Inner-Sphere Cluster Formation by $[Ru(NH_3)_5H_2O]^{3+}$ or $[Os(NH_3)_5H_2O]^{3+}$ in Combination with $[M(CN)_6]^{4-}$ (M = Fe, Ru, or Os)

Vassiliki G. Poulopoulou,[†] **Henry Taube,***[,†] **and Fabio S. Nunes**[‡]

Department of Chemistry, Stanford University, Stanford, California 94305-5080, and Universidade Federal do Parana.Setor de Ciéncias Exatas, Departamento de Quimica, C.P. 19081, CEP 81531-990, Curitiba PR, Brazil

Received August 5, 1998

When the cations $[M'(NH_3)_5H_2O]^{3+}$ or $[M'(NH_3)_5H_2O]^{2+}$ (M′ = Ru, Os) are added in excess of the co-reactants $[M(CN)_6]^{4-}$ (M = Fe, Ru, Os), inner-sphere binding ends abruptly at the 4:1 ratio. The $[M(CN)_6]^{4-} \rightarrow [M'(NH_3)_5]^{3+}$ charge transfer (CT) absorption shifts slightly to higher energy as the cations accumulate in the cluster, and there is a progressive decrease in intensity per additional oscillator introduced. The absorption bands and the electrochemical properties reveal the presence of isomeric forms in complexes of order 2 and above. The successive stages of reduction of $[Ru(NH_3)_5)]^{3+}$ take place in a narrow range of potentials, despite the close proximity of the peripheral cations in a cluster. Clusters containing Ru(II) and Ru(III) show also the $[Ru(NH_3)_5]^{2+} \rightarrow [Ru(NH_3)_5]^{3+}$ CT transition. While $[Ru(NH_3)_5]^{2+}$ has little effect on M(II) → M′(III) CT absorption, accumulation of M′(III) in a cluster containing the M′(II) → M′(III) oscillator, despite an increase in the number of these oscillators, leads to no significant increase in the intensity. The energy of the $[Ru(NH_3)_5]^{2+} \rightarrow [Ru(NH_3)_5]^{3+}$ transition is 1500 cm^{-1} greater when M = Ru than when it is Fe or Os, for which it appears at 8000 cm^{-1}. This difference is attributed to rapid isomerization of the $Ru^{II}CNRu^{III}$ linkage causing a shift to higher energy. This interpretation is in accord with the deep seated degradation of the clusters which occurs whenever $[Ru(NH_3)_5]^{2+}$ is present (complete loss of the M′(II) → M′(III) and M(II) → M′(III) oscillators), which is most rapid when M = Ru(II).

Introduction

In previous reports the effects of outer-sphere clustering of ions of opposite and high charge on the metal-to-metal charge-transfer absorption[1] attending it and the effect of such clustering, anion about cation, on the kinetics of the reaction to form 1:1 inner-sphere species[2] were dealt with. In the work reported here, we pursued our interest in the consequences of inner-sphere complex formation for compositions in which the ratio of the concentration cation to anion, *R*, starting at 1 was increased at integral values until saturation of the affinity is reached. As far as we know, other work of this kind has not been done, perhaps because serious difficulties due to formation of precipitates was anticipated. At the concentration level prevailing in our studies, this is not a serious problem, especially when the ratio of cation to anion is high.

Important among the issues we have addressed in the present work are the properties of the charge-transfer absorptions which arise when $[Ru(NH_3)_5]^{3+}$, alone or with $[Ru(NH_3)_5]^{2+}$ clusters about $[M(CN)_6]^{4-}$ in the inner-sphere mode. This gives rise to the $[M(CN)_6]^{4-} \rightarrow [Ru(NH_3)_5]^{3+}$ transition and, and when $[Ru(NH_3)_5]^{2+}$ is present, also to the interammine transition. Similar studies were also done with $[Os(NH_3)_5]^{3+}$ clustering about $[M(CN)_6]^{4-}$ but in this case, because $[Os(NH_3)_5]^{2+}$ is very difficult to access, only $[M(CN)_6]^{4-} \rightarrow [Os(NH_3)_5]^{3+}$ transitions could be recorded. The electrochemical behavior of the multinuclear centers in close proximity are of interest in their own right and was also investigated. The results provide insight into the stabilization of $[M(CN)_6]^{4-}$ relative to $[M(CN)_6]^{3-}$ by $[M'(NH_3)_5]^{3+}$, and the stabilization by $[M(CN)_6]^{4-}$ of $[M'(NH_3)_5]^{3+}$ relative to $[M'(NH_3)_5]^{2+}$. The formation of inner-sphere clusters of high order when cation is in excess is a multistage process which results in complex kinetics. In our kinetic studies we have limited ourselves to the early stage of the reaction, the rate of formation of the 1:1 complex as the ratio of cation to anion increases being the focus of our interest. The reverse situation, anion clustering about cation to form 1:1 inner-sphere complexes was dealt with in our earlier study.[2]

Experimental Section

$[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ was prepared as described in the literature.[3] The rate constant[3] for the aquation of $[Ru(NH_3)_5(CF_3SO_3)]^{2+}$ is 1.9×10^{-2} s^{-1} at 25 °C; in all experiments the ruthenium solutions were kept for 20 min before mixing with the nucleophiles.

$[Ru(NH_3)_5H_2O]^{2+}$ was prepared by reduction of a solution of $[Ru(NH_3)_5H_2O]^{3+}$ with H_2 over a platinum gauze. The solutions 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.[4,5] Sodium hexacyanoferrate(II) decahydrate (Strem), potassium hexacyanoruthenate(II) trihydrate (Aldrich), and potassium ferricyanide (Sigma) were used as received.

$[Os(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ was prepared from OsO_4 according to the literature procedure.[6,7] The aquation rate[3] for $[Os(NH_3)_5(CF_3$-

---

[†] Stanford University.

[‡] Universidade Federal do Parana.Setor de Ciéncias Exatas.

(1) Poulopoulou, V. G.; Taube H. *Inorg. Chem.* **1997**, *36*, 2240.

(2) Poulopoulou, V. G.; Taube, H. *Inorg. Chem.* **1997**, *36*, 4782.

(3) Dixon, N. E.; Lawrence, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2940.

(4) Howe, J. L. *J. Am. Chem. Soc.* **1986**, *18*, 981.

(5) Curtis, J. C.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1562.

(6) Lay, P. A.; Magnuson, R. H.; Sen, J.; Taube, H. *Am. Chem. Soc.* **1982**, *104*, 7658.

(7) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Chem.* **1989**, *28*, 3001.

