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Solution Characterization of the Iron(II) Bis(1,4,7-Triazacyclononane) Spin-Equilibrium Reaction

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Introduction

Spin-crossover phenomena exert important influences on the properties and reactivities of transition metal compounds.[1−3] Such behavior is particularly common among Fe(II) complexes,[4] where it is of interest with regard to O_2 activation[5] and molecular device operation.[6] Thus, $^1A_1 \rightarrow {}^5T_2$ spin exchange at $Fe^{II}N_6$ centers continues to attract wide attention.[7]

It is curious that the well-known bis(1,4,7-triazacyclononane) complex, $Fe(tacn)_2{}^{2+}$,[8] has been considered to be low spin based on the X-ray crystal structure and infrared spectrum of the isolated solid, $[Fe(tacn)_2]Cl_2{\cdot}4H_2O$.[8b,9] However, we recently reported that $Fe(tacn)_2{}^{2+}$ undergoes $^1A_1 \rightleftharpoons {}^5T_2$ spin exchange in solution and demonstrated that this reaction contributes to the unusually large electrode half-reaction entropy, $\Delta S°_{rc}$, of the $Fe(tacn)_2{}^{3+/2+}$ couple.[12] This Note presents a more complete characterization of the $Fe(tacn)_2{}^{2+}$ spin equilibrium, a study of the influence of solvent and electrolyte on the reaction, and a quantitative description of the contribution of Fe(II) spin exchange to the thermodynamics of the $Fe(tacn)_2{}^{3+/2+}$ half reaction.

Experimental Section

Materials. $[Fe(tacn)_2]Br_2{\cdot}3H_2O$ was prepared as described in ref 8a. The corresponding triflate salt was prepared by adding a large molar excess of $NaCF_3SO_3$ to a solution of $[Fe(tacn)_2]Br_2{\cdot}3H_2O$. After cooling in an ice bath, the resulting precipitate was collected by filtration, washed with ethanol, and dried in a stream of dry N_2. The product assayed as $[Fe(tacn)_2](CF_3SO_3)_2{\cdot}4.5H_2O$ by linear-sweep voltammetry. Preparation and handling of $Fe(tacn)_2{}^{2+}$ and its salts was carried out under an inert atmosphere by use of a glovebox or Schlenk line techniques. Electrochemical solvents acetone, acetonitrile, dimethyl sulfoxide, and dimethylformamide were obtained as distilled-in-glass reagents from Burdick and Jackson and used as received. Deuterated solvents and other reagents were obtained from Aldrich Chemical Co.

Methods. Electrochemical and magnetic susceptibility measurements were carried out using equipment described previously.[12] The electrochemical half-reaction entropy, $\Delta S°_{rc} = F(\partial E°'/\partial T)$, was determined from the temperature dependence of $E°'$ in a nonisothermal three-electrode cell[13] in which the working and reference electrode compartments were thermostated independently by circulating water baths. Solution magnetic susceptibilities were determined as a function of temperature in deuterated solvents by the ^1H NMR method of Evans.[14] TMS was used as the internal reference in nonaqueous solvents; acetone or sodium 3-(trimethylsilyl)propionate was used as the internal reference in D_2O. Mass susceptibility, χ_g, was calculated from

$$\chi_g = -3\Delta f/4\pi fm + \chi_o[1 + (d_o - d_s)/m] \qquad (1)$$

where Δf is the frequency shift in Hz of the reference compound, f is the fixed probe frequency of the spectrometer, χ_o is the mass susceptibility in $cm^3\ g^{-1}$ of the solvent, m is the mass in g of the complex in 1 cm^3 of solution, and d_o and d_s are the densities of the solvent and solution, respectively. For concentrated solutions in D_2O, $d_o - d_s$ was approximated as the density difference between water and a ferric chloride solution of the same concentration.[15] For more dilute solutions (concentration $\leq$ 15 mM), d_s was approximated as $d_o + m$. The molar susceptibility, determined as $\chi_M = \chi_g \times MW$, was corrected for the diamagnetic contributions of the tacn ligands, Fe(II) core electrons, and counterions using tabulated values of Pascal's constants[16] to obtain a corrected molar suceptibility, $\chi_{M'}$. The effective magnetic moment was evaluated as $\mu_{eff} = 2.828\ (\chi_{M'}/T)^{1/2}$ and fit to eq 5 using commercially available software (KaleidaGraph, v. 3.51, Synergy Software, Reading, PA). Variable temperature electronic spectroscopy measurements were made under N_2 in the thermostated sample compartment of a Perkin-Elmer Lambda 19 spectrometer.

