relative Fe–CO bond energies,[21] yet there is no correlation at all with the CO stretching frequencies. In fact the CO stretching frequencies correlate much better with redox potentials, as seen in Figure 6. Morse[22] and Morris[23] have previously found such a correlation for a wide variety of organometallic compounds. We have previously discussed the deceptively simple notion of metal–ligand bond energies in highly covalent synergistic bonding situations.[24] A careful analysis shows that dissociation of CO or MeIm in $FeN_4(MeIm)(CO)$ results in substantial changes in the bond strength of the remaining axial ligand. These changes in the bonds not broken contribute to the kinetic barrier associated with k_{-L}. When a CO bond is stretched slightly, it is unlikely that the other iron–ligand bonds are significantly perturbed. Thus, there are significant energetic factors associated with the Fe–CO bond energy that have no corresponding component in the CO stretching frequency.

While $E_{1/2}$ does not correlate with the MLCT energy for different N_4 ligands, within a given N_4 system, an excellent correlation between $E_{1/2}$ and E_{MLCT} is observed as shown in Figure 7.[25] The slopes of the plots are nearly 1.0 (when identical units are used for both axes), consistent with both $E_{1/2}$ and E_{MLCT} benefitting from the stabilizing of $d_{xz,yz}$ by π-acceptor ligands. It should be noted that rate data and $E_{1/2}$ are correlated in the increasing trans destabilization of MeIm or py in $Fe(dmgH)_2TL$ complexes,[3] the trans effects of anation rates of $Ru(NH_3)_4T(H_2O)^{2+}$ systems,[26] and perhaps the lability of CH_3CN and MeIm in various $FeR_4[TIM]^{2+}$ systems.[5d]

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Solvent Dependence of the Electron Self-Exchange of Hexakis(2,6-diisopropylphenyl isocyanide)chromium(0,I) and -chromium(I,II) and a Comparison with Theoretical Models

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The rate of electron self-exchange between chromium(I) hexakis(2,6-diisopropylphenyl isocyanide) tetrafluoroborate, $Cr(CNdipp)_6BF_4$, and $Cr(CNdipp)_6(BF_4)_2$ has been measured as a function of reactant concentration, temperature, and solvent (acetone, acetonitrile, nitromethane, methylene chloride, methanol) by ^1H NMR line broadening. The rate of electron self-exchange between $Cr(CNdipp)_6$ and $Cr(CNdipp)_6BF_4$ has been measured as a function of temperature in acetone. The Cr(0)/Cr(I) rate constants, ca. 10^8 M^{-1} s^{-1}, are a factor of 10 higher than the Cr(I)/Cr(II) values in methylene chloride and acetone. The Cr(I)/Cr(II) rate constants vary little between the solvents at 298 K. The activation parameters do vary, showing a compensating pattern for the solvents studied. The results for the two systems are compared with the predictions of the standard Marcus collision and solvent dynamic models. The experimental electron self-exchange rate constants are in excellent agreement and the activation parameters are in reasonable agreement with the predictions from the Marcus collision model. The calculated activation parameters from the Marcus collision model show no trend with solvent, and thus do not predict the compensation behavior.

Introduction

Outer-sphere electron self-exchange reactions are of particular interest in the field of mechanistic inorganic chemistry because the electron self-exchange rate constant is characteristic of an oxidation–reduction couple, analogous to a reduction potential. Furthermore, theoretical treatment of these reactions is simpler than the treatment of electron-transfer cross-reactions, which involve net chemical change.[1-5] As part of our ongoing effort to study nonaqueous electron transfer by transition-metal complexes, we have chosen the Cr(0,I,II) hexakis(2,6-diisopropylphenyl isocyanide), $Cr(CNdipp)_6^{0/+}$ and $Cr(CNdipp)_6^{+/2+}$, systems for detailed study. Several features of this class of complexes make them appealing. They are substitution inert in three oxidation states (Cr(0,I,II)), X-ray crystal structures have been determined for four oxidation states (Cr(0,I,II,III)) of $Cr(CNC_6H_5)_6$,[6] a variety of analogous symmetrical complexes with other isocyanide ligands can be synthesized, they have adequate stability and solubility in nonaqueous solvents over a large temperature range, and electron self-exchange can be followed directly by ^1H NMR line broadening.[6-8]

The two couples, $Cr(CNdipp)_6^{0/+}$ and $Cr(CNdipp)_6^{+/2+}$, are identical, having the same metal ion and ligand set, except for charge. In the former the reactants are neutral and singly charged; therefore, there is no Coulombic work term contributing to the electron-transfer rate. In the latter system both reactants are charged and there is Coulombic repulsion between the reactants.

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This is the first case in which electron-transfer rates that have been directly measured[1,2] for two couples of the same metal ion and ligand set have been thoroughly studied in a variety of nonaqueous solvents. This system thus provides a rare opportunity to study the effects of reactant charge on the electron-transfer process in nonaqueous solvents. The electron-transfer rate constant for the Cr(I)/Cr(II) system has been determined in five solvents and as a function of temperature. In addition the self-exchange rate constants of the Cr(0)/Cr(I) reaction in acetone have been measured to add to the previous study of the system in methylene chloride. The change in structure on going from Cr(0) to Cr(I) or Cr(I) to Cr(II) is primarily in the small change in the Cr–C bond length. This bond changes 0.037 and 0.039 Å, respectively, between the two couples. As judged from the X-ray crystal structures of $Cr(CNC_6H_5)_6{}^{0/+/2+}$[7] and $Cr(CNdipp)_6$,[9] these structural changes are similar. The results for the two systems are compared with the predictions of the standard Marcus collision and solvent dynamic models.

Experimental Section

The ligand 2,6-diisopropylphenyl isocyanide was prepared by literature methods.[7,8] The hexakis(2,6-diisopropylphenyl isocyanide)chromium(0) complex, $Cr(CNdipp)_6$, and hexakis(2,6-diisopropylphenyl isocyanide)chromium(I) tetrafluoroborate, $Cr(CNdipp)_6BF_4$, were prepared as described previously.[8] Hexakis(2,6-diisopropylphenyl isocyanide)chromium(II) tetrafluoroborate, $Cr(CNdipp)_6(BF_4)_2$, was prepared according the method of Treichel and Essenmacher[7] except that a slight excess over 2 equiv of $AgBF_4$ (Aldrich) was used as the oxidant and the anion source. The complex was recrystallized from an acetone–hexane mixture to give bright red crystals. Characteristic infrared bands are $\nu_{C\equiv N}$ 2138 cm^{-1} (strong), 1425 cm^{-1} (strong), and 1050 cm^{-1} (medium). Infrared spectra for the Cr(II) complex were collected with a Perkin-Elmer 283-B instrument as Nujol mulls due to the reduction of the Cr(II) complex by the bromide in KBr pellets.