10.1021/ic980932s CCC: $18.00

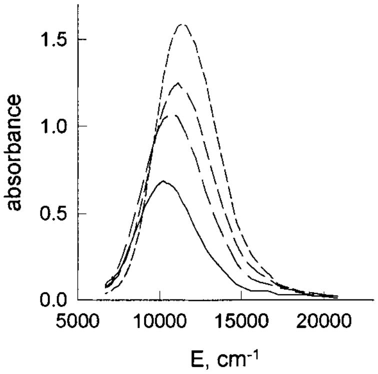

Figure 1. Charge-transfer (CT) bands in mixtures of $[Ru(NH_3)_5H_2O]^{3+}$ and $[Fe(CN)_6]^{4-}$ after substitution is complete at values of ratio *R* equal to 1, 2, 3, 4, 6, and 12 with increasing intensity; $[Fe(CN)_6]^{4-} = 2.5 \times 10^{-4}$ M, D_2O. Profiles for ratios of 4 and above are indistinguishable.

$SO_3)]^{2+}$ is 8.8×10^{-4} s^{-1} at 25 °C. The solutions of $[Os(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ were prepared 2 h before mixing with the nucleophiles and during this time were kept in capped containers in the CAB.

The kinetic measurements were made in aqueous solutions at 25 °C. The materials needed to make up the reaction mixtures were kept in the CAB under N_2 (O_2 content = 5 ppm).

To shorten the reaction time, we resorted to catalysis by Os(IV)[8] when $[Os(NH_3)_5H_2O]^{3+}$ was the cation. There was some difficulty in establishing the terminal composition of the inner-sphere complexes formed in reaction mixtures with a high ratio of $[Os(NH_3)_5H_2O]^{3+}$ to $[Fe(CN)_6]^{4-}$ as being $[(Os(NH_3)_5)_4Fe(CN)_6]^{8+}$ and to bolster the conclusion as reached on the basis of measurements in solution, we sought to prepare a solid from the product solution from a 6:1 ratio of cation to anion. After trying a number of different possible agents, we discovered that the complex cation at 5×10^{-4} M is precipitated by $H_4SiO_4 \cdot 12WO_3 \cdot xH_2O$ at 5.0×10^{-3} M. On the addition of acetone the solid dissolves. The resultant solution with a 1:1 ratio of acetone to water was left to evaporate at room temperature. Blue square very thin platelets appeared which were washed with water and dried under vacuum.

The analysis of the solid (C, 2.32; H, 1.44; N, 5.03; Fe, 0.80; Si, 2.26) shows that it does not conform to any simple composition. Thus the atom ratio of Si to Fe is 5.7. Were the heteropoly anion fully deprotonated it would be two and were it monodeprotonated the ratio would be eight. Carbon is present in excess of that accompanying the iron, presumably because of inclusion of acetone. For present purposes, the critical result is the ratio of N to Fe, 26 expected for 4 $Ru(NH_3)_5{}^{3+}$ per $[Fe(CN)_6]^{4-}$, compared to 25.3 observed.

Instrumentation. UV−vis spectra and kinetic measurements were recorded with a Hewlett-Packard 8453 spectrophometer with a thermostated cell holder. An Mgw Lauda RC 20 Brinkmann circulating water bath was used to maintain the temperature in the cell holder.

The intervalence bands were fitted with Gaussian components by use of Grams/386 software. The areas of the IT bands were calculated as the product of ϵ_{max} (M^{-1} cm^{-1}) and $\Delta_{1/2}$ (cm^{-1}).

Electrochemical experiments were performed under nitrogen in the CAB by using a CV-50W voltammetric analyzer (BAS), a platinum working and counter electrode and an Ag/AgCl reference electrode. The ionic strength was kept constant using LiOTf (0.10 M) as supporting electrolyte. All potentials are reported vs NHE.

Results

A. Inner-Sphere Complex Formation by $[Ru(NH_3)_5]^{3+}$. In Figure 1 are shown the profiles of the charge transfer (CT) bands recorded after substitution is complete in mixtures of $[Ru(NH_3)_5H_2O]^{3+}$ and $[Fe(CN)_6]^{4-}$ at discrete values of the ratio, *R*, of cation to anion ranging from 1 to 12. The experiments were performed in unacidified D_2O solutions with $[Fe(CN)_6]^{4-}$ kept at 2.5×10^{-4} M. Each solution contained 2.5×10^{-5} M $[Ru(NH_3)_5H_2O]^{2+}$ as catalyst[2] for substitution; with its use, substitution is substantially complete after 2 h, at 25 °C. A striking result is that the absorption increases with *R* until 4 is reached, there being no further change as *R* increases to 12. This shows that, in the concentration range under investigation, four and only four cations bind to the core anion. Moreover, because the absorption profiles for $R = 4$ and higher are, within experimental error, superimposable, we can conclude that at $R = 4$, the concentration of $[(Ru(NH_3)_5)_3Fe(CN)_6]^{5+}$ is very low. Thus, the affinity of $[Ru(NH_3)_5]^{3+}$ in the last stage of binding is very high, and there is a very sharp transition from binding to nonbinding as *R* increases beyond 4.

The areas of the absorption bands together with the values of ν_{max} and the values of ϵ_{max} as calculated using the concentration of the anion are recorded in Table 1. The area is a measure of oscillator strength; its increase with R is by no means linear, changing only by a factor of 2.5 when the number of oscillators increases from 1 to 4. Over this range ν_{max} shifts from 1.020×10^3 to a limit at 1.143×10^3 cm^{-1}.

All the absorption bands are asymmetric, excess area appearing on the high energy side of the band maximum, the asymmetry being least for the limiting profile at high *R*. A number of factors contribute to the asymmetry. One is intrinsic and varies depending on the system under study.[9] Spin−orbit coupling, reported[10] as 410 cm^{-1} in $[Fe(CN)_6]^{4-}$ is too small to account for the asymmetry in any of the cases. An expected factor, applicable except when $R = 4$, is the formation of species in composition of order differing from the set value of *R*. Thus, in the 1:1 reaction mixture taken as example, as the 1:1 complex accumulates, the 2:1 will form in competition with the 1:1, leaving uncomplexed an amount of anion equal to that of the 2:1 complex. This does not apply at the 4:1 composition, because the 5:1 complex does not exist. Another source of asymmetry is the coexistence of cis and trans isomers for complexes of order 2, 3, and 4. The compositions of all of the product solutions are under kinetic control; the affinities of the cations for the core are very high so that the rate of dissociation at any stage of binding, even in the presence of catalyst, is very low. Cis−trans isomers are not possible in the case of the 1:1 complex, and for this system a deconvolution of the absorption band was performed. Use was made of the absorption profile of the 1:1 complex as recorded for a reaction solution with anion in excess of the cation, thus ensuring that a single product is being dealt with. It is to be noted that the band for the 1:1 complex is Gaussian. A second condition imposed in the deconvolution was setting the band maximum for the 2:1 complex as determined for the reaction solution with $R = 2$ where the 2:1 is the dominant species. We find that the observed band envelope (Supporting Information, Figure S1) is accounted for by a major contribution by the 1:1 complex, and a minor by the 2:1.

