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Intersystem Crossing Observed by Ultrasonic Relaxation of the $^2\text{T} \rightleftharpoons ^6\text{A}$ Spin Equilibrium of Hexadentate Iron(III) Complexes in Solution

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Abstract: Ultrasonic relaxation techniques have been employed to investigate the dynamics of the spin equilibria of several hexadentate iron(III) complexes in solution. For aqueous solutions of bis(salicylaldiminato)triethylenetetramineiron(III) nitrate-1.5 hydrate, $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$, the relaxation time at 25 °C is 5.33 ± 0.05 ns. From the relaxation amplitude the high-spin state is calculated to be $10.8 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ larger than the low-spin state. From the relaxation time at 25 °C and the equilibrium constant measured by the Evans' ^1H NMR method, the forward (k_{26}) and reverse (k_{62}) rate constants have been calculated to be 8.72×10^7 and $1.01 \times 10^8 \text{ s}^{-1}$, respectively. The temperature dependence of the rate constants implies activation enthalpies for the doublet-sextet interconversion of $\Delta H^\ddagger_{26} = 6.38 \pm 0.28 \text{ kcal mol}^{-1}$ and $\Delta H^\ddagger_{62} = 1.92 \pm 0.28 \text{ kcal mol}^{-1}$. Using absolute rate theory the transmission coefficient, κ , is calculated to be $\geq 10^{-3.4}$ for this formally spin forbidden, $\Delta S = 2$, intersystem crossing process. The value of κ is estimated to lie in the range 10^{-2} - 10^{-3} , indicating that both thermodynamic and electronic factors determine the rate of intersystem crossing. This process can be described as nonadiabatic electron transfer between two electronic isomers possessing distinct, different nuclear geometries. Preliminary observations of ultrasonic relaxations for solutions of $[\text{Fe}^{\text{III}}(\text{acac}_2\text{trien})]\text{NO}_3$ in water and $[\text{Fe}^{\text{III}}(\text{benzac}_2\text{trien})]\text{NO}_3$ in methanol are also described.

Introduction

The relaxation of the thermal spin equilibrium of metal complexes provides a convenient means of determining the dynamics of intersystem crossing processes which are otherwise only accessible in excited states.² Their kinetics are important

for understanding those electron transfer reactions which are accompanied by changes in spin multiplicity and also provide new insights to the intersystem crossing barriers between excited states, especially those of metal complexes. Solution kinetic techniques have been pursued to ensure that the dynamics observed are those of the independent molecules.³

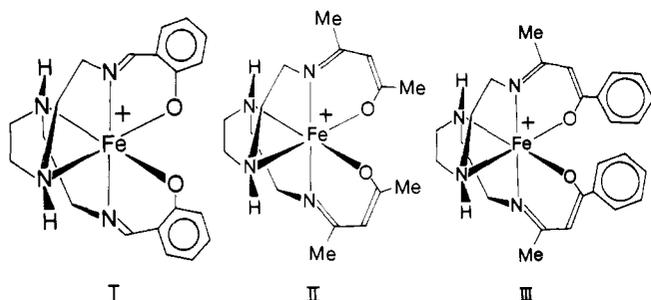
Using ultrasonic relaxation techniques we have previously measured the rates of intersystem crossing between the singlet and quintet states of $[\text{Fe}^{\text{II}}(\text{HB}(\text{pz})_3)_2]$ in THF and of $[\text{Fe}^{\text{II}}(\text{paptH})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ in H_2O . Relaxation times of 33.0 ± 0.7 and 41.00 ± 0.14 ns, respectively, were observed at 25°C .⁴ From the temperature dependence of the relaxation times and of the equilibrium constants the activation barriers for these spin state interconversions were evaluated. As these $\Delta S = 2$ processes are formally spin forbidden they are expected to be associated with a probability factor $\ll 1$ for the crossing. A lower limit to this transmission coefficient, κ , can be estimated from the measured rates and activation barriers for the intersystem crossing process using absolute rate theory. The minimum values of κ were calculated to be $10^{-4.2}$ and $10^{-2.5}$, respectively, for these d^6 ($\Delta S = 2$) spin-forbidden processes.

The recent theoretical treatments of spin equilibria by König and Kremer⁵ have shown that only for the octahedral d^6 case is there no substantial mixing between the states at the cross-over. On this basis the d^5 ($\Delta S = 2$) and d^7 ($\Delta S = 1$) intersystem crossing processes should be more probable than already found in the previous octahedral iron(II) systems.

We now report observations of ultrasonic relaxations ascribed to the spin equilibrium



in aqueous solutions of $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ (compound I). From the temperature dependence of the relaxation



time we can assess the barriers to the intersystem crossing and can calculate the lower limit of the transmission coefficient for the probability of the spin-forbidden intersystem crossing in this pseudooctahedral d^5 iron(III) complex. We also report our preliminary observations of ultrasonic relaxations in aqueous solutions of $[\text{Fe}^{\text{III}}(\text{acac}_2\text{trien})]\text{NO}_3$ (compound II) and methanol solutions of $[\text{Fe}^{\text{III}}(\text{benzac}_2\text{trien})]\text{NO}_3$ (compound III).

