of temperature. In the cobalt, nickel, and zinc lattices the spin crossover does not go to completion, leaving a residual paramagnetism at temperatures well below T_c and a very high "residual diamagnetism" (RD) at temperatures well above T_c. The transition in the mixed crystals is no longer sharp as in the pure [Fe(phen)$_2$(NCS)$_2$], again indicating that the cooperative forces may be considerably weakened on dilution. In the case of [Fe$_x$Co$_{1-x}$(phen)$_2$(NCS)$_2$] as in [Fe$_x$Mn$_{1-x}$(phen)$_2$(NCS)$_2$] the HS $\rightleftharpoons$ LS crossover appears to be quenched at infinite dilution. However, in the cobalt lattice the residual paramagnetism at low temperatures decreases and the residual diamagnetism at high temperatures increases with metal dilution. This would imply that the isolated [Fe(phen)$_2$(NCS)$_2$] molecules buried in the cobalt lattice would tend to stabilize in the ($^1A_1$) low-spin ground state, a result exactly opposite to what was obtained in the case of the Mn-diluted mixed crystals. A similar systematic partial stabilization of the low-spin $^2T_2(O_h)$ ground state in the case of tris(1-pyrrolidinecarbodithioato)iron(III) (FeP) diluted in the corresponding Co(III) lattice has also been reported.[20] Here, too, it was assumed that the structure of the FeP molecule is modified slightly, presumably with shortening of the Fe–S bonds, to approach that of the CoP host lattice which has shorter metal–sulfur bonds.

The Mössbauer spectra of [Fe$_x$Ni$_{1-x}$(phen)$_2$(NCS)$_2$] for $x < 0.1$ were not very satisfactory due to very high electronic absorption of the 14-keV γ rays by the Ni atoms, but the low-spin state appears to be more readily stabilized in the Ni host lattice than in the Fe/Co mixed crystals. In [Fe$_x$Zn$_{1-x}$(phen)$_2$(NCS)$_2$] the HS $\rightleftharpoons$ LS crossover characteristics are almost independent of concentration in the range $x = 0.001$–0.01, although the transition is much more gradual with a high residual paramagnetism and diamagnetism as in the Co and Ni mixed crystals. The rest paramagnetism in the Fe/Zn mixed crystals with $x = 0.01$ and $x = 0.001$ is much higher than in the corresponding Fe/Co or Fe/Ni mixed crystals.

The observations seem to qualitatively show that the amount of rest paramagnetism in the low temperature region and the rest diamagnetism in the high-temperature region, respectively, exhibited by the [Fe$_x$M$_{1-x}$(phen)$_2$(NSC)$_2$] mixed crystals depend on the relative ionic radii of the host M^{2+} and Fe^{2+} ions. The ionic radii are known to decrease in the following order: Mn^{2+} (0.80 Å) > Fe^{2+} (0.74 Å) ~ Zn^{2+} > Co^{2+} (0.72 Å) > Ni^{2+} (0.69 Å).[21]

From our Mössbauer experiments it appears that the host lattices with $r(\mathrm{M}^{2+}) > r(\mathrm{Fe}^{2+})$ favor the stabilization of the HS state as in the case of [Fe$_x$Mn$_{1-x}$(phen)$_2$(NCS)$_2$] and the host lattices with $r(\mathrm{M}^{2+}) < r(\mathrm{Fe}^{2+})$ favor the stabilization of the LS state as in [Fe$_x$Co$_{1-x}$(phen)$_2$(NCS)$_2$] and [Fe$_x$Ni$_{1-x}$(phen)$_2$(NCS)$_2$]. The above suggestion of "negative" and "positive" lattice pressures could decrease or increase the Fe–N bond lengths (R), respectively, leading to an increase or decrease, respectively, of the crystal field potential (which is known to vary as R^{-5}) at the Fe(II) site. This could stabilize the low-spin or high-spin state accordingly. It must be noted that no realistic quantitative analysis based on the simple point-charge approximation can be done on such highly covalent systems, and therefore, our results have only been rationalized in qualitative terms. An X-ray investigation on the whole series of [M$^{\mathrm{II}}$(phen)$_2$(NCS)$_2$] could, however, confirm the above suggestion.

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Registry No. Mn(phen)$_2$(NCS)$_2$, 49809-87-2; Co(phen)$_2$(NCS)$_2$, 14514-45-5; Ni(phen)$_2$(NCS)$_2$, 31084-79-4; Zn(phen)$_2$(NCS)$_2$, 31035-45-7.

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(20) E. J. Cukauskas, B. S. Deaver, Jr., and E. Sinn, *J. Chem. Phys.*, **67**, 1257 (1977).