All deuterated solvents (MSD Isotopes, Merck) were degassed by three freeze–pump–thaw cycles and stored in an evacuated bulb, in the dark, until used. Samples were prepared by weighing the appropriate quantities of solid reagents into a 5-mm NMR tube with a Teflon valve (Wilmad Glass Co.). The samples were placed on a vacuum line where the deuterated solvent was vacuum transferred into the tube. The tubes were kept near the freezing point of the solvent and in the dark until used. Concentrations were calculated from the weight of the solids and the weight of the solvent added to the NMR tube. From the density of the solvent, the molarity was then calculated. The error in each weight is taken as 0.001 g, giving a total concentration error of typically 3%.

Data were collected on a Nicolet NT200WB instrument operating at 200 MHz. Acquisition parameters were a 4.0-μs pulse width, a 50-μs postacquisition delay, a 20 000-Hz sweep width, a 32K block size, and 256 pulses. To obtain accurate line widths, the field homogeneity was carefully adjusted for each spectrum on the basis of the amplitude of the ^2H lock signal and the free induction decay signal. All samples were spun. The accumulation time at each temperature was 9 min.

Temperature was controlled with the built-in gas-flow temperature controller. Dry nitrogen flows through a coil immersed in liquid nitrogen. The accuracy of the control was checked by use of the method of Van Geet[10] as modified by Raiford et al.,[11] corrected to 200 MHz, by adding a sealed capillary of methanol acidified to 0.03% with HCl to the experimental sample. The accuracy is ±1 °C, and the precision is ±0.5 °C. The temperature range used was dictated by the freezing point of the particular solvent and the lack of line broadening observed at higher temperatures. The solvents were chosen on the basis of the stability of the Cr complexes, solubility, availability of the deuterated solvent, and varying dielectric constant.

The stability of the solutions at room temperature was determined by measuring the NMR line width and shift and checking for any new peaks at various time intervals for all the solvents used. Solutions of the Cr(I) complex were stable for days in all solvents used. Solutions of the Cr(0) complex showed some initial (<1%) oxidation and were then stable for 8 h, after which they slowly decomposed. Solutions of the Cr(II) complex showed some initial reduction (≤1%) in CD_2Cl_2, CD_3OD, $(CD_3)_2CO$, and CD_3NO_2 but were then stable for days. Solutions of the Cr(II) complex showed ca. 3% reduction in CD_3CN, after which they were stable for days.

The exact chemical shifts and widths for the Cr(0), Cr(I), and Cr(II) complexes were determined from the pure solutions of each complex at each temperature used and in each solvent used with the exception of the Cr(0) complex in acetone and Cr(II) complex in acetonitrile. The solubility of the Cr(0) complex in acetone is low enough that the chemical shift and width from the pure solutions could not be determined directly. The chemical shift and width of the diamagnetic Cr(0) complex were assumed not to differ significantly from their values in CD_2Cl_2. The chemical shift and width for the Cr(I) complex in CD_3CN did not differ from the chemical shift and width in CD_3NO_2; therefore, it was assumed that the Cr(II) shift and width did not differ in the two solvents. Line widths for all pure Cr complexes were obtained from an IBM-PC Microsoft QuickBasic program that allowed for simulation and superposition of the Lorentzian line shape as predicted by the Bloch equations. The sum of the squares of the difference between the calculated and observed intensity at each point was used to determine the best fit. Typically 300–1000 points were used in the fitting. These widths were found to be independent of the concentration range used for the kinetics. Errors in the ^1H line widths for all the Cr complexes are less then 5%.

The samples for kinetic measurements were 1–9 mM in the Cr(0) complex with 1–10 mM of the Cr(I) complex or were 2–4 mM in the Cr(I) complex with 2–6 mM of the Cr(II) complex. No salt was added to any of the reactions due to NMR dynamic range and solubility limitations. For the Cr(I)/Cr(II) reaction the ionic strength was kept between 0.015 and 0.030 M, averaging 0.020 M, by adjusting the mole fraction and concentration of the reactants. The mole fraction of the Cr complexes was varied in the range 0.1–0.9. It could be most accurately determined from the chemical shift of the meta proton by using eq 1.

$$\nu_{ab} = \chi_a\nu_a + \chi_b\nu_b \qquad (1)$$

Here χ_a and χ_b are the mole fraction of each reactant and ν is the resonance frequency (Hz) in the mixture (ab) and pure reactant (a and b) solutions. These results were found to be within 3% of the values calculated from the solute weights.

The rate analysis program used in this study employs equations[8] derived from the Bloch equations[12] for exchange between two sites with nonequal populations and widths, including multiple pairs, assuming no saturation and steady-state conditions. The NMR data analysis has been fully described previously.[8] The line broadening observed for the meta ^1H doublet was used for all rate measurements. This peak was used because the difference in the chemical shift between the Cr(0) and Cr(I) pair and the Cr(I) and Cr(II) pair was large, the peaks were well separated from other resonances in the sample throughout the temperature range used, and the relative intensity was high.

Results

All proton resonances were observed for the pure Cr(0), Cr(I), and Cr(II) species; the shifts and widths of the meta resonance as a function of temperature and solvent are shown in supplementary material Table 1. The resonance lines for the Cr(0) and Cr(I) complexes in CD_2Cl_2 have been previously described.[8] Line widths for the proton resonances in the Cr(I) complex are narrow, typically 4–6 Hz, and for the Cr(II) complex line widths were typically 10–20 Hz. The resonance shifts, relative to internal TMS, for Cr(I) and Cr(II), vary little between the solvents, typically less then 30 Hz. The paramagnetic shift, $\nu_{Cr(0)} - \nu_{Cr(I)}$, pattern of alternating sign for adjacent aromatic and alkyl protons observed in the Cr(0)/Cr(I) system in CD_2Cl_2[8] is also observed in the Cr(II) system. The only difference is that the $\nu_{Cr(0)} - \nu_{Cr(II)}$ paramagnetic shift is approximately twice the magnitude of that for Cr(0)/Cr(I). In each case, decreasing the temperature caused the paramagnetic shift to increase in magnitude.

For comparison with other systems, the rate constants calculated from the activation parameters for $Cr(CNdipp)_6{}^{0/+}$ at 298 K in CD_2Cl_2 and $(CD_3)_2CO$ are 1.8×10^8 and 1.0×10^8 M^{-1} s^{-1}, respectively. The rate constants for $Cr(CNdipp)_6{}^{+/2+}$ at 298 K in CD_2Cl_2, $(CD_3)_2CO$, CD_3OD, CD_3CN, and CD_3NO_2 are 1.6 $\times 10^7$, 1.3×10^7, 2.4×10^7, 1.5×10^7, and 2.9×10^7 M^{-1} s^{-1}, respectively.