Experimental Section

Materials. The complex $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ was prepared as described in the literature.⁶ The complex was purified by recrystallization from distilled water, dried in vacuo over P_4O_{10} for 36 h, and characterized by elemental analyses. Anal. Calcd for $\text{FeC}_{20}\text{H}_{27}\text{O}_6\text{N}_5$: Fe, 11.23; C, 48.30; H, 5.47; O, 20.91; N, 14.08. Found: Fe, 11.05; C, 48.50; H, 5.30; N, 14.29. Distilled water was used as the solvent for the ultrasonics experiments.

The complex $[\text{Fe}^{\text{III}}(\text{acac}_2\text{trien})]\text{NO}_3$ was prepared as described in the literature,⁷ except that KPF_6 was not added. The deep red methanol solution was filtered, removing a light brown powder. The solvent was removed on a rotary evaporator and the residue was extracted into CH_2Cl_2 (Merck AR). The extract was filtered and an equal volume of CCl_4 added to the filtrate. Most of the CH_2Cl_2 was removed by rotary evaporation and the crude black product which formed was collected, washed with CCl_4 (Merck AR) until the filtrate was colorless, and dried in vacuo. The complex was purified by dissolving it in distilled water, filtering through a $0.45\text{-}\mu$ millipore filter to remove $\text{Fe}(\text{OH})_3$, removing the solvent, repeating the recrystallization from $\text{CH}_2\text{Cl}_2/\text{CCl}_4$, and drying in vacuo over P_4O_{10} for 24 h. The complex was characterized by elemental analyses. Anal. Calcd for $\text{FeC}_{16}\text{H}_{28}\text{N}_5\text{O}_5$: Fe, 13.10; C, 45.08; H, 6.62; N, 16.43; O, 18.77.

Found: Fe, 13.34; C, 44.83; H, 6.44; N, 16.36; O, 18.82. Distilled water was used as the solvent for the ultrasonics experiments.

The complex $[\text{Fe}^{\text{III}}(\text{benzac}_2\text{trien})]\text{NO}_3$ was prepared as described in the literature⁷ except that KPF_6 was not added. Instead the red-purple solution was stirred for 2 h and filtered. The purple residue was extracted into MeOH (Merck AR) and filtered and the solvent was removed. The crude residue was then extracted with CCl_4 (Merck AR) to remove unreacted ligand and the crude product was filtered off and washed with CCl_4 until the filtrate was colorless. This solid was purified by recrystallization from $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ and characterized by elemental analyses. Anal. Calcd for $\text{FeC}_{26}\text{H}_{32}\text{N}_5\text{O}_5$: Fe, 10.15; C, 56.74; H, 5.86; N, 12.72; O, 14.53. Found: Fe, 10.30; C, 56.50; H, 5.81; N, 12.80; O, 14.65. Merck AR methanol was used as the solvent for the ultrasonics experiments. Microanalyses were performed by Alfred Bernhardt Microanalytical Laboratories, West Germany.

Methods. Aqueous solution magnetic moments of 0.02 M $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ were measured using the Evans' ^1H NMR method at 90 MHz (Brüker HX-90). An internal reference of 3% v/v *t*-BuOH was used. Probe temperatures were measured with an internal capillary of ethylene glycol.⁸ The validity of the literature temperature calibration was checked against the melting points of several pure organic liquids and solids.

Ultrasonic absorption measurements were collected in the frequency range 1–150 MHz using a swept frequency acoustic resonance cell between 1 and 25 MHz and a pulsed ultrasonic cell between 10 and 150 MHz as described previously.⁴

Results

The ultrasonic absorption curves for 0.0127–0.0253 M solutions of $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ in H_2O , as shown in Figure 1, represent single ultrasonic relaxation processes. The absorption curves were fitted by nonlinear least-squares analysis to the equation

$$\alpha/f^2 = A(1 + \omega^2\tau^2)^{-1} + B \quad (2)$$

describing a single relaxation process.⁹ Values of A , B , and τ so obtained are listed in Table I, where α is the absorption coefficient (Np cm^{-1}); f is the frequency (Hz), ω is the angular frequency (rad s^{-1}) = $2\pi f$; τ is the relaxation time (s); and A and B are constants for a particular relaxation curve. The relaxation time was found to be concentration independent and the relaxation amplitudes to depend linearly on concentration (Table I), as expected for a unimolecular process.