(21) "Handbook of Chemistry and Physics", 49th ed., CRC Press, Boca Raton, FL, 1968–1969.

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Effect of Spin State on the Redox and Electron-Transfer Properties of the Variable-Spin Family of [Fe$^{\mathrm{II}}$(6-Mepy)$_n$(py)$_{3-n}$tren](PF$_6$)$_2$ Complexes in Solution

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The effect of spin state on the electron-transfer properties of the variable-spin family of [Fe$^{\mathrm{II}}$(6-Mepy)$_n$(py)$_{3-n}$tren](PF$_6$)$_2$ complexes ($n = 1$–3) has been investigated in acetone, benzonitrile, and butyronitrile. For all complexes an Fe(II) $\rightleftarrows$ Fe(III) oxidation wave is observed between +1.05 and +1.30 V vs. a saturated lithium chloride calomel electrode (SLCE). The potential of the reaction is dependent on the number of methyl groups attached to the pyridine rings with $E_{1/2}$ shifting anodically as the number increases from 0 to 3 groups. Heterogeneous electron-transfer rate constants vary between 3.1×10^{-2} and 1.9×10^{-1} cm/s depending on the solvent and the complex. In a given solvent, the standard rate constants are virtually identical for oxidation of the low-spin and high-spin complexes. The k° for the spin-equilibrium complex is smaller than for either the high-spin or the low-spin complex. A discussion of the effect of spin state on rates of electron-transfer is presented.

Introduction

Numerous spin-equilibrium compounds containing Fe(II) and Fe(III) have been prepared and characterized with respect to their electronic and structural properties,[3,4] and much detailed information has been gathered as to how changes in spin state relate to changes in the various physicochemical properties of these complexes. However, one relationship which has not been extensively investigated is how a change of spin state affects the standard redox potential and electron-transfer

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[1] University of Houston.

[2] William Marsh Rice University.

[3] P. Gutlich, *Struct. Bonding (Berlin)*, **44**, 83 (1981).

[4] P. G. Sim, E. Sinn, R. H. Petty, D. L. Merrill, and L. J. Wilson, *Inorg. Chem.*, **20**, 1213 (1981).

0020-1669/82/1321-3433$01.25/0

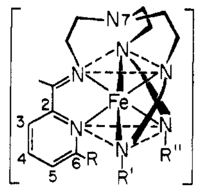

Figure 1. Structure of the $[Fe(6\text{-}Mepy)_n(py)_{3-n}tren]^{2+}$ cations: compound A (R = R' = R'' = H); compound B (R = H, R' = R'' = CH_3); compound C (R = R' = R'' = CH_3).

rate for the reaction Fe(II) $\rightleftharpoons$ Fe(III). Studies of these types are important in order to better understand the mechanism of spin conversion and electron-transfer processes involving Fe(III) and Fe(II) in heme biological systems such as cytochrome P_{450}, myoglobin, and hemoglobin,[5-8] as well as in model systems such as $[(OEP)Fe(L)_2]^+$, where two electronic states of differing spin multiplicity are in thermal equilibrium with one another.[9]

In a recent publication[10] we reported, for the first time, how the electron-transfer rate constant for an Fe(III)/Fe(II) reaction varies as a function of the Fe(III) spin state. In this study, the heterogeneous electron-transfer rate constants for reduction of a series of $[Fe^{III}(X\text{-}Sal)_2trien]^+$ cations in butyronitrile/0.1 M TBAP were found to vary between 2.4×10^{-2} and 4.6×10^{-2} cm/s and to depend on the position of the Fe(III) spin equilibrium.[10] The complexes selected for this initial investigation seemed ideal because the Fe(III) spin equilibrium was well characterized in solution[11] and because there were no changes in coordination number during the Fe(III) $\rightleftharpoons$ Fe(II) redox process.[12]

In this work we wish to report the effect of an Fe(II) spin equilibrium on the rates of electron transfer for the reaction Fe(II) $\rightleftharpoons$ Fe(III). In addition, we have explored how the rates of electron transfer for Fe(II)/Fe(III) complexes depend on the spin state of the products and reactants where there is an *absence* of a spin equilibrium and where there is no change in spin state or coordination number upon electrooxidation. The complexes selected for this study are those of the hexadentate ligands tris[4-(6-R-2-pyridyl)-3-aza-3-butenyl]amines, where R = H or CH_3. The structure of the three cationic complexes $[Fe^{II}(6\text{-}Mepy)_n(py)_{3-n}tren]^{2+}$ (compounds A, B, and C) is shown in Figure 1. The magnetic properties of compounds A, B, and C have been well characterized in both the solid and solution states.[13] In solution, B displays an $^1A \rightleftharpoons {}^5T$ spin equilibrium, whereas A is fully low spin and C is fully high spin over a temperature range of approximately 200 degrees. The relative populations of the high- and low-spin states for the compounds have been shown to depend upon temperature, solvent, and the number of methyl substituents on the pyridine rings. Furthermore, the rates of spin conversion or intersystem crossing (k_1 and k_{-1}) for the