The rate constants as a function of temperature, solvent, and reactant concentration for the Cr(0)/Cr(I) reaction and the Cr(I)/Cr(II) reaction are presented in supplementary material Tables 2a–f. The activation parameters for $Cr(CNdipp)_6{}^{0/+}$ and

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Table I. Comparison of Solvent Effects on the Observed and Calculated[a] Activation Parameters for the $Cr(CNdipp)_6{}^{0/+}$[b] and $Cr(CNdipp)_6{}^{+/2+}$ Self-Exchange Reactions

	$(CD_3)_2CO$	CD_3CN	CD_3NO_2	CD_2Cl_2	CD_3OH
$\Delta H^{\ddagger +/2+}_{obs}$ [c]	5.3	3.1	2.2	2.1	3.7
$\Delta H^{\ddagger +/2+}_{calc}$ [c]	3.3	3.4	3.4	3.1	3.5
$\Delta S^{\ddagger +/2+}_{obs}$ [d]	−8.3	−15	−17	−19	−12
$\Delta S^{\ddagger +/2+}_{calc}$ [d]	−12.0	−11.2	−10.8	−12.0	−11.2
$\Delta H^{\ddagger 0/+}_{obs}$ [c]	4.5			1.5[e]	
$\Delta H^{\ddagger 0/+}_{calc}$ [c]	3.4	3.5	3.3	3.2	3.6
$\Delta S^{\ddagger 0/+}_{obs}$ [d]	−6.6			−16[e]	
$\Delta S^{\ddagger 0/+}_{calc}$ [d]	−8.3	−8.2	−8.6	−6.1	−8.4
$\Delta G^{\ddagger out}_{calc}$ [c,f]	3.3	3.5	3.3	2.6	3.6
w_{cal} [c,g]	0.92	0.63	0.64	1.4	0.68

[a] Where $r = 6.2$ Å and ionic strength = 0.02 M. [b] Abbreviation: CNdipp = 2,6-diisopropylphenyl isocyanide. [c] kcal/mol; errors in the observed values are ±0.2 kcal/mol. [d] cal/(mol K); errors in observed values are ±0.6 cal/(mol K). [e] Anderson, K. A.; Wherland, S. *Inorg. Chem.* **1989**, *28*, 601. [f] Calculated from eq 10 at 273 K; see text. [g] Calculated from eq 7, with $z_1z_2 = 2$ at 273 K; see text.

Table II. Comparison of Solvent Effects on the Calculated[a] Terms Contributing to the Activation Parameters for the $Cr(CNdipp)_6{}^{0/+}$[b] and $Cr(CNdipp)_6{}^{+/2+}$ Self-Exchange Reactions

	$(CD_3)_2CO$	CD_3CN	CD_3NO_2	CD_2Cl_2	CD_3OH
$\Delta H^{*}{}_{in}$ [c]	0.7	0.7	0.7	0.7	0.7
$\Delta H^{*}{}_{out}$ [c]	2.9	3.2	2.9	2.8	3.2
ΔH_{trans} [c]	−0.3	−0.3	−0.3	−0.3	−0.3
$w - T(\partial w/\partial T)$ [c]	−0.09	−0.05	+0.03	−0.13	−0.13
$\Delta S^{*}{}_{out}$ [d]	−1.3	−1.2	−1.6	+0.9	−1.4
$\Delta S^{*}{}_{trans}$ [d]	−7.0	−7.0	−7.0	−7.0	−7.0
$\partial w/\partial T$ [d]	−3.7	−2.5	−2.2	−5.8	−3.0

[a] Where $r = 6.2$ Å and ionic strength = 0.02 M. [b] Abbreviation: CNdipp = 2,6-diisopropylphenyl isocyanide. [c] kcal/mol; error in the $\Delta H^{*}{}_{in}$ calculated value is 0.3 kcal/mol; see text. [d] cal/(mol K). [e] Anderson, K. A.; Wherland, S. *Inorg. Chem.* **1989**, *28*, 601.

Table III. Comparison of Solvent Effects on the Observed[a] and Calculated[b] $Cr(CNdipp)_6{}^{0/+}$[c] and $Cr(CNdipp)_6{}^{+/2+}$ Self-Exchange Rate Constants[d]

	$(CD_3)_2CO$	CD_3CN	CD_3NO_2	CD_2Cl_2	CD_3OH
$k^{0/+}_{obs}$	4.9×10^7			1.8×10^8 [e]	
$k^{0/+}_{calc}$	1.8×10^8	1.2×10^8	1.7×10^8	6.6×10^8	1.0×10^8
$k^{+/2+}_{obs}$	5.2×10^6	8.4×10^6	1.9×10^7	1.0×10^7	1.3×10^7
$k^{+/2+}_{calc}$	3.2×10^7	3.8×10^7	5.3×10^7	4.5×10^7	3.0×10^7

[a] Error on k_{obs} is ±10%. [b] Rate constants at 273 K; $r = 6.2$ Å; ionic strength = 0.02 M. [c] Abbreviation: CNdipp = 2,6-diisopropylphenyl isocyanide. [d] $k = M^{-1}\ s^{-1}$. [e] Anderson, K. A.; Wherland, S. *Inorg. Chem.* **1989**, *28*, 601.

$Cr(CNdipp)_6{}^{+/2+}$ were determined by weighted least-square fits of the variable-temperature data to the Eyring equation, as depicted in Figure 1. The enthalpy and entropy of activation for each reaction in each solvent are presented in Tables I and II. The experimentally determined rate constants at 273 K, a temperature within the range measured in all cases, are shown in Table III.

Discussion

The measured values for the electron self-exchange rate constants of $Cr(CNdipp)_6{}^{+/2+}$ are uniformly 1 order of magnitude lower than the analogous values for the lower charged $Cr(CNdipp)_6{}^{0/+}$ system. For both of the solvents for which both reactions were studied, the lower rate constant of the Cr(I)/Cr(II) reaction arises approximately equally from a higher enthalpy and lower entropy of activation.

