

Properties of Ion Clusters: Interactions of $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and $[\text{Ru}(\text{NH}_3)_6]^{3+}$ with $[\text{Ru}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$

Vassiliki G. Pouloupoulou and Henry Taube*

Department of Chemistry, Stanford University, Stanford, California 94305-5080

Received December 2, 1996

In continuation of work¹ on the rate constants for substitution by hexacyano nucleophiles in the ion pairs formed with $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$, we have observed² that the specific rates—which, with $[\text{Fe}(\text{CN})_6]^{4-}$ as nucleophile, remain strictly first order to more than 90% completion—increase on increasing the ratio, R , of the concentration of the anion to that of the cation (see Supporting Information Figure S1). The solutions were acidified, 1.5×10^{-2} M HO_3SCF_3 , to minimize catalysis by $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$, which is significant for $[\text{Fe}(\text{CN})_6]^{4-}$ but much reduced when it is protonated.

For each nucleophile the data showed a monotonic increase of k with R , k more than tripling at $R = 4$, at which point further increase is modest. This behavior suggests that ion clusters of high order are formed and that the affinity of anion for cation remains high even for the fourth anion being added. These surprising results motivated us to investigate the clustering phenomenon by an alternative method.

In each of the systems an intervalence absorption band appears, and it is expected that its intensity will increase with the number of oscillators and, therefore, increase with R . Although considerable spectrophotometric work has been done with ion pairs,³ we have found nothing in the literature on clusters of higher order. In our investigation, rather than depending on extinction coefficients to measure the oscillator strength of the outer-sphere intervalence absorption, because the band for $[\text{Ru}(\text{CN})_6]^{4-}$ shows asymmetry due to spin-orbit coupling,^{3a} we have measured the areas of the absorption envelopes.⁴ The band maxima are observed to change only slightly as the number of oscillators in a cluster increase (see caption to Figure 2 where the range for the system showing the greatest change is entered).

Experiments were done with $[\text{Ru}(\text{NH}_3)_6]^{3+}$ as well as with $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ in combination with $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Ru}(\text{CN})_6]^{4-}$. The cations were introduced as salts of CF_3SO_3^- , and the anions as the Na^+ salts. A set of experiments was performed in 1.5×10^{-2} M HO_3SCF_3 , the reaction medium of

the kinetic studies, and another set in unacidified solutions. Lacking acid, the interaction of either anion with $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ results in substantial proton transfer—the ion pair $[\text{Ru}(\text{NH}_3)_5\text{OH}]^{2+}, [\text{M}(\text{CN})_6\text{H}]^{3-}$ is formed—and in such solutions our detailed studies were limited to $[\text{Ru}(\text{NH}_3)_6]^{3+}$. To minimize the formation of inner-sphere products, the experiments with the aquo cation were done at 10 °C rather than at ambient temperature, and in the ~15 s interval between mixing and measurement, formation of the inner-sphere product was a minor perturbation. Most of the experiments were done with anion concentration equal to or in excess of that of the cation and with the cation at 2.0×10^{-4} M, a concentration high enough, as shown by the kinetic studies, to result in essentially complete ion pair formation even in 1.5×10^{-2} M H^+ . In some systems, a cation concentration as high as 6×10^{-4} M could be tolerated without serious complication by precipitation. Variation of the cation concentration in such cases showed that the features of the data we shall draw attention to are independent of concentration. Precipitation was a factor in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ – $[\text{Fe}(\text{CN})_6]^{4-}$ system even in the low concentration range, but it is sporadic. By repetition, with selection of only data for which no excess absorption is observed at the far wings of the band, consistent and reproducible results were obtained.

In Figure 1, the data obtained, for the acidic medium, on the areas as a function of R are summarized, while Figure 2 presents the data obtained in the absence of acid. The abscissa “concentration ratio” is to be read as R for the three lower plots, but for the topmost profile it is the inverse, the cation $[\text{Ru}(\text{NH}_3)_6]^{3+}$ being in excess.