$$^1A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^5T$$

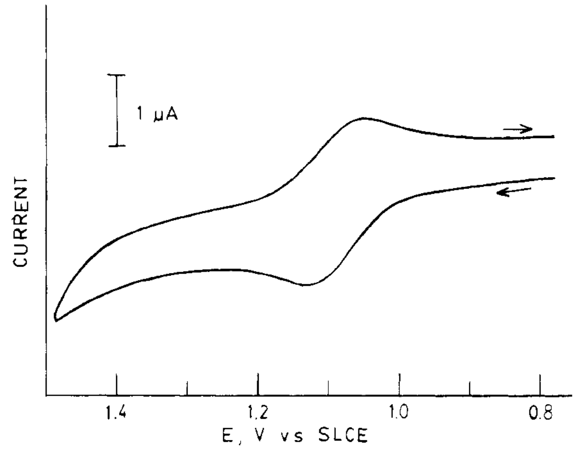

Figure 2. Cyclic voltammogram of 0.25 mM compound B in *n*-PrCN/0.1 M TBAP (scan rate 200 mV/s).

spin equilibrium of B have been measured in solution by a laser-Raman temperature-jump technique and found to be $k_1 = 4 \times 10^6$ s^{-1} and $k_{-1} = 5 \times 10^6$ s^{-1}.[14,15]

Experimental Section

Reagent grade *n*-butyronitrile (*n*-PrCN), benzonitrile (PhCN), and acetone (CH_3COCH_3) were purified according to literature methods[16] and stored over molecular sieves. Solutions were made 0.1 M with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The TBAP was recrystallized from distilled CH_2Cl_2 and dried under reduced pressure. Compounds A, B, and C of Figure 1 were prepared and characterized as described earlier.[13]

Cyclic voltammetric measurements were obtained with a three-electrode system and a PAR Model 173 potentiostat, a PAR Model Universal Programmer, and a Houston Instruments Model 2000 recorder or a storage oscilloscope for fast-scan rates. The working electrode was a platinum button, and a platinum wire served as the counterelectrode. A 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. A Luggin capillary was employed to reduce *iR* loss. The current–voltage curves for fast-scan cyclic voltammograms were taken from an oscilloscope using a C-5A Oscilloscope camera (Tektronix). Variable-temperature cyclic voltammetry was performed as described previously.[12]

Results and Discussion

The spin states of A, B, and C in solution have been characterized as low spin, spin equilibrium, and high spin, respectively, at room temperature.[13] Furthermore, from an electronic spectral study of the analogous Ni(II) complexes,[17] in which $\Delta(10Dq)$ differs by as much as 700 cm^{-1} between the Ni–A and Ni–C analogues, it seems reasonable that the Fe(III) oxidized products of A and C would also be low- and high-spin species, respectively. The spin state of the oxidized form of B is much less certain, and in fact, it too could be a spin-equilibrium species of Fe(III), with the equilibrium position shifted more toward the low-spin form because of the higher positive charge on the metal (of course, in the extreme, it could be essentially low spin by this same reasoning).

Cyclic voltammograms for all three compounds were obtained in the solvents CH_3NO_2, $EtCl_2$, PhCN, *n*-PrCN, CH_3COCH_3, THF, and DMF. In PhCN, *n*-PrCN, and CH_3COCH_3, A and B exhibited a one-electron, diffusion-controlled, reversible Fe(II)/Fe(III) reaction as shown in

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(5) J. H. Dawson, J. R. Trudel, G. Darth, R. E. Linder, E. Bunnenberg, C. Djevasse, R. Chiang, and L. P. Hager, *J. Am. Chem. Soc.*, **98**, 3709 (1976).

(6) E. V. Dose, M. F. Tweedle, L. J. Wilson, and N. Sutin, *J. Am. Chem. Soc.*, **99**, 3886 (1977).

(7) S. C. Tang, S. Kock, G. C. Papaefthymious, S. Foner, R. B. Frankel, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **98**, 2412 (1976).

(8) I. Morishima and T. Lixuka, *J. Am. Chem. Soc.*, **96**, 5270 (1974).

(9) H. A. O. Hill, P. D. Sryte, J. W. Buchler, H. Lueken, M. Tonn, A. K. Gregson, and G. Pellizer, *J. Chem. Soc., Chem. Commun.*, 151 (1979).

