×10^{-3} M (~60 min after the addition), the end of the fast reaction; (c) 24 h later.

Os(IV), though the reaction may proceed through Os(III)·Fe(III) being formed as a reaction intermediate. After following the reaction stage described, a much slower reaction takes place in which absorption in the S_h region grows at the expense of that ascribable to S_i. This phase is essentially complete after 24 h (trace c, Fig. 6). All of the osmium ammine being now converted to a single form, $\epsilon(S_h)$ at 420 nm was calculated as 4.5×10^3 M^{-1} cm^{-1} from the total absorbance after subtracting the contribution by free $Fe(CN)_6{}^{3-}$ remaining. It should be noted that S_i is not oxidized by $Fe(CN)_6{}^{3-}$: the results described are the same when the concentration of $Fe(CN)_6{}^{3-}$ used for the oxidation of Os(III)·Fe(II) is doubled.

The extinction coefficients of S_h and S_l being known, that for S_i can be calculated ($\epsilon(S_i)=1.3\times10^3$ M^{-1} cm^{-1} at 614 nm) from the absorption trace of an equimolar mixture of $[Os(NH_3)_5H_2O]^{3+}$ and $Fe(CN)_6{}^{3-}$ at the end of the substitution phase. From the extinction coefficients for S_l and S_i, we can calculate the relative amounts of these products. In water as solvent, the reaction of $[Os(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6{}^{3-}$ produces S_l and S_i in the ratio 0.38:1 while in 1.5×10^{-2} M H^+, the ratio is 0.56:1.

To check our interpretation of the effect of $Fe(CN)_6{}^{4-}$ on the rate of the reaction of $[Os(NH_3)_5H_2O]^{3+}$ with $Ru(CN)_6{}^{4-}$, we did an experiment in which $Fe(CN)_6{}^{3-}$ was added to a solution in water containing $[Os(NH_3)_5H_2O]^{3+}$ and $Fe(CN)_6{}^{4-}$. The concentrations of these species were 0.1, 1.0 and 0.9 ($M\times10^3$), respectively. The production of Os(III)·Fe(II) in the system is not a zero order reaction as expected if the catalyst concentration was constant, but it is less than first order in the disappearance of the ion pair. To estimate the rate of production of Os(III)·Fe(II) the initial slope for the increase in absorption at 628 nm was taken and it was found to correspond to a rate of production 1.2×10^{-6} M s^{-1}. Taking into account the concentration of $Fe(CN)_6{}^{3-}$ and making the assumption that in this case substitution of $Fe(CN)_6{}^{3-}$ on $[Os(NH_3)_5H_2O]^{3+}$ is rate determining, we calculate this process as 1.2×10^{-2} s^{-1}, to be compared to 1.5×10^{-2} as measured directly. The agreement is within the limits of experimental error, considering the difficulty in measuring the initial slope.

3.3. Effects in D_2O

We used D_2O in order to record the NIR region of the spectrum of the solution mixture of $[Os(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6{}^{3-}$. To our surprise we found that the use of D_2O as solvent has a pronounced effect on the ratio of the products, S_l:S_i (=0.48:1), S_l being more favored in D_2O than in water. The rate constant for substitution (k_l+k_i) was measured at 20 °C at 1.3×10^{-2} s^{-1} and the rate for the transformation of S_l to S_i and S_h as 1.3×10^{-5} s^{-1} (20 °C). These two values are very close to the values measured at 20 °C for the unacidified solution of Os(III) and Fe(III) (1.5×10^{-2} and 1.4×10^{-5} s^{-1}, respectively).

3.4. Absorption data for the ion pairs

The results on the absorption characteristics of the ion pairs are summarized in Table 5 together with literature data for related systems. The spectra were obtained by difference, i.e. by measuring the absorbance of the mixture against the sum when the solutes are kept separate. There was difficulty in the systems with $Co(CN)_6^{3-}$ as reaction partner, because the excess absorption appears at high energy where the separated solutes have very strong absorptions. The difficulty in the case of the Os(III) · Fe(III) system was of a different kind, namely, collapse of the ion pairs to the inner-sphere forms is so rapid that there is an immediate contribution from the absorptions of the latter. By cooling the solutions to 10 °C, by making the measurements as promptly as possible, and by following the change as a function of time, excess absorption on the high energy side of that attributable to S_i was identified. In view of the relatively small value of ϵ we report, it is by no means certain that the maximum for the ion pair has been located. Further reference to this matter appears in Section 4.