Results and Discussion

Electronic Spectroscopy. Figure 1 shows the electronic spectrum of $[Fe(tacn)_2]Br_2{\cdot}3H_2O$ in D_2O between 308 and 358 K. At lower temperatures, the spectrum consists almost entirely of bands at 595 and 390 nm that are characteristic of the

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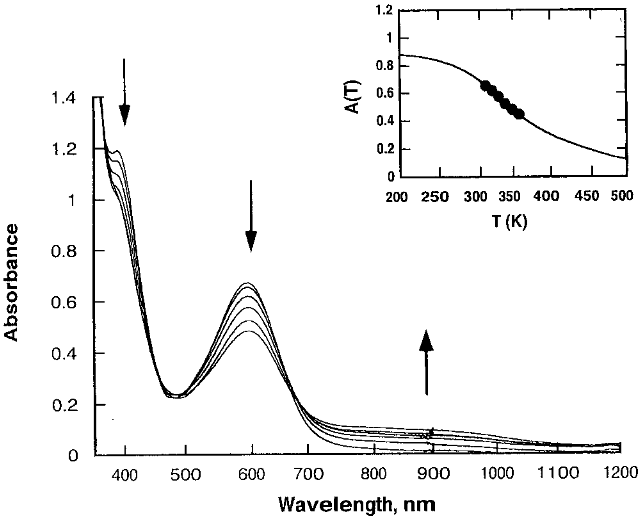

Figure 1. Visible spectrum of $[Fe(tacn)_2]Br_2 \cdot 3H_2O$ in D_2O at 308, 318, 328, 338, 348, and 358 K. Arrows indicate the effect of increasing temperature. Inset: fit of $A(T)$ at 595 nm to eq 4.

$^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions of low-spin Fe(II). As temperature is increased the intensities of these bands decrease, and a weak absorption centered at ca. 900 nm that is characteristic of the $^5T_{2g} \rightarrow {}^5E_g$ transition of high-spin Fe(II)[4c] gains intensity. The behavior is consistent with a temperature-dependent equilibrium between the low- and high-spin forms of $Fe(tacn)_2^{2+}$:

$$\text{LS-Fe(tacn)}_2^{2+}\ ({}^1A_{1g}) \rightleftharpoons \text{HS-Fe(tacn)}_2^{2+}\ ({}^5T_{2g}) \qquad (2)$$

The equilibrium constant, $K_{SE} = x_{HS}/x_{LS}$, where x_{HS} and x_{LS} are the molar fractions of HS- and LS-$Fe(tacn)_2^{2+}$, is defined in terms of the enthalpy and entropy of spin exchange by

$$K_{SE} = \exp(\Delta S^\circ_{SE}/R) \exp(-\Delta H^\circ_{SE}/RT) \qquad (3)$$

The thermodynamic parameters ΔH°_{SE} and ΔS°_{SE} and the temperature, $T_{1/2}$, at which $x_{HS} = x_{LS}$ are obtained by fitting the temperature dependence of the absorbance at 595 nm, $A(T)$, to the following expression:[17]

$$A(T) = A(0)/[\exp(\Delta S^\circ_{SE}/R) \exp(-\Delta H^\circ_{SE}/RT) + 1] \qquad (4)$$

Results are shown in the inset to Figure 1, from which $\Delta H^\circ_{SE} = 19$ kJ mol^{-1}, $\Delta S^\circ_{SE} = 53$ J mol^{-1} K^{-1}, and $T_{1/2} = 358$ K. A molar absorptivity of $\epsilon = 13$ M^{-1} cm^{-1} is calculated for LS-$Fe(tacn)_2^{2+}$ at 595 nm from the limiting value of $A(0)$.