The effects of solvent on the Cr(I)/Cr(II) reaction have been studied in more detail so more comparisons can be made. Figure 1 shows that there is little variation in rate constant with solvent at 298 K but progressively more at lower temperatures. This same trend is demonstrated in the solvent dependence of the activation parameters. Another way to consider the temperature and solvent dependences and the convergence of the rate constants at 298 K is a plot of ΔH^{*} vs ΔS^{*}, as shown in Figure 2. There is a clear pattern of entropy/enthalpy compensation, with smaller enthalpies of activation accompanied by entropies of activation that decrease to more negative values. Although only two solvents were studied for the Cr(0)/Cr(I) reaction, it appears to give the same pattern. These results cannot be extensively compared to other systems because different solvents are often used and temperature-dependence data are seldom collected. However, in the $Fe(cp)_2{}^{0/+}$ reaction (where cp is cyclopentadienide), a qualitative comparison can be made. Among methanol, acetonitrile, nitromethane, acetone, and methylene chloride there was little variation of the self-exchange rate constant.[13] In general the higher rate constants were observed in methanol and nitromethane, while the lowest rate constant was in acetone, as was observed for the $Cr(CNdipp)_6{}^{+/2+}$ reactions. Within the solvents mentioned above there is a similar compensating pattern observed for the activation parameters. A recent correction of the $Fe(cp)_2{}^{0/+}$ rate constants for three of the above solvents does not significantly change this pattern.[14] The solvent dependencies for $Co(cp)_2{}^{0/+}$, $Fe(cp')_2$, and $Co(cp')_2$ (where cp′ is pentamethylcyclopentadienide) are difficult to compare since the same solvents were not studied, although in the solvents that were studied a larger solvent dependence was observed at 298 K.[15] In a system of similar charge type, the electron self-exchange rate constant of $Cu(dmp)_2{}^{+/2+}$ (where dmp is 2,5-dimethyl-1,10-phenanthroline) shows no solvent dependence

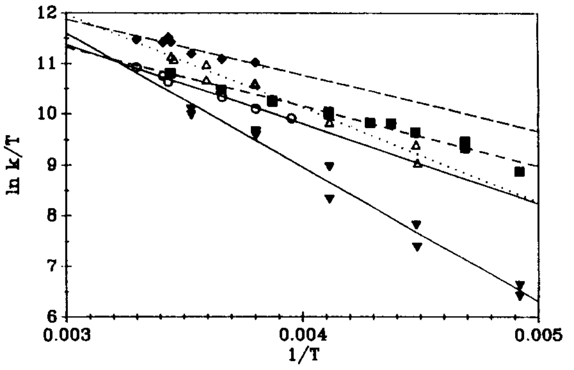

Figure 1. Eyring plots of the temperature dependence of the $Cr(CNdipp)_6{}^{+/2+}$ reaction in the different solvents studied. The ionic strength is ca. 0.02 M in all solvents. Over 30 points were collected in CD_2Cl_2; a representative portion is shown. Key: (■) CD_2Cl_2; (▼) $(CD_3)_2CO$; (△) CD_3OD; (○) CD_3CN; (◆) CD_3NO_2.

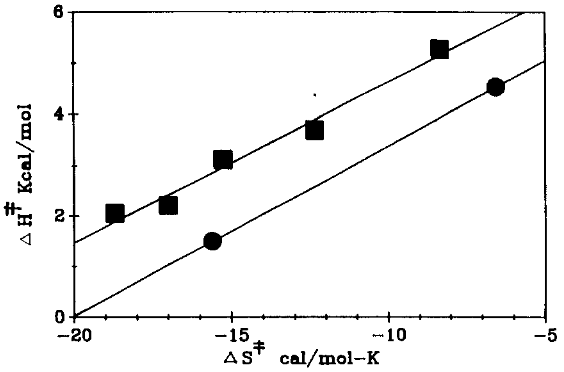

Figure 2. Enthalpy vs entropy of activation for electron self-exchange reactions: (■) $Cr(CNdipp)_6{}^{+/2+}$; (●) $Cr(CNdipp)_6{}^{0/+}$. For the Cr(I)/Cr(II) reactions the order of solvents with increasing enthalpy is CD_2Cl_2, CD_3NO_2, CD_3CN, CD_3OD, $(CD_3)_2CO$. For the Cr(0)/Cr(I) reactions the order of solvents with increasing enthalpy is CD_2Cl_2, $(CD_3)_2CO$.

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between acetone and acetonitrile.[16] In another system of similar charge type the $Mn(CNC_6H_{11})^{+/2+}$ self-exchange reaction showed a larger solvent dependence.[17] In acetonitrile, ethanol, and acetone there was little variation in the rate constant; however, in low-dielectric solvents such as bromobenzene and chloroform significantly lower rate constants were observed. These results are discussed more extensively below.

The electron self-exchange rate constants of ca. 10^8 M^{-1} s^{-1} for the $Cr(CNdipp)_6{}^{0/+}$ reaction and ca. 10^7 M^{-1} s^{-1} for the $Cr(CNdipp)_6{}^{+/2+}$ reaction are some of the highest rate constants measured for neutral and charged systems, respectively.[18-20] On the basis of the Smoluchowski equation and Stokes law,[21,22] eq 2, the rate constant for the $Cr(CNdipp)_6{}^{0/+}$ reaction is a factor

$$k_d^0 = 8RT/3\eta \tag{2}$$

$$k_d = k_d^0(z_1z_2s/r)[\exp(z_1z_2s/r) - 1]^{-1} \tag{3}$$

$$s = (1/4\pi\epsilon_0)e^2/D_sk_BT \tag{4}$$

of 100 lower, at all temperatures measured, than the rate constant for a diffusion-controlled process in acetone. For the charged system, $Cr(CNdipp)_6{}^{+/2+}$, the Debye equation[23] for interacting ions was used (eq 3). This will underestimate the rate constant for reactions between like charged ions if the ionic strength is high enough to lower the electrostatic work required to bring the reactants together. In the equations R is the gas constant, T is the temperature, η is the viscosity, r is the contact distance between the reactants, z_1 and z_2 are the charges on the reactants, ϵ_0 is the permittivity of vacuum, e is the electron charge, and k_B is Boltzman's constant. The dielectric constants and viscosity values were taken from literature sources for each temperature required.[24,25] For all of the solvents at each temperature measured, the calculated rate constants for a diffusion-controlled process were a factor of 50 or larger than the observed rate constant. Diffusion-controlled reactions have been measured for nitromethane[26] and methylene chloride,[27] which confirm that the rates measured for the $Cr(CNdipp)_6$ systems are significantly slower than a diffusion-controlled process. The experimentally observed rates constants are therefore sufficiently slow that it was not necessary to correct for diffusional effects.

