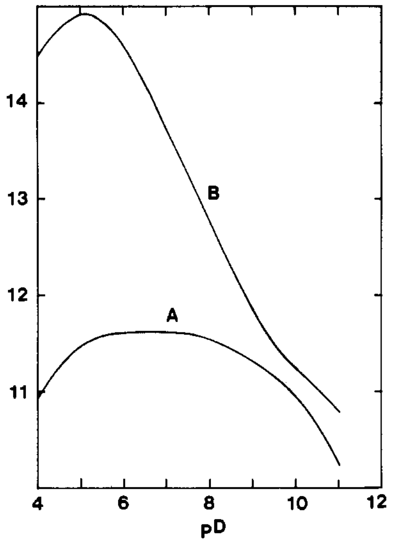

Figure 5. Logarithm of the conditional formation constants vs. pD for the CH_3Hg^{II} complexes of (A) cysteine and (B) selenocysteine.

function of pH in Figure 5. Over the entire pH range, the conditional formation constants are less than those given in Table IV. At high pH (≥12), the difference between the conditional formation constants is the same as the difference in Table IV because both ligands are fully deprotonated and both conditional formation constants are affected equally by the competitive reaction of CH_3Hg^+ with hydroxide. However, as the pH is decreased, the difference increases because competitive protonation of the thiolate group occurs at high pH. The increased stability of the selenol complexes relative to that of the thiol complexes as the pH is decreased is also apparent from the pH dependence of curves C and D in Figure 3; as the pH is decreased, curves C and D shift closer to curve A, indicating a larger fraction of the total MAA has been displaced by selenol.

The conditional formation constants at pH 7.4 are of particular interest with respect to the possible binding of CH_3Hg^{II} by the selenol group of glutathione peroxidase. log K_{fc} for the selenocysteine complex is 13.35, while log K_{fc} of the CH_3Hg^{II} complexes of glutathione and hemoglobin, the two most abundant thiol-containing molecules in human erythrocytes,[2] are 11.55 and 10.7, respectively.[7] With use of the conditional formation constant of the selenocysteine complex as an estimate for the formation constant of the CH_3Hg^{II}–glutathione peroxidase complex and concentrations of 2×10^{-6}, 2×10^{-3}, and 5×10^{-3} M for glutathione peroxidase,[30] glutathione,[2] and hemoglobin in red blood cells, 1.6, 7.7, 14, and 47% of the selenol groups of glutathione peroxidase are predicted to be complexed by CH_3Hg^{II} at total CH_3Hg^{II} concentrations of 1×10^{-6}, 5×10^{-6}, 1×10^{-5}, and 5×10^{-5} M. Even though K_{fc} for the selenocysteine complex is somewhat larger than those of the glutathione and hemoglobin complexes, a somewhat larger fraction of the total amount of CH_3Hg^{II} is complexed by the thiol ligands because of their much higher concentrations. As a reference point, red blood cell concentrations of CH_3Hg^{II} up to $\sim 3 \times 10^{-5}$ M were reported in the 1972 epidemic of CH_3Hg^{II} poisoning in Iraq.[31]

Acknowledgment. This research was supported by a strategic grant to D.L.R. from the Natural Sciences and Engineering Research Council of Canada and by the University of Alberta. Financial support of A.P.A. by an Alberta Heritage Foundation for Medical Research postdoctoral fellowship and of K.S.T. by an AHFMR scholarship is gratefully acknowledged.

