to vary significantly with spin-state changes but only slightly with oxidation-state changes.[24]

Perhaps the most striking aspect of this work is the degree to which the experimental spectra are reproduced by using a simple six-atom model and non-self-consistent calculations. Previous studies[25,26] have suggested that 30–50 atom clusters are required to obtain reasonable agreement with experiment. The outer-shell atoms may well contribute to the detailed structure of metalloporphyrin edges;[26] however, the recent work demonstrates that it is possible to reproduce the major features of the experimental spectra by using only first-shell atoms. The relative ease of our calcultions suggests that it may be feasible to use the MSW Xα extended continuum method to study low-symmetry complexes.

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Registry No. Cr^{IV}(TPP)O, 80584-26-5; Cr^{V}(TPP)M, 84174-28-7.

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Proton NMR Investigation of the Electron-Exchange Reaction between Hexaammineruthenium(II) and Hexaammineruthenium(III) Ions

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The rate of the electron-self-exchange reaction between $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$ has been measured by proton NMR line broadening. The system is complicated by the aquation of $[Ru(NH_3)_6]^{2+}$, which results in reduction of the small amount of $[Ru(NH_3)_6]^{3+}$ present. To reduce this difficulty, measurements were performed at 4 °C. Rate constants are $(6.6 \pm 1.0) \times 10^3$ and $(9.9 \pm 0.2) \times 10^3$ M^{-1} s^{-1} for solutions of 0.125 and 0.250 M $[Ru(NH_3)_6]Cl_2$, respectively. These rate constants are in order-of-magnitude agreement with those previously reported. The reaction appears to be catalyzed by chloride ion. A rate constant for the uncatalyzed reaction at 4 °C and an ionic strength ~0.5 M is estimated to be 3.3×10^3 M^{-1} s^{-1}. The activation enthalpy is about 5 kcal mol^{-1}.

Introduction

The electron-exchange reaction (1) between the hexaammine complexes of ruthenium(II) and ruthenium(III) is of central importance to the study of electron-transfer reactions of metal complexes. Both complexes are relatively substitution-inert, so

$$Ru(NH_3)_6^{2+} + {}^*Ru(NH_3)_6^{3+} \rightleftarrows Ru(NH_3)_6^{3+} + {}^*Ru(NH_3)_6^{2+} \quad (1)$$

that the mechanism of the reaction is outer sphere. With low-spin $(t_{2g})^6$ and $(t_{2g})^5$ 4d electron configurations there are no electronic spin state changes; a single t_{2g} electron is transferred between a singlet and a doublet state. There is little inner coordination sphere reorganization required, for the ruthenium–nitrogen bond lengths differ by only 4 pm between these low-spin states.[1] Consequently, the rate of the reaction is determined largely by outer-sphere, solvation, effects. The importance of the reaction lies in this fact, that it is a probe of the outer-sphere reorganization energy, uncomplicated by other effects.

The rate of the reaction is relatively slow, due at least in part to the small size and consequent strong solvation of the complex ions. The rate was first measured by Meyer and Taube,[2] using an elegant technique that exploited the oxidation state difference in the near-infrared spectrum of the first overtone of the N–H stretching vibration. This provided an isotopic label for the different oxidation states when one state was deuterated. The experiments were difficult, and the rates could not be determined precisely. Furthermore, some unexplained nonreproducibility was encountered. Nevertheless, their rate constant of $(8 \pm 1) \times 10^2$ M^{-1} s^{-1} at 25 °C with $\mu = 0.013$ in trifluoroacetic acid has been used successfully in the calculation of other rate constants by the Marcus cross-reaction relationship. Alternatively, a value of 4×10^3 M^{-1} s^{-1} at $\mu = 0.16$ in acetate buffer has been used, although this value is based on a less precise, indirect measurement of electron-transfer-catalyzed hydrogen–deuterium exchange, also subject to unexplained catalysis. (The value of 4.3×10^3 M^{-1} s^{-1} sometimes quoted[3-5] for $\mu = 0.1$ should in fact be $(4 \pm 3) \times 10^3$ M^{-1} s^{-1} obtained from these results.)

