a ladder composition.[1b] However, the ladder form has been independently synthesized and shows a carbon analysis of 48.45% calculated (48.23% found).[1c] This compares with 42.22% calculated for drum **7** and 41.92% found for the viscous material. Perhaps the drum has opened up[1b] and polymerized to give a chain unit that retains the empirical formula of the drum. The latter would account for the viscous nature of the solution. This suggestion, however, requires further work.

Structural Details. Drums **1** and **2**, which contain only one type of acid residue, are cyclic hexamers with idealized S_6 molecular symmetry. For **1** the crystallographic symmetry is the same as the idealized symmetry, while for **3** the crystallographic symmetry is lower, namely C_i.

The mixed drum **2**, has crystallographic C_2 symmetry with P1, C6, and C7 lying on the 2-fold axis, the methyl hydrogen atoms of C_7 being disordered about this axis. The ideallized molecular symmetry of **2** is D_3 and the molecule is viewed in Figure 2 down the noncrystallographic 3-fold axis. This idealized molecular symmetry is such that all of the tin atoms as well as all of the phosphorus atoms are chemically equivalent.

The framework Sn–O bond lengths for the three drum structures **1**–**3** average to within ±0.01 Å of one another, 2.091 (2) Å for **1**, 2.090 (6) Å for **2**, and 2.103 (5) Å for **3**. These values are similar to that reported for the corresponding cube $[n\text{-Bu}(O)O_2P(C_6H_{11})_2]_4$,[6] i.e., 2.108 (6) Å.

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Registry No. 1, 115270-25-2; **2**, 115288-62-5; **3**, 115270-27-4; **4**, 115270-28-5; **5**, 115270-29-6; **6**, 115270-30-9; **7**, 115270-31-0; **8**, 115270-33-2; $CH_3Sn(O)OH$, 753-61-7; CH_3CO_2H, 64-19-7; $(t\text{-Bu})_2PO_2H$, 677-76-9; $n\text{-BuSn(O)OH}$, 2273-43-0; $(PhO)_2PO_2H$, 838-85-7; $Cl\text{-}p\text{-}C_6H_4CO_2H$, 74-11-3; $\overline{CH_2CH_2CH_2CH}CO_2H$, 3721-95-7; $\overline{CH_2CH_2CH}CO_2H$, 1759-53-1; $C_6H_5CO_2H$, 65-85-0.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom parameters, and additional bond lengths and angles for **1** (Tables S1–S3, respectively) and anisotropic thermal parameters and additional bond lengths and angles for **2** (Tables S4 and S5, respectively) and for **3** (Tables S6 and S7, respectively) (11 pages); listings of observed and calculated structure factors for **1**–**3** (35 pages). Ordering information is given on any masthead page.

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Electron Exchange by Hexakis(*tert*-butyl isocyanide)- and Hexakis(cyclohexyl isocyanide)manganese(I,II). Solvent Effect on the Rate Constant and the Volume of Activation

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The rate of electron self-exchange of $Mn(CNC(CH_3)_3)_6^{+/2+}$ and $Mn(CNC_6H_{11})_6^{+/2+}$ as the BF_4^- salts has been measured by ^{55}Mn NMR line broadening as a function of pressure, temperature, and concentration in acetonitrile, bromobenzene, benzonitrile, acetone, diethyl ketone, methanol, ethanol, methylene chloride, and trimethyl phosphate, and various binary mixtures of methylene chloride, bromobenzene, and acetonitrile. The values of ΔV^* obtained are negative and cover a range of ca. 12 cm³/mol, which is limited by ion pairing in the solvents of lower dielectric constant. The variation of the ambient pressure rate constant with solvent is qualitatively different for the $Mn(CNC(CH_3)_3)_6^{+/2+}$ reaction than was observed for the $Mn(CNC_6H_{11})_6^{+/2+}$ reaction. This is taken as further evidence for a significant influence of rather subtle differences in solvation on the molecular level that are not approximated by dielectric continuum models.

Introduction

The work presented here is a continuation of our study of electron self-exchange in the Mn(I,II)–hexakis(isocyanide) system. Previous work has considered the effects of solvent, temperature, and added electrolyte concentration on the $Mn(CNC_6H_{11})_6^{+/2+}$ reaction,[1] the effect of varying the ligand, including both alkyl[2] and aryl[3] isocyanide ligands, as well as the temperature and electrolyte on reactions in acetonitrile, and the effect of pressure on reactions of a series of alkyl isocyanide complexes in acetonitrile.[4] The purpose of these studies is to provide a body of experimental data on a series of well-defined, outer-sphere electron-transfer reactions in solvents other than water and thus to test the rapidly developing theories for these superficially rather simple reactions.[5,6] The Mn(I,II)–hexakis(isocyanide) system is appealing for a broadly based and thorough study because the electron self-exchange rate constants can be evaluated directly from ^{55}Mn or ^1H NMR line broadening, a series of complexes with both aryl and alkyl ligands can be synthesized that are substitution inert in both oxidation states, the complexes are soluble and stable in a variety of solvents over a large range of temperature, and physical measurements on the complexes are starting to provide information on properties useful in the theoretical analysis of their reactivity.[7,8]