Registry No. $CH_3HgSeCH_2CO_2D$, 102493-99-2; $CH_3HgSeCH_2CH_2CO_2D$, 102494-00-8; $CH_3HgSeCH_2CH_2CH_2CO_2D$, 102494-01-9; $D_3N^+CH(CH_2SeHgCH_3)CO_2D$, 102494-02-0; $D_3N^+CH_2CH_2SeHgCH_3$, 102494-03-1; $D_3N^+CH(C(CH_3)_2SeHgCH_3)CO_2D$, 102494-04-2; $CH_3HgSeCH_2CO_2^-$, 102494-05-3; $CH_3HgSeCH_2CH_2CO_2^-$, 102494-06-4; $CH_3HgSCH_2CH_2CO_2^-$, 102494-07-5; $CH_3HgSeCH_2CH_2CH_2CO_2^-$, 102494-08-6; $CH_3HgSCH_2CH_2CH_2CO_2^-$, 102494-09-7; $CH_3HgSeCH_2CH(NH_2)CO_2^-$, 102494-10-0; $CH_3HgSeCH_2CH_2NH_2$, 102494-11-1; $CH_3HgSCH_2CH_2NH_2$, 102494-12-2; $CH_3HgSeC(CH_3)_2CH(NH_2)CO_2^-$, 102494-13-3; $CH_3HgSeCH_2CH_2OH$, 102494-14-4; CH_3Hg^{II}, 22967-92-6; selenoacetic acid, 25244-47-7; selenopropionic acid, 60746-32-9; selenobutyric acid, 42905-03-3; selenocysteine, 3614-08-2; selenopenicillamine, 36969-38-7; selenocysteamine, 21681-94-7; 2-hydroxyethaneselenol, 60718-59-4.

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(30) This value is calculated for an average selenium blood level of 230 μg/L (Shamberger, R. J. *Biochemistry of Selenium*; Plenum: New York, 1983; p 227) by assuming that all the selenium is in the erythrocytes in the form of glutathione peroxidase and that the blood has a hematocrit of 50%.

(31) Calculated from whole blood mercury concentrations reported in: Bakir, F.; Damluji, S. F.; Amin-Zaki, L.; Murtadha, M.; Khalidi, A.; Al-Rawi, N. Y.; Tikriti, S.; Dhahir, H. K.; Clarkson, T. W.; Smith, J. C.; Doherty, R. A. *Science (Washington, D.C.)* **1973**, *181*, 230. The calculations assume that there was a hematocrit of 50% and that 90% of the whole blood mercury was in the red blood cells.

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Electron Self-Exchange by Hexakis(aryl isocyanide)manganese(I/II): Concentration, Electrolyte, and Temperature Dependences

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The rate of electron self-exchange has been measured for the tetrafluoroborate salts of $Mn(CNR)_6^{+/2+}$ complexes, where R is p-$C_6H_4CH_3$ and p-$C_6H_4OCH_3$, as a function of concentration, temperature, and added tetrabutylammonium tetrafluoroborate in CD_3CN by ^1H NMR line broadening. The measured rate constants ($M^{-1}\ s^{-1}$), at 26 °C and 0.1 M added salt, and the activation parameters ΔH^* (kcal/mol) and ΔS^* (cal/(mol K)) are 3.0×10^7, 2.4, and −16 for the tolyl isocyanide complex and 4.5×10^7, 3.4, and −12 for the anisyl isocyanide complex, respectively. Through an analysis of the ionic strength dependence of the rate constant for the tolyl isocyanide complex, a rate constant of $6.1 \times 10^7\ M^{-1}\ s^{-1}$ was estimated for the condition of no electrostatic interaction between the complexes. These rate constant values are the highest measured for complexes of this type and are ca. 100 times the rate constants previously determined for $Mn(CN(C(CH_3)_3)_6^{+/2+}$ and $Mn(CNC_6H_{11})_6^{+/2+}$. It is concluded that the most likely reason for the rate enhancement is improved overlap between the donor and acceptor orbitals.

Introduction

Significant progress is being made in the understanding of electron-transfer reactions through complementary experimental and theoretical studies.[1,2] In this area we have been especially concerned with the analysis of well-defined, outer-sphere electron-transfer systems that can be studied with the use of solvents other than water. As part of this effort we have sought to ex-

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(1) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437.

(2) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980.

