Photoperturbation of the $^1A \rightleftharpoons {}^5T$ Spin Equilibrium in an Iron(II) Complex in Solution via Ligand Field Excitation

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Received October 8, 1992

Variable-temperature magnetic susceptibility measurements in the solid state of the bis complex of tris(1-pyrazolyl)methane with Fe^{II}, $[Fe(tpm)_2](ClO_4)_2$, suggest the existence of singlet–quintet spin crossover with the singlet isomer largely favored at room temperature. In acetonitrile solution, measurement of the absorption spectrum as a function of temperature reveals a spin equilibrium with the quintet population varying from ca. 6% at 233 K to ca. 30% at 295 K. When the complex in solution is irradiated with a laser pulse at wavelengths within the ligand field absorption band of the singlet isomer, ground-state depletion occurs within the pulse duration followed by fast recovery to the original absorbance level with a time constant of 25 ± 5 ns. The recovery time is virtually independent of temperature over the range +23 to –43 °C, but the signal:noise ratio of the transient signals increases with decreasing temperature. The effect was observable at several monitoring wavelengths spanning the LF and MLCT absorption regions of the complex but only when the irradiation wavelength fell within the LF absorption region. Irradiation within the MLCT band produced no effect other than that of laser pulse scatter. The observations are interpreted in terms of photoperturbation of the singlet–quintet spin state equilibrium, which in this case occurs solely through excitation in the ligand field absorption region of the complex and is the first reported instance of this type for a spin-crossover complex in solution.

Introduction

Complexes of Fe^{II} and Fe^{III} which exhibit electronic spin-state isomerism continue to generate interest because of the biological relevance of the spin-crossover phenomenon as well as its significance in a photophysical context when viewed as an intersystem-crossing process.[1] Photoperturbation of spin-crossover equilibria using pulsed lasers is well established as a technique for studying the kinetics of the spin-conversion processes $^1A \rightleftharpoons {}^5T$ and $^2T \rightleftharpoons {}^6A$ in Fe^{II} and Fe^{III} complexes, respectively[2–4] and has been used to study the interconversion as a function of both temperature and pressure.[5,7]

In all of the examples reported to date for Fe^{II} systems in solution, photoperturbation is effected through excitation in the intense metal–ligand charge-transfer (MLCT) transition of the low-spin isomer with subsequent efficient relaxation resulting in crossover into the potential well of the high-spin isomer,[2] as depicted schematically in Figure 1.

We now wish to report an instance in which perturbation of the spin equilibrium is brought about solely via ligand field (LF) excitation, with excitation through MLCT transitions being ineffective in promoting the perturbation. The species concerned is the bis complex of the tripodal ligand tris(1-pyrazolyl)methane (tpm) with Fe^{II}, $Fe(tpm)_2ClO_4$ (**1**). Spin-state isomerism in the solid state for the PF_6 salt of **1** has been recently demonstrated by Mossbauer spectroscopy.[8]

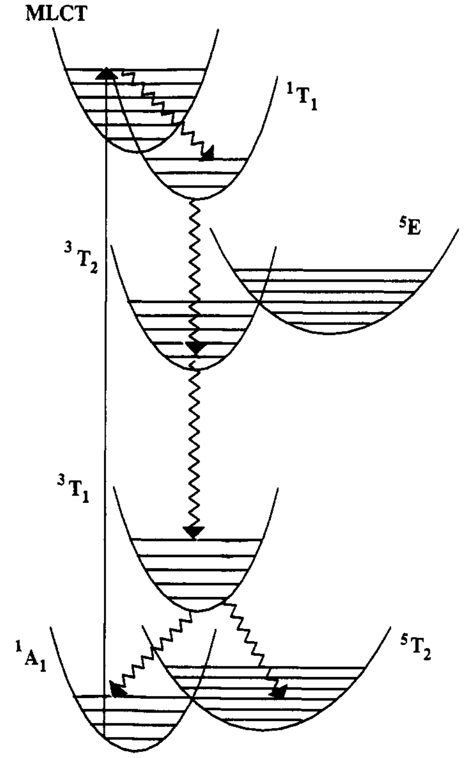

Figure 1. Schematic diagram of ground and excited LF and MLCT states and photophysical pathways in an Fe(II) complex exhibiting spin crossover.

Experimental Section

Laser Flash Photolysis. The irradiation source was a Q-switched Nd-YAG laser (pulse duration ca. 8 ns) described previously.[6,9] Laser excitation wavelengths spanning the LF and MLCT absorption regions

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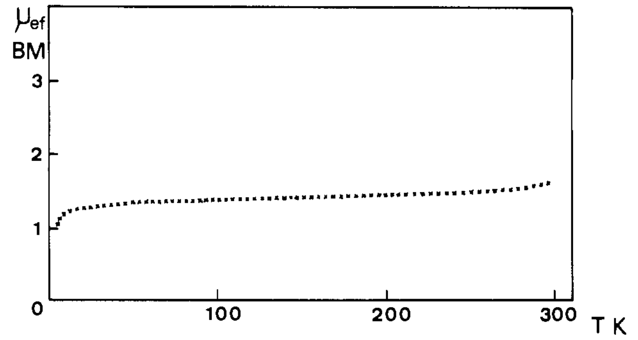

Figure 2. Curie plot of μ_{eff} vs temperature for $[Fe(tpm)_2](ClO_4)_2$.

of the complex were generated by means of frequency-doubling and-tripling crystals or by stimulated Raman scattering[6] in either H_2 or CH_4. For kinetic measurements, absorbance changes following the laser pulse were monitored spectrophotometrically[9] at monitoring wavelengths in the range 370–560 nm in a 1 cm path length quartz fluorimeter cell held in a thermostated (±1 °C) copper block. A gated multichannel diode array detector (Princeton Instruments Model DIDA 700G) was also used to record transient absorption spectra following the laser pulse.