The direct measurement of the self-exchange rate gave an unexpectedly high activation energy of 10.3 ± 1.0 kcal mol^{-1}. More recently, Brown and Sutin[5] measured the rate of the cross-reaction between $[Ru(en)_3]^{3+}$ and $[Ru(NH_3)_6]^{2+}$. With the assumption that the self-exchange rate constants are the same for the hexaammine and the tris(ethylenediamine) complexes, they extracted a self-exchange rate constant of 3.2×10^3 M^{-1} s^{-1} at 25 °C and $\mu = 0.1$ in CF_3SO_3H solution. The activation enthalpy of the self-exchange reaction was calculated with the use of some additional thermodynamic data to be a more reasonable 4.5 kcal mol^{-1}.

In view of the uncertainties inherent in the original work and the assumptions now known to be incorrect required in the cross-reaction study, we have made another attempt at a direct measurement of the rate of the self-exchange reaction.

Experimental Section

Materials. Except for the weighing of solids and the purification of $[Ru(NH_3)_6]Cl_3$, all procedures were carried out under an atmosphere of

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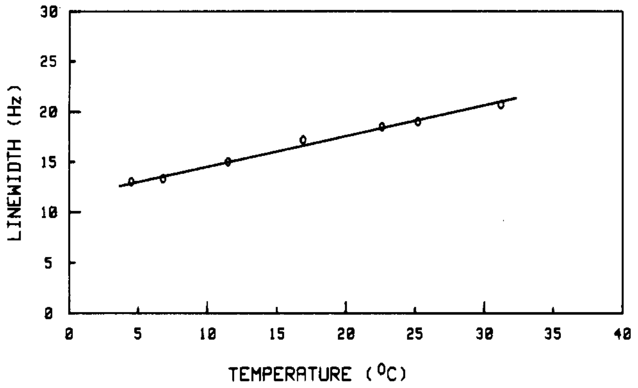

Figure 1. Temperature dependence of the line width of the 90-MHz proton NMR spectrum of $[Ru(NH_3)_6]Cl_2$ at pH 6.

argon. Trace oxygen was removed by passage of the gas through a heated column of BASF catalyst R3-11. Schlenk techniques and syringe transfers with platinum needles were employed.

The method of Lever and Powell[6] was used to prepare $[Ru(NH_3)_6]Cl_2$; $[Ru(NH_3)_6]Cl_3$ was purchased from Johnson Matthey Ltd. and purified according to a published procedure.[7] Solutions of $[Ru(NH_3)_6]Cl_2$ were prepared by weighing the solid salt directly into a 5-mm NMR tube, sealing the tube with a serum cap, and deoxygenating it with a stream of argon. Deoxygenated water at the desired pH adjusted with trifluoroacetic acid or sodium hydroxide and containing 2% v/v dioxane as an internal reference was added by syringe just prior to recording the NMR spectrum. For the exchange studies a known volume of the Ru(II) solution was added by syringe to a deoxygenated NMR tube containing a weighed sample of $[Ru(NH_3)_6]Cl_3$.

NMR Techniques. Spectra were obtained on a Bruker HX-90 instrument. The pulsed free precession mode was used due to the large solvent resonance. A Varian XL-100 FT instrument was used for the ^{14}N-decoupling experiments. A capillary of D_2O was used for an internal lock. The probe temperatures were controlled with Bruker and Varian variable-temperature units, respectively, but were measured directly with a methanol capillary in the sample.[8]

Results

$[Ru(NH_3)_6]^{2+}$ Spectrum. The ^1H NMR resonance of the $[Ru(NH_3)_6]^{2+}$ species consists of a single broad line 2.1 ppm downfield from Me_4Si. The line width is temperature-dependent, as illustrated in Figure 1. The broad line width is due to coupling with the quadrupolar ^{14}N nucleus. Decoupling of ^{14}N (at 36 °C in the Varian XL-100 spectrometer) by irradiation at 7 227 324 Hz (4180 Hz from formamide at 7.23 Mz) reduced the ^1H resonance line width from 23 to 1.6 Hz. No shift in the ^1H resonance occurred on decoupling.

