Note also that these deductions are not dependent upon the assumed value of $E°$ for ferrichrome or ferrichrome A. If we assume $E° = -0.23$ V (an impossibly low value because the reduction by vanadium(II) goes to completion) rather than $E° = -0.16$ V, then the values of $(\Delta G_{11}^*)_{app}$ for the metal ion reductions of the ferrichromes decrease by 1.6 kcal mol^{-1}. The demonstrated differences in reactivity remain. If we assume $E° = -0.12$ V (the measured value for ferrioxamine B at low pH), then the values of $(\Delta G_{11}^*)_{app}$ for the metal ion reductions of the ferrichromes increase by almost 1 kcal mol^{-1}.

Thus, the three hydroxamate siderophores ferrioxamine B, ferrichrome, and ferrichrome A display an interesting variety of electron-transfer reactivities even though their coordination geometries and redox potentials are quite similar. Table VI summarizes the kinetic data. Ferrioxamine B undergoes efficient outer-sphere electron transfer at a rate that is very well predicted by Marcus theory. This complex is also very labile and is susceptible to rapid reduction by chromium(II) via inner-sphere attack. The redox active site of ferrichrome is kinetically less accessible than that of ferrioxamine B to metal ion reductants. Outer-sphere electron transfer requires greater activation, and inner-sphere reduction is rate limited by slow dissociation of an hydroxamate from iron(III). Ferrichrome A has the least accessible redox active site. Even greater activation energies are required, and the inner-sphere pathway is unavailable. Parallel paths are operating in the reduction of ferrichrome A. Two species, which probably are H_3FcA and H_2FcA^-, are reduced at similar rates. The different reactivity may be due to simple charge effects, or it may be due to association of M(II) with one carboxylate to produce a bridged outer-sphere redox mechanism. The small reductant SO_2^- interestingly shows similar reactivity with all three siderophore complexes. It apparently has nearly equal access to each of the three redox active sites.

The pH range employed in this study is somewhat limited. Reactions involving metal ion reductants were performed below pH 4.5 due to the insolubility and unknown reducing properties of M(II) at higher pH. The lower limit of pH is dictated by the pK_a of about 1.5 for the dissociated bis(hydroxamato) complex.[39] The lower limit of pH is 2.6 so that the fully coordinated tris(hydroxamato)iron(III) siderophore complex was kept in at least 12-fold excess over the bis(hydroxamato) ferric siderophore complex. Nevertheless, we can provide partial characterization of the redox properties of the three iron(III) siderophore complexes. The reductant SO_2^- reduces each of the iron(III) siderophores with equal efficiency and suggests that if a common in vivo reductant exists, it is a small highly reactive species. Each of the complexes is capable of fast outer-sphere electron transfer with such a species. The effect of pH is most interesting. The iron(II)/iron(III) redox couple for each complex becomes more positive with increasing proton concentration. Reductive release of iron from the complexes therefore might be assisted by a mechanism that involves proton transfer or a high local proton concentration. Protonation also renders ferrioxamine B and ferrichrome susceptible to inner-sphere attack. In contrast, ferrichrome A is well insulated against inner-sphere reduction. Ferrichrome A carries a large charge that may contribute significantly to its redox characteristics.

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Registry No. Cr, 7440-47-3; Eu, 7440-53-1; V, 7440-62-2; Fc, 15630-64-5; FcA, 15258-80-7; dithionite, 14844-07-6.

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High-Pressure Stopped-Flow Study of Complex Formation on Nickel(II) Ion in Dimethylformamide. Possible Existence of a 5-Coordinate Intermediate