The cyclic voltammograms obtained after 3 h. for reaction solutions with *R* set at 1, 2, and 3 are shown in Figure 2 and are summarized in Table 2. In the more positive range of potentials the cation will be in the 3+ state and here we observe the response of the iron core to the changes in composition. For the solution with $R = 1$, the major signal at $E_{1/2} = 0.63$ V is assigned to the $[Ru(NH_3)_5Fe(CN)_6]^{0/1-}$ couple. Free $[Fe(CN)_6]^{4-}$ in our solutions registers at $E_{1/2} = 0.41$ V; as expected, attachment of the tripositive cation is found to stabilize the anion of more negative charge. In the 1:1 mixture, a small signal is

---

(8) Poulopoulou, V. G.; Takahashi, M.; Takeda, M.; Hasegawa, T.; Taube, H. *Inorg. Chem.* **1996**, *35*, 4622.

(9) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(10) Casabo, J.; Ribas, J. *Inorg. Chem. Acta* **1977**, *21*, 5.

Table 1. Properties of the Charge Transfer Bands for Mixtures of $[Ru(NH_3)_5H_2O]^{3+}$ and $[Os(NH_3)_5H_2O]^{3+}$ with $M(CN)_6^{4-}$ at Discrete Values of the Ratio, *R*

ion ratio $[M'(NH_3)_5]^{3+}/M(CN)_6^{4-}$	$Fe(CN)_6^{4-}$ ν_{max} (10^{-1} cm^{-1})	$Fe(CN)_6^{4-}$ ϵ^c (10^{-3} M^{-1} cm^{-1})	$Fe(CN)_6^{4-}$ area^d (10^{-1})	$Ru(CN)_6^{4-}$ ν_{max} (10^{-1} cm^{-1})	$Ru(CN)_6^{4-}$ ϵ^c (10^{-3} M^{-1} cm^{-1})	$Ru(CN)_6^{4-}$ area^d (10^{-1})	$Os(CN)_6^{4-}$ ν_{max} (10^{-1} cm^{-1})	$Os(CN)_6^{4-}$ ϵ^c (10^{-3} M^{-1} cm^{-1})	$Os(CN)_6^{4-}$ area^d (10^{-1})
1[a]	1020	2.9	320	1457	2.5	282	1215	3.1	410
2[a]	1090	4.5	540	1488	4.4	509	1280	5.2	793
3[a]	1123	5.2	630	1516	5.4	650	1306	6.4	999
4[a]	1131	6.5	774	1560	6.8	710	1359	7.2	1120
1[b]	1599	1.6	180	2033	1.8	230	1777	1.9	344
2[b]	1639	2.8	350	2033	3.2	400	1812	3.4	652
3[b]	1664	3.6	430	2081	4.2	510	1834	5.2	900
4[b]	1664	4.3	472	2081	4.6	540	1834	6.0	968

[a] M′ = Ru. [b] M′ = Os. [c] As determined by having the tetranegative ions in excess the true ϵ values for the 1/1 complexes are 3.0, 2.7, and 3.4 for $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$ and $Os(CN)_6^{4-}$, respectively, when the cation is $[Ru(NH_3)_5H_2O]^{3+}$, and 1.7, 1.9, and 2.1 when the cation is $[Os(NH_3)_5H_2O]^{3+}$. [d] The oscillator strength (*f*) for the 1/1 complexes when the anion is in excess was calculated as 0.053, 0.052, and 0.071 for $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Os(CN)_6^{4-}$, respectively, when the cation is $[Ru(NH_3)_5H_2O]^{3+}$, and 0.031, 0.039, and 0.045 when the cation is $[Os(NH_3)_5H_2O]^{3+}$.

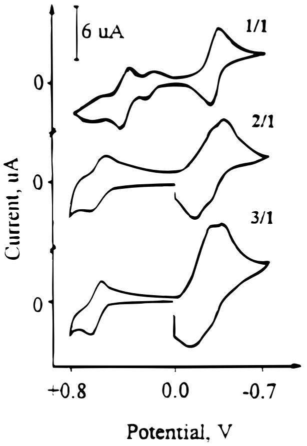

Figure 2. Cyclic voltammograms for reaction solutions with *R* ($[Ru(NH_3)_5H_2O]^{3+}/[Fe(CN)_6]^{4-}$) equal to 1, 2, and 3; $[Fe(CN)_6]^{4-} = 2.5 \times 10^{-4}$ M, D_2O.

observed at $E_{1/2} = 0.84$ V, as well as a signal corresponding to free $[Fe(CN)_6]$,$^{4-}$ observations compatible with the asymmetry noted in the charge-transfer band and with the electrochemical observations made with the 2:1 complex. The signals at 0.84 and 0.41 V corresponding to the 2:1 complex and to $[Fe(CN)_6]^{4-}$ respectively are expected on the basis of arguments already made. The catalyst at the end of the reaction is not free, and in the nominal 1:1 product mixture it will be bound mainly to the abundant 1:1 species, but partly to $[Fe(CN)_6]$,$^{4-}$ causing a depletion of $[Fe(CN)_6]^{4-}$ relative to the 2:1 species as observed. Similar effects apply in the other cases.

When $R = 2$, as expected from the foregoing, the major signal corresponding to the $[(Ru(NH_3)_5)_2Fe(CN)_6]^{3+/2+}$ couple appears at 0.84 V. The shift in the potential of the iron couple caused by addition of the second cation is 0.21 V, 0.01 V smaller than that for the first stage of complexation. In this case the product solution was subjected to chromatography on a cation exchange column packed with Sephadex C-25, 0.30 M KCl being used as elutant. The anionic 1:1 complex is not retained by the column. Analysis of the later eluate led to an estimate of 1.9% of the $[Fe(CN)_6]^{4-}$ being present as the 1:1 complex, but according to arguments just made this figure is only a lower limit on the extent to which the reaction of the cation with the 2:1 complex competes with its reaction with the 1:1.

In the 3:1 reaction mixture, the only electrochemical signal in the high potential range observed is that for the $[(Ru(NH_3)_5)_2Fe(CN)_6]^{3+/2+}$ couple, the expected value for the 3:1 species at ca. 1.03 V being unobservable while in the 4:1 reaction mixture the only responses observed are in the lower potential region. In the lower reduction potential range the anion is in the reduced state, and we now observe the response of the Ru(III)/Ru(II) couple to the changes in composition. In the cyclovoltammetric traces we find for the solution with $R = 1$ a single wave at −0.04 V shifted from that for $[Ru(NH_3)_5H_2O]^{3+/2+}$ at $E_{1/2} = 0.10$ V. The shift to a lower potential reflects the greater stabilization by $[Fe(CN)_6]^{4-}$ of the higher oxidation state of ruthenium compared to the lower. The traces for solutions at compositions $R = 2$, 3, and 4 each have two components, these features being reproduced in differential pulse voltammetry, which has the advantage of improving the resolution and was relied on to define the response of the $[Ru(NH_3)_5]^{3+/2+}$ couple to changes in the composition of the solutions.