We are especially interested in pursuing measurements of the volumes of activation for these reactions under a variety of conditions. Relatively few measurements of volumes of activation for electron-transfer reactions have been made[9-17] compared to

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the recent intensive activity in measurements on solvent exchange and ligand substitution.[18,19] This is partly because volumes of activation for reactions between ionic reactants are more difficult to interpret.[19,20] However, the interpretation is unlikely to be more difficult than the interpretation of entropies of activation, and the investigation of reactions of and between ions is necessary if volumes of activation are to become a useful tool in the study of inorganic reactions.

The work presented here is primarily an extensive investigation of the solvent and total electrolyte concentration dependence of the volume of activation. By studying a wide range of solvents and concentrations, we hope to be able to find what aspects of the medium most affect the volume of activation. These measurements also extend previous studies on the solvent and temperature dependences of the rate constants for electron exchange at 1 atm pressure, and the results for $Mn(CNC(CH_3)_3)_6^{+/2+}$ presented here are significantly different from those for the previously studied system[1] $Mn(CN(C_6H_{11}))_6^{+/2+}$.

Experimental Section

The manganese complexes were made and the solvents acetonitrile, acetone, and ethanol were purified as previously described.[2] Methylene chloride was dried over Drierite and then distilled, trimethyl phosphate (Aldrich) was dried over P_2O_5 and then vacuum distilled, benzonitrile (Aldrich) was dried by refluxing over P_2O_5 and then fractionally distilled under vacuum, and diethyl ketone (Aldrich Gold Label) and methanol (Fisher, 0.02% H_2O) were used without further purification. The high-pressure NMR measurements were made on an instrument developed for the purpose as previously described.[4,22] Pressures up to ca. 200 MPa were used. Two samples were in the pressure bomb simultaneously. Each had the same Mn(I) complex concentration, and one also contained the Mn(II) complex. At each pressure, spectra of each sample were obtained and the line widths were extrapolated to a zero rf level. The temperature dependence data were obtained on a Nicolet 200WB instrument.[1] Typical concentrations for the pressure dependence studies were 0.15 M of the Mn(I) complex and 0.005 M for the Mn(II) complex. Temperature-dependence measurements were done with ca. 0.02 M Mn(I) and 0.005 M Mn(II), made up to 0.12 M total salt concentration with tetrabutylammonium tetrafluoroborate. The only exception to the above was the temperature dependence for CH_2Cl_2 as the solvent. This was done under the conditions of the high-pressure experiment and in the spectrometer used for those experiments. All temperature dependence data were fit to the Eyring expression by using a least-squares procedure[23] that allowed for error in both the temperature and the rate constant. Errors in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were derived from the estimated errors in the rate constants and temperatures.

The rate of the electron-exchange process, eq 1, was obtained from the ^{55}Mn NMR line widths by using eq 2, where $\Delta\nu_D$ is for the diamagnetic complex and $\Delta\nu_P$ is for the Mn(I) complex in the presence of the Mn(II) form.

$$Mn(CNR)_6^+ + Mn(CNR)_6^{2+} \rightleftharpoons Mn(CNR)_6^{2+} + Mn(CNR)_6^+ \qquad (1)$$

$$k = \frac{2\pi(\Delta\nu_P - \Delta\nu_D)}{[Mn(CNR)_6^{2+}]} \qquad (2)$$

Here $\Delta\nu$ is half of the width of the dispersion curve as measured between the maximum and the minimum. This equation is applicable if the reaction is in the limiting slow-exchange regime, characterized by broadening but no shift of the $^{55}Mn(CNR)_6^+$ resonance with increasing concentration of $Mn(CNR_6)^{2+}$. This was the case for all reactions studied.

Within transition-state theory, the volume of activation is defined by eq 3 and the compressibility of activation by eq 4.[21] The data are thus analyzed as plots of ln k vs P.

$$\left[\frac{\partial(\ln k)}{\partial P}\right]_T = \frac{-\Delta V^\ddagger}{RT} \qquad (3)$$

$$-\left[\frac{\partial \Delta V^\ddagger}{\partial P}\right]_T = \Delta\beta^\ddagger \qquad (4)$$