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The complex formation of (thiocyanato)nickel(II) and bis(diethyldithiocarbamato)nickel(II) in dimethylformamide (DMF) has been studied as a function of temperature and pressure. The kinetic parameters obtained are $k_f^{298} = (3.1 \pm 0.2) \times 10^4$ M^{-1} s^{-1}, $\Delta H_f^* = 66.0 \pm 1.0$ kJ mol^{-1}, $\Delta S_f^* = +62.7 \pm 3.7$ J K^{-1} mol^{-1}, and $\Delta V_f^* = +8.8 \pm 0.5$ cm^3 mol^{-1} for the SCN^- reaction and $k_f^{298} = (3.03 \pm 0.03) \times 10^4$ M^{-1} s^{-1}, $\Delta H_f^* = 62.0 \pm 0.4$ kJ mol^{-1}, $\Delta S_f^* = +48.8 \pm 1.3$ J K^{-1} mol^{-1}, and $\Delta V_f^* = +12.4 \pm 0.2$ cm^3 mol^{-1} for Et_2DTC^-. The discussion centers on whether to assign I_d or D mechanisms to nickel(II) complexation in DMF. Earlier work has shown that the DMF exchange rate is invariant with DMF concentration for exchange on $Ni(DMF)_6^{2+}$ in DMF/nitromethane mixtures.[1] This fact and the above results are indicative of a D mechanism.

Introduction

In recent years, our kinetic interests have been mainly focused on the elucidation of the mechanisms that govern solvent exchange on divalent and trivalent transition-metal centers, in both aqueous[2,3] and nonaqueous media,[4,5] using high-pressure NMR.[6] For the first-row transition-metal ions, it is now apparent that the mechanism for solvent exchange is not unique for all cations but changes from an associative activation mode for the early elements to a dissociative activation mode for the later ones.

We have recently extended our interests to the wider class of complex formation reactions on divalent cations. To this purpose, a high-pressure stopped-flow spectrophotometer was built and the formation of $V(H_2O)_5SCN^+$ from $V(H_2O)_6^{2+}$

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was studied in water as a function of pressure.[7] The results confirmed the identity of behavior for water exchange and water replacement in aqueous solutions.

The present study is concerned with complex formation reactions in nonaqueous solvents, which is a much less studied area. For octahedral divalent metal ions, the first two high-pressure mechanistic studies have only appeared recently. Caldin and Greenwood[8] have studied the reactions of Ni^{2+} and Co^{2+} with PADA (pyridine-2-azo-*p*-dimethylaniline) in DMF and Me_2SO by laser *T*-jump methods, and Tanaka et al.[9] have studied the reaction of Ni^{2+} with isoquinoline in DMF, CH_3CN, MeOH, and EtOH by stopped-flow techniques. Both reports were rationalized according to I_d substitution mechanisms. However, Frankel[1] had observed that the rate of DMF exchange on $Ni(DMF)_6{}^{2+}$ is independent of the DMF concentration when nitromethane is added as an inert cosolvent. Hence, this author proposed a limiting D mechanism for this process. This would imply that the mechanism for solvent exchange on $Ni(DMF)_6{}^{2+}$ in DMF is different from the mechanism for complex formation in this solvent, whereas in water an I_d mechanism adequately explains both processes.[2,10] To further investigate the reactions of $Ni(DMF)_6{}^{2+}$ in DMF, we have studied the effect of pressure on the formation of nickel(II) complexes with thiocyanate and diethyldithiocarbamate (Et_2DTC^-) in DMF.

Experimental Section

All solutions were prepared in a glovebox under an inert nitrogen atmosphere at room temperature. Concentrations are given uncorrected for volume changes due to variation in temperature and/or pressure.[11] $Ni(DMF)_6(ClO_4)_2$ was prepared by following the method of Selbin et al.[12] for the preparation of Me_2SO salts. EDTA titration gave % Ni = 8.37 (calculated % Ni = 8.43). $NaClO_4{\cdot}H_2O$ (Merck, p.a.) and KSCN (Merck, p.a.) were dried in an oven at 120 °C for 48 h and stored in a desiccator over $CaCl_2$. Sodium diethyldithiocarbamate trihydrate (Fluka, p.a.) was recrystallized from acetone/ether shortly before use. Dimethylformamide (Fluka, p.a.) was dried over 4-Å molecular sieves for 24 h, stored over KOH pellets for a further 24 h, and finally distilled under reduced pressure and stored over 4-Å molecular sieves in a glovebox. The ionic strength was fixed at 0.10 M for the Et_2DTC^- study and at 0.20 M for the SCN^- study. $NaClO_4$ was added as necessary in both studies. The wavelengths of observation were λ_{obsn} = 330 nm (Et_2DTC^-) and λ_{obsn} = 320 nm (SCN^-).