An especially significant observation was made in checking the absorption of $Fe(CN)_6^{3-}$ immediately after mixing with $[Os(NH_3)_5H_2O]^{3+}$. The Fe(III) species has a strong absorption band at 420 nm ($\epsilon = 1050$ M^{-1} cm^{-1}) where neither of the cations contributes significantly. While in the formation of $[Ru(NH_3)_5H_2O]^{3+} \cdot [Fe(CN)_6]^{3-}$ the absorption at 420 nm is hardly affected (2% increase), in forming the corresponding Os(III) ion pair at pH 3.8, we observed an initial decrease of 22% at 420 nm, much greater than can be accounted for by the formation of S_i. At pH 2.9 this decrease was only 2%.

Table 5
Spectrophotometric properties of the ion pairs[a,b], metal to metal charge transfer

Ion pair	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})
$[Ru(NH_3)_5H_2O]^{3+} \cdot [Fe(CN)_6]^{3-}$	440	30 ± 5
$[Ru(NH_3)_5H_2O]^{3+} \cdot [Fe(CN)_6]^{4-}$	718	25
$[Ru(NH_3)_6]^{3+} \cdot [Fe(CN)_6]^{4-}$	714	
$[Ru(NH_3)_5H_2O]^{3+} \cdot [Ru(CN)_6]^{4-}$	538	24
$[Ru(NH_3)_5Cl]^{2+} \cdot [Ru(CN)_6]^{4-}$	510 [2]	20
$[Ru(NH_3)_6]]^{3+} \cdot [Ru(CN)_6]^{4-}$	549 [16]	
$[Ru(NH_3)_5H_2O]^{3+} \cdot [Co(CN)_6]^{3-}$	$230 < \lambda < 260$	30 ± 5
$[Os(NH_3)_5H_2O]^{3+} \cdot [Fe(CN)_6]^{3-}$	520	15 ± 5
$[Os(NH_3)_5H_2O]^{3+} \cdot [Fe(CN)_6]^{4-}$	476	47.7
$[Os(NH_3)_5Cl]^{2+} \cdot [Fe(CN)_6]^{4-}$	438 [4]	
$[Os(NH_3)_5H_2O]^{3+} \cdot [Ru(CN)_6]^{4-}$	392	40
$[Os(NH_3)_5Cl]^{2+} \cdot [Ru(CN)_6]^{4-}$	372 [4]	
$[Os(NH_3)_5H_2O]^{3+} \cdot [Co(CN)_6]^{3-}$	$240 < \lambda < 280$	20 ± 5

[a] Where no literature reference, present work, some of which are repetition of earlier work, with agreement.

[b] Concentration range for present work 1.0×10^{-3} to 2.5×10^{-3} M; temperature 23–25 °C except in the case of [Os(III) · [Fe(III)] where measurement was made at 10 °C.

The ion pair $[Ru(NH_3)_5H_2O]^{3+}$ precipitates as an orange solid when the concentration exceeds 3.0×10^{-3} M. The IR spectrum of the solid (KBr disc) showed the C≡N stretch at 2112 cm^{-1} as a narrow peak, close to that of $K_3Fe(CN)_6$ (2122 cm^{-1}) and far removed from that of $K_4Fe(CN)_6$ (2033 cm^{-1}). The crystal structure of the solid has been determined [17] and will be reported in a separate publication.