To interpret these results it is necessary to know the equilibrium constants and thermodynamic parameters associated with equilibrium 1 under the conditions of the ultrasonics experiments. Therefore, the effective magnetic moment of $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ in H_2O was measured using the Evans' NMR method between 24 and 82°C .¹⁰ The data are listed in Table II and μ_{eff} values at the temperatures of the ultrasonics experiments are given in Table I. These data were corrected for changes in solvent density and hence for sample concentration with temperature. To calculate the equilibrium constants the magnetic moment of the high-spin state was taken as $6.0 \mu_{\text{B}}$ and that of the low-spin state as $1.9 \mu_{\text{B}}$.⁶ The data were fitted as $\ln K$ vs. T^{-1} by linear least-squares regression and are plotted in Figure 2. From the temperature dependence of the equilibrium constant between the two states ΔH° is calculated to be $4.46 \pm 0.22 \text{ kcal mol}^{-1}$, and ΔS° to be $14.7 \pm 0.7 \text{ cal deg}^{-1} \text{ mol}^{-1}$. Although the previous results reported by Wilson et al.⁶ did not include measurements in water, these values lie in the middle of the range they found for a variety of solvents.

The ultrasonic absorption of 0.1 M solutions of $[\text{Fe}^{\text{III}}(\text{acac}_2\text{trien})]\text{NO}_3$ in H_2O at 25°C also revealed a single relaxation process with a relaxation time of 2.12 ± 0.06 ns. However, the complex slowly hydrolyzes over the several hours time scale of the ultrasonics experiment with a small amount of $\text{Fe}(\text{OH})_3$ being formed. Although this does not greatly affect the accuracy of the ultrasonic absorption measurements, it was felt that there could be a serious effect on the magnetic sus-

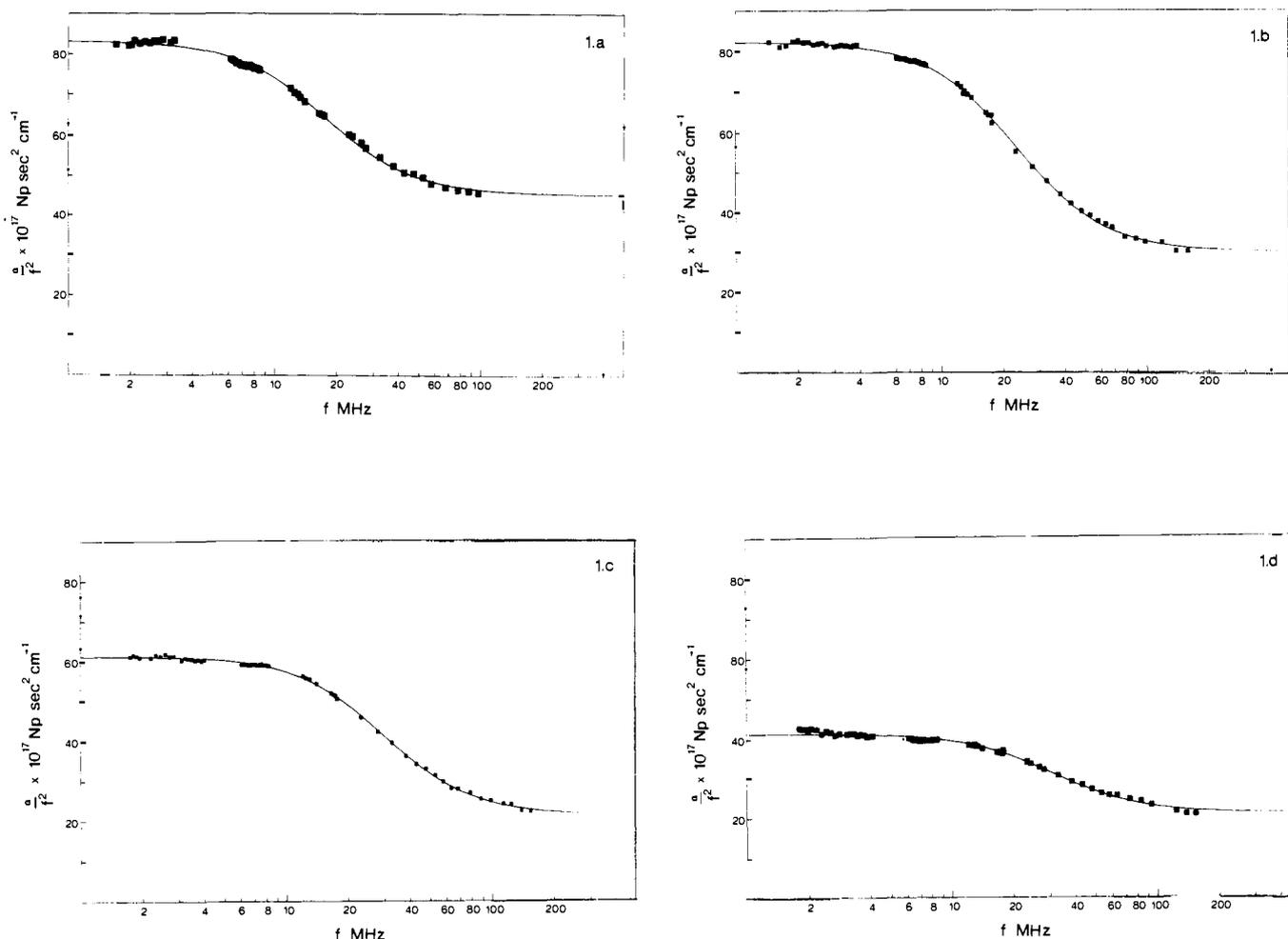


Figure 1. The ultrasonic absorption of aqueous solutions of $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$: (a) 5 °C, 0.0150 M; (b) 15 °C, 0.0253 M; (c) 25 °C, 0.0253 M; (d) 25 °C, 0.01274 M.

ceptibility measurements. The complex has therefore not been investigated further.