The line width is independent of pH within the range 3–12 at 34 °C. Below pH 3 the line width broadens significantly, perhaps indicating a proton-catalyzed exchange of the ammine hydrogens. Between pH 3 and pH 12 the ammine protons undergo only slow exchange with the solvent, as evident from the separate ammine and solvent proton resonances and the pH independence of the line width. Nevertheless, it is necessary to use H_2O as the solvent to avoid electron-exchange-catalyzed proton substitution by deuterium.[2] Because of the consequent large solvent resonance signal, the spectrometer was operated in a continuous wave mode.

Loss of $[Ru(NH_3)_6]^{2+}$. Addition of small quantities of $[Ru(NH_3)_6]Cl_3$ to solutions of $[Ru(NH_3)_6]Cl_2$ causes additional broadening of the diamagnetic Ru(II) resonance, but this additional broadening decays rapidly. The disappearance of the Ru(III)-induced broadening is illustrated in Figure 2 for a 0.25 M solution of $[Ru(NH_3)_6]Cl_2$ at pH 6 and 25 °C. The rate of decay of the Ru(III)-induced broadening of the Ru(II) resonance increases with the concentration of $[Ru(NH_3)_6]Cl_2$ in the range 0.10–0.37 M, with an increase in acidity from pH 6 to pH 3, and with an increase in temperature from 25 to 35 °C.

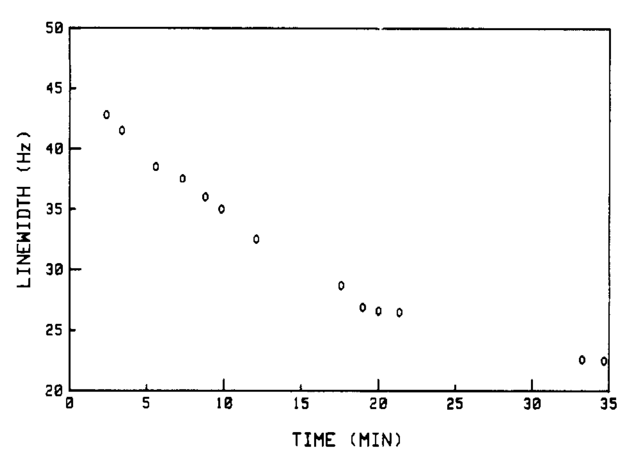

Figure 2. Time dependence of the $[Ru(NH_3)_6]Cl_3$-induced broadening of the proton NMR spectrum of 0.250 M $[Ru(NH_3)_6]Cl_2$ at pH 6 and 25 °C.

The following reaction scheme is consistent with these observations:

$$\mathrm{Ru(NH_3)_6^{2+} + H_2O \xrightarrow{k_1 + k_2[H^+]} Ru(NH_3)_5(H_2O)^{2+} + NH_3} \tag{2}$$

$$\mathrm{Ru(NH_3)_5(H_2O)^{2+} + Cl^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ru(NH_3)_5Cl^+ + H_2O} \tag{3}$$

$$\mathrm{Ru(NH_3)_5Cl^+ + Ru(NH_3)_6^{3+} \overset{K_4}{\rightleftharpoons} Ru(NH_3)_5Cl^{2+} + Ru(NH_3)_6^{2+}} \tag{4}$$

Hydrolysis of hexaammineruthenium(II) ion gives the aquapentaammineruthenium(II) complex which, in the presence of chloride, forms the chloropentammineruthenium(II) complex. The potential of this complex is such that it reduces the hexaammineruthenium(III) ion. The net effect of these reactions is to convert some $[Ru(NH_3)_6]^{3+}$ into $[Ru(NH_3)_6]^{2+}$ and hence remove this Ru(III) species as a source of electron-exchange-induced line broadening.

It is reasonable to assume that the rate of establishing equilibrium in reaction 4 by electron transfer is rapid relative to substitution reactions 2 and 3. From the known rate constants[9] k_3 of 9.0 $M^{-1}\ s^{-1}$ and k_{-3} of 6.3 s^{-1} and the high chloride ion concentration, it can be seen that equilibrium 3 is also established rapidly relative to the slower aquation reaction 2. At pH 6 the thermal aquation reaction is rate-determining ($k_1 = 9.3 \times 10^{-6}$ s^{-1}),[10] but as the acidity is increased to pH 3 the acid-catalyzed process begins to contribute to the aquation ($k_2 = 1.24 \times 10^{-3}$ $M^{-1}\ s^{-1}$),[11] accounting for the increased rate of disappearance of the Ru(III)-induced broadening at the lower pH.