Magnetic Susceptibility. Temperature-dependent magnetic susceptibility measurements employing the Evans ^1H NMR method were conducted to explore the influence of solvent, counterion, and electrolyte concentration on the thermodynamics of reaction 2. Magnetic data were analyzed by fitting the observed magnetic moment, $\mu_{eff}(T)$, to the expression

$$\mu_{eff}(T) = \{\mu_{LS}^2[\exp(-\Delta H^\circ_{se}/RT) \exp(\Delta S^\circ_{se}/R) + 1]^{-1} + \mu_{HS}^2[\exp(\Delta H^\circ_{se}/RT) \exp(-\Delta S^\circ_{se}/R) + 1]^{-1}\}^{1/2} \qquad (5)$$

where μ_{LS} and μ_{HS} are the limiting magnetic moments of low- and high-spin $Fe(tacn)_2^{2+}$. Results determined over a temperature range of 223−363 K in dimethylformamide-d_7 are shown in Figure 2. Values of $\Delta H^\circ_{SE} = 21(1)$ kJ mol^{-1}, $\Delta S^\circ_{SE} = 61(3)$ J mol^{-1} K^{-1}, and $T_{1/2} = 344$ K are obtained from the fit of eq 5 to these data. Because the temperature range available in each solvent is inadequate to encompass the gradual character of spin equilibria in solution, it is not possible to drive reaction 2 to its low- or high-spin limit and obtain the limiting magnetic moments. Therefore, μ_{LS} and μ_{HS} are obtained from the fit of μ_{eff} vs T. The resulting quantities are larger than the spin-only values of 0 and 4.9 μ_B and suggest the presence of orbital contributions to the observed magnetic moments.

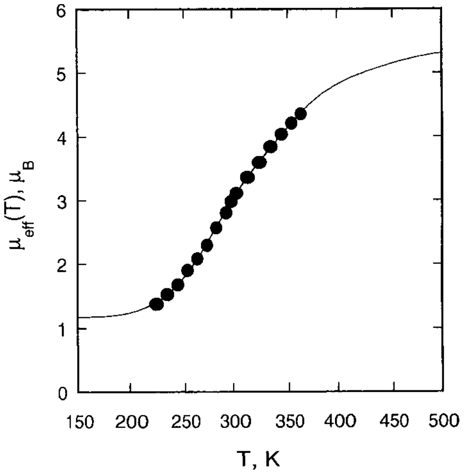

Figure 2. Fit of $\mu_{eff}(T)$ to eq 5 for $[Fe(tacn)_2](CF_3SO_3)_2 \cdot 4.5H_2O$ in dimethylformamide-d_7 from 223 to 363 K.

Data collected as a function of solvent, counterion, and electrolyte concentration are reported in Table 1. Relatively large uncertainties are observed in some instances, possibly because a small temperature range is investigated. However, mean values of $\Delta H^\circ_{SE} = 23$ kJ mol^{-1}, $\Delta S^\circ_{SE} = 67$ J mol^{-1} K^{-1}, and $T_{1/2} = 335$ K in Table 1 are consistent with the spectroscopic result in Figure 1, with our previous determination of $\Delta H^\circ_{SE} = 24$ kJ mol^{-1}, $\Delta S^\circ_{SE} = 68$ J mol^{-1} K^{-1}, and $T_{1/2} = 349$ K for $[Fe(tacn)_2]Br_2 \cdot 3H_2O$ in D_2O,[12] and with thermodynamic parameters reported for other $Fe^{II}N_6$ LS-HS equilibria.[3,4a]

The data in Table 1 show that $Fe(tacn)_2^{2+}$ spin exchange exhibits little dependence on solvent, counterion, and the presence of excess electrolyte. Such behavior is anticipated in dilute solution where cooperative effects are absent. The thermodynamic parameters obtained under these conditions reflect the intramolecular structural changes that accompany LS → HS conversion. The positive value of ΔH°_{SE} is a consequence of the increase in metal−ligand bond distance (∼0.2 Å for $Fe^{II}N_6$ centers)[4] that results from a gain of two σ-antibonding e_g^* electrons. The positive value of ΔS°_{SE} arises from increases in vibrational partition functions as metal−ligand bonds are weakened and increases in electronic partition functions as multiplicity increases.