0020-1669/86/1325-2437$01.50/0

Table I. Summary of Kinetic Data for Electron Self-Exchange by $Mn(CNR)_6^{+/2+}$ at 0.1 M Tetrabutylammonium Tetrafluoroborate and 26 °C

ligand	$10^{-5}k$, $M^{-1}\ s^{-1}$	ΔH^*, kcal/mol	ΔS^*, cal/(mol K)	$10^{-5}k_\infty$, $M^{-1}\ s^{-1}$	r_μ, Å
$C_6H_5CH_3$	299 ± 13	2.4 ± 0.1	−16 ± 1	613 ± 19	13.5
$C_6H_4OCH_3$	448 ± 29	3.4 ± 0.2	−12 ± 1	*d*	*d*
	438 ± *a*	3.8 ± 0.2	−11 ± 1	*d*	*d*
CH_3[b]	206 ± 27	1.8 ± 0.1	−20 ± 2	924 ± 17	8.75
CH_2CH_3[b]	19.7 ± 0.6	3.6 ± 0.2	−18 ± 3	90.1 ± 5.4	8.50
$CH_2C_6H_5$[b]	13.0 ± 0.2	2.0 ± 0.3	−24 ± 2	52.2 ± 3.4	9.25
$CH(CH_3)_2$[b]	2.61 ± 0.09	4.8 ± 0.1	−18 ± 1	8.04 ± 0.41	10.25
$C(CH_3)_3$[b]	0.65 ± 0.01	5.4 ± 0.1	−19 ± 1	2.03 ± 0.11	10.25
C_6H_{11}[c]	4.38 ± 0.07	3.4 ± 0.1	−21 ± 1	13.4 ± 3.4	11.00

[a] Single point at 26 °C; 0.04 M total ionic strength. [b] From ref 4. [c] From ref 3. [d] Ionic strength dependence data not obtained.

tensively characterize the electron-self-exchange reaction of complexes of the type $Mn(CNR)_6^{+/2+}$. Previous work has employed the measurement of ^{55}Mn NMR line broadening to study the effect of concentration, solvent, temperature, pressure, and added electrolyte on the reactivity of the cyclohexyl, methyl, ethyl, isopropyl, *tert*-butyl, *n*-butyl, and benzyl isocyanide complexes.[3-6] A variety of physical studies of these complexes have also been pursued in order to better understand them and better interpret the kinetics.[7,8] This series of complexes was chosen because the electron-self-exchange reaction can be studied directly, the compounds are substitution-inert in both oxidation states, a variety of symmetric complexes can be readily synthesized, and they have adequate stability and solubility in a variety of solvents over a large temperature range.

In this paper we extend our previous work through the study of complexes of aryl isocyanides. These were not studied previously because the rates could not be measured by ^{55}Mn line broadening, but they can be studied by ^1H NMR line broadening if a methyl group is in the ligand. These complexes are of particular interest because the electron being transferred is in an orbital that is delocalized onto the C≡N and the benzene ring.[7] The alkyl complexes, including benzyl isocyanide, do not have this conjugation. Since the alkyl isocyanide complexes showed a marked rate decrease with increasing bulk of the alkyl group,[4] it is significant to know whether the conjugated systems will react as did the larger alkyl isocyanides or whether the rates will be higher.

Experimental Section

The complexes $Mn(CNR)_6(BF_4)$ and $Mn(CNR)_6(BF_4)_2$, where R is p-$C_6H_4CH_3$ (tolyl) and p-$C_6H_4OCH_3$ (anisyl), and tetrabutylammonium tetrafluoroborate ($(TBA)BF_4$), were prepared as previously described.[3,7] Acetonitrile-d_3 (Aldrich) was used without further purification.

Samples were made in 1-mL volumetric flasks and transferred to 5-mm NMR tubes under argon, by using syringe techniques and septa. The tubes were then kept at 4 °C and in the dark until used. Such solutions were stable for 2 days.

Data were collected on a Nicolet NT200WB instrument operating at 200 MHz. Acquisition parameters were a 3-μs pulse width, a 500-ms postacquisition delay, a 2000–4000-Hz sweep width, a 32K block size, and 256 pulses. The temperature was controlled within 0.5 °C by using a built-in gas-flow temperature controller. To obtain accurate line widths, the field homogeneity was carefully adjusted for each sample on the basis of the intensity of the lock signal and the area of the free induction decay signal. Line widths were obtained from the single Lorentzian lines by using the program LF on the Nicolet instrument. Typically, 150–200 points were used in the fitting.