In the calculation of k, the $\Delta\nu_D$ vs pressure data were first smoothed by fitting ln $\Delta\nu_D$ to a second-order polynomial in pressure, and the polynomial values were used to calculate k from $\Delta\nu_P$ and $[Mn(CN(C(CH_3)_3)_6^{2+}]$ values. Comparable results were obtained when $(\Delta\nu_P - \Delta\nu_D)$ was calculated for each pressure value, and this difference was used to calculate k. The plots of ln k vs P are typically curved, with the magnitude of the slope decreasing with increasing pressure. There is no single theoretical treatment that can be used to fit such data, but a common empirical treatment that fits our data reasonably well is eq 5. The data were fit to eq 5, with or without the c term,

$$\ln k = a + bP + cP^2 = \ln k_{P=0} - \left[\frac{\Delta V^\ddagger}{RT}\right]_{P=0} P + \left[\frac{\Delta\beta^\ddagger}{2RT}\right]_{P=0} P^2 \qquad (5)$$

by using least-squares methods,[24] and the errors in the parameters were calculated based on the scatter about the fit lines. The decision to include the c term, and thus calculate $\Delta\beta^\ddagger$, was made based on the reduced χ^2 value and the magnitude of the errors in the parameters. Inclusion of the quadratic term typically increased the magnitude of $\Delta V^\ddagger$ by about 2 cm^3/mol compared to a linear fit of the lower pressure data, P up to 100 MPa. Thus there is some curvature affecting data below 100 MPa. We wish to emphasize that we found it important to collect on the order of 15 points in the range of 0–200 MPa in order to properly define $\Delta V^\ddagger$ and give even an approximate value of $\Delta\beta^\ddagger$. Further, data must be of good precision or consistent results will not be obtained, as indicated by much different values of $\Delta V^\ddagger$ obtained from the initial slope of ln k vs P and the full quadratic treatment. The results are presented in Tables I and II as the fit parameters.

Discussion

In our previous work on the volumes of activation of $Mn(CNR)_6^{+/2+}$ complexes in acetonitrile,[4] we found that $\Delta V^\ddagger$ varied by 20 cm^3/mol with the R group, giving more negative values for the larger and more flexible ligands. However, we did not find it possible to predict $\Delta V^\ddagger$ from the theoretical approaches that we tried. The systems $Mn(CNC_6H_{11})_6^{+/2+}$ and $Mn(CN(C(CH_3)_3)_6^{+/2+}$ were chosen for further study because the complexes are especially stable.

Values of $\Delta V^\ddagger$ in this study were found to vary by 12 cm^3/mol. This is not a small variation, but it is smaller than we expected to observe for the wide range of conditions we used. The variation of $\Delta V^\ddagger$ does not correlate directly with solvent parameters such as molal volume, viscosity, dielectric constant (ϵ), index of refraction (n), the combined solvent parameter $((1/n^2) - (1/\epsilon))$ from Marcus theory, dipole moment, donor or acceptor number, HOMO or LUMO energies,[25] the variation of the dielectric constant with pressure[21,26] ($\phi = (1/\epsilon)(\partial \ln \epsilon)/\partial P)$), or a variety of other parameters often used to correlate solvent effects.

A more complex approach for predicting $\Delta V^\ddagger$ is based on Marcus theory and has been presented in the most detail by Swaddle and co-workers.[27] The volume of activation is calculated as the sum of several terms

$$\Delta V^\ddagger = \Delta V^\ddagger_{IR} + \Delta V^\ddagger_{SR} + \Delta V^\ddagger_{COUL} + \Delta V^\ddagger_{DH} \qquad (6)$$

The first term represents internal rearrangement of bond lengths and angles, and is negligible here. The second term represents solvent reorganization, and the last two terms are for the precursor complex formation. $\Delta V^\ddagger_{COUL}$ represents the formation of the precursor complex at zero ionic strength, and $\Delta V^\ddagger_{DH}$ is the correction to the ionic strength of the experiment using an extended Debye–Hückel activity coefficient formula. The equations used here do not include consideration of the pressure dependence of reactant radii. This parameter was omitted due to the uncertainty

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Table I

A. Volume of Activation as a Function of Solvent and Reactant Concentration for $Mn(CNC(CH_3)_3)_6(BF_4)_{1,2}$

solvent	[Mn(I)], *m*	[Mn(II)],[a] *m* × 10^3	no. of points	*T*, °C	$\Delta V^{\ddagger}$, cm^3/mol	$\Delta\beta^{\ddagger}$,[b] $cm^3/(mol\ MPa)$ × 10^2	predicted[c] $\Delta V^{\ddagger}$, cm^3/mol
CH_3CN	0.19	6.9	12	0	−11 ± 2	−3 ± 2	−16/−15/−14
	0.25	8.4	13	6	−12 ± 2	−5 ± 2	
	0.32	8.4	14	6	−13 ± 2	−5 ± 1	
	0.69	4.5	10	6	−12 ± 1	−4 ± 1	−17/−15/−14
CH_3OH	0.17	6.6	6	6	−20 ± 2	−9 ± 3	−24/−20/−16
		7.1	5				
	0.18	10.5	13	3	−20 ± 3	−9 ± 4	
C_6H_5CN	0.52	5.6	9	12	−9 ± 2	−8 ± 4	
CH_3CH_2OH	0.16	5.7	9	7	−16 ± 2	−6 ± 2	−23/−19/−15
$(CH_3)_2CO$	0.16	3.9	10	6	−20 ± 2	−7 ± 1	−32/−23/−14
$(CH_3O)_3PO$	0.16	3.7	6	6	−10 ± 2		
$(CH_3CH_2)_2CO$	0.18	4.9	7	7	−22 ± 2	−9 ± 4	
CH_2Cl_2	0.11	3.0	11	0	−18 ± 2	−7 ± 1	−51/−27−/−2