(10) K. M. Kadish, C. H. Su, and L. J. Wilson, *Inorg. Chem.*, **21**, 2312 (1982).

(11) M. F. Tweedle and L. J. Wilson, *J. Am. Chem. Soc.*, **98**, 4824 (1976).

(12) K. M. Kadish, K. Das, D. Schaeper, C. L. Merrill, B. R. Welch, and L. J. Wilson, *Inorg. Chem.*, **19**, 2816 (1980).

(13) M. A. Hoselton, L. J. Wilson, and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 1772 (1975).

(14) M. A. Hoselton, L. J. Wilson, R. S. Drago, and N. Sutin, *J. Am. Chem. Soc.*, **98**, 6967 (1976).

(15) E. V. Dose, M. A. Hoselton, N. Sutin, M. F. Tweedle, and L. J. Wilson, *J. Am. Chem. Soc.*, **100**, 1141 (1978).

(16) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals", 2nd ed., Pergamon Press, New York, 1980.

(17) L. J. Wilson, D. Georges, and M. A. Hoselton, *Inorg. Chem.*, **14**, 2968 (1975).

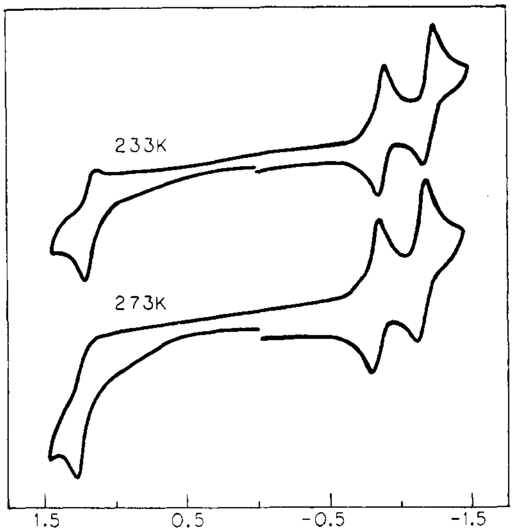

Figure 3. Cyclic voltammograms of 0.5 mM compound C in acetone/0.1 M TBAP at 273 and 233 K (scan rate 100 mV/s).

Table I. Half-Wave Potentials (V vs. SLCE) for the $[Fe^{II}(6\text{-}Mepy)_n(py)_{3-n}tren]^{2+}$ Complexes in Various Solvents at 22 °C

compd	reaction	solvent C_6H_5CN	solvent *n*-PrCN	solvent CH_3COCH_3
A	$Fe^{II}_{LS} \rightleftarrows Fe^{III}_{LS}$	+1.05	+1.07	+1.10
B	$Fe^{II}_{SE} \rightleftarrows Fe^{III\,a}$	+1.08	+1.10	+1.13
C	$Fe^{II}_{HS} \rightleftarrows Fe^{III}_{HS}$	+1.25	+1.23	+1.30

[a] SE = spin equilibrium; the spin state of oxidation product of B is not established. See discussion in text.

Figure 2. On the other hand, the oxidation of C at slow-scan rates was characterized by a peak that was not coupled to a corresponding reduction peak upon reversing the scan direction. The anodic peak current, i_{pa}, was proportional to the square root of scan rate, and the anodic peak potential shifted by 30 mV for each 10-fold increase in scan rate at low scan. At fast-scan rates the cathodic peak became well defined and no shift in $E_{1/2}$ was observed. This behavior is characteristic of a coupled irreversible chemical reaction following electron transfer, i.e., an EC mechanism.[18] The presence of an EC mechanism was further confirmed by variable-temperature cyclic voltammograms of C in acetone at 0.1 V/s. As seen in Figure 3, a more reversible reaction is obtained at 233 K than at 273 K. Variable-temperature studies of the other two complexes gave reversible redox reactions in the temperature range 298–230 K.

Complications were also present in that compounds A and B exhibited evidence of adsorption on the electrode surface in $EtCl_2$, while ill-defined current–voltage curves were obtained for A and C in CH_3NO_2 and THF. For these reasons, we have limited our discussion in this paper to reactions in PhCN, *n*-PrCN, and CH_3COCH_3, where the current–voltage curves were well-defined and no evidence of adsorption was present. As can be seen in Figure 3, for C, two reversible reductions are obtained at rather negative potentials. Because we have restricted our studies to the interrelationship between spin state and the Fe(II)/Fe(III) redox couple, these two reductions have not been further characterized at this time.