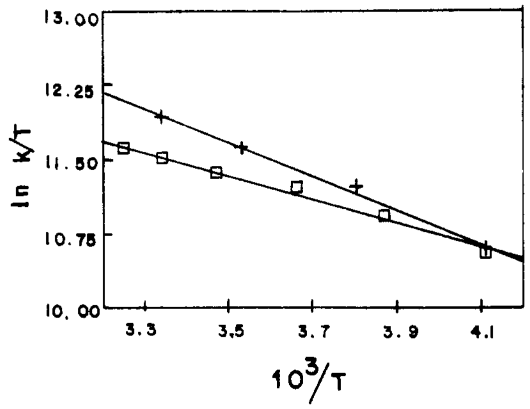

Figure 1. Eyring plots for electron-self-exchange rate constants of $Mn(CNR)_6^{+/2+}$ in the presence of 0.1 M tetrabutylammonium tetrafluoroborate in CD_3CN: (□) R = p-tolyl; (+) R = p-anisyl.

In solutions that are mixtures of the diamagnetic $Mn(CNR)_6^+$ and the paramagnetic $Mn(CNR)_6^{2+}$ complexes, the ^1H NMR resonance shifts are the weighted averages of those of the complexes measured individually. This averaging indicates that the electron-exchange process is in the fast-exchange region. Wahl has shown that in the fast-exchange limit, eq 1 can be used to calculate the rate constant for electron exchange.[9]

$$k = \frac{x_D x_P (4\pi)(\Delta\nu)^2}{c(w_{DP} - x_D w_D - x_P w_P)} \tag{1}$$

Here k is the second-order rate constant, x_D and x_P are the mole fractions of the diamagnetic and paramagnetic species, $\Delta\nu$ is the difference in resonance frequency (Hz), for the line of interest, between the pure diamagnetic and pure paramagnetic samples, w_D, w_P, and w_{DP} are the NMR line widths (Hz) at half-height for the pure diamagnetic, pure paramagnetic, and mixed samples, respectively, and c is the total molarity of the manganese complexes.

For each rate constant calculation, the spectra were obtained and the CH_3 resonances analyzed for the mixture of $Mn(CNR)_6^+$ and $Mn(CNR)_6^{2+}$, the pure $Mn(CNR)_6^+$ complex, and the pure $Mn(CNR)_6^{2+}$ complex. The last two were determined at the same total salt concentration as for the mixed sample.

Solutions of $Mn(CNR)_6^{2+}$ have been found to slowly decompose to $Mn(CNR)_6^+$ and free Mn^{2+}.[8,10,11] The presence of a very small quantity of $Mn(CNR)_6^+$ in the $Mn(CNR)_6^{2+}$ solution drastically increases the ^1H NMR line width. To avoid this, the samples prepared to contain only $Mn(CNR)_6^{2+}$ also contained a small amount of the oxidant $NOBF_4$. Total salt concentration was controlled by adding $(TBA)BF_4$.

The concentration of $Mn(CNR)_6^{2+}$ in the solution containing both oxidation states of the complex is quite low, and it can be most accurately determined from the chemical shift results by using eq 2, where the

$$x_P = \frac{\nu_{DP} - \nu_D}{\nu_P - \nu_D} \tag{2}$$

subscripts are as used before, and ν is the resonance frequency for the methyl group protons.

Results

The results of the concentration, temperature, and ionic strength dependences are summarized in the Table I. The Eyring plot of the temperature dependence data and a plot of the ionic strength

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(3) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 1338.
(4) Nielson, R. M.; Wherland, S. *J. Am. Chem. Soc.* **1985**, *107*, 1505.
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(7) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1985**, *24*, 1803.
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(9) Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542.
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(11) Fantucci, P.; Naldini, L.; Cariati, F.; Valenti, V. *J. Organomet. Chem.* **1974**, *64*, 109.