For the solution at $R = 2$, a shoulder is revealed at the higher potential side of the major peak. We attribute the two signals to the presence of cis and trans isomers, an interpretation borne out by the results obtained at higher values of *R*. The two major fractions which were collected by cation ion exchange chromatography (vide supra), after $[Ru(NH_3)_5Fe(CN)_6]^-$ had washed through the column, were subjected to differential pulse voltammetry. Separation was apparently not complete, the first fraction showing signals at −0.04 and 0.00 V, the former being greater, and the second showing a signal only at −0.04 V. The intervalence absorption for the second fraction appears at 872 nm, and for the first fraction, still a mixture, it appears at 880 nm. The difficulty in separating the two species indicates that they carry the same charge, confirming them to be isomers.

In experiments on inner-sphere cluster formation between $[Ru(NH_3)_5H_2O]^{2+}$ and $[Fe(CN)_6]^{4-}$ the properties of the pyridinepentaammineruthenium(II) complex were exploited to detect free $[Ru(NH_3)_5H_2O]^{2+}$. The aquo ion reacts rapidly to form the pyridine complex which is highly colored ($\lambda_{max} = 407$ nm; $\epsilon = 7.8 \times 10^3$ M^{-1} cm^{-1}).[11] A solution was prepared containing 5×10^{-5} M $[Fe(CN)_6]$,$^{4-}$ and $[Ru(NH_3)_5H_2O]^{2+}$ at 4-fold this level (ratio accurate to within about 3%). After completion of substitution, pyridine was added to bring its concentration to 5×10^{-3} M. The color of $[Ru(NH_3)_5(py)]^{2+}$ was not observed but it did appear when a slightly higher ratio of $[Ru(NH_3)_5H_2O]^{2+}$ to $[Fe(CN)_6]^{4-}$ was used. The experiments show that even at low concentration four $[Ru(NH_3)_5]^{2+}$ bind strongly to $[Fe(CN)_6]^{4-}$ and that the affinity of the resulting cluster for $[Ru(NH_3)_5]^{2+}$ is very low.

In Figure 3 are shown the spectrophotometric traces recorded for a series of experiments in which the ratio of $[Ru(NH_3)_5H_2O]^{2+}$ to $[Ru(NH_3)_5Fe(CN)_6]^-$ was increased, while the

---

(11) Ford, P.; Gaunder, R. G.; Rudd De. F. P.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.

Table 2. Summary of the Cyclic Voltammograms for Reaction Solutions with Different Ratios *R*

$[(NH_3)_5Ru]^{3+}$/ $M(CN)_6{}^{4-}$	$E_{1/2}$ (V vs NHE)										
	$Fe(CN)_6{}^{4-}$					$Fu(CN)_6{}^{4-}$		$Os(CN)_6{}^{4-}$			
1	(+0.41)[a]	+0.63	(+0.84)	−0.04		−0.02		(+0.63)	+0.83	−0.05	
2		(+0.63)	+0.84	−0.04	(0.00)	−0.01	(+0.05)		(+0.83)	−0.07	(+0.03)
3			(+0.84)	−0.06	+0.04	−0.02	+0.06			−0.04	+0.03
4				−0.06	+0.05	−0.02	+0.08			−0.04	+0.03

[a] Relatively weak features in parentheses.

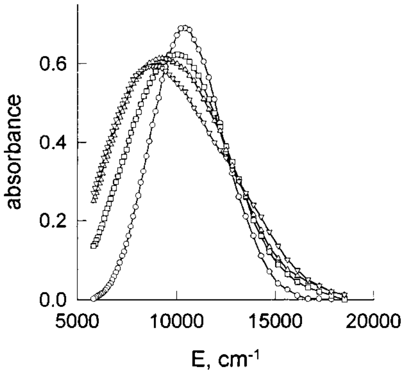

Figure 3. Spectra of reaction mixtures of $[Ru(NH_3)_5H_2O]^{2+}$ with $[Ru(NH_3)_5Fe(CN)_6]^-$ at values of ratio *R* equal to 0 (○), 1 (●), 2 (▽), and 3 (▼); $[Ru(NH_3)_5Fe(CN)_6]^- = 2.5 \times 10^{-4}$ M, D_2O.

latter was kept at 2.5×10^{-4} M, D_2O as solvent. Because the Ru(II) solution, as prepared by the reduction of Ru(III) with H_2, contains acid at the same concentration as that of the cation, these solutions were buffered (pH = 4.1, citrate buffer at 5×10^{-3} M). The traces were recorded ca. 15 min. after mixing, a time long enough to ensure completion of substitution by Ru(II). In line with results already dealt with, the maximum number of ruthenium cations accommodated by the anion is 4. Deconvolution, with the constraint that the known half width of the $[Ru(NH_3)_5Fe(CN)_6]^-$ CT band is applied, shows that two components are present, one at 1.067×10^4 cm^{-1} which we assign to Fe(II) → Ru(III) charge transfer and one at 8.00×10^3 cm^{-1} which we assign to Ru(II) → Ru(III) charge transfer. The results (ν_{max} and ϵ) of the deconvolution are shown in Table 3. As $[Ru(NH_3)_5]^{2+}$ accumulates, the $[Fe(CN)_6]^{4-} \rightarrow [Ru(NH_3)_5]^{3+}$ transition moves to higher energy and decreases in intensity while that for $[Ru(NH_3)_5]^{2+} \rightarrow [Ru(NH_3)_5]^{3+}$ changes little, ϵ increasing almost linearly with the number of oscillators.

For completeness, experiments were done keeping the ratio of $[Ru(NH_3)_5]^{2+}$ to $[Fe(CN)_6]^{4-}$ at 1, but increasing the ratio of Ru(III) to Ru(II). The energies of Fe(II) → Ru(III) transition increase slightly as the ratio of Ru(III) to Ru(II) increases: 1067, 1080, 1120 (cm^{-1} × 10^{-1}) for the ratios 1, 2, and 3 respectively, almost the same as without Ru(II). While ϵ increases, it falls somewhat short of doubling with a 3-fold increase in the number. Within experimental error, the energy of the interammine transition does not change with increasing Ru(III). Quite astonishing is the finding that despite the increase in number of oscillators, ϵ for the transition, if anything, shows a slight decrease.

When solutions containing $[Ru^{III}(NH_3)_5(Fe(CN)_6)Ru^{II}(NH_3)_5]^+$ are stored for a long time, light being excluded, changes in the absorption spectrum are observed, which are much more rapid at higher ratios of $[Ru(NH_3)_5]^{2+}$ to $[Ru(NH_3)_5]^{3+}$. When the ratio is 3, after 3 days the intensity of the absorption at the maxima for the two transitions has decreased by a factor of at least 3 resulting in a rather featureless absorption over a wide range in wavelength, except for a new maximum at $1.724 \times 10^{4-}$ cm^{-1}, and the appearance of a blue precipitate.