4. Discussion

The emphasis of this study being on the substitution rates, the most significant result of it is the high rate of collapse to the inner-sphere products of the $[Os(NH_3)_5H_2O]^{3+} \cdot [Fe(CN)_6]^{3-}$ ion pair as compared to that of $[Os(NH_3)_5H_2O]^{3+} \cdot [Co(CN)_6]^{3-}$, $[Ru(NH_3)_5H_2O]^{3+} \cdot [Fe(CN)_6]^{3-}$ and $[Ru(NH_3)_5H_2O]^{3+} \cdot [Co(CN)_6]^{3-}$. It was in fact some of these comparisons, seen in preliminary semiquantitative experiments that led us to pursue the investigations. The rates for the four cases being considered are (s^{-1}, 20 °C, 1.5×10^{-2} M H^+): 3.7×10^{-3}, 2.1×10^{-6}, 5.9×10^{-5}, 5.9×10^{-5}, respectively. To be noted is that the rate of substitution by $Fe(CN)_6^{3-}$ on $[Os(NH_3)_5H_2O]^{3+}$ is 1500-fold greater than that by $Co(CN)_6^{3-}$, while, when $[Ru(NH_3)_5H_2O^{3+}]$ is being acted on, these rate constants are nearly the same. The important difference between $Fe(CN)_6^{3-}$ and $Co(CN)_6^{3-}$ for present purposes is that the former is a much stronger oxidizing agent than the latter. We infer that this difference is felt in the case of $[Os(NH_3)_5H_2O]^{3+}$ but not of $[Ru(NH_3)_5H_2O^{3+}]$ because the former is more easily oxidized than is the latter. This conclusion follows from experience with the general chemistry of the respective ammine complex, there being a considerable body of descriptive chemistry for the Os(IV) tetraammines [18], but none for the ruthenium analogues. It also follows from observations made on charge transfer absorption for the respective ion pairs. For $[Os(NH_3)_5H_2O]^{3+} \cdot [Fe(CN)_6]^{3-}$, a maximum is observed at 520 nm, while for the ruthenium analogue, the maximum is at 440 nm. The energy difference corresponds to an equilibrium constant 10^{14} greater for the oxidation of the osmium ammine, and, because of the uncertainty in the maximum for Os, this is probably a lower limit. Though this energy difference is not directly applicable to the equilibrated 4+ states, it is unlikely that it would be fully compensated for when the species relax following instantaneous electron loss. Perhaps the most direct evidence on the point at issue is that in the ion pair with $[Os(NH_3)_5H_2O]^{3+}$, $Fe(CN)_6^{3-}$ is partially reduced, but not in that with $[Ru(NH_3)_5H_2O]^{3+}$. The increase in the extent of reduction of $Fe(CN)_6^{3-}$ in the ion pair as the pH increases shows that deprotonation of H_2O in the coordination sphere of Os(III) plays a role in the equilibrium process. Moreover, because oxidation results in a πd^4 system, structural readjustments following electron loss can be expected.

That substitution lability can be very sensitive to electronic structure has long been recognized. A striking illustration is provided by the disparity in rates of exchange of water between the aquo ions of V^{3+} ($k_{\text{ox.}}=1.3\times10^3$ at 25 °C [19a]; the more recent value reported here is from Ref. [19b]), Cr^{3+} (0.1, 7×10^{-6} s^{-1}) [20a]; more recent value reported here is from Ref. [20b] and was obtained at a much lower salt concentration) and Fe^{3+} [21] and the solvent where the rate constants at 25 °C are 5×10^2, 2.4×10^{-6} and 1.6×10^2 s^{-1}, respectively. But it must be noted that a change in oxidation state alone can have a very large effect on substitution lability, because of a general weakening of bonds to the ligands on reduction. An example is afforded by the $[Ru(NH_3)_5H_2O]^{3+/2+}$ couple (measured for $[Ru(NH_3)_5H_2O]^{3+}$ as 1.8×10^{-6} s^{-1} at 25 °C [22a]; estimated for $[Ru(NH_3)_5H_2O]^{2+}$ as 0.27 s^{-1} [22b]), where an increase in the rate of water exchange by a factor of $\sim10^5$ is observed on $1e^-$ reduction. Here a πd^5 electron system is replaced by a πd^6, but the effect of the bond loosening more than compensates for the change in πd electron count, which taken alone would lead to a decrease in rate of substitution. In catalysis by Cr(II) of substitution on Cr(III) complexes, both effects are exploited (catalytic conversion by Cr^{2+} of $[Cr(NH_3)_5X]^{2+}$ to $[Cr(H_2O)_5X]^{2+}$ [23]). In the case of catalysis by Ru(II) of substitution on Ru(III) complexes, an example of which is reported by Gaswick and Haim [6] for the $[Ru(NH_3)_5H_2O]^{3+}\cdot[Fe(CN)_6]^{4-}$ system, the second effect is operative.