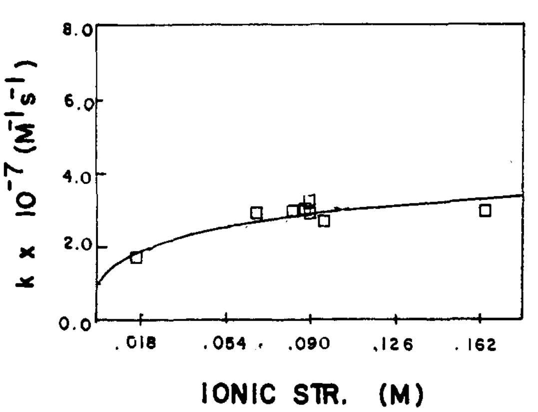

Figure 2. Ionic strength dependence for the electron-self-exchange rate constants of $Mn(CN\text{-}p\text{-}C_6H_4CH_3)_6^{+/2+}$ in CD_3CN. Ionic strength was calculated as described in the text.

dependence data are presented in Figures 1 and 2. More studies were done on the tolyl isocyanide system because more precise rate constants could be obtained for this system. This is primarily because $\Delta\nu$ is typically 14.3 ppm for the tolyl isocyanide pair, while it is only 3.1 ppm for the anisyl isocyanide pair of complexes. Activation parameters were calculated by a weighted least-squares method, assuming a 10% error in each rate constant and a 0.5 °C error in the temperature.

The ionic strength dependence data were fit to the same expressions used previously.[3] This model attributes the variation of the rate consatnt to the variation in the electrostatic work required to form the electron-transfer precursor complex. This work term decreases with increasing ionic strength; thus the measured rate increases. On the basis of earlier conductivity measurements[3] on $Mn(CNC_6H_{11})_6BF_4$, $Mn(CNC_6H_{11})_6(BF_4)_2$, and $(TBA)BF_4$, we assumed that, at the concentrations used, the $Mn(CNR)_6^+$, and $Mn(CNR)_6^{2+}$ complexes were not ion-paired, and an association constant of 7 M^{-1} was used for $(TBA)BF_4$. As an approximation, and for consistency with the value of the association constant, an extended Debye–Hückel equation for the activity coefficient was used. The result of the fit is a value of the rate at infinite ionic strength and a value for the radius term r_μ. The assumptions for this model are not strictly valid, especially the attempt to calculate activity coefficients in order to estimate the ion association of the electrolyte. However, we have not found a better method, and the whole process is used only to estimate the rate when electrostatic work is minimal. This extrapolation of the data to infinite ionic strength is not large since k_∞, 6.13×10^7 M^{-1} s^{-1}, is only twice the 0.1 M total salt value. The value of r_μ, 13.5 Å, is also consistent with previous measurements for larger complexes.[4]

The activation parameters are generally quite negative values of ΔS^* and small values of ΔH^*. For the the anisyl isocyanide complexes, the activation parmeters were also measured at low ionic strength. These data indicate a distinct change in the activation parameters, with a more favorable entropy accompanied by a less favorable enthalpy of activation for the anisyl complexes compared to the tolyl isocyanide complexes.

Discussion

The results obtained in this work can be compared to the results of Chan and Wahl[12] on complexes of the type $Ru(hfacac)_n(bpy)_{3-n}^{3-n/2-n}$, where hfacac is hexafluoroacetylacetonate, bpy is 2,2′-bipyridyl, and n is 2 or 3. Their results are generally for conditions of lower ionic strength and for different sizes and charge types, but there is a slight decrease in the measured rate constant brought on by the substitution of the conjugated bpy ligand for the hfacac ligand.

The principal conclusion of the present study, in contrast to the results for the Ru systems, is that electron self-exchange is more rapid for the aryl isocyanide complexes of the type $Mn(CNR)_6^{+/2+}$ than for any alkyl isocyanide complex. The only possible exception is the rate constant for the complexes $Mn(CNCH_3)_6^{+/2+}$ extrapolated to infinite ionic strength in order to compensate for the electrostatic work required to form the precursor complex. Thus, the phenyl groups, with their delocalized π systems conjugated with the π system of the C≡N and the Mn t_{2g} orbitals, facilitate electron transfer compared to the case of alkyl isocyanide complexes. Other general observations are that the rate is somewhat less affected by ionic strength than the other reactions, since $k_\infty/k_{\mu=0.1}$ is only 2 for the tolyl isocyanide system and is 3–4.5 for the alkyl isocyanide systems. The anisyl isocyanide complexes react somewhat more rapidly than the tolyl isocyanide ones; this difference originates from a more favorable ΔS^* despite a 1 kcal/mol less favorable ΔH^*.