Next, the result of the Cr(0)/Cr(I) reaction in CD_2Cl_2[8] and $(CD_3)_2CO$ and the Cr(I)/Cr(II) reaction in CD_2Cl_2, $(CD_3)_2CO$, CD_3NO_2, CD_3CN, and CD_3OD will be compared with the predictions of two theories. The first model that will be discussed is the Marcus collision theory. In this model, the rate constant is the product of a collision frequency Z and an exponential energy term with three contributions, w for the work to bring the reactants together, $\Delta G^*{}_{in}$ for the energy required to reorganize the coordination sphere to the compromise geometry required for electron transfer, and $\Delta G^*{}_{out}$ for the analogous energy to rearrange the solvent. The alternative precursor complex preequilibrium Marcus model considers that the reaction occurs by electron transfer within a previously formed bimolecular assembly.[1] The difference between the models is the way in which the preexponential term is calculated,[28] and the difference will be small for small reactants but significant for larger reactants such as the $Cr(CNdipp)_6$ complexes. It has been previously observed that the collision model works better with large reactants.[28] We also found that the collision model gives more accurate predictions for the $Cr(CNdipp)_6$ calculations; therefore, it is this model that will be used. The observed rate constants for the two reactions in different solvents along with the rates calculated by using eqs 5–10 at 273 K are summarized in Table III.

$$k = Z\kappa' \exp[-(w_r + \Delta G^*{}_{in} + \Delta G^*{}_{out})/RT] \tag{5}$$

$$Z = N[8\pi k_BT(m_1 + m_2)/m_1m_2]^{1/2}r^2/1000 \tag{6}$$

$$w = [z_1z_2e^2/D_sr][(\exp(\beta\sigma))/(1 + \beta\sigma)][\exp(-\beta r)] \tag{7}$$

$$\beta = [(8\pi N\mu e^2)/(1000D_sk_BT)]^{1/2} \tag{8}$$

$$\Delta G^*{}_{in} = (6f_lf_{l+1}(\Delta a)^2)/2(f_l + f_{l+1}) \tag{9}$$

$$\Delta G^*{}_{out} = (e^2/8r)(1/D_{op} - 1/D_s) \tag{10}$$

In the equations, Z is the collision frequency of neutral molecules in solution; eq 6 has been derived for gas-phase collisions.[28] The probability of electron transfer, κ', was assumed to be one.[28] In reactions with poor orbital overlap between the electron donor and acceptor, or other restrictions, this value can fall far below unity. The masses of the two reactants are m_1 and m_2, r is the separation of the metal centers at the time of electron transfer, and N is Avogadro's number. The Coulombic work, w,of bringing the reactants together, corrected to finite ionic strength, is given by eq 7.[21,22] In (7), σ is equal to the hard-sphere radius of the reactant plus the radius of the ion of opposite charge, μ is the ionic strength, and β is the ion interaction parameter given by eq 8. In eq 6, f_l and f_{l+1} are the breathing mode force constants of the two reactants and Δa is the difference between the equilibrium metal–ligand bond distances of the two reactants. In eq 10, D_{op} is the optical dielectric constant, which is equal to the square of the index of refraction for the solvent. All other symbols are as described above.

In the calculated work term σ was determined to be 8.4 Å. The anion, $BF_4{}^-$, radius of 2.2 Å was taken from tabulated values,[29] and the $Cr(CNdipp)_6$ radius of 6.2 Å is from the Cr–Cr distance in the crystal structure of $Cr(CNdipp)_6$.[9] For all the solvents considered z_1z_2 was set equal to 2 for the $Cr(CNdipp)_6{}^{+/2+}$ system and 0 for the $Cr(CNdipp)_6{}^{0/+}$ system. For the Cr(I)/Cr(II) reaction a value for the ionic strength is required. A typical value of 0.02 M was used in all the calculations, but the results are insensitive to the precise value. The Coulombic work term calculated for each charge type and in each solvent is given in Table I. The collision frequency, Z, was calculated to be 2.7 × 10^{11} at 273 K.

For the inner-sphere reorganization term, $\Delta G^*{}_{in}$, the Cr–C bond length [Cr(0), 1.938 ± 0.003 Å;[31] Cr(I), 1.975 ± 0.007 Å;[6] Cr(II), 2.0144 ± 0.002 Å[6]] and force constants are required. The force constants were estimated from Raman data on the isoelectronic $Mn(CNC_6H_{11})_6{}^+$ and $Mn(CNC_6H_{11})_6{}^{2+}$ (f_0 = 1.8 mdyn/Å; f_1 = 2.1 mdyn/Å).[30] For $Cr(CNdipp)_6{}^{2+}$ f was extrapolated from the lower oxidation state data (f_2 = 2.5 mdyn/Å). From the uncertainty in Δa and f_l, $\Delta G^*{}_{in}$ is taken as 0.7 ± 0.3 kcal/mol for both reactions.

For the outer-sphere reorganization energy of the surrounding solvent, $\Delta G^*{}_{out}$, D_{op} and D_s were calculated[24,25] for each solvent used at 298, 273, and 248 K, temperatures within the range measured in all solvents.[24,25] The value of $\Delta G^*{}_{out}$ at 273 K for each solvent used is given in Table III.

The agreement between the observed and calculated rate constants, in Table III, is excellent. Other attempts to calculate

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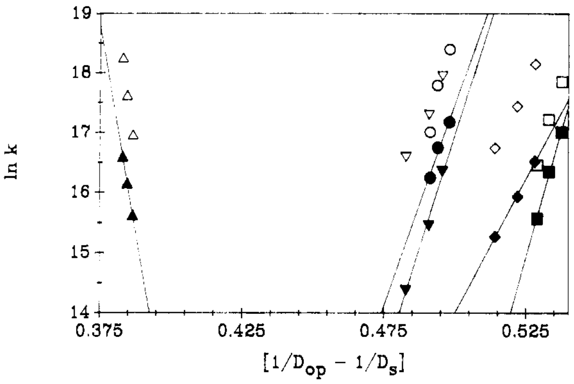

Figure 3. Dependence of ln k with $(1/D_{op} - 1/D)$ at 298, 273, and 248 K. The open symbols are the calculated values at each temperature (see text); the filled symbols are the observed values. The highest rate constants for each solvent are at 298 K and the lowest rate constants are at 248 K. Key: (△) CD_2Cl_2; (▽) $(CD_3)_2CO$; (○) CD_3NO_2; (◇) CD_3CN; (□) CD_3OD.

rate constants with this model have given agreement within a factor of 10–100,[1,13,19,28] again with the calculated values typically larger then the observed ones. This may arise if reactions occur only after collisions with specific orientations of the reactants. The theory treats the reactants as uniform spheres; adding a steric factor of less than 1 in the preexponential would lower the predicted rate constants. The calculated rate constants based on the above equations are only a factor of 2.3–6.1 higher than the observed rate constants for the $Cr(CNdipp)_6^{+/2+}$ self-exchange reaction at 273 K. The calculated rate constants for $Cr(CNdipp)_6^{+/2+}$ in methanol and nitromethane are the most accurately predicted by the Marcus collision theory, and both are less than a factor of 3 higher then the observed rates. The calculated rate constants for the $Cr(CNdipp)_6^{0/+}$ self-exchange reaction are only about a factor of 3.7 higher than the observed rate constants. Another example of the success of the prediction involves the comparison between the two charge types. The observed rate constants in the $Cr(CNdipp)_6^{0/+}$ self-exchange reaction in methylene chloride and acetone are a factor of 13 and 10 faster, respectively, than the observed rate constants in the $Cr(CNdipp)_6^{+/2+}$ system. The analogous calculated rate constant ratios are 15 and 6.