The loss of the Ru(III)-induced broadening is initially linear, since the loss of $[Ru(NH_3)_6]^{3+}$ is directly proportional to the rate of aquation of $[Ru(NH_3)_6]^{2+}$. Increasing the concentration of $[Ru(NH_3)_6]^{2+}$ increases the *rate* of aquation and hence the rate of loss of broadening. The concentration of $[Ru(NH_3)_6]^{3+}$ required to produce the observed broadening is obtained from the rate of electron exchange established below. The rate of loss of the broadening is then a measure of the rate of aquation of $[Ru(NH_3)_6]^{2+}$. From the data in Figure 2 this rate constant is estimated to be 1.0×10^{-5} s^{-1} (25 °C, pH 6, μ = 0.75 M). This is in satisfactory agreement with the previously reported rate constant of 9.3×10^{-6} s^{-1} (25 °C, pH 5, μ = 0.10).[10] The value of 1.0×10^{-5} s^{-1} is only an estimate, however, both because of the indirect way in which it was obtained and because of the uncertainty of the positions of the equilibria of reactions 3 and 4.

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The nonlinear portion of the curve in Figure 2 indicating a decrease in the rate of loss of $[Ru(NH_3)_6]^{3+}$ is inconsistent with the above simple interpretation. Since the concentration of Ru(II) is much greater than that of Ru(III), the rate of loss of $[Ru(NH_3)_6]^{3+}$ is essentially the constant rate at which a small fraction of $[Ru(NH_3)_6]^{2+}$ hydrolyzes. The chloride ion concentration is constant so the equilibrium of reaction 3 is unaffected by the extent of reaction. The position of equilibrium 4, however, does change as $[Ru(NH_3)_6]^{3+}$ is consumed. The reduction potentials for the half-reactions $[Ru(NH_3)_5Cl]^{2+/+}$ and $[Ru(NH_3)_6]^{3+/2+}$ are −42 and +51 mV, respectively.[12,13] Hence the equilibrium constant K_4 is approximately 40. As the aquation reaction proceeds, $[Ru(NH_3)_6]^{3+}$ is consumed and $[Ru(NH_3)_5Cl]^{+}$ is produced. Reaction 4 does not then proceed completely to the right, and the rate of reduction of $[Ru(NH_3)_6]^{3+}$ becomes less than the rate of aquation.

Although the presence of chloride ion exacerbates the problem of the disappearance of $[Ru(NH_3)_6]^{3+}$ because of the low reduction potential of $[Ru(NH_3)_5Cl]^{+}$, removal of chloride does not eliminate the problem. The $[Ru(NH_3)_5(H_2O)]^{2+}$ complex generated by the aquation reaction has a potential of +67 mV,[12,13] so that some $[Ru(NH_3)_6]^{3+}$ could be reduced directly by this species. Other cmplexes with much higher reduction potentials[13] can be generated from $[Ru(NH_3)_5(H_2O)]^{2+}$, such as $[Ru(NH_3)_5py]^{2+}$ (298 mV) or $[Ru(NH_3)_5(CH_3CN)]^{2+}$ (426 mV), but a kinetics difficulty ensues. To be effective, the capture of $[Ru(NH_3)_5(H_2O)]^{2+}$ by a substitution reaction must occur more rapidly than its oxidation by $[Ru(NH_3)_6]^{3+}$. Since the second-order rate constants for ligand substitution[14] are of the order 10^{-1} M^{-1} s^{-1} and those for electron transfer likely to be at least 10^3 M^{-1} s^{-1}, the dominance of substitution over oxidation can only be achieved at very high ratios of ligand to ruthenium(III), conditions unsuitable for the exchange experiment.

Electron-Exchange Rates. To reduce the effects of the aquation of $[Ru(NH_3)_6]^{2+}$ on the measurement of its exchange reaction with $[Ru(NH_3)_6]^{3+}$, we have adopted the alternative of working at a lower temperature. Measurements were made at 4 °C, at which temperature the extent of aquation is not significant during the time of the experiment. A few measurements were performed at 25 °C, and the $[Ru(NH_3)_6]^{3+}$-induced broadening was obtained by back-extrapolation to zero time.