The origin of these differences can be pursued within the currently available theory for outer-sphere electron-transfer reactions.[1,2] Since the reactants and products are identical, self-exchange reactions are among the best opportunites for testing these theories. The second-order rate constant, k, is represented as the product of a precursor association constant, K_a, and the first-order rate constant for electron transfer within this complex, k_{et}:

$$k = K_a k_{et} \tag{3}$$

The electron-transfer rate constant can be further represented as the product of several terms

$$k_{et} = \nu_{n,eff}\kappa_{el}(S(r,\theta))e^{-(\Delta G_{in}+\Delta G_{out})/RT} \tag{4}$$

where $\nu_{n,eff}$ is an effective nuclear frequency, κ_{el} is the electronic transmission coefficient, $S(r,\theta)$ is a steric factor, ΔG_{in} is the energy required to reorganize the complexes for electron transfer, and ΔG_{out} is the analogous energy for the solvent reorganization that must precede electron transfer. The effective nuclear frequency depends on solvent frequencies, frequencies for vibrations associated with ΔG_{in}, and the energies ΔG_{in} and ΔG_{out}. The solvent frequencies are the same as for the alkyl isocyanide complexes because the solvent is the same, and the Mn–C A_{1g} vibrational frequencies are comparable for $Mn(CNC_6H_5)_6BF_4$ and $Mn(CNC_6H_5)(BF_4)_2$ and the larger alkyl isocyanide complexes.[7] Thus $\nu_{n,eff}$ values should not be significantly different between the alkyl and aryl complexes. Similarly, values for ΔG_{in} and ΔG_{out} should be little different because the force constants for the Mn–C bonds, the sizes of the complexes, and the differences in Mn–C bond lengths between the Mn(II) and Mn(I) complexes should be similar. This leaves the precursor association constant, the steric factor, and the electronic transmission coefficient to be discussed. The steric factor and the precursor formation constant can be considered together. To the extent that only electrostatics are involved, the larger alkyl isocyanide complexes and the aryl isocyanide complexes should have similar K_a values. The rate constants for the aryl isocyanide complexes may be augmented because they have somewhat more open space between the ligands than a complex with *tert*-butyl isocyanide or cyclohexyl isocyanide ligands. This will allow somewhat closer approach with less specific angular requirements to fit the ligands together. Whatever this advantage is, it is not going to make the complexes as free to approach each other as the ethyl isocyanide complex, which still reacts 7–15 times more slowly than the aryl isocyanide complexes. A factor that is less easily evaluated is the possibility for nonelectrostatic interaction between the ligands, such as phenyl ring stacking, that stabilizes the precursor complex. Such interactions are probably not large and should be less for the anisyl complex than for the tolyl complex because the methoxy group should interfere more than the in-plane methyl group. This leaves κ, the electronic transmission coefficient, to be considered. The value of κ is 1 for limiting adiabatic behavior and decreases for other cases. Orbital overlap, and thus electron-transfer distance, will strongly influence the value of κ once the overlap decreases from some critical value. Our previous observation that the rate for electron self-exchange decreases with increasing ligand bulk for the alkyl isocyanide complexes[4] indicates that these reactions do not have a κ of 1. Thus the most likely explanation for the

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[12] Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1982**, *86*, 126.

increase in rate constant when alkyl ligands are replaced by aryl ligands is that donor-acceptor overlap is enhanced and thus κ is increased.

The interpretation of the rate variation can be tested by consideration of the activation parameters. If κ is increasing, then $\Delta S^\ddagger$ should increase toward zero and $\Delta H^\ddagger$ should be constant. The value of $\Delta S^\ddagger$ at 0.1 M salt is somewhat lower for the tolyl and anisyl isocyanide complexes than it is for the alkyl complexes. The value of $\Delta H^\ddagger$ varies for all of the reactions. There is thus some corroboration of the interpretation, but the interpretation of $\Delta S^\ddagger$ values is difficult, and the differences are small considering the precision of the measurements. Some of the complications in the interpretation of $\Delta S^\ddagger$ have been previously discussed for the manganese alkyl isocyanide complexes[4] and for ionic strength effects.[13]

In summary, we have found that electron self-exchange in the series of complexes $Mn(CNR)_6^{+/2+}$ is facilitated if the R group is aromatic and thus conjugated with the Mn—C≡N unit. The most likely reason for this rate enhancement is enhanced overlap between the donor and acceptor orbitals and thus an increase in the electronic transmission coefficient κ.