Half-Wave Potentials and Spin State. The half-wave potentials for oxidation of each complex in the three solvents are given in Table I. Within a given solvent, the half-wave potential for the Fe(II) ⇄ Fe(III) couple varies as a function of the number of methyl groups. Generally, adding an electron-donating group to a ligand should produce an easier oxidation while addition of an electron-withdrawing group should produce the opposite effect.[19] If all other factors are neglected, it would be expected that electron-donating methyl groups would make the Fe(II) center more electron rich, thus producing an easier oxidation. For example, it has been reported[13] that substitution of two methyl groups for protons in the 6-position for the low-spin complexes of $[Fe(6\text{-}Mepy)_2trien]^{2+}$ and $[Fe(py)_2trien]^{2+}$ (note: trien, not tren) results in a cathodic potential shift of 20 mV for $E_{1/2}$. However, the reverse is observed in the present study as shown in Table I. A 30-mV anodic potential shift of $E_{1/2}$ was seen on going from the totally low-spin complex, A, to the intermediate-spin-equilibrium complex, B, which contains two methyl substituents. Furthermore, we also observe an additional 130–170-mV anodic potential shift of $E_{1/2}$ on going from B to the totally high-spin complex, C, which contains three methyl substituents. Since the effects of solvent, ionic strength, and ion-pair formation should be almost identical for the three complexes, the most reasonable factor responsible for the anodic shift of potential is the change of the Fe(II) spin state from low to intermediate to high spin. Thus, on the basis of the positive potential shift with increasing number of methyl groups, it seems that the half-wave potentials reflect not only the inductive and/or polar effects of the substituent but also the effect of the metal ion spin state.

Table II. Heterogeneous Rate Constant Determination for the Fe(II) ⇄ Fe(III) + e^- Reaction of B in *n*-PrCN/0.1 M TBAP at 22 °C

scan rate, V/s	(scan rate)$^{1/2}$, (V/s)$^{1/2}$	ΔE, mV	Ψ^a	$10^2k°$, cm/s
2.0	1.41	73	1.87	6.5
5.0	2.24	81	1.15	6.3
10.0	3.16	88	0.87	6.7
20.0	4.47	101	0.56	6.2
			av	6.4

[a] Reference 20.

Electron-Transfer Rate Constants and Spin State. Measurements of electron-transfer rate constants can be obtained by using cyclic voltammetry as demonstrated by Nicholson.[20] For each of the three complexes of this study the separation of peak potentials was measured as a function of scan rate. Shifts of the peak potentials from the reversible value of 57 mV are considered quasireversible, and under these conditions the rate of electron transfer can be calculated from the relationship[20]

$$k^\circ = \Psi\gamma^\alpha\left(\frac{nFv}{\pi RT}D\right)^{1/2} \qquad (1)$$

where k° is the heterogeneous electron-transfer rate constant (cm/s), n is the number of electrons transferred in each step, v is the potential sweep rate (V/s), D is the diffusion coefficient of the reacting species, and $\gamma = (D_0/D_r)^{1/2}$ (where D_0 is the diffusion coefficient of the reduced form of the reactant, α is the electron-transfer coefficient; π, F, and RT have their usual significance. Ψ is related to ΔE_p, the potential difference between the cathodic and anodic peak potentials. Values of Ψ, as defined by eq 1 for various values of ΔE_p, have been tabulated after the solution of the appropriate equations by numerical analysis.[20]

Typical data for the determination of heterogeneous electron-transfer rate constants of compound B are shown in Table II and a summary of the data in three solvents is given in Table

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(18) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(19) P. Zuman, "Substituent Effects in Organic Polarography", Plenum Press, New York, 1967.

(20) R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1965).

Table III. Summary of Electron-Transfer Rate Constants, $k°$, for the Variable-Spin $[\mathrm{Fe^{II}(6\text{-}Mepy)}_n\mathrm{(py)}_{3-n}\mathrm{tren}](\mathrm{PF_6})_2$ Compounds in Nonaqueous Solvents at 22 °C

		$k°$, cm/s		
compd	reaction	C_6H_5CN	*n*-PrCN	CH_3COCH_3
A	$\mathrm{Fe^{II}}_{\mathrm{LS}} \rightleftarrows \mathrm{Fe^{III}}_{\mathrm{LS}}$	4.7×10^{-2}	8.5×10^{-2}	1.9×10^{-1}
B	$\mathrm{Fe^{II}}_{\mathrm{SE}} \rightleftarrows \mathrm{Fe^{III}}$ [a]	3.1×10^{-2}	6.4×10^{-2}	1.4×10^{-1}
C	$\mathrm{Fe^{II}}_{\mathrm{HS}} \rightleftarrows \mathrm{Fe^{III}}_{\mathrm{HS}}$	4.3×10^{-2}	7.4×10^{-2}	1.5×10^{-1}

[a] SE = spin equilibrium; the spin state of oxidation product for B has not been established.