Experiments were also done with $[Ru(CN)_6]^{4-}$ and $[Os(CN)_6]^{4-}$ as the nucleophiles, following the routine described for $[Fe(CN)_6]$.$^{4-}$ The spectra obtained are deposited as Supporting Information, Figs. S2 and S3. Here as well, binding of cation to anion terminates sharply at a ratio of 4:1. Asymmetry of the absorption envelope is now even more pronounced than it is for $[Fe(CN)_6]^{4-}$, because, while the factors which contribute to asymmetry there are still operative, the effect of spin−orbit coupling is more prominent. Its effect is obvious in the trace for the complex $[Ru(NH_3)_5Os(CN)_6]^-$ where a bulge appears on the high-energy side of the maximum. The gross features of the spectra, ν_{max} and areas, are summarized in Table 1.

The electrochemical results for the $[Ru(NH_3)_5]^{3+/2+}$ couple with the two additional nucleophiles are also summarized in Table 2 and in the lower potential range they closely parallel those obtained for $[Fe(CN)_6]$.$^{4-}$ For the $[Os(CN)_6]^{3-/4-}$ couple we were able to observe only the signal for the 1:1 species, shifted 0.20 V above that of the free anion at 0.63 V, while for $[Ru(CN)_6]^{3-/4-}$, the potential for the free anion being at 0.83 V, even that for the 1:1 complex is shifted to the breakthrough region.

The trends in the intensities of the transitions when $[Ru(NH_3)_5]^{2+}$ is also a component of the clusters follows those described for $[Fe(CN)_6]$,$^{4-}$ including the observation than when the number of $[Ru(NH_3)_5]^{3+}$ attached to $[Ru(NH_3)_5M(CN)_6]^{2-}$ increases, the intensity of the interammine transitions remains almost constant. In respect to energies, there is an outstanding exception to expectation. Although the energies of the interammine transitions in the 1:1:1 complexes with $[Fe(CN)_6]^{4-}$ and $[Os(CN)_6]^{4-}$ are the same (8.00×10^3 cm^{-1}), expected because the immediate environments of the cations are identical, that for $[Ru(CN)_4]^{4-}$ appears at 9.40×10^3 cm^{-1}, a similar difference being maintained for other $[Ru(NH_3)_5]^{3+}$/$[Ru(NH_3)_5]^{2+}$ ratios. A deconvolution of the spectrum for $[Ru(NH_3)_5Os(CN)_6Ru(NH_3)_5]^+$ appears as Figure S4; a summary of the properties of the CT transitions for $[Ru(CN)_6]^{4-}$ and $[Os(CN)_6]^{4-}$ is included in Table 3.

As with $[Fe(CN)_6]^{4-}$ as core, all the solutions containing also $[Ru(NH_3)_5]^{2+}$ undergo slow decomposition, which is the most rapid with $[Ru(CN)_6]^{4-}$ as cation, leading to featureless absorption except for a peak, also at 1.724×10^4 cm^{-1}.

B. Inner-Sphere Complex Formation by $[Os(NH_3)_5]^{3+}$. The investigation of inner-sphere clustering was extended to $[Os(NH_3)_5H_2O]^{3+}$ as the cation. In these experiments as well, the nucleophile was kept at 2.5×10^{-4} M. Advantage was taken of the known catalysis by Os(IV) of substitution on Os(III)[8] which we generated by the addition of $[Fe(CN)_6]^{3-}$ at the 2.5×10^{-5} M level. This reduces the concentration of $[Os(NH_3)_5]^{3+}$ so that in the 1:1 reaction mixture, it is present at 2.2×10^{-4} M. By use of the catalyst substitution is complete in 3 h. when the cation to nucleophile concentration does not exceed 4 (above this ratio there is a marked decrease in the rate of substitution). With $[Os(NH_3)_5H_2O]^{3+}$, we encountered the complication that

Table 3. Results of the Deconvolution of the Charge-Transfer Band Envelopes of Solution Mixtures That Contain $[Ru(NH_3)_5H_2O]^{3+}$ and $[Ru(NH_3)_5H_2O]^{2+}$; Set: Ru(II) Increasing at Fixed $[(NH_3)_5RuM(CN)_6]^-$; Lower, Ru(III) Increasing at Fixed $[(NH_3)_5RuM(CN)_6]^{2-}$

	C. T. $[M(CN)_6]^{4-} \rightarrow [Ru(NH_3)_5]^{3+}$						C. T. $(NH_3)_5]^{2+} \rightarrow [Ru(NH_3)_5]^{3+}$					
	$Fe(CN)_6{}^{4-}$		$Ru(CN)_6{}^{4-}$		$Os(CN)_6{}^{4-}$		$Fe(CN)_6{}^{4-}$		$Ru(CN)_6{}^{4-}$		$Os(CN)_6{}^{4-}$	
ion ratio	ν_{max} (10^{-1} cm^{-1})	ϵ (10^{-3} M^{-1} cm^{-1})	ν_{max} (10^{-1} cm^{-1})	ϵ (10^{-3} M^{-1} cm^{-1})	ν_{max} (10^{-1} cm^{-1})	ϵ (10^{-3} M^{-1} cm^{-1})	ν_{max} (10^{-1} cm^{-1})	ϵ (10^{-3} M^{-1} cm^{-1})	ν_{max} (10^{-1} cm^{-1})	ϵ (10^{-3} M^{-1} cm^{-1})	ν_{max} (10^{-1} cm^{-1})	ϵ (10^{-3} M^{-1} cm^{-1})
1[a]	1067	2.6	1496	2.4	1220	2.8	800	1.0	944	0.5	800	0.9
2[a]	1131	2.4	1510	2.3	1340	2.5	800	1.8	950	1.0	800	1.7
3[a]	1253	1.7	1570	2.1	1417	1.8	800	2.9	950	1.5	800	3.0
1[b]	1067	2.6	1496	2.4	1220	2.8	800	1.0	944	0.5	800	0.9
2[b]	1080	4.1	1560	4.2	1328	4.8	800	0.9	950	0.5	810	0.9
3[b]	1120	4.6	1587	5.2	1373	5.6	800	0.9	945	0.6	810	0.9

[a] $[(NH_3)_5Ru]^{2+}/[(NH_3)_5Ru^{III}M(CN)_6]^-$. [b] $[(NH_3)_5Ru]^{3+}/[(NH_3)_5Ru^{II}M(CN)_6]^{2-}$.

a secondary reaction sets in after substitution is complete. When the solutions are stored many hours, the maximum for the $[M(CN)_6]^{4-} \rightarrow [Os(NH_3)_5]^{3+}$ CT band shifts to higher energy, and a new absorption band grows at 320 nm. The effect is more marked at high values of the ratio of cation to anion, but in no case is significant at 3 h.