Ultrasonic absorption measurements on $[\text{Fe}^{\text{III}}(\text{benzac}_2\text{trien})]\text{NO}_3$ were frustrated by low solubility. However, at 0.02 M in methanol a small excess absorption of $\sim 2 \times 10^{-17} \text{ Np s}^2 \text{ cm}^{-1}$ was observed, from which an upper limit of 1 ns can be calculated for the relaxation time (see below), consistent with that observed in water for the structurally and electronically similar $[\text{Fe}^{\text{III}}(\text{acac}_2\text{trien})]^+$ complex.^{7,11}

Discussion

Solutions of $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ in water exhibit single ultrasonic relaxations with concentration-independent relaxation times (for $1.3\text{--}2.5 \times 10^{-2} \text{ M}$ solutions), as expected for a unimolecular isomerization process. The observed relaxation time of $5.33 \pm 0.05 \text{ ns}$ for $\sim 10^{-2} \text{ M}$ solutions at 25 °C is consistent with the recent work of Sutin and Wilson et al. Using the laser Raman temperature-jump technique, these authors have found the relaxation time to be less than the 30 ns lower limit of the apparatus.¹¹ An estimate of 10–20 ns for the relaxation time was obtained for $4\text{--}5 \times 10^{-3} \text{ M}$ solutions in methanol at 25 °C by means of a deconvolution procedure.¹⁷ Their previously reported value of $35 \pm 8 \text{ ns}$ was obtained for $2\text{--}5 \times 10^{-4} \text{ M}$ solutions in methanol at 20 °C, without the deconvolution procedure.¹⁷ While these results indicate the possibility of some contribution from a concentration-dependent relaxation pathway, no concentration dependence was apparent in the relaxation time from the ultrasonic relaxation measurements. Over the twofold concentration range studied such a concentration dependence would have been readily

detected. Furthermore, since the relaxation amplitude depends both on the concentration and the relaxation time (eq 4), the linear concentration dependence of the relaxation amplitude (Table I) also indicates that the relaxation time is concentration independent. Since the amplitude of the ultrasonic relaxation displays a temperature dependence consistent with the temperature dependence of the spin equilibrium, the ultrasonic relaxation is therefore ascribed to a unimolecular isomerization of the Fe(III) complex between two states of different spin multiplicity.

A measure of the volume difference between the doublet and sextet isomers can be obtained from the amplitude of the ultrasonic absorption. Equation 2 can be written as

$$\frac{\alpha}{f^2} = \frac{2\pi^2\rho v}{RT} \left(\Delta V^\circ - \frac{\alpha_p}{\rho C_p} \Delta H^\circ \right)^2 \frac{\Gamma\tau}{1 + \omega^2\tau^2} + B \quad (3)$$

Hence the excess absorption due to chemical relaxation for $\omega \ll \tau$ is

$$A = \frac{2\pi^2\rho v}{RT} \left(\Delta V^\circ - \frac{\alpha_p}{\rho C_p} \Delta H^\circ \right)^2 \Gamma\tau \quad (4)$$

where ρ is the solution density, v the sound velocity, α_p the coefficient of thermal expansion, C_p the specific heat, and Γ the concentration dependence ($\Gamma^{-1} = [\text{LS}]^{-1} + [\text{HS}]^{-1}$ where $[\text{LS}]$ and $[\text{HS}]$ are the concentrations of the doublet and sextet isomers, respectively). Values of ΔH° and Γ are obtained from the determination of the equilibrium constant by the NMR method. The other quantities are taken from the literature.^{12,13} These are listed in Table I, together with the values of ΔV° calculated using eq 4 from the experimental results at three

Table I. Collected Data and Results for $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ ^a