III. It can be seen that in Table II a constant and self-consistent rate constant is obtained over a scan variation of better than a factor of 10, which is a good indication of the reliability of the rates. Similar self-consistent rate constants were obtained for all values listed in Table III. Here, the heterogeneous rate constants are presented to only two significant figures because of the ±2 mV uncertainty in measuring the trace on the picture taken by the Polaroid camera.

In order to interpret the results in Table III, it is necessary to examine the possible mechanistic pathways for the oxidation of compounds A, B, and C. Although differences in $k°$ for the same compound in different solvents are large, it is interesting to note that the same relative trend is observed for the three compounds in each solvent. As seen in Table III, rate constants for the oxidation of A and C may be considered identical within experimental error or, at best, only slightly greater for the oxidation of the low-spin A when compared to that of high-spin C. In the case of compounds A and C the reaction scheme appears to be straightforward and is represented by eq 2 and 3, where LS and HS represent the low-spin and high-spin forms of the complex, respectively.

$$\mathrm{Fe(II)_{LS}} \rightleftarrows \mathrm{Fe(III)_{LS}} + e^- \qquad (2)$$

$$\mathrm{Fe(II)_{HS}} \rightleftarrows \mathrm{Fe(III)_{HS}} + e^- \qquad (3)$$

It has been suggested by Orgel[21] that spin state may account for the effect of ligands on the rates of electron transfer. As a general rule, providing all other factors for a given couple are invariant, the rates (both heterogeneous and homogeneous) are generally expected to decrease according to the following order: low spin/low spin > high spin/high spin > low spin/high spin. For example, as has been pointed out by Gurira[22] the Fe(III)/Fe(II) redox reaction in aqueous media has a $k°$ of 6.49×10^{-2} cm/s, where both the product and reactant are high-spin species. In contrast, reduction of $[\mathrm{Fe(phen)_3}]^{3+}$ to $[\mathrm{Fe(phen)_3}]^{2+}$ has $k° > 10$ cm/s, where both the product and reactant are low spin. In a similar manner, the low-spin/low-spin reaction of the $[\mathrm{Co(phen)_3}]^{3+}/[\mathrm{Co(phen)_3}]^{2+}$ couple has a $k°$ of 3.3×10^{-2} cm/s while that for the low-spin to high-spin reaction of $[\mathrm{Co(NH_3)_6}]^{3+}/[\mathrm{Co(NH_3)_6}]^{2+}$ has $k° < 10^{-5}$ cm/s. Differences in heterogeneous electron-transfer rate constants, as a function of spin state, have been discussed by Kadish and Jordan[23] for the hypothetical electrode reactions of cytochrome *c*, hemoglobin, and myoglobin. For these systems, the largest rate constant was calculated for the oxidation/reduction of cytochrome *c*, where both the Fe(II) reactant and Fe(III) product are low spin.

The conclusion that faster rates are obtained for electrooxidation/electroreduction of low-spin complexes when compared to those of similar high-spin or spin-equilibria complexes was also reported by Yasuda et al.[24] This conclusion was based on a study of variable-spin tris(N,N-disubstituted-dithiocarbamato)iron(III) complexes using galvanostatic techniques. A similar conclusion was also reached earlier by Kadish and Davis[25] for electroreduction of several synthetic porphyrin complexes. In the porphyrin systems a much larger difference existed in the rates, and it was postulated that the order of the rate constants should be $\mathrm{Fe(III)_{LS}/Fe(II)_{LS}} > \mathrm{Fe(III)_{HS}/Fe(II)_{HS}}$. This postulation, however, was based on limited data in which not a great deal was known about the actual iron spin state in solution and for complexes in which there may have been a change of coordination number upon reduction. In our present study, however, the spin state is well-defined and it is rather certain that no change of coordination number occurs during the redox reaction.