The high-pressure and conventional stopped-flow spectrophotometers have been described previously.[7] First-order rate constants, k_{obsd}, were obtained from weighted linear least-squares analyses of at least the first 3 half-lives. Second-order rate constants, k_f, were determined by weighted linear least-squares analyses of the variation of k_{obsd} with concentration of excess reagent.[13] Activation parameters were calculated from weighted nonlinear least-squares analyses according to the Eyring equation for ΔH^* and ΔS^* and eq 1 for ΔV^*, where k_0 represents the rate constant at 0 MPa.

$$\ln k = (\ln k_0) - \Delta V^* P/RT \qquad (1)$$

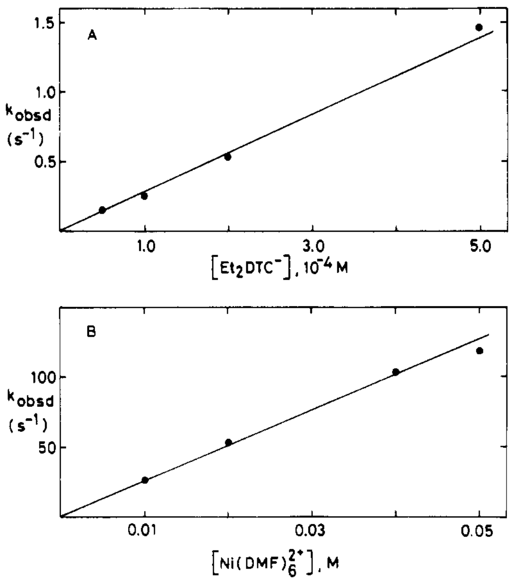

Figure 1. Variation of first-order rate constants with the concentration of excess reagent for the formation of $Ni(Et_2DTC)_2$ (A) and $NiSCN^+$ (B) in DMF at 273.2 K.

Table I. Second-Order Rate Constants as a Function of Temperature for the Reactions of $Ni(DMF)_6{}^{2+}$ with SCN^- and Et_2DTC^- in DMF[a]

SCN^- [b]		Et_2DTC^- [c]	
T, K	k_f, M^{-1} s^{-1}	*T*, K	$10^{-4}k_f$, M^{-1} s^{-1}
233.2	15.0 ± 0.9	273.2	0.275 ± 0.019
243.2	53.2 ± 9.9	283.2	0.755 ± 0.028
253.2	194 ± 43	293.2	1.94 ± 0.10
263.2	817 ± 46	298.2	3.11 ± 0.15
273.2	2530 ± 110	303.2	4.85 ± 0.15
		313.2	10.7 ± 0.3
		323.2	22.7 ± 0.3

[a] Errors quoted are standard deviations. [b] $[Ni(DMF)_6{}^{2+}]$ between 0.005 and 0.05 M; $[SCN^-]$ between 5×10^{-4} and 0.004 M. [c] $[Ni(DMF)_6{}^{2+}]$ between 2×10^{-6} and 2×10^{-5} M; $[Et_2DTC^-]$ between 5×10^{-5} and 5×10^{-4} M.

Results

Thiocyanate Reaction. The reaction between $Ni(DMF)_6{}^{2+}$ and SCN^- was studied under conditions of excess metal ion (≥10:1) to ensure mono complex formation and pseudo-first-order kinetics. Figure 1 shows the variation of the first-order rate constants, k_{obsd}, with concentration of the excess reagent. The kinetics are consistent with eq 2, for which the observed rate constant is given by eq 3.

$$Ni(DMF)_6{}^{2+} + SCN^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ni(DMF)_5SCN^+ + DMF \qquad (2)$$

$$k_{obsd} = k_f[Ni(DMF)_6{}^{2+}] + k_r \qquad (3)$$

Under the conditions of this study, the equilibrium is essentially displaced to the products and k_r, the intercept of k_{obsd} vs. $[Ni(DMF)_6{}^{2+}]$ is 0 within experimental error. Accordingly, k_r was set equal to 0 in the fit of the data to eq 3. The reaction was studied as a function of temperature, and the results are presented in Table I. Table II lists the calculated activation parameters.