The CT bands for $[Fe(CN)_6]$,$^{4-}$ $[Ru(CN)_6]^{4-}$, and $[Os(CN)_6]^-$ as nucleophiles are deposited as Supporting Information, Figures S4, S5, and S6. The figures serve to show that, as when $[Ru(NH_3)_5H_2O]^{3+}$ is the cation, the terminal species at high ratios of cation to anion has four cations attached to the anion. A complication in all the data appears at the high energy side of the maximum, where in each case there is absorption which we are at present unable to account for. Because the traces at $R = 4$ and above for each anion track closely, we believe that the complications noted on the high energy wings are inherent in the systems and probably reflect unexplored chemistry of Os(IV) interacting with other species in the systems. The shapes on the low energy side of the maximum in each case are Gaussian so that it is unlikely that spurious absorption contributes here. The deconvolutions to obtain the areas were done by making use of the low energy region, a strategy which also minimizes the complication introduced by the shoulder on the high energy side. The spectrophotometric properties are summarized in Table 1. For the 1:1 complexes, the values of f ($= 4.6 \times 10^{-9}\ \epsilon_{max} \cdot \Delta\nu_{1/2}$) have been calculated.[9]

Useful electrochemical data for the inner-sphere clusters formed by $[Os(NH_3)_5]^{3+}$ are meager. In the low potential range, that for the $[Os(NH_3)_5]^{3+/2+}$ couple is shifted into the breakthrough range while at potentials where the response of the $[M(CN)_6]^{3-/4-}$ couple is registered, complex uninterpretable behavior was observed for M = Ru and Os, and failing to identify the source of the difficulty, we have data only for the $[Fe(CN)_6]^{3-/4-}$ couple. The response in differential pulse voltammetry for $[Os(NH_3)_5Fe(CN)_6]^-$ consists of a broad envelope which contains also the signal for the Os(IV)/Os(III) couple in the complex. The observations are consistent with a shift in the Fe(III)/Fe(II) couple much the same as is observed when the cationic fragment is $[Ru(NH_3)_5]^{3+}$.

C. Kinetics of the Formation of $[Ru(NH_3)_5Ru(CN)_6]^-$ with Cation in Excess. Outer-sphere clustering of tripositive ions about anions of high charge, as monitored by the areas of the charge-transfer absorption bands, has been demonstrated.[1] Though the effects of such clustering on the kinetics of substitution when the cation is at the core have been recorded[2], those for the present case were not examined. We here report the results of experiments done on the kinetics of substitution in the $[Ru(NH_3)_5H_2O]^{3+}/[Ru(CN)_6]^{4-}$ system when the ratio of the concentration of cation to anion ranges from 1 to as high as 16. By choice of $[Ru(CN)_6]^{4-}$ as anion, catalysis by $[Ru(NH_3)_5H_2O]^{2+}$, generated by the reduction of the cation by the anion, is avoided. The concentration of the anion was kept at 2.5×10^{-4} M, temperature 25.0 °C. To maximize outer-sphere clustering, the only electrolyte present was that needed to meet the experimental conditions imposed. In one series of experiments, the pH was adjusted to 3.0 (by titration with HO_3SCF_3), and in the other, the reagents were dissolved in water.

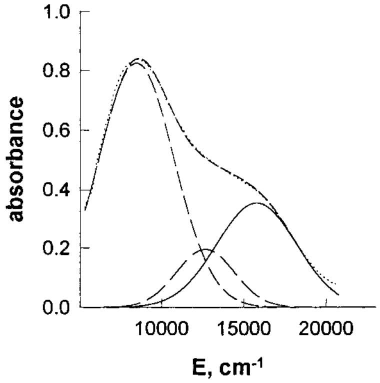

Figure 4. Deconvolution of the spectrum of a mixture containing $[Ru(NH_3)_5H_2O]^{2+}$ and $[Ru(NH_3)_5Os(CN)_6]^-$ at a ratio $R = 3$. From left to right: $[Ru(NH_3)_5]^{2+} \rightarrow [Ru(NH_3)_5]^{3+}$ charge transfer, and the two components (due to the spin−orbit coupling) of the Os(II) → $[Ru(NH_3)_5]^{3+}$ charge-transfer band; (•••) experimental spectrum; (- - -) fitted spectrum; $[Ru(NH_3)_5Os(CN)_6]^- = 2.5 \times 10^{-4}$ M, D_2O.

The kinetics of the reaction, proceeding full course, are complicated by its multistage nature, and as a result, we restricted our interest to the early reaction stage involving the 1:1 complex. Initial rates were determined by collecting numerous readings of the absorbance over 1% of the reaction, and taking the slopes. The data we have obtained are shown in Figure 5, each point being the average of at least 5 determinations. We note for the unbuffered solutions a monotonic increase in reaction rate with an increase in the ratio of cation to anion until a plateau is reached. At pH = 3.0 the core anion, at least when the ion ratio is 1, is monoprotonated and in this experiment structure is observed before a plateau value is reached. At pH 3.6 where the anion is mainly unprotonated and the cation is mainly in the aquo rather than hydroxo form, the behavior is intermediate between the other two.

D. Solubility Considerations. In the course of trying to prepare solids from some of our product solutions, we made some observations on solubilities, which though qualitative, are unusual enough to merit a brief mention. The product solutions we are dealing with contain, in addition to the clusters, K^+ and $CF_3SO_3{}^-$ as counterions.

In general the difficulty of preparing solids increases with the ratio of cation to anion. Thus while $K[Ru(NH_3)_5Fe(CN)_6]$ precipitates readily from aqueous solution on the addition of ethanol, the solid which is left on evaporating the product

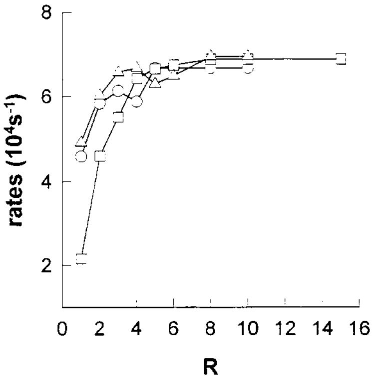

Figure 5. Initial rates for the formation of the 1/1 complex as the ratio of cation to anion increases in mixtures of $[Ru(NH_3)_5H_2O]^{3+}$ and $[Ru(CN)_6]^{4-}$ (neutral solution (○), pH = 3.0 (●), pH = 3.6 (▽)); $[Ru(CN)]^{4-} = 2.5 \times 10^{-4}$ M, pH was adjusted by titration with HO_3SCF_3, 25.0 °C.

solution resulting from a 4:1 ratio of $[Ru(NH_3)_5H_2O](O_3SCF_3)_3$ and $K_4Fe(CN)_6$ dissolves readily even in 2-propanol. When the product solution was evaporated to a small volume, and after the addition of $K_4Fe(CN)_6$ was then stored in the refrigerator, long, very thin needles were formed, which however proved to be unsuitable for structure determination by X-ray diffraction.