One of the most surprising results in Table III is that, independent of solvent, rate constants for the oxidation of B are measurably smaller than for oxidation of either A or C. This is consistent with the findings of Yasuda et al.,[24] which further indicates that oxidation of a complex undergoing a spin equilibrium may, in general, be slower than that for which no change of spin state occurs. As already discussed above, the oxidation product of B has not been firmly determined but, based on comparisons with the analogous Ni(II) systems,[17] it is likely to be either totally low spin, or possibly a spin-equilibrium system. If the former situation is the case, the electrode reaction would be

$$\mathrm{Fe(II)_{SE}} \rightleftarrows \mathrm{Fe(III)_{LS}} + e^- \qquad (4)$$

and the observed rate constant for electron transfer might depend on the rate of spin conversion concomitant with electron transfer if the chemical (spin) conversion were slow. Unfortunately, data in the literature suggest that spin conversion rates are not slow. For compound B, laser-Raman *T*-jump kinetic measurements in solution have shown that the forward (k_1) and reverse (k_{-1}) first-order rate constants for the

$$\mathrm{Fe^{II}}_{\mathrm{LS}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Fe^{II}}_{\mathrm{HS}} \qquad (5)$$

spin conversion are 4×10^6 s^{-1} and 5×10^6 s^{-1}, respectively.[14,15] In CH_3COCH_3, the electron-transfer rate constant is 1.4×10^{-1} cm s^{-1}, which can be translated into a first-order rate constant on the order of 10^6 s^{-1} when a reaction layer of ~10-Å thickness is assumed. An even smaller rate constant is observed in C_6H_5CN and *n*-PrCN. Therefore, in all the solvents examined the rate of spin conversion between the high- and low-spin states appears to be greater than the electron-transfer rate by a factor of at least 5–10.

In our earlier study involving reduction of $[\mathrm{Fe^{III}(X\text{-}Sal)_2trien}]^+$, the electron-transfer rate constant was found to be between 2.4×10^{-2} and 4.6×10^{-2} cm/s, depending on the position of the spin equilibrium.[10] Again, with the assumption of a reaction layer thickness of 10 Å, this corresponds to a first-order electron-transfer rate constant of $(2.4\text{–}4.6) \times 10^5$ s^{-1}, which is substantially less than the spin conversion rate of 10^7–10^8 s^{-1} as measured in the bulk of solution by laser-Raman *T*-jump and ultrasonic relaxation kinetics.[6,26] Differences between a slow, rate-determining spin conversion observed under our electrochemical conditions and that observed in the bulk of solution by laser-Raman *T*-jump methods were attributed possibly to an interaction between the electrical field in the Helmholtz reaction layer and the magnetic field of the diffusing species. This may also be the case for the compounds investigated in this study, although not as large a decrease in spin conversion would be needed for the two processes (spin conversion and electron transfer) to become

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[21] L. E. Orgel, *Inst. Int. Chim. Solvay, Cons. Chim.* [*Rapp. Discuss.*], **10**, 289 (1956).

[22] R. C. C. Gurira, Thesis, The Pennsylvania State University, 1973.

[23] K. M. Kadish and J. Jordan, *J. Electrochem. Soc.*, **8**, 1250 (1978).

[24] H. Yasuda, K. Suga, and S. Aoyagui, *J. Electroanal. Chem.*, **86**, 259 (1978).

[25] K. M. Kadish and D. G. Davis, *Ann. N.Y. Acad. Sci.*, **206**, 495 (1973).

[26] R. A. Binstead, J. K. Beattie, E. V. Dose, M. F. Tweedle, and L. J. Wilson, *J. Am. Chem. Soc.*, **100**, 5609 (1978).

Inorg. Chem. **1982**, *21*, 3437–3442

competitive. Whatever the reason, however, there is no doubt that the electron-transfer rate constant is slowest for compound B, regardless of the solvent used.

Attempts to determine whether spin conversion occurs before or after electron transfer have, to date, proven unsuccessful. Variable-scan measurements did not reveal the presence of either an EC (*e*lectrochemical–*c*hemical) mechanism or a CE (*c*hemical–*e*lectrochemical) mechanism. Differentiation between these mechanisms might be achieved by measurements of electron-transfer rates for a series of intermediate-spin (spin-equilibrium) complexes that possess differing populations of the high-spin and low-spin states (as was possible for the [Fe(X-Sal)$_2$trien](PF$_6$)$_2$ spin-equilibrium complexes).[10] Unfortunately, complexes of this type are not widely available.

In summary, we have measured electron-transfer rate constants for three similar Fe(II) complexes, differing mainly in these spin states in order to determine the effect of spin state on heterogeneous electron-transfer rates. Contrary to initial expectation, similar rate constants were obtained for the Fe(II)$_{\mathrm{HS}}$/Fe(III)$_{\mathrm{HS}}$ and Fe(II)$_{\mathrm{LS}}$/Fe(III)$_{\mathrm{LS}}$ complexes, while the rate constant for the oxidation of a spin-equilibrium Fe(II) complex was slower than for either the purely high- or low-spin species, and this appears true independent of the solvent system utilized. Finally, similar to our earlier results for reduction of an Fe(III) spin-equilibrium system, the rates of spin conversion for the present Fe(II)$_{\mathrm{LS}}$ $\rightleftarrows$ Fe(II)$_{\mathrm{HS}}$ spin-equilibrium process may be slower at the electrode surface than in the bulk of solution. It would seem that this possibility needs to be investigated further, both theoretically and experimentally.