This reaction has been studied previously at different temperatures,[14] but we have repeated the work at conditions involving much higher concentrations of reagents, in an effort to learn more about the mechanism of reaction (see later discussion). The earlier study reported the following results calculated for zero ionic strength: $k_f^{293} = 1.3 \times 10^6$ M^{-1} s^{-1}, ΔH_f^* = 69.0 kJ mol^{-1}, ΔS_f^* = +89.5 J K^{-1} mol^{-1}. These

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Table II. Activation Parameters for DMF Exchange and Replacement on Ni(DMF)$_6^{2+}$ in DMF[a,b]

	$10^{-3}k_f^{298}$, M^{-1} s^{-1}	ΔH_f^*, kJ mol^{-1}	ΔS_f^*, J K^{-1} mol^{-1}	ΔV_f^*, cm^3 mol^{-1}	ref
DMF[c]	3.8	62.8 ± 2.1	+33.5 ± 8.4	+9.1 ± 0.3 (297 K)	6
isoquinoline	2.4	51.9 ± 1.7	−8 ± 4	+9.3 ± 0.3 (298 K)	16, 9
PADA	1.2 ± 0.1	31.4 ± 2.1	−82.6 ± 6.7	+9.1 ± 2.7 (298-323 K)[d]	17, 8
SCN$^-$	31 ± 2	66.0 ± 1.0	+62.7 ± 3.7	+8.8 ± 0.5 (264 K)	this work
Et$_2$DTC$^-$	30.3 ± 0.3	62.0 ± 0.4	+48.8 ± 1.3	+12.4 ± 0.2 (298 K)	this work

[a] Ionic strength (NaClO$_4$) was 0.10 M for the Et$_2$DTC$^-$ study and the isoquinoline variable-pressure study and was 0.20 M for the SCN$^-$ study but was not controlled for the remaining studies. [b] Errors quoted are standard deviations. [c] First-order-exchange rate constant (s^{-1}) and related activation parameters. [d] Average of four values given in ref 8.

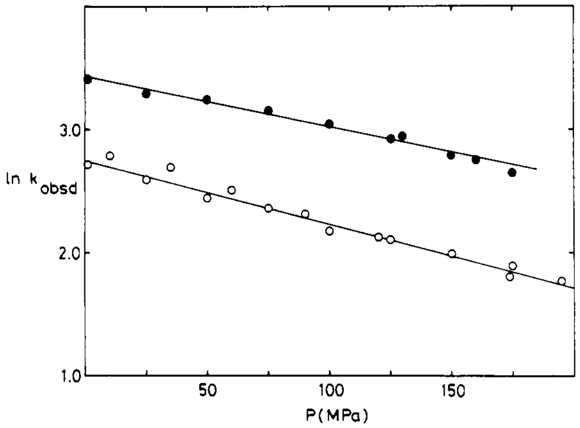

Figure 2. Effect of pressure on first-order rate constants for the formation of NiSCN$^+$ (●) and Ni(Et$_2$DTC)$_2$ (○) in DMF.

numbers are consistent with those obtained in our study, considering the difference in ionic strength (0.20 M in this work).

The first-order rate constants for NiSCN$^+$ formation for solutions containing 0.0400 M Ni(DMF)$_6^{2+}$ and 0.00400 M SCN$^-$ at 263.8 K were measured at pressures varying from 1 to 175 MPa. Since there is no significant contribution from the reverse reaction, the k_{obsd} values are directly proportional to the second-order formation constants, k_f, and hence ΔV_f^* obtained from eq 1. Figure 2 indicates the change in k_{obsd} with pressure. The volume of activation is calculated to be ΔV_f^* = +8.8 ± 0.5 cm^3 mol^{-1} with k_{obsd}(0 MPa) = 30.7 ± 0.7 s^{-1}, which is close to the value (32.8 s^{-1} at 263.8 K) observed on the conventional stopped-flow instrument.

Diethyldithiocarbamate Reaction. The reaction between the nickel(II) cation and Et$_2$DTC$^-$ has been studied previously in Me$_2$SO.[15] It has been found that the stable product is Ni(Et$_2$DTC)$_2$ and that conditions of excess metal ion result in complicated kinetics. For excess ligand, the kinetics simplify and the observed rate of formation of the bis complex is equal to the rate of formation of the mono complex. The reaction proceeds to completion. The same behavior is observed in DMF solution. The reaction was therefore studied with an excess of ligand present (≥10:1). Figure 1 shows the change in first-order rate constant, k_{obsd}, with the concentration in Et$_2$DTC$^-$. The trihydrate salt of the ligand was used, and to check whether this source of water (<2 × 10^{-3} M for the most concentrated solution) affected the reaction rate and the spectra, approximately 10^{-2} M H$_2$O was added to a test solution but had negligible effect. Variable-temperature and variable-pressure results are presented in Tables I and II and are similar to those observed for the SCN$^-$ system.