The $Cr(CNdipp)_6^{+/2+}$ self-exchange rate constant shows very little solvent dependence. Although only two solvents were studied in the $Cr(CNdipp)_6^{0/+}$ exchange, the rate constant increases with decreasing dielectric parameter, $(1/D_{op} - 1/D_s)$, precisely as predicted from the ΔG^*_{out} term of the Marcus collision model. The observed rate constants for the $Cr(CNdipp)_6^{+/2+}$ reaction show a similar correlation with the dielectric parameter for the same two solvents but no correlation overall. The calculated values, $k_{calc}^{+/2+}$, also show little dependence on the solvent. The origin of this behavior is the contribution from the work term. In going to the lower dielectric solvents, the work term increases more than ΔG^*_{out} decreases. This is illustrated in Figure 3, which shows observed and calculated rate constants at three temperatures as a function of the Marcus dielectric parameter.

The observed and calculated activation parameters for the self-exchange by $Cr(CNdipp)_6^{0/+}$ and $Cr(CNdipp)_6^{+/2+}$ in each solvent measured are presented in Tables I and II. The prediction of the activation parameters is a severe test of a theory, since 1.4 kcal in the activation parameters is equivalent to a factor of 10 in the rate constant.

In a comparison of the observed parameters for the two systems, the enthalpy of activation in methylene chloride is quite small, 1.5 and 2.1 kcal/mol for the $Cr(CNdipp)_6^{0/+}$ and $Cr(CNdipp)_6^{+/2+}$ self-exchange reactions, respectively. However methylene chloride has the most negative entropies of any of the solvents studied, −16 and −19 cal/(mol K). Acetone has the largest enthalpies and the least negative entropies of all the solvents, 4.5 and 5.3 kcal/mol and −7 and −8 cal/(mol K).

The observed enthalpies do show some solvent dependence varying from 2.1 to 5.3 kcal/mol while the entropies vary from −8.3 to −19 cal/(mol K) in the $Cr(CNdipp)_6^{+/2+}$ self-exchange. The large, negative entropies accompany the small enthalpies; this compensation leads to little change in the rate constants among the solvents. In Figure 2 a plot of observed enthalpy versus entropy for the $Cr(CNdipp)_6^{+/2+}$ exchange is linear for the five solvents measured. This type of solvent influence on the enthalpy and entropy has been previously observed for $Fe(cp)_2^{0/+}$ and other types of reactions.[13,19,32–34] A similar plot of the calculated enthalpy versus entropy is however not linear.

The variation and compensation in ΔS^* and ΔH^* are not predicted by the model, and the origin of these patterns must be sought elsewhere. Both methylene chloride and nitromethane have very small donor numbers of 1.2 and 4.8,[35] respectively, and both have small enthalpies and large negative entropies of activation. Methanol and acetonitrile have similar observed activation parameters and similar donor numbers, 12 and 13, respectively. Acetone with the largest ΔH^*_{obs} and the least negative S^*_{obs} has the largest donor number 17. There is no apparent correlation between the observed rate constants and activation parameters with acceptor numbers. For all of the solvents studied, the small enthalpy and large negative entropies of activation correlate with the weak donor solvents and the large enthalpies of activation and small negative entropies of activation correlate with the stronger donor solvents. This may suggest that with the weak donor solvents the solvents are more ordered around the reacting complexes than the typically solvated reactants, but equally strongly interacting; therefore, there is a large entropy price for electron transfer. Conversely in the strong donor solvents the solvent is comparably structured about the reactants and the complexes undergoing electron transfer, and therefore a smaller entropy of activation is observed. This leads to a picture of the reacting complexes as having highly ordered solvent about them, independent of the solvent donor number. Although the correlation is not exact, possibly due to the small change in rate constant with solvent, the rate constants tend to decrease with increasing solvent donor strength. This would suggest that positive charge is spread out in the transition state. In a comparable system, $Mn(C_6H_{11})_6^{+/2+}$ shows the opposite trend for the solvents studied.[17,35,36] The rate constant increases with increasing solvent donor strength and the large enthalpies, and small entropies, are associated with the high donor strength solvents. Again this difference may be attributed to the fact that the Mn complexes are not conjugated; therefore, they are influenced more by the charge and factors that affect the charge distribution such as solvent donor strength.

The terms contributing to the calculated enthalpy and entropy of activation for the self-exchange reactions are given by eqs 13 and 14.

$$\Delta S_{trans} = R \ln (hZ/k_BT) - R/2 \tag{11}$$

$$\Delta H_{trans} = -RT/2 \tag{12}$$

$$\Delta S^* = \Delta S_{trans} - \partial w/\partial T + \Delta S^*_{out} + \Delta S^*_{in} \tag{13}$$

$$\Delta H^* = (w - T\partial w/\partial T) + \Delta H_{trans} + \Delta H^*_{out} + \Delta H^*_{in} \tag{14}$$

Here ΔH^*_{out} and ΔS^*_{out} were calculated from the temperature dependence of ΔG^*_{out} in eq 10. The energy required to rearrange the inner coordination sphere is simply bond stretching, and therefore, ΔS^*_{in} is set equal to zero and all the ΔG^*_{in} energy appears as ΔH^*_{in}.[17,28,37] The temperature dependence of the work term was calculated to give the $\partial w/\partial T$ and $(w - T\partial w/\partial T)$ terms. From the nomenclature of Brown and Sutin,[28] the entropy and enthalpy contributions from the preexponential term are ΔS_{trans} and ΔH_{trans}, given by eqs 11 and 12.

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The calculated entropy of activation for all of the solvents only varies from −11 to −12 cal/(mol K). $\Delta S_{\mathrm{trans}}$ accounts for −7 cal/(mol K) for all of the solvents. The $\partial w/\partial T$ term contributed the next largest amount to the entropy term. The negative numbers with the largest magnitude are for solvents with the lowest dielectric constants. Methylene chloride is −5.8 cal/(mol K), while nitromethane is only −2.2 cal/(mol K). The smallest contribution to the entropy term comes from $\Delta S^*_{\mathrm{out}}$. For all of the solvents $\Delta S^*_{\mathrm{out}}$ is about −1 cal/(mol K) except for methylene chloride in which it is about +1 cal/(mol K). This result is in part due to the small dielectric term, $(1/D_{\mathrm{op}} - 1/D_{\mathrm{s}})$, for methylene chloride. Another interesting characteristic of the temperature dependence of methylene chloride is that the work term (eq 7) decreases with an increasing dielectric term unlike all of the other solvents studied where work increases with an increasing dielectric term. Also the dielectric term increases with decreasing temperature in methylene chloride unlike all of the other solvents studied. This can be seen in Figure 3.