In contrast to the two cases referred to above, labilization for substitution in the Os(III)·Fe(III) system takes place by decreasing the electron count on the target molecule. While raising the oxidation state strengthens the bonds to the ligands, an electronic effect more than compensates for this. A special attribute of the πd^4 electronic structure which results on $1e^-$ oxidation of Os(III) is that it can lend itself to S_N2 attack by an incoming ligand. This contrasts with catalysis by $[Ru(NH_3)_5]^{2+}$ of substitution on $[Ru(NH_3)_5]^{2+}$; rate comparisons with a variety of incoming ligands suggests that substitution on $[Ru(NH_3)_5H_2O]^{2+}$ is far toward the S_N1 limit [24]. A 'gedanken' illustration of substitution closely coupled to electron transfer would be the reaction of Br with $V(H_2O)_6^{2+}$ (πd^3) where it can be imagined that Br in approaching a face of the octahedron extracts an electron, the resulting Br^- occupying, at least temporarily, the orbital thus vacated. Whether substitution in $[Os(NH_3)_5H_2O]^{3+}\cdot[Fe(CN)_6]^{3-}$ is coupled in this sense to electron transfer remains to be seen. The fact that there is partial oxidation of osmium in the ion pair – presumably by the formation of $[Os(NH_3)_5OH]^{3+}\cdot[Fe(CN)_6H]^{3-}$ – would argue the contrary. However, the rate of inner-sphere complex formation is not directly proportional to the concentration of this species: its concentration decreases by a factor of 10 when the pH changes from 3.8 to 2.9 while the reaction rate decreases by a factor of only 4.3 and reaction continues at even higher acidities.

We infer that the catalytic impurity which enhances the rate of substitution by $Ru(CN)_6^{4-}$ in $[Os(NH_3)_5H_2O]^{3+}$ is $Ru(CN)_6^{3-}$. At first sight it seems remarkable that the catalyzed reaction is also simply first order in the concentration of the ion pair $[Os(NH_3)_5H_2O]^{3+}\cdot[Ru(CN)_6]^{4-}$. This however is the natural outcome if $Ru(CN)_6^{3-}$ reacts rapidly with $[Os(NH_3)_5H_2O]^{3+}$, to form the inner-sphere complex $[Os^{IV}\cdot Ru^{II}(CN)_6]$, and the rate determining step is the reaction:

$$\begin{aligned}&[Os^{IV}\cdot Ru^{II}(CN)_6]\\&\quad+[Os(NH_3)_5H_2O]^{3+}\cdot[Ru(CN)_6]^{4-}\longrightarrow\\&\qquad\qquad[Os(NH_3)_5{}^{3+}\cdot Ru(CN)_6{}^{4-}]\\&\quad+[Os(NH_3)_5H_2O]^{3+}\cdot[Ru(CN)_6]^{3-}\end{aligned}\tag{1}$$

$$\begin{aligned}&[Os(NH_3)_5H_2O]^{3+}\cdot[Ru(CN)_6]^{3-}\\&\quad=[Os^{IV}\cdot Ru^{II}(CN)_6]\ \text{rapid}\end{aligned}\tag{2}$$

The notation Os(IV) is used to acknowledge that the state of protonation of NH_3 on Os(IV) is not known. The rate of reaction is given by $k_1[[Os^{IV}\cdot Ru^{II}(CN)_6]]$ $[[Os(NH_3)_5H_2O]^{3+}\cdot[Ru(CN)_6]^{3-}]$. Because the concentration of $[Os^{IV}\cdot Ru^{II}(CN)_6]$ remains constant throughout, the reaction remains first order. The compositional and structural changes which accompany the change from Os(III) to Os(IV) can explain why reaction (1) can be slow, for what otherwise would be a simple electron transfer. While in the case of the stronger oxidizing agent, the rate determining step in the catalyzed substitution is the redox change, reaction (2), with the weaker oxidant $Fe(CN)_6^{3-}$ it appears to be the substitution reaction itself, an understandable outcome if the rate of formation of Os(IV)·M(II) from Os(III)·M(III) depends on the driving force of the reaction. This is entirely reasonable in view of the simplicity of action of the oxidants. As a significant side implication of this experiment, because the product of the catalyzed substitution reaction is identical to that of the uncatalyzed, we can conclude that in forming Os(IV)·Ru(II) from the ion pair, NH_3 is not lost from the coordination sphere of the osmium moiety.