A striking feature of the data for the systems with the anion in excess is that as R increases at constant cation concentration the areas level off to a constant value at $R = 8$. This feature is displayed most prominently in the data for $[\text{Ru}(\text{CN})_6]^{4-}$ in Figure 1 but is realized in the other cases as well. In contrast to this when the cation clusters about the anion, the “break” in the profile appears not at 8 but when the concentration ratio reaches 6 (Figure 2). For the inverse case the experiments in nonacidified media were feasible only with $[\text{Ru}(\text{NH}_3)_6]^{3+}$ in combination with $[\text{Ru}(\text{CN})_6]^{4-}$, inner-sphere complex formation interfering when $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ is used in place of the hexaammine and precipitation vitiating attempts to use $[\text{Fe}(\text{CN})_6]^{4-}$.

For cation in excess (Figure 2) there is a monotonic increase of area with concentration ratio, but for the inverse case, there is an abrupt interruption when the concentration ratio is raised above 2, exhibited also for the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ – $[\text{Fe}(\text{CN})_6]^{4-}$ system. In acidic solution (Figure 1) interruptions, which are especially noticeable for the $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ – $[\text{Ru}(\text{CN})_6]^{4-}$ system, are also observed, but now they occur at higher values of R (~5).

The gross features thus far described suggest that when the cation is in excess, it is held to the central ion by hydrogen bonding, and this structure is retained in the terminal cluster. In the reverse case, under comparable conditions (no added electrolyte) the hydrogen-bonded structure is maintained only

(1) Pouloupoulou, V. G.; Li, Z.-W.; Taube, H. *Inorg. Chim. Acta* **1994**, 225, 173.

(2) A more complete report on the kinetics of substitution is in preparation.

(3) (a) Curtis, J. C.; Meyer, T. J. *J. Inorg. Chem.* **1982**, 21, 1562. (b) Miralles, A. J.; Szecsy, A. P.; Haim, A. *Inorg. Chem.* **1982**, 21, 697. (c) Haim, A. *Comments Inorg. Chem.* **1985**, 4, 113. (d) Vogler, A.; Osman, A. H.; Kunkely, H. *Coord. Chem. Rev.* **1985**, 64, 159. (e) Curtis, J. C.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, 100 (19), 6284. (f) Kremer, E.; Cha, G.; Morkevicius, M.; Seaman, M.; Haim, A. *Inorg. Chem.* **1984**, 23, 3028. (g) Rybak, W.; Haim, A.; Netzel, T. L.; Sutin, N. *J. Phys. Chem.* **1981**, 85, 2856. (h) Toma, H. E. *J. Chem. Soc., Dalton Trans.* **1980**, 471. (i) Toma, H. E. *Can. J. Chem.* **1979**, 57, 2079. (j) Billing, R.; Khoshtariya, D. E. *Inorg. Chem.* **1994**, 33, 4038. (k) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, 90, 3657. (l) Khoshtariya, D. E.; Kjaer, A. M.; Marsagishvili, T. A.; Ulstrup, J. *J. Phys. Chem.* **1991**, 95, 8797. (m) Khoshtariya, D. E.; Kjaer, A. M.; Marsagishvili, T. A.; Ulstrup, J. *J. Phys. Chem.* **1992**, 96, 4154.

(4) An HP 8452A diode array spectrophotometer was used, with a 5 cm path length cell. The intervalence bands were fitted with two Gaussian components by use of Grams/386 software. In the case of $[\text{Ru}(\text{CN})_6]^{4-}$, the bands were fitted well with the two components at an intensity ratio 2/1 and split by $3\lambda/2$ with $\lambda = 1000 \text{ cm}^{-1}$, and for $[\text{Fe}(\text{CN})_6]^{4-}$, bands were fit with $\lambda = 410 \text{ cm}^{-1}$. The areas of the intervalence bands were calculated as the product of $\epsilon_{\text{max}} (\text{M}^{-1} \text{cm}^{-1})$ and $\Delta\nu_{1/2} (\text{cm}^{-1})$.