	5 °C	15 °C	25 °C ^d
$A \times 10^{17}$, Np s ² cm ⁻¹	38.0 ± 0.4	52.3 ± 0.3	39.91 ± 0.17
$B \times 10^{17}$, Np s ² cm ⁻¹	45.2 ± 0.3	29.9 ± 0.2	21.35 ± 0.15
τ , ns	8.94 ± 0.16	6.80 ± 0.06	5.33 ± 0.05
μ_{eff} , μ_{B} ^b	3.80	4.07	4.32
K_{26}	0.505	0.668	0.867
ΔH° , kcal mol ⁻¹			4.46 ± 0.22
ΔS° , cal deg ⁻¹ mol ⁻¹			14.7 ± 0.7
C_{total} , M	0.014 77	0.025 27	0.025 32
$\Gamma \times 10^3$, M	3.292	6.066	6.298
ρ , g cm ⁻³ ^c	0.999 99	0.999 13	0.997 07
v , cm s ⁻¹ ^c	144 900	147 300	149 700
$\alpha_p/\rho C_p$, cm ³ kcal ⁻¹ ^c	0.015 92	0.150 90	0.258 25
ΔV° , cm ³ mol ⁻¹	10.29	10.90	11.16
k_{26} , s ⁻¹	3.75×10^7	5.89×10^7	8.72×10^7
k_{62} , s ⁻¹	7.44×10^7	8.82×10^7	10.06×10^7
ΔG^\ddagger_{26} , kcal mol ⁻¹			6.62 ± 0.40
ΔG^\ddagger_{62} , kcal mol ⁻¹			6.53 ± 0.40
ΔH^\ddagger_{26} , kcal mol ⁻¹			6.38 ± 0.28
ΔH^\ddagger_{62} , kcal mol ⁻¹			1.92 ± 0.28
ΔS^\ddagger_{26} , cal deg ⁻¹ mol ⁻¹			-(0.8 ± 1.0)
ΔS^\ddagger_{62} , cal deg ⁻¹ mol ⁻¹			-(15.5 ± 1.0)

^a The quoted error bars are for one standard deviation. ^b The estimated error is ± 0.03 μ_{B} . ^c Pure solvent values were assumed for the physical constants. ^d At 0.012 74 M, $A = (20.2 \pm 0.3) \times 10^{-17}$ Np s² cm⁻¹, $B = (20.9 \pm 0.3) \times 10^{-17}$ Np s² cm⁻¹, $\tau = (5.16 \pm 0.15)$ ns.

Table II. Magnetic Susceptibility Measurements for $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ in H₂O^a

Δf , Hz ethylene glycol	T , K	Δf , Hz <i>t</i> -BuOH	$\chi_{\text{g}} \times 10^6$, ^b cgs	$\chi_{\text{m}}^{\text{cor}} \times 10^3$ ^c	μ_{eff} , ^d μ_{B}
148.920	296.7	30.664	15.28	7.788	4.32
137.622	309.5	32.718	16.31	8.302	4.55
127.499	321.0	34.332	17.16	8.723	4.75
117.375	332.5	36.533	18.31	9.295	4.99
107.105	344.2	36.973	18.63	9.458	5.12
97.422	355.2	37.853	19.19	9.732	5.28

^a $C_{\text{total}} = 0.0225$ M at $T = 21.6$ °C. The data were corrected for changes in solvent density with temperature. ^b Includes $\chi_0(\text{H}_2\text{O}) = 0.718 \times 10^{-6}$ cgs. ^c Includes $\chi_{\text{D}} = 0.191 \times 10^{-3}$ mol⁻¹, which was obtained using Pascal's constants and constitutive corrections. ^d The estimated error is ± 0.03 μ_{B} .

different temperatures, the average value being 10.8 ± 0.5 cm³ mol⁻¹ for $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$.

Solutions of $[\text{Fe}^{\text{III}}(\text{acac}_2\text{trien})]^+$ in water also exhibit single ultrasonic relaxations. The observed relaxation time of 2.12 ± 0.06 ns for these 10^{-1} M solutions at 25 °C is also consistent with the recent laser temperature-jump results where the relaxation time was found to be less than 30 ns¹¹ for $\sim 10^{-3}$ M solutions,¹⁸ with the previously measured value of 45 ± 10 ns⁷ being measured for $\sim 10^{-4}$ M solutions.¹⁸ As the complex undergoes a slow hydrolysis in water producing $\text{Fe}(\text{OH})_3$ no further ultrasonic relaxation measurements have been pursued owing to the likelihood of inaccurate magnetic susceptibility measurements in aqueous solutions. Although the complex is stable in methanol, the ultrasonic amplitude is too small to yield useful data due to the unfavorable relative magnitudes of ΔV° and ΔH° (eq 4).

Similarly, solutions of $[\text{Fe}^{\text{III}}(\text{benzac}_2\text{trien})]^+$ in methanol only yield a small excess ultrasonic absorption of $\sim 2 \times 10^{-17}$ Np s² cm⁻¹. However, it is possible to set an upper limit for τ in this case using eq 4 if one knows both ΔV° and ΔH° . Using the value of ΔV° found for $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ and the value previously found for ΔH° ,⁷ an upper limit of 1 ns is calculated for τ in good agreement with the observed relaxation time for the structurally and electronically similar $[\text{Fe}^{\text{III}}(\text{acac}_2\text{trien})]^+$ in aqueous solutions.