B. Volume of Activation and Ambient Pressure Rate Constant as a Function of Solvent for $Mn(CNC(CH_3)_3)_6(BF_4)_{1,2}$

solvent mole ratios	[Mn(I)], *m*	[Mn(II)],[a] *m* × 10^3	no. of points	*T*, °C	$\Delta V^{\ddagger}$, cm^3/mol	$\Delta\beta^{\ddagger}$, $cm^3/(mol\ MPa)$ × 10^2	k_0, $M^{-1}\ s^{-1}$ × 10^{-4}
$CH_3CN:CH_2Cl_2$							
9:1	0.15	4.4	10	1	−12 ± 2	−5 ± 2	3.6 ± 0.1
4:1	0.17	4.2	14	0	−14 ± 2	−4 ± 3	3.1 ± 0.2
7:3	0.18	10.6	23	1	−15 ± 2	−5 ± 7	3.0 ± 0.1
3:2	0.16	4.1	13	0	−15 ± 2	−5 ± 2	3.8 ± 0.2
1:1	0.14	3.6	14	1	−14 ± 2	−4 ± 2	4.1 ± 0.2
2:3	0.12	7.0	19	2	−19 ± 3	−10 ± 3	3.8 ± 0.2
3:7	0.12	3.1	13	1	−15 ± 3	−5 ± 3	4.7 ± 0.3
1:4	0.12	3.2	14	2	−13 ± 3	−4 ± 3	5.7 ± 0.3
1:9	0.11	2.8	8	2	−15 ± 2	−4 ± 3	6.5 ± 0.3
$CH_3CN:BrC_6H_5$							
4:1	0.15	3.4	10	2	−12 ± 4	−5 ± 3	2.8 ± 0.2
1:1	0.15	8.9	18	2	−15 ± 3	−7 ± 4	2.6 ± 0.2
1:4	0.11	6.9	14	2	−13 ± 3	−10 ± 5	3.2 ± 0.2
$CH_2Cl_2:BrC_6H_5$							
4:1	0.08	2.3	14	1	−17 ± 2	−7 ± 2	5.9 ± 0.2
1:1	0.11	6.3	19	1	−21 ± 3	−15 ± 3	4.2 ± 0.2
3:7	0.14	5.4	18	3	−16 ± 2	−5 ± 2	3.0 ± 0.1

[a] When two $Mn(CNC(CH_3)_3)_6^{2+}$ concentrations were studied, the data were analyzed simultaneously. [b] Where no value is given, the data did not require the quadratic term. [c] Prediction from the Marcus theory equations as given by Swaddle.[26] The first value is for a charge product of 2, the second for 1, and the last for 0. In all cases, the ionic strength was taken as the [Mn(I)]. The solvent parameters were taken or derived from data in ref 20, 25, and 28. For acetone, data at 10 °C were used, for acetonitrile, methanol, and ethanol, 20 °C data were used, and for methylene chloride and bromobenzene, 30 °C data were used. The radius of the *tert*-butyl isocyanide complex was taken as 5.4 Å. This is an average of the maximum and minimum radius estimated for the complex in ref 1. The radius used for calculating the Debye–Hückel term was 10.25 Å, also from ref 1.

Table II. Volume of Activation as a Function of Solvent and Reactant Concentration for $Mn(CNC_6H_{11})_6(BF_4)_{1,2}$

solvent	[Mn(I)], *m*	[Mn(II)], *m* × 10^3	no. of points	*T*, °C	$\Delta V^{\ddagger}$, cm^3/mol	$\Delta\beta^{\ddagger}$,[a] $cm^3/(mol\ MPa)$ × 10^2	predicted[c] $\Delta V^{\ddagger}$, cm^3/mol	k_0, $M^{-1}\ s^{-1}$ × 10^{-4}
CH_3CN	0.20	4.1	11	2	−17 ± 1	−6 ± 1	−14/−13/−13	18.9 ± 0.4
CH_3OH	0.18	3.3	18	2	−16 ± 2		−21/−18/−14	14.5 ± 0.3
$(CH_3)_2CO$	0.19	3.2	17	3	−20 ± 2	−8 ± 2	−28/−20/−13	14.5 ± 0.4
CH_2Cl_2	0.12	3.0	15	3	−21 ± 4	−8 ± 4	−46/−24/−2	6.9 ± 0.4
BrC_6H_5	0.17	13.9	10	2	−9 ± 2		−38/−20/−1	5.1 ± 0.5
$CH_2Cl_2:BrC_6H_5$[b]								
7:3	0.09	3.2	21	3	−17 ± 2	−3 ± 2		5.8 ± 0.2
1:1	0.10	7.7	18	3	−18 ± 2	−3 ± 3		4.9 ± 0.1
3:7	0.10	6.9	18	3	−10 ± 4			5.0 ± 0.2