Again, since the reaction is irreversible, a single solution mixture (5.00 × 10^{-4} M Et$_2$DTC$^-$ and 5.00 × 10^{-5} M Ni(DMF)$_6^{2+}$) was studied as a function of pressure. Figure 2 shows the variation of k_{obsd} with pressure at 298.2 K. The calculated volume of activation is ΔV_f^* = +12.4 ± 0.2 cm^3 mol^{-1}, and the rate constant at zero pressure, k_{obsd}(0 MPa) = 15.0 ± 0.2 s^{-1}, is comparable to k_{obsd} = 16.9 s^{-1} measured on the conventional stopped-flow instrument.

Discussion

Table II is a compilation of rate constants and activation parameters for Ni(DMF)$_6^{2+}$ reactions in DMF for which data are available from high-pressure studies. On the basis of these data, an attempt can be made to decide on the exact nature of the reaction mechanism.

The activation entropy, ΔS_f^*, is large and positive in three cases, very negative but poorly defined (20 K temperature range) when PADA is the ligand, and slightly negative for isoquinoline complexation (30 K range). Therefore, as observed on other occasions, with the large error inherent in its determination,[6] this activation parameter does by no means offer conclusive evidence on the mechanism. The volume of activation, ΔV_f^*, on the other hand, is clearly positive for all five processes, undoubtedly showing the expected dissociative character of substitution on Ni^{2+} in dimethylformamide.

For complex formation reactions, both D (eq 4) and I$_d$ (eq 5) mechanisms can be described as a preequilibrium followed by the incorporation of a ligand into the first coordination sphere of the metal.[10] Hence, these reactions can exhibit

$$\begin{gathered}\mathrm{Ni(DMF)_6^{2+}} \underset{k_s}{\overset{k_{ex}}{\rightleftharpoons}} \mathrm{Ni(DMF)_5^{2+}} + \mathrm{DMF} \\ \mathrm{Ni(DMF)_5^{2+}} + \mathrm{L}^{n-} \xrightarrow{k_L} \mathrm{Ni(DMF)_5L^{(2-n)+}}\end{gathered} \qquad (4)$$

$$\begin{gathered}\mathrm{Ni(DMF)_6^{2+}} + \mathrm{L}^{n-} \overset{K_{os}}{\rightleftharpoons} [\mathrm{Ni(DMF)_6 \cdots L}]^{(2-n)+} \\ [\mathrm{Ni(DMF)_6 \cdots L}]^{(2-n)+} \xrightarrow{k_I} \mathrm{Ni(DMF)_5L^{(2-n)+}} + \mathrm{DMF}\end{gathered} \qquad (5)$$

either second-order or limiting first-order kinetics, depending on the relative rate constants and concentration conditions.

When the metal ion is in excess, pseudo-first-order kinetics are observed for the reaction between Ni(DMF)$_6^{2+}$ and thiocyanate. The observed first-order rate constant, k_{obsd}, is then given by eq 6 for a D mechanism and eq 7 for an I$_d$

$$k_{obsd} = \frac{k_{ex}k_L[\mathrm{Ni(DMF)_6^{2+}}]}{k_s[\mathrm{DMF}]} \qquad (6)$$

$$k_{obsd} = \frac{K_{os}k_I[\mathrm{Ni(DMF)_6^{2+}}]}{1 + K_{os}[\mathrm{Ni(DMF)_6^{2+}}]} \qquad (7)$$

mechanism.[18] Equation 7 indicates that k_{obsd} will approach

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(18) There are two limiting types of behavior for a D mechanism. If the initial DMF dissociation is rate determining, then k_{obsd} is independent of [Ni(DMF)$_6^{2+}$] and equal to k_{ex}. If the ligand incorporation is rate determining, then k_{obsd} varies with [Ni(DMF)$_6^{2+}$] (as we observed) and eq 6 applies. If the two steps occur at comparable rates, then non-first-order curves result. For an I$_d$ mechanism the preequilibrium is diffusion controlled and is much faster than the interchange step. The observed first-order rate constant may be invariant with [Ni(DMF)$_6^{2+}$] due to the saturation kinetics indicated in eq 7.