The average of 10.8 ± 0.5 cm³ mol⁻¹ obtained for the volume difference between the low-spin and high-spin isomers of $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ can be compared with the known metal-ligand bond length differences between the low-spin (1.94 μ_{B}) $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]\text{Cl} \cdot 2\text{H}_2\text{O}$ and high-spin (5.9 μ_{B}) $[\text{Fe}^{\text{III}}(\text{acac}_2\text{trien})]\text{PF}_6$.¹⁴ From these data one calculates that the effective radius from the central metal to the peripheral hydrogen atoms on the trien backbone of $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ is 4.0 Å. If 4.0 Å is used as the radius of a sphere describing the low-spin state, then using the equation

$$\Delta V^\circ = N_{\text{A}} \frac{4\pi}{3} (r^3_{\text{HS}} - r^3_{\text{LS}}) \quad (5)$$

the measured volume difference of 10.8 ± 0.5 cm³ mol⁻¹ corresponds to a radial extension of 0.09 Å on passing to the larger high-spin state. This can be considered a minimum change in metal-ligand bond lengths between the low-spin and high-spin isomers, since examination of the crystal structure reveals that the surface is deeply indented with space between the planes formed by the trien backbone. The volume change due to an extension of the metal-ligand bonds is less for this indented surface than for a sphere. Hence the measured ΔV° is consistent with the measured average bond length difference of 0.12 Å.¹⁴ The effect of the large salicylaldehyde rings has been ignored in these calculations as there is only a small bond length difference of 0.04 Å for the Fe-O bonds resulting in a tilting rather than extension of the salicylaldehyde rings. Within the errors of these simple calculations, the ultrasonic relaxation amplitudes are consistent with our assignment of the absorption to the spin equilibrium relaxation.

The rate constants for the intersystem crossing between spin states can be calculated from the relaxation times. For a unimolecular isomerization process between the low-spin doublet state and high-spin sextet state:

$$\tau^{-1} = k_{26} + k_{62} = k_{62}(K_{26} + 1) \quad (6)$$

Using the equilibrium constants determined by the NMR method, the rate constants given in Table I are calculated.

The most significant aspect of these results is the temperature dependence of the rate constants (Figure 3). The free energy barriers calculated from the rate constants at 25 °C and the activation parameters obtained from their temperature dependence using absolute rate theory (eq 7) are given in Table

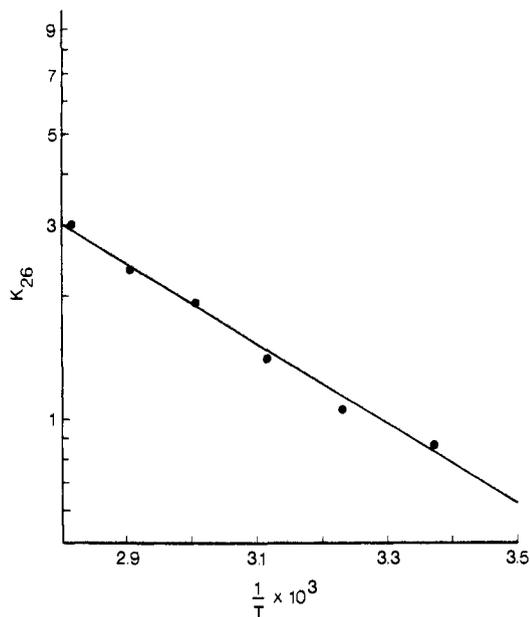


Figure 2. The temperature dependence of the equilibrium constant for $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ in H_2O .

I and illustrated in Figure 4.

$$k = \left(\frac{k_B T}{h}\right) e^{-\Delta G^\ddagger_{\text{obsd}}/RT} = \left(\frac{k_B T}{h}\right) e^{-\Delta H^\ddagger_{\text{obsd}}/RT} e^{\Delta S^\ddagger_{\text{obsd}}/R}$$

$$= \kappa \left(\frac{k_B T}{h}\right) e^{-\Delta H^\ddagger_{\text{obsd}}/RT} e^{\Delta S^\ddagger/R} \quad (7)$$

From these results an assessment can be made of the magnitude of κ , the transmission coefficient, which reflects the probability of the spin-forbidden intersystem crossing.

For $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ the rate constants k_{26} of $8.72 \times 10^7 \text{ s}^{-1}$ and k_{62} of $1.01 \times 10^8 \text{ s}^{-1}$ at 25°C correspond to activation free energies ΔG^\ddagger_{26} of $6.62 \text{ kcal mol}^{-1}$ and ΔG^\ddagger_{62} of $6.53 \text{ kcal mol}^{-1}$, the difference of $0.09 \text{ kcal mol}^{-1}$ being ΔG°_{26} . For the doublet–sextet process the activation enthalpy ΔH^\ddagger_{26} is $6.38 \text{ kcal mol}^{-1}$ but this comprises $4.46 \text{ kcal mol}^{-1}$ due to the endothermic enthalpy difference ΔH°_{26} . For the reverse sextet–doublet process the activation enthalpy ΔH^\ddagger_{62} is therefore $1.92 \text{ kcal mol}^{-1}$. Hence the rate constant k_{62} is determined by a small enthalpy barrier and an entropy barrier equivalent to $-T\Delta S^\ddagger_{\text{obsd}}$ of $4.62 \text{ kcal mol}^{-1}$. This entropy barrier comprises both κ and other entropy terms so that the relative magnitudes of these two factors cannot be separated experimentally. To estimate κ requires an additional assumption.