It is necessary to establish that the line broadening is in the slow-exchange regime of NMR relaxation processes.[15] Customarily this is done by observation of the temperature dependence of the process, but this is precluded by the thermal hydrolysis reaction described above. Alternatively, a direct assessment of the slow-exchange conditions can be made. These are that $(\Delta\omega)^2 >> T_2^{-2}, \tau^{-2}$, where $\Delta\omega$ is the chemical shift difference (in radians) between the exchanging sites, $T_2^{-1} = \pi(\Delta\nu)$, where $\Delta\nu$ is the line width of the dilute paramagnetic site (in hertz), and τ is the lifetime of a nuclear spin in the paramagnetic site. For the second-order electron-exchange reaction $\tau = (k[\mathrm{Ru(III)}])^{-1}$. The proton NMR spectrum of $[Ru(NH_3)_6]^{3+}$ has been reported[16] to be a single broad line with a chemical shift of 14 kHz and a relaxation time T_2^{-1} of 4×10^3 s^{-1}. Hence $(\Delta\omega)^2 > 10^9$ s^{-2} while $T_2^{-2} \approx 10^7$ s^{-2} and $\tau^{-2} < 10^7$ s^{-2} for an exchange rate constant of 10^4 M^{-1} s^{-1}. The slow-exchange conditions appear to be satisfied. Consequently, the exchange rate constant is related to the exchange-induced line broadening as $\pi(\Delta\nu_{ex}) = k[\mathrm{Ru(III)}]$.

The dependence of the exchange-induced broadening of the $[Ru(NH_3)_6]^{2+}$ resonance on the $[Ru(NH_3)_6]^{3+}$ concentration is shown in Figure 3 for two sets of experiments using $[Ru(NH_3)_6]Cl_2$ concentrations of 0.125 and 0.250 M. With no other added electrolyte the chloride ion concentrations were 0.250 M and 0.500 M and the ionic strengths 0.375 and 0.750, respectively. According to the slow-exchange conditions, the line broadening should be independent of the concentration of $[Ru(NH_3)_6]^{2+}$. This was tested in an experiment using 0.125 M $[Ru(NH_3)_6]Cl_2$ to which was added 0.125 M $BaCl_2$ to bring the chloride concentration to 0.500 M and the ionic strength to 0.750 M. The induced broadening was the same as that observed when 0.250 M $[Ru(NH_3)_6]Cl_2$ was used (see data point * in Figure 3), consistent with slow exchange.

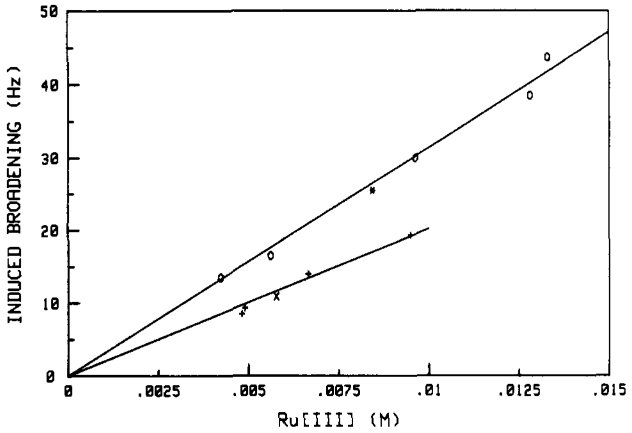

Figure 3. Dependence of the proton NMR line width of $[Ru(NH_3)_6]Cl_2$ on the concentration of $[Ru(NH_3)_6]Cl_3$ at 4 °C: (○) 0.250 M $[Ru(NH_3)_6]Cl_2$; (+) 0.125 M $[Ru(NH_3)_6]Cl_2$; (*) 0.125 M $[Ru(NH_3)_6]Cl_2$ and 0.125 M $BaCl_2$; (×) 0.125 M $[Ru(NH_3)_6]Cl_2$ and 0.375 M ammonium trifluoroacetate.