In all cases the rates of reactions decrease when the solutions are acidified. The effects for Ru(III) are small, less than a factor of 2 for $Co(CN)_6^{3-}$ as the nucleophile, somewhat greater for $Fe(CN)_6^{4-}$, presumably because it protonates in 1.5×10^{-2} M acid. For $Fe(CN)_6^{3-}$ the decrease is only slightly greater than it is for $Co(CN)_6^{3-}$.

The product distribution however is markedly affected, the ratio Ru(III)·Fe(III)/Ru(IV)·Fe(II) changing from 2.3 to 12 on acidification. As would be expected were deprotonation a factor in stabilizing the higher oxidation state, it becomes more abundant in higher pH, the partition into the different products taking place after substitution. Acidification decreases the rates at which $Fe(CN)_6^{3-}$ substitutes on Os(III) more than is the case when Ru(III) is acted on, the ratios being 4.3 and 2.3, respectively. For Os(III) two paths for the collapse of the ion pair must be invoked, one inverse in some power of $[H^+]$ and another independent of $[H^+]$. The latter would account for considerably less than 1/2 of the reaction in the unacidified solutions, whereas in the acidified it would account for the bulk of the reaction. The product distribution is relatively insensitive to these changes, in contrast to the behavior of the Ru(III) system.

At this stage, the studies with D_2O in place of H_2O as solvent show only that the outcome is sensitive to the change, the product distribution being more affected than the rate of substitution. This is not a surprising outcome, considering the compound nature of the substitution rate: k_l+k_i. A change in one coefficient, the others remaining constant would produce this effect. Further studies of this kind, in which the ammines are also deuterated are in progress and may shed light on how the mechanisms for the separate paths differ.

The kinetic analysis of the more complex reactions – this includes all of those involving $[Os(NH_3)_5H_2O]^{3+}$ and that of $[Ru(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6^{3-}$ – is not complete but some features of the kinetic results merit consideration at this point. When $[Os(NH_3)_5H_2O]^{3+}$ reacts with $Fe(CN)_6^{3-}$ three products appear, S_l and S_i. The conclusion that they are formed by parallel paths follows from the observation that the appearance of at least one of them, in this case S_i, is a strictly first-order reaction. In the absence of a complication such as the induction period which, in an unacidified medium, confuses the issue when the growth of S_l is followed, the measured value of the rate constant is given by k_l+k_i, no matter which species is being monitored. We can therefore be confident that in spite of the induction period observed, k_l+k_i governs the substitution which eventually leads to S_l. It needs to be mentioned that at the wavelength selected for S_i, there is little interference by absorption by S_l.

Because the analysis of the results shows that substitution itself does not involve an induction period, its appearance in the formation of S_l in non-acidified solution indicates that the initial product of the substitution is not S_l but is a species which has a relatively small extinction coefficient and which converts to S_l. If this secondary reaction has a rate constant substantially greater than that of substitution, a steady state will be reached in which the measurements obey first-order kinetics, and yield a rate constant which has the same value as that determined in monitoring S_i. This is in fact the case as shown in Section 3.

When the kinetic data obtained for $[Os(NH_3)_5H_2O]^{3+}$ – leaving aside those in which electron transfer plays a role – are compared with those for $[Ru(NH_3)_5H_2O]^{3+}$, a quantitative difference can be noted which we believe is significant. The range in rates for the latter (Table 1) is less than a factor of two. In fact that for water exchange, 1.2×10^{-4} s^{-1} at 20 °C (in 0.010 M H^+) [25] is not much different from those recorded in Table 1. As expected, because of the enhanced ligand field barrier, substitution on $[Os(NH_3)_5H_2O]^{3+}$ is somewhat slower than it is for $[Ru(NH_3)_5H_2O]^{3+}$, but the disparity in rates between substitution by trinegative as compared to tetranegative ions is considerably greater for Os(III) than for Ru(III). In considering the data $Co(CN)_6^{3-}$ can be taken as representative of an orthodox trinegative ion. The rate constant for substitution by this nucleophile on Os(III) is approximately a factor of 10 smaller than it is for the tetranegative ions, while for Ru(III), the ratio is less than a factor of 3. The greater sensitivity to the nature of the entering nucleophile in the case of Os(III) indicates greater bond making during substitution on it, in line with expectation based on the larger size of Os(III).