[a] Where no value is given, the data did not require the quadratic term. [b] Mole ratios of the solvents are given. [c] The parameters used are as in Table IA, except the radius of the cyclohexyl isocyanide complex is taken as 6 Å and the Debye–Hückel radius as 11 Å.

in the Coulombic terms, but it has been included in the analysis of simpler systems by Swaddle and co-workers.[17,26] The results of the calculations, assuming reactants of various charges in order to approximate ion pairing, are presented in Tables IA and II. In all tables, the solvents are in the order of decreasing dielectric constant. At 25 °C the dielectric constants are as follows:[28,29] CH_3CN, 36.0; CH_3OH, 32.6; C_6H_5CN, 25.2; CH_3CH_2OH, 24.3; $(CH_3)_2CO$, 20.7; $(CH_3O)_3PO$, 20.6; $(CH_3CH_2)_2CO$, 16.6; CH_2Cl_2, 8.9; C_6H_5Br, 5.4; $CHCl_3$, 4.7.

We have previously attempted to analyze the effect of added electrolyte on the rate constant for electron self-exchange in the $Mn(CNC_6H_{11})_6^{+/2+}$ system.[1] In that study, we concluded that

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there was no ion pairing in acetonitrile, complete ion pairing in bromobenzene, and partial ion pairing in acetone and ethanol. These estimates are for the solvents at atmospheric pressure. As pressure is increased, ion pairing should decrease, thus increasing the Coulombic term and decreasing the rate constant. On the basis of the ambient pressure results, the charge product of the reactants should be +2 for acetonitrile and +2 or +1 for methanol, +1 or 0 for acetone and ethanol, and 0 for methylene chloride and bromobenzene. Since the $Mn(CNC(CH_3)_3)_6^{+/2+}$ complexes are similar in size to the $Mn(CNC_6H_{11})_6^{+/2+}$ complexes, the ion pairing should be similar. The predicted values of $\Delta V^{\ddagger}$ as a function of solvent and charge product demonstrate, within this model, how ion pairing leads to a small range of $\Delta V^{\ddagger}$ values. The values in acetonitrile are generally more positive than can be predicted, while at the opposite end of the solvent range, bromobenzene and methylene chloride give a more negative value than is predicted. For the latter two solvents, the predicted value for $\Delta V^{\ddagger}$ is especially sensitive to the charge on the reactants. Either some contribution from reaction between ions or inclusion of consideration of the large dipole interaction between the reactant ion pairs could account for the more negative values. It is not clear why the acetonitrile values are so positive for $Mn(CNC(CH_3)_3)_6^{+/2+}$. A preliminary measurement for the same system with $CF_3SO_3^-$ as the anion instead of BF_4^- gives the more negative value of about −20 cm^3/mol.

The solvent mixture experiments will now be discussed. Because of the precision of the $\Delta V^{\ddagger}$ measurements and the rather small range of observed values, the trends are not strong ones, but some discussion can be suggested. Three studies on $Mn(CNC(CH_3)_3)_6^{+/2+}$ in mixed solvents were performed, CH_3CN with CH_2Cl_2, CH_3CN with C_6H_5Br, and CH_2Cl_2 with C_6H_5Br. The reaction could not be studied in pure C_6H_5Br, but based on the trends demonstrated in the mixed solvents, $\Delta V^{\ddagger}$ should be about −10 cm^3/mol in this solvent. This is similar to the value of −9 cm^3/mol measured for $Mn(CNC_6H_{11})_6^{+/2+}$ in C_6H_5Br, and again shows that this solvent produces one of the most positive $\Delta V^{\ddagger}$ values. In the mixture of CH_3CN with C_6H_5Br, there is a clear minimum in $\Delta V^{\ddagger}$ at an equimolar mixture of the two solvents. A similar trend is apparent but not so clearly demonstrated in the other two solvent mixtures. If the dielectric constant of the two solvent mixtures with acetonitrile is calculated as the weighted average of the pure solvent values, then the dielectric constants of the mixtures that show the minimum value for $\Delta V^{\ddagger}$, 2:3 CH_3CN:CH_2Cl_2 and 1:1 CH_3CN:C_6H_5Br, are about 20, and $\Delta V^{\ddagger}$ matches the value for acetone, which has a dielectric constant of 20.7 at 25 °C. Although the situation is quite complex, it appears that ion pairing strongly influences the measured values for $\Delta V^{\ddagger}$. Over limited ranges of dielectric constant, between acetonitrile and acetone, increasing dielectric constant leads to a less negative $\Delta V^{\ddagger}$, as is predicted for the pure solvents. For the solvent mixtures that give dielectric constants somewhat below that of acetone, ion pairing reduces the charge product and $\Delta V^{\ddagger}$ becomes more positive. For the mixtures of bromobenzene and methylene chloride, complete ion pairing is expected, and other factors are controlling $\Delta V^{\ddagger}$, such as the dipole–dipole interaction mentioned above. The $Mn(CNC_6H_{11})_6^{+/2+}$ system was studied in only one solvent mixture, CH_2Cl_2 with C_6H_5Br, and showed an essentially monotonic change of $\Delta V^{\ddagger}$ with solvent composition. For this system, $\Delta V^{\ddagger}$ could be measured in C_6H_5Br, and the value falls on the line with the mixture results.