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Ferric Ion Sequestering Agents. 10. Selectivity of Sulfonated Poly(catechoylamides) for Ferric Ion[1]

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Complexation equilibria have been evaluated by potentiometric titration of several biologically significant divalent metals as well as Fe(III) with the sulfonated poly(catecholate) ligands 1,6-bis(2,3-dihydroxy-5-sulfobenzoyl)-1,6-diazahexane (4-LICAMS), 1,3,5-tris(((2,3-dihydroxy-5-sulfobenzoyl)amino)methyl)benzene (MECAMS), and 1,5,10,14-tetrakis-(2,3-dihydroxy-5-sulfobenzoyl)-1,5,10,14-tetraazatetradecane (3,4,3-LICAMS). For all ligands studied the titrations demonstrate the following relative stabilities Fe(III) >> Cu(II) > Zn(II) > Ni(II), Co(II) > Mg(II) > Ca(II). These poly(catechoylamide) ligands possess great selectivity for ions of high charge to ionic radius ratios such as Fe(III) and Pu(IV); their selectivity is similar to that shown by desferrioxamine B, the current chelating agent for iron overload, and is greater than that demonstrated by DTPA, the chelating agent most often used for plutonium and other heavy-metal ion decorporation.

Introduction

Chelation therapy as a means of treatment for removal of metals or metalloids from the body has been used since British antiLewisite (2,3-dimercaptopropanol) was discovered to be an effective sequestering agent for arsenic in the early 1940s.[2] Subsequent development of amine polycarboxylates such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), effective in vivo sequestering agents for a variety of metal ions,[3] has spurred the search for the development of other effective chelating agents.

Although the synthetic chelating agents EDTA and DTPA effectively remove toxic metals from the body, they also bind divalent calcium and zinc[4] and must be administered as the calcium or zinc salts to avoid depletion of these elements from the body. Even then, toxicity results when these ligands are administered to test animals over prolonged periods.[5] Laboratory animals die, apparently at least in part as a result of Zn(II) depletion, when a high level of DTPA is maintained in the blood by multiple injections.[6] Thus, there is a need for development of chelating agents that are capable of selectively chelating the toxic metal without removing biologically significant divalent metal ions.

The in vivo sequestering of ferric ion is of particular interest because of its toxicity if in excess in the body. With the microbial iron sequestering agent enterobactin[7,8] as a model, synthetic catechoylamide ligands have been designed to bind ferric ion.[9] This work has recently been reviewed.[10]

In addition to binding ferric ion, synthetic catechoylamide ligands will bind other metals with high charge to ionic radius ratios such as Pu(IV), the oxidation state most likely to exist under physiological conditions. Pu(IV) and Fe(III) possess notable chemical similarities: (1) they have similar charge to ionic radius ratios (4.2 and 4.6 e/Å, respectively);[11] (2) both have large hydrolysis constants; (3) Pu(IV) is known to follow biological iron-transport pathways.[12] With these similarities

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(1) Previous paper in this series: Weitl, F. L.; Raymond, K. N. *J. Org. Chem.* **1981**, *46*, 5234–37.

(2) Peters, R. A.; Stocken, L. A.; Thompson, R. H. S. *Nature (London)* **1945**, *156*, 616–19.

(3) Seven, M. J., Johnson, L. A., Eds. "Metal Binding in Medicine"; Lippincott: Philadelphia, 1959.

(4) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1977.

(5) Foreman, H. "Metal Binding in Medicine"; Seven, M. J., Johnson, L. A., Eds.; Lippincott: Philadelphia, 1959; pp 82–94.

(6) Taylor, G. N.; Williams, J. L.; Roberts, L.; Atherton, D. R.; Shabestari, L. *Health Phys.* **1974**, *27*, 285–88.

(7) O'Brien, I. G.; Gibson, F. *Biochim. Biophys. Acta* **1970**, *215*, 393–402.

(8) Pollack, J. R.; Neilands, J. B. *Biochem. Biophys. Res. Commun.* **1970**, *38*, 989–92.

(9) Weitl, F. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 2728–30.

(10) Raymond, K. N.; Harris, W. R.; Carrano, C. J.; Weitl, F. L. *ACS Symp. Ser.* **1980**, *No. 140*, 313–332.

(11) Shannon, R. D. *Acta Crystallogr., Sect A* **1976**, *A32* (5), 751–67.

0020-1669/82/1321-3437$01.25/0