the limiting value k_I as the $K_{os}[Ni(DMF)_6^{2+}]$ term becomes much greater than unity. This would be reflected in a curvature of the k_{obsd} vs. $[Ni(DMF_6^{2+}]$ plot. If an I_d mechanism is really operative in the case of thiocyanate complexation, the linear plot in Figure 1 should correspond to the very first linear part of the curve, taking into account the experimental errors. The maximum curvature to allow for this linear portion, however, would require a K_{os} value inferior to 2 M^{-1}. A calculation of the theoretical value of K_{os} using the Fuoss equation,[19] with an estimated distance of closest approach of 7 Å, yields a value of 5 M^{-1}. Considering the approximations used in the calculation, the two values are not very different and one cannot dismiss an I_d mechanism. However, a K_{os} value less than or equal to 2 M^{-1} introducted into eq 7 implies an interchange rate constant, k_I, greater than or equal to 1.4×10^4 s^{-1}, whereas the solvent-exchange rate constant k_{ex} is 3.8×10^3 s^{-1}.[4] This is contrary to what is expected for an I_d mechanism for which a statistical model predicts k_I equal to $0.75k_{ex}$.[20] Experimentally, for nickel(II) complex formation in water, k_I is observed to be even less, about $0.2k_{ex}$.[21]

When the ligand is in excess, discrimination between D and I_d mechanisms could be easier since high concentrations of ligand may effect a change of the rate-determining step for the D mechanism. Equations 8 and 9 give the dependences

$$k_{obsd} = \frac{k_{ex}k_L[L]}{k_s[DMF] + k_L[L]} \tag{8}$$

$$k_{obsd} = \frac{K_{os}k_L[L]}{1 + K_{os}[L]} \tag{9}$$

of the observed first-order rate constants on ligand concentration for D and I_d mechanisms, respectively. For the dithiocarbamate reaction, plots of k_{obsd} vs. $[Et_2DTC^-]$ are linear (Figure 1) but only low concentrations of ligand were present and either eq 8 or 9 adequately explains the results.[22] For the thiocyanate reaction, the rate was much slower than expected,[23] suggesting that complexes of higher stoichiometry are formed; hence, no conclusive evidence could be obtained for this system.

The volumes of activation listed in Table II were all determined under conditions where the reactions obey second-order rate laws. They are therefore composite values according to eq 10 (D mechanism) and 11 (I_d mechanism). For a D

$$\Delta V_f^* = \Delta V_{6\to5}^0 + \Delta V_L^* \tag{10}$$

$$\Delta V_f^* = \Delta V_{os}^0 + \Delta V_I^* \tag{11}$$

mechanism a common volume of reaction for the 6-coordinate to 5-coordinate dissociation preequilibrium, $\Delta V_{6\to5}^0$, is present along with a potentially ligand-dependent volume of activation, ΔV_L^*, corresponding to the ligand bonding to the metal center. ΔV_L^* is influenced by the nucleophilicity and stereochemistry of the ligand as well as by the effects of electrostatic charge cancellation. For an I_d mechanism, electrostatic effects would, in the same way, influence the ΔV_{os}^0 term in eq 11.[24] The volume of activation for the interchange step, ΔV_I^*, is dominated by the solvent dissociation and hence can be equated to a constant, ΔV_{ex}^*. Considering the 1–2 cm^3 mol^{-1} uncertainty in their measured values,[27] the ΔV_f^* values do not vary significantly with the nature of the entering ligand. A distinction between D and I_d mechanisms cannot therefore be based on this parameter.