The compressibility of activation, $\Delta\beta^{\ddagger}$, is poorly defined. A major problem is that there is no theoretical expression for the dependence of ln k on P that can be used with confidence. The polynomial can fit the data reasonably well, but $\Delta\beta^{\ddagger}$ and to a certain extent even $\Delta V^{\ddagger}$ are sensitive to the exact pressure range chosen and the distribution of data points. Therefore, no interpretation of these values will be attempted.

Table III. Enthalpy and Entropy of Activation as a Function of Solvent

A. $Mn(CNC(CH_3)_3)_6(BF_4)_{1,2}$[a]

solvent	no. of points	T range, °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)	$k(T = 0\ °C)$,[d] $M^{-1}\ s^{-1} \times 10^{-4}$
CH_3CN[b]	6	−35 to +30	5.4 ± 0.1	−19 ± 1	2.7
C_6H_5CN	6	−15 to +35	5.0 ± 0.2	−19 ± 1	5.3
CH_3CH_2OH	4	0 to 35	5.7 ± 0.4	−17 ± 2	3.3
$(CH_3)_2CO$	6	−30 to 35	4.3 ± 0.1	−22 ± 1	3.3
$(CH_3O)_3PO$	5	−15 to +35	5.1 ± 0.1	−18 ± 1	5.4
$(CH_3CH_2)_2CO$	6	−15 to +35	4.3 ± 0.1	−22 ± 1	2.9
CH_2Cl_2[c]	11	−15 to +16	4.0 ± 0.1	−21 ± 1	6.5

B. $Mn(CNCC_6H_{11})_6(BF_4)_{1,2}$[e]

solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)	$k(T = 0\ °C)$,[e,f] $M^{-1}\ s^{-1} \times 10^{-4}$
CH_3CN	3.4	−21	17.7
CH_3CH_2OH	3.5	−22	11.7
$(CH_3)_2CO$	3.5	−22	13.6
$CHCl_3$	4.3	−22	2.7
BrC_6H_5	6.0	−15	4.8

[a] All at 0.020 M $Mn(CNC(CH_3)_3)_6^+$, ca 6 × 10^{-3} M $Mn(CNC(CH_3)_3)_6^{2+}$, and 0.10 M tetrabutylammonium tetrafluoroborate unless otherwise indicated. [b] From ref 2. [c] 0.20 M $Mn(CNC(CH_3)_3)_6^+$ and 7.6 mM $Mn(CNC(CH_3)_3)_6^{2+}$. [d] Additional 0 °C rate constant ($M^{-1}\ s^{-1} \times 10^{-4}$): CH_3OH, 2.1. [e] Calculated from data in ref 1. [f] Additional 0 °C rate constants ($M^{-1}\ s^{-1} \times 10^{-4}$): CH_3OH, 13.6; CH_2Cl_2, 6.5.

This study has also produced a set of rate constants and activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, as a function of solvent at 1 atm pressure. In addition, the rate constant as a function of solvent composition has been established for the solvent mixtures (Table III). These results can be compared to the previous study of the solvent dependence of electron exchange in the system $Mn(CNC_6H_{11})_6^{+/2+}$.[4] In the earlier study, enough information was available to attempt to separate the reaction paths for the various ion paired species, by using the dependence of the observed rate constant on added electrolyte and estimates of the ion association constants. The data are not available to do this here, although the ion pairing pattern should be similar. For the point to be made, it is adequate to compare the measured rate constants at a single salt concentration. In the case of $Mn(CNC(CH_3)_3)_6^{+/2+}$, the range of rate constants is smaller. With the exception of those for the solvent mixtures of C_6H_5Br with CH_2Cl_2, the rate constants have the opposite dependence on the dielectric constant or the solvent parameter $1/n^2 - 1/\epsilon$, which varies monotonically with the dielectric constant, as does that for $Mn(CNC_6H_{11})_6^{+/2+}$. The complex nature of the solvent dependence of the $Mn(CNC_6H_{11})_6^{+/2+}$ reaction may be related to the flexibility of the ligands and the larger spaces between them compared to the more rigid *tert*-butyl isocyanide ligands. The much more negative $\Delta V^{\ddagger}$, −17 cm^3/mol in acetonitrile at 0.1 M salt concentration, for the $Mn(CNC_6H_{11})_6^{+/2+}$ reaction compared to about −12 cm^3/mol for the $Mn(CNC(CH_3)_3)_6^{+/2+}$ system, has already been partially attributed to this difference.[4]