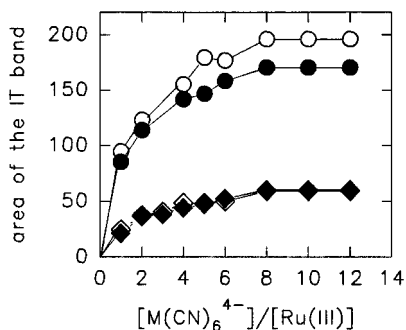


Figure 1. Areas of the intervalence absorption bands as a function of the concentration ratio, R , in $\text{CF}_3\text{SO}_3\text{H}$ (1.5×10^{-2} M). $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} = [\text{Ru}(\text{NH}_3)_6]^{3+} = 2.0 \times 10^{-4}$ M. Key: ●, $[\text{Ru}(\text{CN})_6]^{4-}/[\text{Ru}(\text{NH}_3)_6]^{3+}$ ($E_{\text{max}} = 19.7 \times 10^3 \text{ cm}^{-1}$); ○, $[\text{Ru}(\text{CN})_6]^{4-}/[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ($E_{\text{max}} = 20.0 \times 10^3 \text{ cm}^{-1}$); ◆, $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Ru}(\text{NH}_3)_6]^{3+}$ ($E_{\text{max}} = 16.2 \times 10^3 \text{ cm}^{-1}$); ◇, $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ($E_{\text{max}} = 16.8 \times 10^3 \text{ cm}^{-1}$).

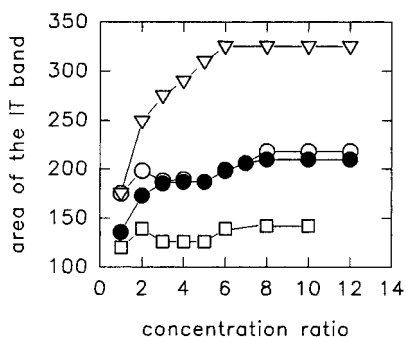


Figure 2. Areas of the intervalence absorption bands as a function of the concentration ratio in neutral solutions. The center ion concentration is 2.0×10^{-4} M. Key: ▽, $[\text{Ru}(\text{NH}_3)_6]^{3+}/[\text{Ru}(\text{CN})_6]^{4-}$ ($E_{\text{max}} = 18.0\text{--}18.4 \times 10^3 \text{ cm}^{-1}$); ○, $[\text{Ru}(\text{CN})_6]^{4-}/[\text{Ru}(\text{NH}_3)_6]^{3+}$ ($E_{\text{max}} = 18.0 \times 10^3 \text{ cm}^{-1}$); ●, $[\text{Ru}(\text{CN})_6]^{4-}/[\text{Ru}(\text{NH}_3)_6]^{3+}$ in 1.5×10^{-2} M LiO_3SCF_3 ($E_{\text{max}} = 18.1 \times 10^3 \text{ cm}^{-1}$); □, $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Ru}(\text{NH}_3)_6]^{3+}$ ($E_{\text{max}} = 13.1 \times 10^3 \text{ cm}^{-1}$).

to $R = 2$, after which there is collapse to a structure in which the anions begin to occupy the 8 octahedral faces. While there is an energy benefit for such change when CN^- approaches the central ion positive charge, there is none in the reverse case. Interanion repulsion is reduced on protonation; the change in structure then does not take place until a higher value of R is reached.

It needs to be pointed out that the kinetic data that indicate that four anions cluster about the central cation are not in conflict with the higher order terminal clusters suggested by the spectrophotometric measurements. Were substitution largely $\text{S}_{\text{N}}1$ in character it is not impossible that four anions in the complex suffice to prevent re-entry of H_2O into $[\text{Ru}(\text{NH}_3)_5]^{3+}$, additional anions having no effect.²

The repulsion between the peripheral ions leads to a loosening of the cluster (i.e., to an increase in the central ion–peripheral ion distance) which results in a decrease in oscillator strength. This may account for the difference in area observed for