At an early stage of our work with $[Os(NH_3)_5]^{3+}$ as the cation, before we were aware of the slow decomposition of the complexes, the observation made with solutions kept for a long time indicated that more than 4 cations could attach to $[Fe(CN)_6]$,$^{4-}$ and the need to prepare a solid for analysis appeared. After trying a dozen or so salts containing anions of high charge, and meeting with no success, we discovered that on adding, $H_4SiO_4 \cdot 12WO_3 \cdot xH_2O$ to the reaction solution a precipitate forms. Remarkably the precipitate dissolves when acetone is added to the aqueous solution. Under conditions of slow precipitation well formed square platelets appear which proved to scatter X-rays as an amorphous solid.

Discussion

The spectrophotometric properties of the 1:1 complexes as prepared from mixtures of $[M'(NH_3)_5H_2O]^{3+}$ and $[M(CN)_6]^4$ at the 1:1 ratio are summarized in the body of the table, and as prepared by use of anion in excess, the method used by Burewicz and Haim[12] for M = Fe and Ru, appear in a footnote to Table 1. As expected, because of the formation of side products in the former case, the extinction coefficients are somewhat lower than they are for the latter method. The following, prepared by separation of solids, have also been reported: $[Ru(NH_3)_5Ru(CN)_6]^-$ [13] and $[Os(NH_3)_5M(CN)_6]^-$ (M = Fe, Ru, Os).[14] Where comparisons can be made between the two methods, the agreement is satisfactory.

The agreement between the energy differences that exist for the intervalence transitions and those for the relevant potentials of the redox couples for the free ions has been commented on,[12,14,15] and is not materially affected by the use of the potentials for the couples in the 1:1 complexes. A feature of the data for the 1:1 complexes which appears not to have been touched on previously is based on a comparison of the half-width of the absorption bands as determined experimentally with those calculated from the equation $\Delta\upsilon_{1/2} = [2310(\nu_{max} - \Delta E_o)]$ which is derived[9,16] on the assumption that delocalization is weak. It provides a qualitative guide to deciding whether the particular system is in Class 2[17] or has substantial Class 3 character. In a large number of cases,[16] in which there are other grounds for concluding that the electronic interaction is significant but weak (Class 2), the experimental value of $\Delta\nu_{1/2}$ exceeds that calculated by 10% or so. When delocalization becomes substantial, the experimental value decreases relative to that calculated.

When this criterion is applied to the M(II) → M′(III) transitions we find for the case of M(II) = $[Fe(CN)_6]^{4-}$, and M′(III) = $[Ru(NH_3)_5]^{3+}$, $\Delta\nu_{1/2}$(ex) = 3822 cm^{-1} while that calculated is 4217 cm^{-1}, but when M′(III) is $[Os(NH_3)_5]^{3+}$, the values are 4050 and 3962 cm^{-1}, respectively. That there is more delocalization in the former case than in the latter is attributable partly to the larger difference in the energies of the ground-state orbitals when $[Os(NH_3)_5]^{3+}$ substitutes for $[Ru(NH_3)_5]^{3+}$. This is borne out by including $[Os(NH_3)_5Ru(CN)_6]^-$ in the comparison, where the difference in ground-state energies is maximum and $\Delta\nu_{1/2}$(ex) at 4414 cm^{-1} exceeds $\nu_{1/2}$(theor) at 4004.

The extent of mixing the excited states, [M′(II)·M(III)], into the ground states, [M′(III)·M(II)], can also contribute to the extent of delocalization. This will be the greatest for the stronger oxidizing agent among the cations, namely $[Ru(NH_3)_5]^{3+}$, in combination with the strongest reducing agent, $[Fe(CN)_6]$.$^{4-}$ It can account for the fact that f for $[Ru(NH_3)_5Fe(CN)_6]^-$ is as great as it is for $[Ru(NH_3)_5Ru(CN)_6]^-$ while f for $[Os(NH_3)_5\text{-}Fe(CN)_6]^-$ where the energy of the [Os(II)·Fe(III)] excited state lies much higher relative to the ground state, is considerably lower than it is for $[Os(NH_3)_5Ru(CN)_6]^-$, so that the contribution by mixing is reduced.

The increase in the energies of the M(II) → M′(III) transitions as the number of tripositive cations bound to the anion increases has already been noted, and is attributable to the greater stabilization by the cation of $[M(CN)_6]^{4-}$ compared to $[M(CN)_6]^{3-}$. Each cation contracts the electron cloud of the anion, but the polarizability of the anion is expected to decrease as the number of bound cations increases, so that resultant effect, a decrease in orbital overlap in the interaction of cation with anion, will not be a linear function of the number of cations added, in accordance with the experimental observations.

A measurable difference in the reduction potentials for isomeric couples has been demonstrated by partial separation of the two forms for the 2:1 species. The more abundant species gave a good response in cyclovoltammetry with a peak-to-peak separation of 0.07 V, showing that the couples for the two stages of reduction of the cationic centers differ only very slightly in energy. That the multistage reductions occur with very little change in potential for each stage is indicated also by the fact that for each core anion the $[Ru(NH_3)_5]^{3+/2+}$ couple is reduced at a potential which remains almost constant (within 0.01 V of mean) irrespective of the stage of reduction. This means that the relative affinities of $[M(CN)_6]^{4-}$ for the cations is almost constant as the ratio of $[Ru(NH_3)_5]^{3+}$ to $[Ru(NH_3)_5]^{2+}$ changes. Moreover, in referring to Table 2 we note that the reduction

---

(12) Burewicz, A.; Haim, A. *Inorg. Chem.* **1988**, *27*, 1611.

(13) Siddiqui, S.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1987**, *26*, 3101.

(14) Vogler, A.; Osman, S. H., Kunkely, H. *Inorg. Chem.* **1987**, *26*, 2337.

(15) Forlano, P.; Baroldo, L. M.; Globe, J. A.; Della Védova, C. O. *Inorg. Chim. Acta* **1994**, *223*, 37. $[(NH_3)_5RuOs(CN)_6]^-$ prepared by the solution method.[12]

(16) Creutz, C. *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley and Sons: New York, 1983; Vol. 30, p 1. A modification of the equation of ref 9 appears herein, which corrects for the difference in the reduction potentials of the two sites, ΔE_o.

(17) Robin, M. D.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1971**, *10*, 1543.

potentials remain almost constant as the ratio of cation to anion changes. These are surprising results in view of the very high affinities which prevail.