Some features of the spectrophotometric properties remain to be dealt with. To be noted is that the energy of the Ru(IV)·Fe(II) charge transfer transition, which leads to Ru(III)*·Fe(III)* is, as expected, lower than it is for the corresponding change in Os(IV)·Fe(II). This energy difference is 0.69 V for an unacidified solution and 0.69 V in 1.5×10^{-2} M H^+, which is surprisingly good agreement. The oxidation states 4+ are involved also in light induced charge transfer in $[M(NH_3)_5H_2O^{3+}\cdot M(CN)_6^{3-}]$ and $[M(NH_3)_5^{3+}\cdot M(CN)_6^{3-}]$, processes which will now be considered.

The spectrophotometric data for inner-sphere and outer-sphere complexes are summarized in Table 6 except those which apply to the Os(IV)·Fe(II) and Ru(IV)·Fe(II) systems which were considered above. As expected on the basis of distance alone, the energies of the transitions for the outer-sphere forms are greater than for the corresponding inner-sphere. Were the metal to metal distance the only factor, the entries in the last column would be the same, but it is seen that those for osmium are consistently higher than they are for ruthenium, outside the range attributable to the slightly greater radius of Os^{3+} as compared to Ru^{3+}. The results for three ruthenium complexes agree reasonably well, as do two of the values for osmium. The aberrant value (Os(III)·Fe(III)) has been declared suspect on other grounds, and an estimated value for it has been arrived at by assuming that Δ (see Table 6) for it is the average of the two values which are in

Table 6
Summary of selected spectrophotometric data

	λ_{max} (cm$^{-1}\times10^{-1}$)		
	Outer sphere	Inner sphere	Δ [(o.s.) − (i.s.)]
Ru(III) + Fe(III)	2273	1852	421
	(0.43)^a (0.68)^{*,b} a_{os}^c	(0.79) a_{is}^c	
Os(III) + Fe(III)	1923 1720*	1211	713 518*
	(1.09)	(1.03)	
Ru(III) + Fe(II)	1393	1020	372
	(0.88) b_{os}^c (0.22) (0.47)*	(0.71) b_{is}^c (0.47)	
Os(III) + Fe(II)	2101	1592	508
	(0.58)	(0.57)	
Ru(III) + Ru(II)	1859	1479	379
	(0.86) (0.56)	(0.68) (0.54)	
Os(III) + Ru(II)	2551	2024	527

[a] The numbers in parentheses are the magnitudes of the differences between the numbers indicated, expressed in V (eV).
[b] The asterisk identifies the estimated value of λ_{max} for Os(III) + Fe(III) and of quantities derived from it.
[c] See text.

harmony. The figures which depend on the estimated value are identified by asterisks. That Δ appears in distinct sets for the two metal centers indicates that specific bonding effects involving the bridging CN$^-$ play a role.

The difference between the Fe(CN)$_6^{3-/4-}$ and Ru(CN)$_6^{3-/4-}$ couples as determined by use of Ru(NH$_6$)$_5^{3+}$ are 0.58 (o.s.) and 0.57 (i.s) V; as by use of Os(NH$_3$)$_5^{3+}$ they are 0.56 (o.s.) and 0.54 (i.s.) V which is remarkable internal agreement. The difference as determined electrochemically is 0.40 V (for the Fe(CN)$_6^{3-/4-}$ couple, E° is reported as 0.36 V; for the Ru(CN)$_6^{3-/4-}$ couple, the recorded value is 0.86 V [26]). It is to be noted that the difference calculated from the mixed valence properties of the hexacyanides with the cation [Osen$_2$(H)(H$_2$O)$_2$]$^{2+}$ is 0.47 V [10]. Similarly the difference between the Os(NH$_3$)$_5^{3+/2+}$ and the Ru(NH$_3$)$_5^{3+/2+}$ couples can be estimated by resort to the data for Fe(CN)$_6^{4-}$ as the common nucleophile and also for Ru(CN)$_6^{4-}$. The outcome is: for Fe(CN)$_6^{4-}$ as nucleophile 0.88 (o.s.) and 0.71 (i.s.) V; for Ru(CN)$_6^{4-}$ as nucleophile, 0.86 (o.s.) and 0.68 (i.s.) V. Here there is a definite difference between inner-sphere and outer-sphere readings, Os(III) being stabilized relative to Ru(III) in collapsing to the inner sphere. The difference determined electrochemically for [M(NH$_3$)$_5$H$_2$O]$^{3+/2+}$ is ~0.80 V.