Physical Measurements. Visible absorption spectra were measured on Cary 219 and HP 8452 diode array spectrophotometers, the latter being used for variable-temperature studies over the range 295–230 K in a thermostated cell (±1 °C) encased in a polystyrene jacket. The continuously stirred sample was cooled by means of a controlled flow of cold, dry N_2. Magnetic susceptibilities were measured by the Faraday method using equipment described earlier.[10] The molar susceptibilities were corrected for ligand diamagnetism using Pascal's constants.

Synthesis of 1. A solution of iron(II) perchlorate hexahydrate (0.97 g, 0.27 mmol) in ethanol (5 mL) was added to a solution of tris(1-pyrazolyl)methane (0.13 g, 0.59 mmol) in ethanol (5 mL) under a nitrogen atmosphere. Pink crystals of the product precipitated within 30 min. The precipitate was washed with 96% ethanol and dried in air. Yield: 0.12 g (65.8%). Anal. Calc for $[FeC_{20}H_{20}N_{12}Cl_2O_8]$: C, 35.16; H, 2.95; N, 24.60; Cl, 10.38. Found: C, 34.73; H, 2.96; N, 24.03; Cl, 9.96. (Analyses were carried out at the H. C. Oersted Institute, Copenhagen, Denmark.)

Results

The magnetic susceptibility of solid $[Fe(tpm)_2](ClO_4)_2$ has been recorded from 4.5 to 295 K. A plot of μ_{eff} versus temperature is shown in Figure 2. In the temperature range from 50 to 200 K the magnetic moment has a rather constant value of ca. 1.35 μ_B, which is mainly ascribed to the temperature-independent paramagnetism of the low-spin form. In the temperature range 150–295 K, the magnetic moment increases from 1.40 to 1.58 μ_B, indicating a slight population of a paramagnetic state at room temperature. Assuming a $^1A_1 \rightleftharpoons {}^5T_2$ equilibrium with $\mu(ls) = 0.9\ \mu_B$ and $\mu(hs) = 4.9\ \mu_B$, a high-spin population of 7.3% is estimated at 295 K. Hence the present compound is expected to exhibit spin-crossover behavior similar to that reported[11] for $[Fe(HB(pz)_3)_2]$ ($HB(pz)_3$ = hydrotris(pyrazolyl)borate) at temperatures above room temperature. Heating of complex **1** above room temperature was not attempted because of the explosive nature of the perchlorate salt. However, in the case of the corresponding PF_6 salt, spin crossover above room temperature has indeed been observed in a recent Mossbauer study.[8] Investigations of the spin equilibrium in solution are more directly relevant in the present context, and these are considered below.

The perchlorate salt is soluble in MeCN, and the electronic absorption spectrum shown in Figure 3 is very similar to that reported[11] for the $[Fe(HB(pz)_3)_2]$ complex referred to above. It is interesting that the ligand field strength of the present neutral tpm ligand is almost the same as that of the anionic $HB(pz)_3^-$. The latter ligand is expected to be a better σ-donor than tpm. However tpm might very well be a better π-acceptor than $HB(pz)_3^-$. The electronic spectral data suggest that the two effects compensate each other.