Electrode Half-Reaction Entropy. When a large structural change accompanies an electrochemical reaction it makes significant intramolecular contributions to the electrode half-reaction entropy.[18] The origins of these terms are similar to those that produce the entropy change associated with a spin-crossover reaction. Thus, the ΔS°_{rc} of an electrode reaction accompanied by a complete or partial spin exchange reflects contributions from both processes.

Electrochemical reduction of $Fe(tacn)_2^{3+}$ consists of the following reactions:

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Table 1. Thermodynamic and Magnetic Properties of $Fe(tacn)_2^{2+}$ Spin Equilibrium[a]

solvent	temp range (K)	ΔH°_{SE} (kJ mol^{-1})	ΔS°_{SE} (J mol^{-1} K^{-1})	μ_{LS} (μ_B)	μ_{HS} (μ_B)	$T_{1/2}$ (K)
deuterium oxide	278−348	23(4)	67(14)	0.9	5.6	343
deuterium oxide[b]	283−353	24(8)	70(29)	0.3	5.3	343
deuterium oxide[c]	278−348	23(10)	67(37)	0.7	5.6	343
dimethylformamide-d_7	223−363	21(1)	61(3)	1.2	5.6	344
dimethyl sulfoxide-d_6	297−373	22(8)	68(20)	1.1	5.5	324
acetonitrile-d_3	233−323	21(2)	66(6)	1.3	5.8	318
acetone-d_6	243−313	24(8)	73(37)	1.2	4.8	328

[a] From fits of effective magnetic moment to eq 5 over the indicated temperature range for the $CF_3SO_3^-$ salt of $Fe(tacn)_2^{2+}$, except as noted. [b] Br^- salt. [c] Br^- salt plus 0.1 M $LiClO_4$.

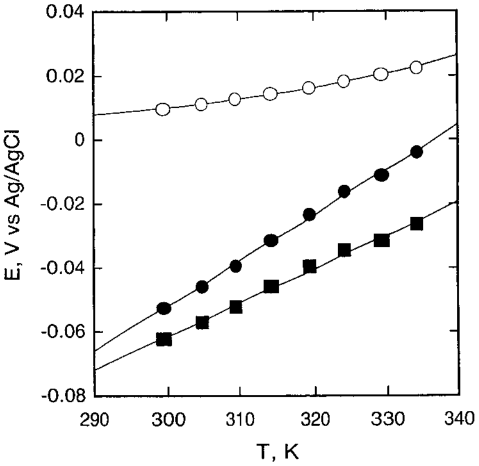

Figure 3. Plots of $E^{\circ\prime}_{obs}$ (●), $(RT/F)\ln(1 + K_{SE})$ (○), and $E^{\circ\prime}_{LS-LS} = E^{\circ\prime}_{obs} - (RT/F)\ln(1 + K_{SE})$ (■) versus temperature for reduction of $Fe(tacn)_2^{3+}$ in dimethyl sulfoxide containing 0.1 M $LiClO_4$.

$$\text{LS-Fe(tacn)}_2^{3+} + e^- \rightleftharpoons \text{LS-Fe(tacn)}_2^{2+} \quad E^{\circ\prime}_{LS-LS} \tag{6}$$

$$\text{LS-Fe(tacn)}_2^{2+} \rightleftharpoons \text{HS-Fe(tacn)}_2^{2+} \quad K_{SE} \tag{7}$$

The observed electrode potential and half-reaction entropy are given by

$$E^{\circ\prime}_{obs} = E^{\circ\prime}_{LS-LS} + (RT/F)\ln(1 + K_{SE}) \tag{8}$$

$$(\Delta S^\circ_{rc})_{obs} = (\Delta S^\circ_{rc})_{LS-LS} + x_{HS}\Delta S^\circ_{SE} - x_{LS}R\ln(x_{LS}) - x_{HS}R\ln(x_{HS}) \tag{9}$$