$[\text{Ru}(\text{NH}_3)_6]_2^{3+}, [\text{Ru}(\text{CN})_6]^{4-}$ as compared to $[\text{Ru}(\text{NH}_3)_6]^{3+}, -[\text{Ru}(\text{CN})_6]_2^{4-}$, 249 and 198 respectively; the electrostatic attraction terms are the same, but the repulsion terms are in the ratio of 9 to 16. This factor, together with the change in structure when the anion is peripheral, contributes to, and may be the major cause of, the remarkably small increase in area noted in Figure 2, on proceeding from the ion pair to $R = 8$, 175 to 218 for $[\text{Ru}(\text{CN})_6]^{4-}$ about $[\text{Ru}(\text{NH}_3)_6]^{3+}$ and 120 to 142 for $[\text{Fe}(\text{CN})_6]^{4-}$ about the same cation.

A surprising result is that the oscillator strength for $[\text{Ru}(\text{NH}_3)_6]^{3+}, [\text{Ru}(\text{CN})_6]^{4-}$ is greater than it is for $[\text{Ru}(\text{NH}_3)_6]^{3+}, -[\text{Fe}(\text{CN})_6]^{4-}$, the ratio being 1.5. The values of E_{max} for the two systems are 18.0×10^3 and $13.1 \times 10^3 \text{ cm}^{-1}$, respectively, so that the electronic coupling for $[\text{Ru}(\text{CN})_6]^{4-}$ is about 1.4-fold greater than it is for $[\text{Fe}(\text{CN})_6]^{4-}$ as electron donor. Because the proton affinity of $[\text{Fe}(\text{CN})_6]^{4-}$ is considerably higher than that of $[\text{Ru}(\text{CN})_6]^{4-}$, a tighter hydrogen bond is expected for it (the differences in affinity for protons accounts for the greater disparity in areas for the two nucleophiles in acidic solution (Figure 1) as compared to nonacidic solution (Figure 2), protonation leading to a loosening of structure). Moreover, to the extent that the charge transfer state mixes into the ground state, this contribution to the electronic coupling is expected to be greater for $[\text{Fe}(\text{CN})_6]^{4-}$. The comparison suggests that the delocalization leading to increased oscillator strength is not through the hydrogen bonds but arises from face to face overlap—enabled by the hydrogen bond interaction—the radial extension of the πd orbitals being greater for $[\text{Ru}(\text{CN})_6]^{4-}$ than for $[\text{Fe}(\text{CN})_6]^{4-}$. That the area for the ion pair $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}, [\text{Ru}(\text{CN})_6]^{4-}$ in Figure 1 is seen to be slightly greater than that for $[\text{Ru}(\text{NH}_3)_6]^{3+}, [\text{Ru}(\text{CN})_6]^{4-}$, 94 compared to 85, suggests that in the former case H_2O rather than NH_3 is involved in hydrogen bonding, but the slight increase for the former may be purely geometric in origin.

The major effect of an acidic medium arises from protonation of the anions. Acid will exert an additional effect, acting as electrolyte. The results shown in Figure 2 for an experiment with LiO_3SCF_3 present at 1.5×10^{-2} M shows a marked effect of the electrolyte in “loosening” the hydrogen-bonded structures but having virtually no effect on the oscillator strength in the more compact structure which we infer as taking over at $R = 3$. Whether or not extra electrolyte is present, the counterions, Na^+ for $[\text{M}(\text{CN})_6]^{4-}$ in excess and O_3SCF_3^- for cation in excess, must play a role in stabilizing the cluster, but the nature of their participation is not revealed by these studies.

Acknowledgment. This work was supported by the NSF (Grant No. CHE9120158-AO1).

Supporting Information Available: Figure S1 (first-order reaction rates for the collapse of the outer-sphere complexes of $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ to the inner-sphere products) and Figure S2 (intervalence charge transfer absorption bands for the $[\text{Ru}(\text{CN})_6]^{4-}-[\text{Ru}(\text{NH}_3)_6]^{3+}$ system, as a function of increasing R) (3 pages). Ordering information is given on any current masthead page.

IC9614428