The recently published reports[28] on the exchange of DMF on lanthanide cations have shown that a mechanistic crossover occurs across the series from an I_d mechanism (Tb^{3+}) to a D mechanism (Tm^{3+}, Yb^{3+}) with an intermediate member (Er^{3+}) reacting via both mechanisms. The mechanisms were deduced from the variation of the observed exchange rate constant, k_{obsd}, with the concentration of DMF in DMF/CH_3NO_2 mixtures. Equations 12 and 13 describe the behavior for D and I_d

$$k_{obsd} = k_{ex} \tag{12}$$

$$k_{obsd} = \frac{K_{os}k_I[DMF]}{1 + K_{os}[DMF]} \tag{13}$$

mechanisms, respectively. Frankel[1] had performed similar experiments for DMF exchange on $Ni(DMF)_6^{2+}$. He observed that the exchange rate constants were independent of the composition of the DMF/CH_3NO_2 solutions and proposed a D mechanism to explain these results. They could also be explained by the saturation kinetics predicted by eq 13 for an I_d mechanism. However, this would require a large K_{os} value, and this requirement cannot be fulfilled if $Ni(DMF)_6^{2+}$ is preferentially solvated by CH_3NO_2,[29] as found by Frankel.[32]

Although a D mechanism best describes the exchange of DMF on $Ni(DMF)_6^{2+}$,[33] for complex formation, the assignment of a mechanism is less straightforward. Nevertheless, the value of k_I being too large compared to that of k_{ex} is a good

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(22) For an I_d mechanism, the results require only that $K_{os} \leq 2000$ M^{-1}. If a D mechanism is operating, then the second-order rate constant is given by $k_f = k_{ex}k_L/k_s[DMF]$, from which one calculates $k_L/k_s = 102$. Since $[Et_2DTC^-]/[DMF]$ is always less than 4×10^{-5}, then $k_s[DMF] \gg k_L[Et_2DTC^-]$, consistent with the observed linearity of k_{obsd} vs. $[Et_2DTC^-]$.

(23) For low-excess thiocyanate concentrations both the D and I_d mechanisms predict a common second-order rate constant equal to the constant measured under excess metal conditions. The observed reaction rate was much slower than that for comparable excess metal conditions, indicating that a different reaction was occurring. From the excess-metal results, a k_L/k_s ratio of 106 is calculated, assuming a D mechanism (eq 6). This would imply that saturation kinetics would have become apparent for $[SCN^-] \geqslant 0.05$ M. The curvature would have been much more pronounced than for an I_d mechanism with the constraint of $K_{os} \leqslant 2$ M^{-1}.

(24) For uncharged ligands, ΔV_{os}^0 is close to zero. For charged ligands, the equation of Hemmes[25] can be used to calculate ΔV_{os}^0. In water, values of +3.2, +5.3, and +7.3 cm^3 mol^{-1} are calculated (distance of closest approach, a, taken as 5 Å) for products of charges −2, −3, and −4, respectively. In CH_3CN, a value of +8.9 cm^3 mol^{-1} (a = 7 Å) has been calculated[26] for a −3 charge product. There are insufficient data for such calculations of ΔV_{os}^0 in DMF, since the pressure dependence of the dielectric constant has not been reported.

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indication that the mechanism is the same for both processes. In DMF, substitution on Ni^{2+} appears to be going through a 5-coordinate intermediate whereas, in water, substitution proceeds via a concerted process. A more dissociative substitution behavior in DMF than in water has also been noted by Tanaka et al. for Fe^{3+} complexation reactions.[26] Steric arguments might be evoked to explain such a trend whereby the change from small water molecules to bulky DMF molecules bonding to the metal cations results in destabilization of solvates of higher coordination number.

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Registry No. DMF, 68-12-2; $Ni(DMF)_6^{2+}$, 33789-00-3; SCN^-, 302-04-5; diethyldithiocarbamate, 147-84-2.

Supplementary Material Available: First-order rate constants for the formation of $NiSCN^+$ and $Ni(Et_2DTC)_2$ as a function of concentration of reagents and temperature (Table SI) and as a function of pressure (Table SII) (2 pages). Ordering information is given on any current masthead page.