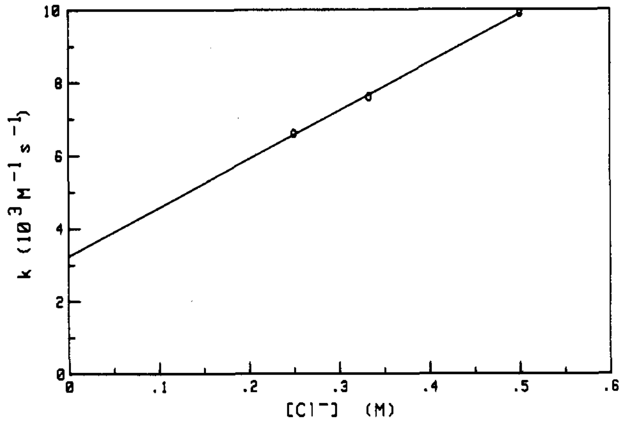

Figure 4. Dependence of the exchange broadening interpreted as a chloride ion dependence.

The exchange rate constants at 4 °C obtained from the slopes of the lines in Figure 3 are $(6.6 \pm 1.0) \times 10^3$ and $(9.9 \pm 0.2) \times 10^3$ M^{-1} s^{-1} for the 0.125 M (μ = 0.375 M) and 0.250 M (μ = 0.750 M) solutions of $[Ru(NH_3)_6]Cl_2$, respectively.

The difference in rate between the 0.125 and 0.250 M $[Ru(NH_3)_6]Cl_2$ solutions is therefore due either to the difference in ionic strength between the two solutions or to the difference in chloride ion concentrations. To distinguish between these possibilities a further experiment was performed with 0.125 M $[Ru(NH_3)_6]Cl_2$ but with the ionic strength increased to 0.75 M by using an ammonium trifluoroacetate solution instead of barium chloride (see data point × in Figure 3). In this case no increase in rate was observed over that for a solution of 0.125 M $[Ru(NH_3)_6]Cl_2$ without added electrolyte. Hence, it appears that in these rather concentrated solutions ionic strength effects are saturated and the difference in rates is due to a specific chloride ion effect.

This is consistent with the final observation in this series of experiments, which is that the observed broadening increases linearly with the concentration of $[Ru(NH_3)_6]Cl_2$ in the absence of other added electrolyte (Figure 4). Extrapolation to zero concentration gives an intercept of 3.3×10^3 M^{-1} s^{-1}, which can be interpreted as the rate constant at 4 °C for electron exchange without participation of a chloride ion, but in solutions of high ionic strength. Evaluation of a comparable second-order rate constant for electron transfer involving chloride ion from the slope

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in Figure 4 requires knowledge of the ion-pair equilibrium constant. This has been measured at higher temperatures for ion pairs of $[Ru(NH_3)_6]^{3+}$ with halide ions.[17] From the temperature dependence a value of 11 M^{-1} is calculated at 4 °C and zero ionic strength. This value, however, depends on ionic strength. From the Debye–Hückel parameters obtained from spectrophotometry at 25–50 °C, we calculate that at 4 °C the fraction of ion-paired $[Ru(NH_3)_6]^{3+}$ increases from 0.45 to 0.71 as the chloride ion concentration increases from 0.25 to 0.50 M. Hence, these parameters do not predict the linear increase illustrated in Figure 4. It is likely that these data reflect a mixture of both ionic strength and specific ion effects. They do indicate that chloride ion can facilitate electron transfer between ruthenium complexes. Chloride ion participation was previously observed in the oxidation of $[Ru(NH_3)_6]^{2+}$ by $[Fe(H_2O)_6]^{3+}$.[2] A second-order rate constant of the order of 1×10^4 M^{-1} s^{-1} can be estimated for the electron-exchange reaction between the $[Ru(NH_3)_6]^{3+},Cl^-$ ion pair and $[Ru(NH_3)_6]^{2+}$. Considerable further work would be required to elucidate properly the role of counterions in this electron-transfer reaction.

A few measurements of the exchange rate were made at 25 °C by a back-extrapolation procedure. With 0.25 M $[Ru(NH_3)_6]Cl_2$ solutions a rate constant of 2.2×10^4 M^{-1} s^{-1} was obtained. From the data at 4 and 25 °C a value for ΔH^* of 5 kcal mol^{-1} can be calculated. While this is in good agreement with the results of Brown and Sutin,[5] a detailed study was not pursued because of the experimental difficulties and the composite nature of the observed rate constant.