The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are similar to the values measured for other systems, nearly constant $\Delta S^{\ddagger}$ and quite similar values of $\Delta H^{\ddagger}$. Recently a correlation between $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ has been discussed for ligand substitution reactions.[30] The data presented here for the $Mn(CNC(CH_3)_3)_6^{+/2+}$ reaction show no such correlation, since the values of $\Delta V^{\ddagger}$ vary by 12 cm^3/mol, while $\Delta S^{\ddagger}$ varies by only 5 cal/mol K) and in no regular way. It remains intriguing that the solvent that gives the least negative value for $\Delta V^{\ddagger}$, C_6H_5Br, gives the only activation parameters that show really significant differences. The $Mn(CNC(CH_3)_3)_6^{+/2+}$ reaction could not be studied in C_6H_5Br, but mixed-solvent studies indicate that $\Delta V^{\ddagger}$ is less negative here also.

Conclusion

The value of $\Delta V^{\ddagger}$ for the electron self-exchange reactions of $Mn(CNC(CH_3)_3)_6^{+/2+}$ and $Mn(CNC_6H_{11})_6^{+/2+}$ has been shown to be solvent dependent and to vary by only 12 cm^3/mol in the

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(30) Phillips, J. C. *J. Phys. Chem.* **1985**, *89*, 3060.

range of solvents tested. These solvents have a wide range of properties, including dielectric constant and its pressure derivative as well as molar volume, index of refraction, viscosity, and compressibility. No simple correlations between the solvent properties and $\Delta V^{\ddagger}$ were found. However, an analysis of the data within a Marcus theory framework that has had reasonable success in predicting $\Delta V^{\ddagger}$ values demonstrates that ion pairing can lead to a great diminution of the range of $\Delta V^{\ddagger}$ values compared to what would be expected without ion pairing. Doine and Swaddle[17] have found better agreement with the Marcus theory predictions in their study of tris(hexafluoroacetylacetonato)ruthenium(II,III) in various solvents. This system is a 0/−charge type, and therefore does not suffer from as many complications from ion pairing and Coulombic interaction as the manganese isocyanides. Nevertheless, they also observed an apparent influence of ion pairing on $\Delta V^{\ddagger}$ in chloroform.

In order to better interpret these results, more information on the ion paired species present is required, as well as more data on the physical properties of the solvents as a function of pressure in order to apply the Marcus theory and related equations. A better understanding of molar volumes of ions in nonaqueous solvents will also help, and development of equations for predicting molar volumes would allow $\Delta V^{\ddagger}$ to be predicted by direct consideration of the reactant and transition-state structures. More sensitive instrumentation will also help improve the precision and allow us to work at a wider range of concentrations in order to manipulate the extent of ion pairing.

Further results of this study involve the variation of the ambient-pressure rate constant with solvent and the temperature dependence of the rate constants. The rate constants were found to vary in the opposite manner as did those for complexes of cyclohexyl isocyanide studied earlier. This again indicates that the specifics of the molecular interactions in solvation and not just bulk properties are significant. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were typical of others measured, and did not show the correlation between $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ previously observed for substitution reactions.[30]

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Registry No. $Mn(CNC(CH_3)_3)_6^+$, 18972-33-3; $Mn(CNC(CH_3)_3)_6^{2+}$, 19154-91-7; $Mn(CNC_6H_{11})_6^+$, 52438-24-1; $Mn(CNC_6H_{11})_6^{2+}$, 52438-27-4.

Notes

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Synthesis, Structure, and Spectroscopic Properties of (σ-Alkyl)iron(II) Phthalocyanines

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Many years ago, it was shown that the doubly reduced iron phthalocyanine $[Fe^{I}Pc(-3)]^{2-}$ (Pc = phthalocyanine) reacts with alkyl and aryl halides to produce σ-bonded alkyl- and aryliron(II) phthalocyanine derivatives.[2] However, these complexes were never completely characterized and their chemistry has so far not been explored. The analogous iron(II) porphyrin species have been mentioned in the literature as very unstable species that form by electrochemical reduction of the corresponding iron(III) porphyrin complexes, but they were never isolated.[3–6] We have now isolated several σ-bonded alkyliron(II) phthalocyanine complexes. We describe here the synthetic methods used for the preparation of these complexes and their spectroscopic and structural properties.