A consideration of the data in Table 3, in harmony with some of the comments already made, suggests that in the compact systems we are dealing with, electron distribution effects must be invoked to account for them. Noteworthy is the increase in the energies of the $[M(CN)_6]^- \rightarrow [Ru(NH_3)_6]^{3+}$ transitions when $[Ru(NH_3)_5]^{2+}$ is added to $[Ru(NH_3)_5M(CN)_6]^-$. On the addition of three $[Ru(NH_3)_5]^{2+}$, for M = Fe, Os, Ru, respectively, they are 1.23, 1.18, 1.07, in order of decreasing oxidizability of the anion. For M = Fe and Os, the ratios are even greater than that following the addition of $[Ru(NH_3)_5]^{3+}$. Because $[Ru(NH_3)_5]^{2+}$ has a lower charge than $[Ru(NH_3)_5]^{3+}$, the explanation offered for the change in energy on the addition of the latter is not applicable. Net transfer of electron density from $[Ru(NH_3)_5]^{2+}$ to the bridging ligands (back-bonding), in view of the negative charge they carry is likely to be small, and in any case, taken alone, would lead to a decrease in energy of the transition. However, net electron transfer from $[Ru(NH_3)_5]^{2+}$ to $[Ru(NH_3)_5]^{3+}$, that is replenishment by $[Ru(NH_3)_5]^{2+}$ of electron density withdrawn from the bridging group by $[Ru(NH_3)_5]^{3+}$, would weaken the oxidizing power of the latter and lead to an increase in energy. The number of core to $[Ru(NH_3)_5]^{3+}$ oscillators is not affected on the addition of $[Ru(NH_3)_5]^{2+}$ to the 1:1 complex, and the electron redistribution postulated would result in a decrease in their intensity as is observed.

While the number of core to $[Ru(NH_3)_5]^{3+}$ oscillators is not affected by disporportionation equilibria, established by intramolecular electron-transfer reactions such as

$$2[Ru(III)M(CN)_6Ru(II)] = [Ru(III)M(CN)_6Ru(III)] + Ru(II)M(CN)_6Ru(II)$$

the number of interammine oscillators is sensitive to the values of the associated equilibrium constants, as then will be their intensities. Because the successive redox potentials for the clusters span a rather narrow range for the 4:1 species, it appears that the equilibrium constants for the disproportionation reactions approach the statistical values, and that other causes must be found to account for the remarkable observations made on intensities, namely that while, when $[Ru(NH_3)_5]^{3+}$ is added to $[Ru(NH_3)_5M(CN)_6]^-$ the intensities of the interammine transitions increase almost linearly with the number of cations introduced, while, when $[Ru(NH_3)_5]^{3+}$ is added, the intensities remain almost the same.

It is to be noted that Ru(III) has a much greater effect on electron redistribution than does Ru(II), the excited-state $Ru(II)\cdot[Fe(CN)_6]^{3-}\cdot Ru(II)$ lying much lower in energy than $[Ru(III)\cdot[Fe(CN)_6]^{5-}\cdot Ru(III)]$, the former derived by electron transfer from $[Fe(CN)_6]^{4-}$ to Ru(III).

In the face of the stability of complexes with only $[Ru(NH_3)_5]^{3+}$ present, the instability when $[Ru(NH_3)_5]^{2+}$ is included in the assembly came as a surprise. The decomposition is most rapid with $[Ru(CN)_6]^{4-}$ as the core ion, and there being evidence that in this case, rapid linkage isomerization takes place, we attribute the instability to this cause. Nitrogen replacing carbon at the core ruthenium, slow replacement by the solvent follows, and the resultant altered core now is subject to further linkage isomerization. Earlier work[19] has shown that CN^- labilizes the release from the complex of NH_3 trans to CN^-, the product undergoing polymerization. The color which develops is attributed to the inclusion of $[Ru(NH_3)_5CN]^{2+}$ into the polymer, the high energy of the band being ascribed to end effects where the terminal metal ion has an environment different from that of an included ion. As observed, the energy of the resulting valence band is expected to be independent of the identity of M. If the suggestion as as to the nature of the decomposition of the inner-sphere clusters is borne out by future work, the associated reactions can have considerable preparative utility.

Our present studies of the effects of outer-sphere clustering on the rates of inner-sphere complex formation complement our earlier studies made with anion concentration equal to, or in excess of that of cation. As in the earlier work, plateau values of the rates are reached as the ion ratio increases, those in acidic solution also showing structure before the plateau is reached. The large contrast in rate in unacidified solutions, a factor of more than 3 for the limiting rate compared to that in the ion pair, is mainly ascribable to internal proton transfer: $[Ru(NH_3)_5H_2O^{3+}\cdot Ru(CN)_6{}^{4-}]^- = [Ru(NH_3)_5OH\cdot Ru(CN)_5(CNH)]^-$, which is largely overcome with the addition of a second cation. The most notable result of the new work, is that when acid is present to eliminate the adverse effect of internal proton transfer the rate increase, despite the added opportunities for substitution offered by each additional cation accumulated in the cluster,[1] is only a factor of 1.5 or so, whereas, in the inverse case, protonated anion about cation, the rate increase is a factor of 3.3. Asymmetry in the action of cations and anions in accelerating the rate of substitution at a cation was first documented by Garrick,[20] in showing that the rate of aquation of $[Co(NH_3)_5Cl]^{2+}$ is accelerated by electrolytes, and is sensitive to the concentration and nature of the anion, much more than that of the cation. Despite a statistical factor of 6 favoring substitution in the terminal outer sphere cluster,[1] the rate increase compared to that in the ion pair, as observed in the present study, is very small.

Acknowledgment. This work was supported by National Science Foundation Grant Number CHE-9505379-003.

Supporting Information Available: Deconvolution of the charge-transfer band of a solution mixture with 1/1 ratio of $[Ru(NH_3)_5H_2O]^{3+}$ and $[Fe(CN)_6]^{4-}$ (Figure S1). Charge-transfer bands in mixtures of $[Ru(NH_3)_5H_2O]^{3+}$ and $[Ru(CN)_6]^{4-}$ (Figure S2) or $[Os(CN)_6]^{4-}$ (Figure S3) at values of ratio *R* from 1 to 12. Charge-transfer bands for reaction mixtures of $[Os(NH_3)_5H_2O]^{3+}$ with $[Fe(CN)_6]^{4-}$ (Figure S4) or $[Ru(CN)_6]^{4-}$ (Figure S5) or $[Os(CN)_6]^{4-}$ (Figure S6) at values of ratio *R* from 1 to 12. This material is available free of charge via the Internet at http://pubs.acs.org.

IC980932S

---

(18) Reference 16, Table 18. Separation of the centers must be taken into account when making comparisons of the energies of the transitions.

(19) (a) Isied, S. S.; Taube, H. *Inorg. Chem.* **1975**, *14*, 2561. (b) See also thesis: Stanford University, 1973, p 100 et seq.

(20) Garrick, F. J. *Trans. Faraday Soc.* **1938**, *34*, 1088.