The last two terms on the right hand side of eq 9 are small. Neglect of these quantities yields the simplified expression $(\Delta S^\circ_{rc})_{LS-LS} \cong (\Delta S^\circ_{rc})_{obs} - x_{HS}\Delta S^\circ_{SE}$ that has been used in related form[19,20] to describe the entropy change of coupled electron-transfer and spin-exchange reactions. However, x_{HS} is noticeably temperature dependent over the range of conditions employed. A more accurate procedure for obtaining the half-reaction entropy of reaction 6 is illustrated in Figure 3. The filled circles define a plot of $E^{\circ\prime}_{obs}$ versus T for the reduction of $Fe(tacn)_2^{3+}$ in dimethyl sulfoxide from which a value of $(\Delta S^\circ_{rc})_{obs} = 138$ J mol^{-1} K^{-1} is obtained. A corrected electrode potential is calculated as $E^{\circ\prime}_{LS-LS} = E^{\circ\prime}_{obs} - (RT/F)\ln(1 + K_{SE})$, using for K_{SE} the value determined at each temperature from ΔH°_{SE} and ΔS°_{SE} (eq 3, Table 1). A plot of the resulting quantity versus T is illustrated by the filled squares in Figure 3 and yields a corrected half-reaction entropy of $(\Delta S^\circ_{rc})_{LS-LS} = 103$ J mol^{-1} K^{-1}. Values of $(\Delta S^\circ_{rc})_{LS-LS}$ determined in this way in five solvents are collected in Table 2.

Table 2. Observed and Spin Equilibrium Corrected Half-Reaction Entropies (J mol^{-1} K^{-1})

solvent	$(\Delta S^\circ_{rc})_{obs}$[a]	$(\Delta S^\circ_{rc})_{LS-LS}$[b]	$(\Delta S^\circ_{rc})_{Ru}$[c]
deuterium oxide	41	23	25
dimethyl sulfoxide	138	103	110
dimethylformamide	163	137	129
acetontirile	152	122	117
acetone	157	122	130

[a] Value of ΔS°_{rc} for $Fe(tacn)_2^{3+/2+}$ determined over the temperature interval 290−320 K in 0.1 M $LiClO_4$, from ref 12. [b] Value of ΔS°_{rc} for $Fe(tacn)_2^{3+/2+}$ corrected as described in text. [c] Value of ΔS°_{rc} for $Ru(tacn)_3^{3+/2+}$ determined over the temperature interval 290−320 K in 0.1 M $LiClO_4$, from ref 12.

The accuracy of the correction procedure is assessed by comparing values of $(\Delta S^\circ_{rc})_{LS-LS}$ with ΔS°_{rc} for a reaction with components of similar size, charge, stoichiometry, and which are known to involve only LS forms. A suitable half-cell reaction is

$$\text{LS-Ru(tacn)}_2^{3+} + e^- \rightleftharpoons \text{LS-Ru(tacn)}_2^{2+} \quad E^{\circ\prime}_{Ru} \tag{10}$$

The half-reaction entropies of reaction 10 are listed as $(\Delta S^\circ_{rc})_{Ru}$ in Table 2. $(\Delta S^\circ_{rc})_{obs}$, $(\Delta S^\circ_{rc})_{LS-LS}$, and $(\Delta S^\circ_{rc})_{Ru}$ all exhibit large solvent-dependent contributions that arise from the extent to which solvent order is created or destroyed by the change in charge of the reactant.[21] However, after subtraction of the spin-exchange contribution from $(\Delta S^\circ_{rc})_{obs}$, good agreement between $(\Delta S^\circ_{rc})_{LS-LS}$ and $(\Delta S^\circ_{rc})_{Ru}$ is observed in all solvents. The agreement confirms the validity of the correction procedure and quantifies the magnitude of the spin-exchange contribution to ΔS°_{rc} for $Fe(tacn)_2^{3+/2+}$.

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