A minimum value of κ and hence the lowest probability of intersystem crossing is obtained by assuming that the entropy of the transition state equals that of the high-spin state, provided that there is no minimum in $-T\Delta S^\ddagger$ between the two spin states. This latter restriction is not required thermodynamically, but we believe this restriction on the transition state entropy to be reasonable considering the nature of the isomerization process; it is certainly valid in the case of $[\text{Fe}^{\text{II}}(\text{HB}(\text{pz})_3)_2]$ where ΔH^\ddagger_{51} is only $0.62 \text{ kcal mol}^{-1}$, equal to the thermal energy at room temperature.^{4,15} With the assumption that the entropy of the transition state is not greater than the sextet isomer, then if the entire entropic barrier for the sextet–doublet process of 4.62 kcal/mol is due to κ , the minimum value of κ is $10^{-3.4}$.

Examination of the x-ray crystal structure of $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ reveals a distortion from octahedral symmetry which would be expected to split the ${}^2\text{T}$ state into ${}^2\text{A}$ and ${}^2\text{E}$ states.¹⁴ The effect of the splitting is to introduce a degeneracy barrier as well for the intersystem crossing, as given by the

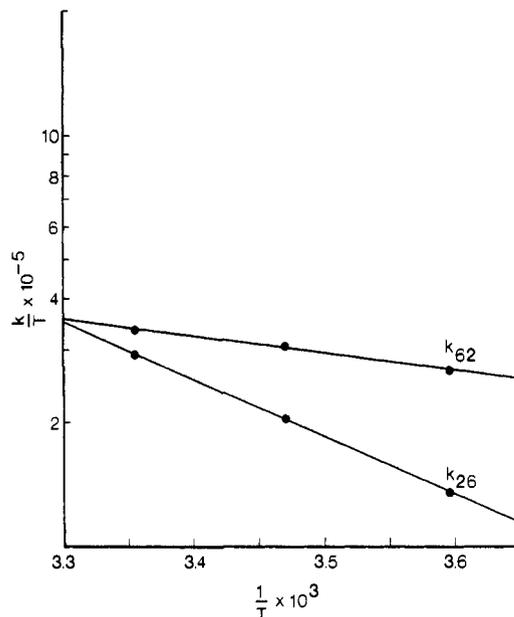


Figure 3. Eyring plots of the temperature dependence of the rate constants k_{26} and k_{62} for the $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$ system.

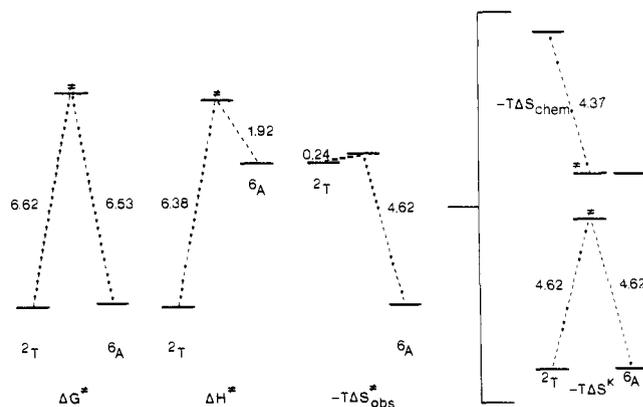


Figure 4. Activation parameters for the intersystem crossing process in $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$, with $-T\Delta S^\ddagger_{\text{obsd}}$ partitioned to give the minimum value of κ as described in the text.

equation

$$-T\Delta S_{\text{deg}} = -RT \ln \frac{[\text{HS}]_{\text{deg}}}{[\text{LS}]_{\text{deg}}} \quad (8)$$

For the ${}^2\text{T} \rightleftharpoons {}^6\text{A}$ process the degeneracies are equal ($-RT \ln 6/6 = 0$) but for the ${}^2\text{E} \rightleftharpoons {}^6\text{A}$ and ${}^2\text{A} \rightleftharpoons {}^6\text{A}$ processes the degeneracies of the two states are unequal causing additional entropy barriers of $-RT \ln 6/4$ and $-RT \ln 6/2 \text{ cal mol}^{-1}$, respectively. In the transition from doublet to sextet the complex acquires this additional entropy but this presumably must occur after passage from the doublet state. This implies by microscopic reversibility that for the sextet to doublet process the sextet state must lose entropy equivalent to the spin degeneracy to reach the transition state. This restriction imposes minimum entropy barriers of 0.24 (${}^2\text{E}$) or $0.65 \text{ kcal mol}^{-1}$ (${}^2\text{A}$) and hence increases the minimum probability for intersystem crossing, κ , to $10^{-3.2}$ (${}^2\text{E}$) or $10^{-2.9}$ (${}^2\text{A}$).