The calculated enthalpy of activation also varys little, only from 3.1 to 3.5 kcal/mol. The $\Delta H^*_{\mathrm{out}}$ term is the largest contributor to the enthalpy of activation. Again for the $\Delta H^*_{\mathrm{out}}$ term there is little difference among the solvents. The next largest contributor is ΔH^*_{in}, which is simply ΔG^*_{in} as discussed above, and therefore is constant for all of the solvents. A small part of ΔH^* is from $\Delta H_{\mathrm{trans}}$ from eq 12, which is also constant for all of the solvents at −0.3 kcal/mol. The smallest contribution to enthalpy is from the temperature dependence of the work term. This value is 0.1 kcal/mol or less for each solvent.

The experimental activation parameters are compared with the calculated values in Tables I and II. The calculated values of ΔS^* and ΔH^* are from eqs 13 and 14, respectively. Both parameters are in excellent agreement in methanol. Given the precision of the observed values, there is also very good agreement for acetonitrile. For both nitromethane and methylene chloride the calculated ΔH^* is about 1 kcal/mol too large and the ΔS^* is about 6.5 cal/(mol K) less negative then the observed values. In acetone the $\Delta H^*_{\mathrm{calc}}$ is about 2 kcal/mol smaller then the observed value and the $\Delta S^*_{\mathrm{calc}}$ is about 4 cal/(mol K) too negative. The calculated values show no trend with solvent, as was observed, and thus do not predict the compensation behavior.

From this pattern it is difficult to say why the model is not as accurate for these solvents. Since rate constants are quite well predicted and activation parameters are not, the deviation from the theory seems to be caused by the same factors that lead to compensation behavior. The model considers the solvent as a dielectric continuum and the reactants as hard spheres. The molecular features of the solvation process and the nonuniform surface of the complexes are clearly oversimplified.

For the low-dielectric solvents such as methylene chloride and to a lesser extent acetone, ion pairing would be expected.[35,37,38] However the rate constants were found to be in much greater error when a lower charge type was used. For instance, the $k^{0/+}_{\mathrm{calc}}$ values can be used as an estimate of the calculated rate constant with ion pairing since the work term in these calculations is zero. As can be seen in Table III, the calculated rate constants for $\mathrm{Cr(CNdipp)_6}^{+/2+}$ that are already too high would increase a factor of 6–14 if the work term were ignored for these two solvents. The activation parameters would also be less accurately predicted if lower charge types were used. The apparent lack of effect from ion pairing may be in part from the large size of the reactants. The charge density of these large ions is small, and there is no dipole moment for the complex. This same argument may also suggest that the reactants are weakly solvated.

Conversely, the complexes could be ion paired but the ion pairing does not affect the rate. The ion pairs would have large dipole moments, thus involving some electrostatic interaction in bringing them together. The conjugated ligands extend the π-symmetry orbitals involved in the electron-transfer process, thus giving excellent orbital overlap. Slight disturbances of this overlap by the anions may still leave adequate remaining overlap so that the electron-transfer rate is unaffected.

Table IV. Comparison of the Observed and Calculated[a] Solvent Continuum Parameters for $\mathrm{Cr(CNdipp)_6}^{+/2+}$ [b] Self-Exchange

	$\mathrm{(CD_3)_2CO}$	$\mathrm{CD_3CN}$	$\mathrm{CD_3NO_2}$	$\mathrm{CD_2Cl_2}$	$\mathrm{CD_3OH}$
τ_{L}, 10^{-12} s	0.3	0.2	0.2	0.4	8.2
ν_{calc}, 10^{12} s^{-1}	2.2	3.4	3.3	1.5	0.08
ν_{obs}, 10^{12} s^{-1}	0.015	0.015	0.021	0.003	0.032

[a] From eqs 12–14; see text. [b] Abbreviation: CNdipp = 2,6-diisopropylphenyl isocyanide.

Other systems studied in this laboratory have shown a quite different reactivity pattern. In the $\mathrm{Mn(CNC_6H_{11})_6}^{+/2+}$ system it was found that the rate constants were a factor of 10 smaller in low-dielectric solvents.[17,35] This was attributed to a slow ion pair pathway for electron transfer. Ion pairs in this system may have more of an effect because the Mn complexes are not conjugated and therefore have less orbital overlap. In this case, orbital overlap will be quite distance dependent. This has been shown[36] by the dependence of the electron self-exchange rate constant on the size of the alkyl R group in complexes of the type $\mathrm{Mn(CNR)_6}^{+/2+}$. The presence of a counterion between or mutually in contact with two reactants can thus increase the electron-transfer distance and decrease κ' and the electron-transfer rate constant. This interpretation is further supported by the high rate constant for the conjugated system $\mathrm{Mn(CNC_6H_5)_6}^{+/2+}$, which is about the size of $\mathrm{Mn(CNC_6H_{11})}^{+/2+}$ but has an electron self-exchange rate constant comparable to that of $\mathrm{Mn(CNCH_3)_6}^{+/2+}$. Recent work on the reduction of $\mathrm{Cr(CNdipp)_6}^{2+}$ by $\mathrm{Co(nox)_3(B\text{-}nBu)_2}$ has shown that the reaction is insensitive to added salt.[39]

The other model that will be considered is the solvent dynamic model. This model treats the solvent polarization dynamics as being overdamped, where the motion along the reaction coordinate associated with dipole reorientation is impeded by dielectric friction from the surrounding solvent molecules.[15,40] It is thus a modification of the preexponential term of the Marcus model. The observed frequency factor, $\nu^{\mathrm{n}}_{\mathrm{obs}}$, is calculated from eq 15, and the

$$\nu^{\mathrm{n}}_{\mathrm{obs}} = k\{K_{\mathrm{p}} \exp[-(\Delta G^*{}_{\mathrm{out}} + \Delta G^*{}_{\mathrm{in}})/RT]\}^{-1} \qquad (15)$$

$$K_{\mathrm{p}} = (4\pi r^3 N/3000) \exp(-w/RT) \qquad (16)$$

$$\nu^{\mathrm{out}}_{\mathrm{calc}} = \tau_{\mathrm{L}}^{-1}(\Delta G^*{}_{\mathrm{out}}/4\pi k_{\mathrm{B}} T)^{1/2} \qquad (17)$$

predicted relative frequency factor, $\nu^{\mathrm{out}}_{\mathrm{calc}}$, is calculated from $\Delta G^*_{\mathrm{out}}$, as predicted from the dielectric continuum model of solvent relaxation (eq 17). For eqs 15 and 16, r, w, ΔG^*_{in}, and $\Delta G^*_{\mathrm{out}}$ are all calculated as described above from eqs 7–10. Here k is the observed rate constant. In eq 16 τ_{L} is the longitudinal solvent relaxation time. In Table IV, τ_{L}^{-1}, $\nu^{\mathrm{n}}_{\mathrm{obs}}$, and $\nu^{\mathrm{out}}_{\mathrm{calc}}$ are presented.