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Solvent and Structure Effects on the Spin-Crossover and Electron-Transfer Properties of $[Fe^{III}(X\text{-}Salmeen)_2](PF_6)$ and $[Fe^{III}(X\text{-}Sal)_2trien](PF_6)$ Complexes

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The electron-transfer reactions for a series of five $[Fe^{III}(X\text{-}Salmeen)_2](PF_6)$ and six $[Fe^{III}(X\text{-}Sal)_2trien](PF_6)$ complexes were investigated in nonaqueous media. In the former series, X = 3-NO_2, 5-NO_2, H, 4-OCH_3, and 3-OCH_3. In the latter series, X = 3-NO_2, 5-NO_2, H, Cl, Br, and 5-OCH_3. Both series of Fe(III) complexes undergo an Fe(III)/Fe(II) reaction as well as a low-spin ⇄ high-spin Fe(III) spin equilibrium. Each redox reaction was measured as a function of temperature between 220 and 320 K, and the corresponding magnetic moments were recorded in up to seven different nonaqueous solvents. Heterogeneous electron-transfer rate constants, k_s, were also measured at room temperature and correlations made between the position of the spin equilibria and the reversible half-wave potential and/or the electron-transfer rate constant. Correlations were between the substituent constant of the X group and the $E_{1/2}$, k_s, or magnetic moment of each complex as well as between the total entropy of electron transfer and the magnetic moment of Fe(III) under the same solution conditions. On the basis of these correlations, some attempts were made to determine the factors influencing electron-transfer reactions of spin-equilibria systems.

Introduction

Recent electrochemical studies in our laboratory have focused on how spin equilibria affect the standard redox potentials and electron-transfer rates for oxidation or reduction of Fe(III),[4–6] Fe(II),[7] and Co(II)[8] six-coordinate complexes. In the most detailed study of an Fe(III) spin equilibrium for the $[Fe^{III}(X\text{-}Sal)_2trien]^+$ cation, it was illustrated how changes in ligand substituent and the solvent media affected the position of the $^2T \rightleftharpoons {}^5A$ spin crossover. More importantly, it was illustrated how variable-temperature electrochemistry could be used to investigate the spin-crossover process as it relates to redox potentials and electron-transfer rates.[5]

This work represents a continuation of our studies in this area and incorporates new data for the variable-spin $[Fe^{III}(X\text{-}Salmeen)_2]^+$ series of complexes shown in Figure 1a for the purpose of comparison with results reported earlier[5] for the structurally similar $[Fe^{III}(X\text{-}Sal)_2trien]^+$ cations (Figure 1b). Both series of six-coordinate iron(III) complexes exhibit

$$^{2}\mathrm{T}(\text{low-spin}) \underset{k_{-1}}{\overset{k}{\rightleftharpoons}} {}^{6}\mathrm{A}(\text{high-spin})$$

spin equilibria in the solid and solution states with $k_{1,-1} \geq 10^{-7}$ s^{-1} in solution for dynamic spin-crossover processes,[9–11] but the former series are bis(tridentate) species while the latter contain hexadentate ligands.

Experimental Section

Chemicals. $[Fe^{III}(X\text{-}Sal)_2trien](PF_6)$ (X = 3-NO_2, 5-NO_2, H, Cl, Br, 5-OCH_3) and $[Fe^{III}(X\text{-}Salmeen)_2](PF_6)$ (X = 3-NO_2, 5-NO_2, H, 4-OCH_3, 3-OCH_3) were prepared and characterized as described earlier.[9,10] Reagent grade methylene chloride (CH_2Cl_2), acetone ($(CH_3)_2CO$), dimethylformamide (DMF), *n*-butyronitrile (*n*-PrCN), dimethyl sulfoxide (Me_2SO), and pyridine (py) were purified according to literature methods[12] and stored over molecular sieves prior to use. For the electrochemistry, each solution was made with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The TBAP was purified by recrystallization from ethyl acetate/ether and dried under reduced pressure.

Instrumentation and Methods. Cyclic voltammetric measurements were obtained with a three-electrode system using either an IBM Model EC 225 voltammetric analyzer or a PAR Model 173 potentiostat and a PAR Model 175 universal programmer coupled with a Houston Instruments Model 2000 recorder or a storage oscilloscope for rapid scan rates. The working electrode was a platinum button, and a platinum wire served as the counterelectrode. A commercial saturated calomel electrode (SCE) or commercial saturated lithium calomel electrode (SLCE) was used as the reference electrode and was separated from the bulk of the solution by a fritted glass bridge with the same solvent and supporting electrolyte. An SLCE electrode

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