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Registry No. $Mn(CN\text{-}p\text{-}C_6H_4CH_3)_6^+$, 48243-20-5; $Mn(CN\text{-}p\text{-}C_6H_4CH_3)_6^{2+}$, 48243-19-2; $Mn(CN\text{-}p\text{-}C_6H_4OCH_3)_6^+$, 48244-70-8; $Mn(CN\text{-}p\text{-}C_6H_4OCH_3)_6^{2+}$, 52394-17-9.

Supplementary Material Available: Tables of reactant concentrations, temperatures, chemical shift values, and line widths (2 pages). Ordering information is given on any current masthead page.

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Formation and Photophysical Properties of Tetranuclear Bipyridyl Complexes of the Type $\{[(bpy)_2Ru(L\text{-}L)]_3Fe\}$

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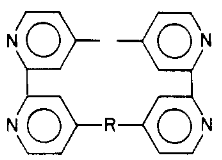
The synthesis of a series of covalently linked bipyridines, L-L, having alkyl linkages ranging from $(CH_2)_2$ to $(CH_2)_{12}$ is described. The ligands are used to prepare a series of ruthenium complexes of the type $[(bpy)_2Ru(L\text{-}L)]^{2+}$. These complexes may be used as ligands in the formation of tetranuclear complexes having a central Fe^{2+}, $\{[(bpy)_2Ru(L\text{-}L)]_3Fe\}^{8+}$. The equilibrium constants for formation of the complexes as a function of the length of the alkyl bridge between the bipyridines are determined by spectrophotometric and fluorescence quenching methods. The emission decay of the ruthenium complexes in solutions containing Fe^{2+} is a double exponential. The fast component of the decay corresponds to emission from ruthenium "ligands" complexed to iron, and the long component of the decay is from uncomplexed ruthenium centers. The rapid decay of the complexed ruthenium results from energy transfer to the iron bipyridyl center of the complex.

Introduction

With the increasing interest in interfacial photoprocesses and the photochemistry of large aggregated chromophores,[1] there is a growing need to prepare and spectroscopically characterize small clusters of chromophores that may serve as models for larger, more complex systems. A significant body of literature exists describing supersensitization of semiconductors[1b,2] and intermolecular quenching and excimer formation processes of chromophores adsorbed to numerous colloids.[1a,3] Among the various chromophores used in these studies, derivatives of $[Ru(bpy)_3]^{2+}$ have been widely applied.[2d,4-9] Recently, covalently linked 2,2′-bipyridine derivatives (**1**-**4**) have been synthesized[10] (vide infra) that allow for the preparation of particular polynuclear bipyridine-containing complexes that are soluble in a variety of solvents. In this work we report the in situ complexation of $[(bpy)_2Ru(L\text{-}L)]^{2+}$ complexes (**1a**-**4a**) with iron(II) to form the tetranuclear complexes $\{[(bpy)_2Ru(L\text{-}L)]_3Fe\}^{8+}$ (**1b**-**4b**).

Excitation-energy transfer from coordinated ruthenium centers to the central iron bipyridyl complex occurs for each of the four complexes. The intramolecular energy transfer is analogous to that observed in organic donor-acceptor complexes linked by an alkyl chain[11] and represents a rare example of intramolecular energy transfer in an inorganic system having no ground-state electronic interaction between the donor and acceptor.



L-L

1, R = $(CH_2)_2$
2, R = $(CH_2)_5$
3, R = $p\text{-}(CH_2)_2(C_6H_4)(CH_2)_2$
4, R = $(CH_2)_{12}$

[†] Tulane University.

[‡] Colorado State University.

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