The measurements with Fe(CN)$_6^{3-}$ as nucleophile lead to estimates of the differences in the Ru(NH$_3$)$_5^{4+/3+}$ and Os(NH$_3$)$_5^{4+/3+}$ couples. As expected the ruthenium couple is more strongly oxidizing, the difference being 0.68 V as measured in the outer-sphere mode (here the estimated value of λ_{max} for the osmium outer-sphere complex is used), and 0.79 V for the inner-sphere mode. For reasons already mentioned, the values need not agree exactly, but it should be noted that when the experimental value for Os(III) in the o.s. complex is used, 0.68 is replaced by 0.43. We believe that the estimated value of λ_{max} is the better.

Included in Table 5 which is devoted to ion pairs are literature data on related complexes, which provide a basis for the estimation of useful differences in redox potential from spectrophotometric data. By the use of Ru(CN)$_6^{4-}$ as common reductant, we find that [Ru(NH$_3$)$_5$Cl]$^{2+}$ is a weaker oxidant than [Ru(NH$_3$)$_5$H$_2$O]$^{3+}$, by 0.12 V. For [Os(NH$_3$)$_5$Cl]$^{2+}$ compared to [Os(NH$_3$)$_5$H$_2$O]$^{3+}$, the corresponding value as determined by use of Ru(CN)$_6^{4-}$ is 0.17 V, and 0.20 V as determined by Fe(CN)$_6^{4-}$. The comparisons imply that the affinity for Cl$^-$ of the higher oxidation state is greater than for the lower and that the disparity in the affinities is greater for Os(III) than for Ru(III). Unfortunately, an experimental test of the latter conclusion is rendered difficult because of the instability of the osmium ammines in water. The close agreement between the maxima for [Ru(NH$_3$)$_5$H$_2$O]$^{3+}\cdot$[Ru(CN)$_6$]$^{4-}$ and [Ru(NH$_3$)$_6$]$^{3+}\cdot$[Ru(CN)$_6$]$^{4-}$ suggests the use of [Os(NH$_3$)$_6$]$^{3+}$ as a stand-in for [Os(NH$_3$)$_5$H$_2$O]$^{3+}$ in locating the λ_{max} for the ion pair of the latter with Fe(CN)$_6^{3-}$. Experiments to this end are underway.

Our work has revealed many more facets, particularly with Fe(CN)$_6^{3-}$ as a reactant, than are dealt with in this communication. Of paramount interest is research already underway which has as goal the detailed determination of the composition and structures of the various species formed by the oxidizing nucleophiles. We believe that the assignment of oxidation states for S_l and S_h in the case of the ruthenium system and S_l and S_i in the case of the osmium system is correct. As to S_h in the case of Os(III), preliminary observations suggest that it is a form of Os(VI), a corresponding amount of Os(III)·Fe(II) being produced (disproportionation of Os(IV)).

Rotation of the bridging CN^- to ligate carbon to the cation has been suggested as cause of the induction periods. It provides a reasonable explanation of the mitigation of the effects of the induction period on acidifying the reaction solutions. Especially in the case of Os(III), the rate of substitution is decreased considerably as the acidity is raised, but it is unlikely that the rate of the suggested linkage isomerization would be affected. As a result, in acidic solutions the induction period would involve a smaller fraction of the total reaction than in water. Moreover, because of the greater ligand field stabilization of the πd electrons for Os(III) compared to Ru(III), the change in the nature of the donor atom would make a greater difference for it. The fact that an induction period is not observed in the formation of $[Os^{IV}\cdot Fe^{II}(CN)_6]$ may be attributable to the generally greater substitution lability of πd^4 compared to πd^5 or πd^6 systems so that the 'flip' occurs more rapidly. The formation of the 4+ oxidation state by the relatively weak oxidizing agent $Fe(CN)_6^{3-}$ is an unexpected result. The rearrangement of the bridging CN^-, as suggested, can contribute to the stabilization of the 4+ state. To our knowledge, no prior example of net $1e^-$ oxidation of the pentaammines at relatively low pH has been reported. In the case of $[Os(NH_3)_5H_2O]^{3+}$, the oxidation is observed even in the ion pair with $Fe(CN)_6^{3-}$, where it is probably promoted by deprotonation of the coordinated water molecule.

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