The solvent-dependent $\nu^{\mathrm{n}}_{\mathrm{obs}}$ values show no correlation with the $\nu^{\mathrm{out}}_{\mathrm{calc}}$ values. The ν_{obs} values range from 0.006 to 0.03, only a factor of 5. However, the ν_{calc} values vary from 0.08 to 3.3, a factor of 40. All of the ν_{calc} values are a factor of 100 larger then the observed values except for methanol where ν is less then a factor of 3 larger. As can be seen from eqs 15–17, a larger τ_{L} should result in lower k and small τ_{L} should result in higher k's until the solvent reorganization is no longer the rate-determining step. Comparisons of τ_{L} show that there is no correlation between τ_{L} and the observed rate constants.

In summary, the experimental self-exchange rate constants are in excellent agreement and the activation parameters are in reasonably good agreement with the predictions from the Marcus collision model. The rate constants show little solvent dependence, but the experimental activation parameters show a compensation pattern with solvent. However, the calculated activation parameters show no trend with solvent, and thus do not predict the compensation behavior. With the exception of acetone the deviations between the observed and calculated values of $\Delta H^*_{\mathrm{obs}} < \Delta H^*_{\mathrm{calc}}$ and $\Delta S^*_{\mathrm{obs}} < \Delta S^*_{\mathrm{calc}}$ have been observed before.[19] These

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deviations maybe from reactant–reactant and reactant–solvent interactions, which the model does not address. There is a correlation between large negative entropies and weak donor solvents. This work is being extended with the study of cross-reactions with the $Cr(CNdipp)_6^{2+}$ complex.

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Supplementary Material Available: Tables of reactant concentrations, temperatures, chemical shift values, and line widths (Tables 1 and 2a–f) (7 pages). Ordering information is given on any current masthead page.

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Interactions in Aqueous Solution at 25 °C of Palladium(II) and Mercury(II) with 1,4-Dithia-18-crown-6 and 1,10-Dithia-18-crown-6. A Thermodynamic, Spectral, and X-ray Crystallographic Study

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log K, ΔH, and ΔS values for the interactions of Hg(II) and Pd(II) with 1,4-dithia-18-crown-6 (1,4-$T_2$18C6) and 1,10-dithia-18-crown-6 (1,10-$T_2$18C6) were determined in aqueous solution at 25 °C by polarography and competitive calorimetry. The reaction stoichiometries of either metal ion with 1,4-$T_2$18C6 and 1,10-$T_2$18C6 are 1:2 and 1:1, respectively. The formation of both metal complexes of 1,10-$T_2$18C6 is favored by both ΔH and ΔS, while that of both metal complexes of 1,4-$T_2$18C6 is favored by ΔH only. The thermodynamic results have been interpreted in terms of ligand field stabilization energy (LFSE), charge-transfer, and macrocyclic effects. The UV/vis absorption spectra of Pd(II) complexes with both crown thioethers in 0.5 M HNO_3 show that LFSE and charge-transfer effects make large contributions to the formation of the very stable complex $Pd(1,4\text{-}T_2 18C6)_2^{2+}$. The molecular structures of Pd(II) complexes with both crown thioethers have been determined by single-crystal X-ray analysis. The complex $Pd(1,10\text{-}T_2 18C6)(NO_3)_2$ crystallizes in the orthorhombic $Pna2_1$ space group with $a = 10.508$ (4) Å, $b = 13.871$ (7) Å, $c = 13.772$ (7) Å, $Z = 4$, and $R = 0.064$. The complex $Pd(1,4\text{-}T_2 18C6)_2(NO_3)_2$ crystallizes in the orthorhombic $Pbca$ space group with $a = 8.474$ (2) Å, $b = 18.349$ (5) Å, $c = 148.969$ (25) Å, $Z = 8$, and $R = 0.083$. A cis-square-planar configuration is found for the $Pd(1,10\text{-}T_2 18C6)^{2+}$ complex.

Introduction

Crown thioether ligands are noted for their significant affinity for Cu(I), Cu(II), Pd(II), Ag(I), Pt(II), Pt(IV), Au(I), Au(III), Hg(I), and Hg(II) in aqueous solution.[1-5] Hence, these crown thioethers represent potentially useful reagents for these specific metal ions in analytical determinations, recovery and separation processes, and homogeneous catalysis. Complexes of Pd and Pt have been shown to act as active homogeneous catalysts in reactions of industrial importance.[6,7] The coordination chemistry of Pd and Pt complexes with open-chain and crown thioethers has been elucidated by using X-ray diffraction results.[8,9] However, few thermodynamic quantities for crown thioether–Pt group metal interactions have been reported,[10] probably because of the difficulty in the determination of these quantities, particularly in aqueous media.[11]

In the present study, this difficulty is circumvented by using a competitive procedure combining calorimetric[11] and polarographic data. Since log K values for the formation of Pd(II)–thioether complexes are expected to be very large, determination of these constants is not possible by using direct methods.[12,13] For instance, potentiometric and spectrophotometric methods become invalid because Pd(II) forms very stable complexes with thioethers. Also, the polarographic method cannot be used because of the irreversibility of the reduction of the Pd(II) complex at the dropping-mercury electrode in aqueous solution. However, the polarographic determination of K values for Hg(II)–thioether interaction is not difficult. As will be seen in the Results and Discussion sections, the differences between log K (Δ log K) values for Hg(II) and Pd(II) interactions with these thioethers are of the correct magnitude to allow them to be determined by a competitive calorimetric technique. The combination of these Δ log K values with those for Hg(II) interaction with thioethers should lead to corresponding Pd(II) values. This method should be useful for the determination of the log K values for other Pd(II)–ligand interactions. Since Hg(II) is one of the few metal ions that can bind strongly to thioethers in aqueous media, these systems may provide the possibility of selective removal of Hg(II) from the environment. In the present paper, attention is directed to the investigation of K, ΔH, and ΔS values for the interaction of sulfur-substituted macrocyclic ligands with Pd(II) and Hg(II) and to the correlation of these quantities with structural data for the Pd(II) complexes.

Experimental Section

Materials. The crown thioethers and metal salts were obtained in the best purity available from the sources indicated and used without further purification: 1,10-dithia-18-crown-6 (1,10-$T_2$18C6) and 1,4-dithia-18-crown-6 (1,4-$T_2$18C6) (Parish Chemical Co.) (molecular structures shown in Figure 1); $Pd(NO_3)_2$ and $Hg(NO_3)_2$ (Morton Thiokol); HNO_3 (Mallinckrodt).

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