Discussion

Proton magnetic resonance provides a direct but not entirely satisfactory means of investigating the electron-exchange reaction between $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$. A major difficulty arises from the instability of $[Ru(NH_3)_6]^{2+}$ to hydrolysis during the minutes required to acquire a spectrum (Figure 2). Because of the relative redox potentials involved, hydrolysis of a small fraction of the diamagnetic $[Ru(NH_3)_6]^{2+}$ present in excess leads to the consumption of a large fraction of the paramagnetic $[Ru(NH_3)_6]^{3+}$, which is present in low concentration. Lowering the concentration of $[Ru(NH_3)_6]^{2+}$ to reduce the rate of its hydrolysis only lengthens the time required to acquire its spectrum. Increasing the concentration of $[Ru(NH_3)_6]^{3+}$ causes an unacceptably broad resonance. Consequently, the experimental conditions under which the reaction can be studied are limited. These observations may account, however, for some of the difficulties encountered in the original work, for it is apparent that variations in the time used for experimental procedures could lead to variations in effective concentrations and results.

The rate constants found in the present work are in reasonable agreement with those reported previously by Meyer and Taube[2] and by Brown and Sutin.[5] Our absolute values are somewhat higher, reflecting both the higher ionic strength of the solutions used in these NMR studies and the presence of chloride ions in the place of trifluoroacetate or trifluoromethanesulfonate ions. Significantly, the activation enthalpy was found to be approximately 5 kcal mol^{-1}, which is in agreement with that obtained indirectly by Brown and Sutin[5] but is only half that reported by Meyer and Taube.[2]

Because of the difficulty of making reliable corrections for differences in ionic strength,[5] it is not appropriate to make detailed comparisons among the various rate constants and conditions under which the reaction has been studied. The present results serve to confirm the order-of-magnitude correctness of the previously reported rate constants, to remove the anomaly of the unreasonably large activation enthalpy originally reported, and to emphasize the desirability of examining the role of anions in these outer-sphere electron-transfer reactions by using a technique that allows studies at low ionic strengths.

Acknowledgment. This work was supported by the Australian Research Grants Scheme.

Registry No. $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(NH_3)_6^{2+}$, 19052-44-9; Cl^-, 16887-00-6.

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Weak Curie-Type Paramagnetism of High-Nuclearity Platinum Carbonyl Clusters: Anomalous Magnetic Behavior

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This paper reports the magnetic behavior of large platinum carbonyl clusters: $(Bu_4N)_2[Pt_6(CO)_{12}]$ (**1**), $(Bu_4N)_2[Pt_9(CO)_{18}]$ (**2**), $(Bu_4N)_4[Pt_{19}(CO)_{22}]$ (**3**), and $(PPN)_2[Pt_{38}(CO)_{44}H_x]$ (**4**). We found these platinum clusters to be "diamagnetic" at room temperature but "weakly paramagnetic" at low temperature. The observed paramagnetism (which is an anomaly considering that these are all even-electron clusters) can be described by the simple Curie law. The Van Vleck temperature-independent paramagnetic susceptibility χ_p increases with cluster size. Such marked increase in χ_p with increasing cluster size can be attributed to the decrease in the energy gap between the occupied states and the unoccupied states as the cluster size increases. Another important result is that the effective magnetic moment, μ_{eff}, falls in the narrow range of 0.35–0.55 μ_B per cluster. From the observed magnetic moments, we calculated the μ_{eff} value per atom to be 0.1 ± 0.02 μ_B, a value very close to the corresponding value of 0.09 μ_B observed by Marzke et al. for platinum crystallites containing approximately 400 atoms. The fact that these molecular platinum clusters have magnetic properties very similar to (indeed approaching) those of the small crystallites is a strong indication that these clusters begin to enter the *quantum-size regime* where the magnetic properties are distinctly different from those of the bulk as well as those of the molecules.

Introduction

Recently there has been considerable interest in the magnetic behavior of high-nuclearity transition-metal clusters since they represent ideal models for the transition of molecular units to small particulates to bulk metal.[1,2] These molecular clusters, synthesized by chemical means,[3] have a single *size* and *shape* as opposed to

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