Experimental Section

General Procedures. All experiments were done under an inert atmosphere by Schlenk techniques. Solvents used were rigorously purified and dried under argon. Iron(II) phthalocyanine was prepared by using known methods[7] and purified at 400 °C under reduced pressure (10^{-4}–10^{-5} Torr). The compounds 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), lithium aluminum hydride, sodium borohydride, and 2-methyl-2-propanethiol were purchased from Aldrich-Chimie (France). Potassium 2-methyl-2-propanethiolate was prepared by reaction of a 10-fold excess of 2-methyl-2-propanethiol with potassium hydroxide in ethanol, precipitated by addition of diethyl ether, filtered, dried under vacuum, and stored in a glovebox. The visible spectra were recorded in chlorobenzene or THF on a Cary 210 spectrometer. The ^1H NMR spectra were obtained in deuteriated DMSO or THF with a 200-MHz Bruker SY 200 instrument in tubes sealed under argon. Chemical shifts are indicated in ppm relative to TMS. Coupling constants are indicated in Hz. Elemental analyses were obtained from the Centre de Microanalyse, Département de Chimie de l'Université Louis Pasteur de Strasbourg. All the analytical and spectroscopic results described here were obtained with small crystals that were sorted out under the microscope.

Synthesis of $[Fe(R)Pc(-2)]^-$ (R = CH_3 (1), C_2H_5 (2), $(CH_3)_2CH$ (3)). $LiAlH_4$ (0.035 mmol, 13 mg) and 18-crown-6 (0.077 mmol, 20.3 mg) were mixed with a suspension of iron(II) phthalocyanine [Fe(R)Pc(−2)] (0.0355 mmol, 20 mg) in THF (15 mL), and the mixture was stirred until the color of the resulting solution became violet. This color indicated the formation of the doubly reduced species $[Fe^{I}Pc(-3)]^{2-}$. After filtration under an inert atmosphere a 15–20 fold excess of one of the halides CH_3I (0.56 mmol, 80 mg), C_2H_5I (0.064 mmol, 100 mg), or $(CH_3)_2CHBr$ (0.65 mmol, 80 mg) was added and the stirring was continued until the solution became green. Red crystals of **3** mixed with colorless crystals of 18-crown-6 were obtained after filtration under an inert atmosphere and slow diffusion of pentane into these green solutions enclosed in sealed tubes.

Alternative Procedures. (a) Sodium borohydride (0.035 mmol, 1.3 mg) can also be used as reducing agent in place of lithium aluminum hydride.

(b) Potassium 2-methyl-2-propanethiolate can also be used as reducing agent. A chlorobenzene solution (10 mL) containing potassium 2-methyl-2-propanethiolate (0.21 mmol, 26.6 mg) and 18-crown-6 ($\subset$18c6; 0.077 mmol, 20.3 mg) was added under argon to a suspension of $[Fe^{II}Pc]$ (0.035 mmol, 20 mg) in 12 mL of chlorobenzene and stirred until the resulting solution became violet. The procedure followed from this point on was then identical with that described above.

$[Fe(CH_3)Pc][Li(\subset 18c6)]\cdot THF$ (1). UV–vis (C_6H_5Cl; λ_m, nm (log ε)): 479 (4.94), 540 (4.75), 639 (4.75), 675 (4.76), 707 (4.96). ^1H NMR (δ, deuteriated DMSO): 7.70 (H_a, Pc); 8.84 (H_b, Pc); −7.65 (CH_3); 3.34 ($\subset$18c6). Anal. Calcd for $FeLiC_{49}H_{51}N_8O_7$: C, 63.51; H, 5.50; N, 12.09. Found: C, 62.5; H, 5.2; N, 11.8.

$[Fe(C_2H_5)Pc][Li(\subset 18c6)]\cdot THF$ (2). UV–vis (C_6H_5Cl; λ_m, nm (log ε)): 479 (4.87), 550 (4.74), 657 (4.70), 677 (4.71), 702 (4.90). ^1H NMR (δ, deuteriated DMSO): 7.63 (H_a, Pc); 8.87 (H_b, Pc); −6.27 (H_α, C_2H_5), −3.01 (H_β, C_2H_5), $J(H_\alpha H_\beta) = 7.5$ Hz); 3.34 ($\subset$18c6). Anal. Calcd for $FeLiC_{50}H_{52}N_8O_7$: C, 63.84; H, 5.61; N, 11.91. Found: C, 63.6; H, 5.6; N, 12.0.

$[Fe(CH(CH_3)_2)Pc][Li(\subset 18c6)]\cdot THF$ (3). UV–vis (C_6H_5Cl; λ_m, nm (log ε)): 479 (4.81), 545 (4.64), 651 (4.63), 676 (4.64), 699 (4.82). ^1H

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