The activation free energy of $6.62 \text{ kcal mol}^{-1}$ for the doublet to sextet process is almost entirely due to the activation enthalpy of $6.38 \text{ kcal mol}^{-1}$. This implies a correlation between the magnitude of the transmission coefficient, κ , and the chemical entropy of the transition state. If $\kappa \sim 1$, the entropy of the activated complex is that of the low-spin doublet state; if κ approaches its minimum value of about 10^{-3} , the entropy

of the activated complex approaches that of the high-spin sextet state. Although a strong inference cannot be drawn, it is likely that the entropy of the activated complex is closer to that of the high-spin than of the low-spin state, implying that κ is closer to 10^{-3} than to 1. This is suggested by the observation that the overall free-energy change for the spin-state transition is close to zero; so the enthalpy difference between the states is compensated by the entropy difference. Since the enthalpy of the transition state is closer to that of the high-spin state, its entropy may similarly resemble that of the high-spin state.

This interpretation is physically reasonable if the higher enthalpy of the activated complex is due to an expansion of the coordination sphere to resemble the larger high-spin state. Such an activated complex would possess greater entropy owing to increased vibrational partition functions, a consequence of longer, weaker bonds, and owing to decreased solvation. To determine the volume of activation experimentally, however, the more difficult measurement of relaxation times as a function of applied pressure would be required. At present we can only surmise that the activated complex resembles the high-spin state and that κ is therefore of the order of 10^{-2} – 10^{-3} .

A similar argument can be applied to the results previously obtained for the iron(II) complex $[\text{Fe}(\text{paptH})_2]^{2+}$. Again in this case the entropy of activation for the low-spin to high-spin transition is essentially zero, implying a similar correlation between κ and the chemical entropy difference. In this case the minimum value of κ was found to be $10^{-2.5}$. Hence for both an iron(II) and an iron(III) complex it is reasonable to infer that κ lies within an order of magnitude of 10^{-2} . There is no significant difference in the probability of intersystem crossing between the Fe(II) and Fe(III) $\Delta S = 2$ processes for these two six-coordinate complexes.

A value of 10^{-2} for κ implies an energy separation between the two states at the crossover point of $\sim 38 \text{ cm}^{-1}$, for both complexes.⁴ This similarity in the energy separation between spin states for both an Fe(II) and an Fe(III) complex is not expected theoretically. In the d^6 case there is no substantial mixing between spin states in octahedral symmetry, whereas mixing can occur in d^5 systems.⁵ The present results indicate that the theoretical considerations are insufficient to account for the observed rates of intersystem crossing. The smaller minimum value for κ of $10^{-4.2}$ found for $[\text{Fe}^{II}(\text{HB}(\text{pz})_3)_2]$ may indicate differences in the extent of mixing among different complexes. Hence, both electronic and thermodynamic factors determine the rates of intersystem crossing.

A probability of intersystem crossing at the order of 10^{-2} for some $\Delta S = 2$ transitions would explain why we observe no excess ultrasonic absorption due to the spin equilibrium of tris(diethyldithiocarbamate)iron(III). For this complex the enthalpy difference between the two states is only about 1 kcal mol^{-1} and the volume difference only about 5 $\text{cm}^3 \text{ mol}^{-1}$.^{1,7,16} With such a small enthalpy difference between the ground states, the activation enthalpy is unlikely to exceed about 2 kcal mol^{-1} , leading to a predicted relaxation time of 10^{-9} – 10^{-10} s. Since the relaxation amplitude depends linearly on the relaxation time and on the square of the volume change (eq 4), a process with such a short relaxation time and small volume difference would have a relaxation amplitude too small to observe.

In summary, ultrasonic absorption experiments reveal a relaxation time of 5 ns for the spin equilibrium in the iron(III) complex $[\text{Fe}^{III}(\text{Sal}_2\text{trien})]^+$ in water. For two related complexes the ultrasonic absorptions are consistent with similar rapid relaxations but experimental limitations prevent acquisition of reliable data. Using absolute rate theory a minimum value for the probability of the $\Delta S = 2$ intersystem crossing is $10^{-3.4}$. It is suggested that a probable value for this transmission coefficient is of the order of 10^{-2} – 10^{-3} . This can be compared with the estimates of 10^{-3} – 10^{-6} made on the basis of the laser temperature-jump results.¹⁷ The more accurate ultrasonics experiments allow the determination of activation parameters and reveal a significant activation enthalpy barrier. This leads to the conclusion that the intersystem crossing process is less forbidden, with a minimum value for κ of $10^{-3.4}$, and our estimate of the probable value is in the range 10^{-2} – 10^{-3} . Thus both the thermodynamic barrier and electronic factors contribute substantially to the free-energy barrier for intersystem crossing. Hence, in these complexes we conclude that the intersystem crossing process involves nonadiabatic electron transfer¹⁷ between two electronic isomers possessing distinct, different nuclear geometries.

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