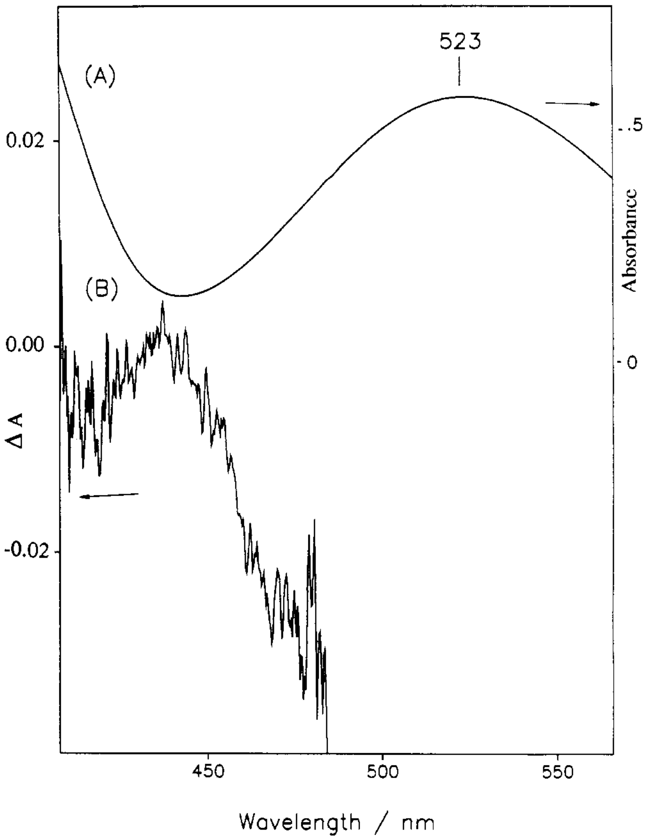

Figure 3. Trace A: absorption spectrum ($^1A_1 \rightarrow {}^1T_1$ ligand field band) of $[Fe(tpm)_2](ClO_4)_2$ in CH_3CN. Trace B: ground-state depletion spectrum following pulsed laser irradiation at 532 nm of $[Fe(tpm)_2](ClO_4)_2$ in CH_3CN. The spectrum was recorded using a gated diode array multichannel detector (Princeton Instruments Model DIDA 700G) (gate width 7 ns; gate delay following laser pulse 15 ns; laser pulse energy 7 mJ). The abrupt cutoff on the long-wavelength side of the spectrum is due to the onset of laser scatter.

The band in Figure 3 with λ_{max} at 523 nm ($\epsilon_{523} = 56\ dm^3\ mol^{-1}\ cm^{-1}$) is assigned to the d–d transition, $^1A_1 \rightarrow {}^1T_1$, of the low-spin isomer of **1**. The steeply rising absorption toward the blue region is assigned to the $^1A_1 \rightarrow {}^1MLCT$ transition.

An estimate of the high-spin–low-spin distribution in acetonitrile solutions was obtained from the variable-temperature spectra in the range −40 to +22 °C. The maximum of the first ligand field band exhibits a blue shift from 523 to 518 nm on cooling, and more significantly, the intensity of the same band increases upon cooling. According to the vibronic ligand field model of Liehr and Ballhausen,[12] such a band should experience a decrease in intensity upon cooling, as described by the expression

$$I = I_0 \coth \hbar\omega/2kT$$

where $\hbar\omega$ is the active (enabling) vibrational quantum of the ground state. In the present case, we have chosen a symmetric Fe–N stretching frequency[13] of 380 cm^{-1} as the intensity-creating mode. The Raman spectrum of the complex in acetonitrile excited at 457.9 nm shows a band at 382 cm^{-1}. Using the above equation to correct the observed intensity of the spectra recorded at ca. 10 °C intervals over the range −40 to +22 °C, we have estimated equilibrium constants $K = [HS]/[LS]$ for each temperature from the corrected intensities. The corresponding thermodynamic

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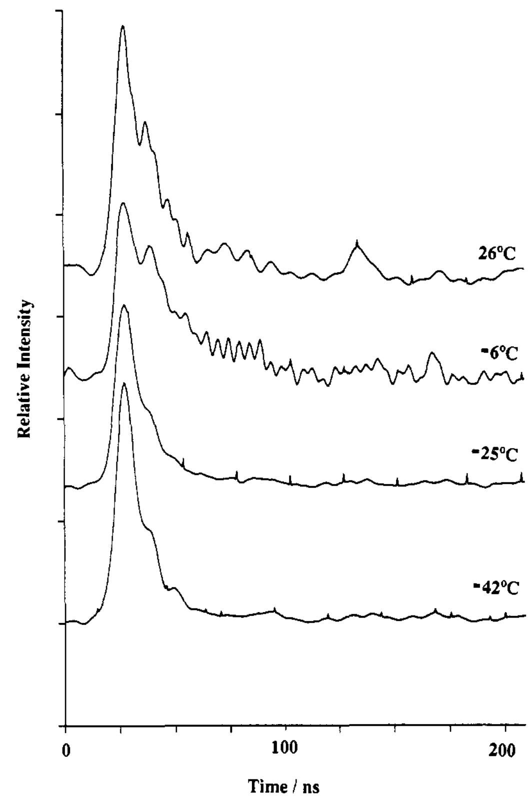

Figure 4. Traces showing ground-state depletion and relaxation to the original absorbance level following pulsed laser irradiation of $[Fe(tpm)_2](ClO_4)_2$ at 532 nm in CH_3CN at different sample temperatures (monitoring wavelength 490 nm; laser pulse energy 12 mJ).

parameters derived from a ln K vs $1/T$ plot, $\Delta H° = 18$ kJ mol^{-1} and $\Delta S° = 53$ J K^{-1} mol^{-1}, though preliminary values only, are close to the parameters reported[14,15] for the related complex $[Fe(HB(pz)_3)_2]$ in CH_2Cl_2 and THF. Compared to the solid state behavior, it is evident that the high-spin population of the present system in solution has been increased considerably. In the range −40 to +22 °C, the high-spin population increases from ca. 6% to almost 30%. Similar patterns have been reported for several other systems.[16]

Pulsed irradiation of a solution of **1** (ca. 5×10^{-3} mol dm^{-3}) in MeCN at 355 nm, a wavelength which falls within the range of the $^1A_1 \rightarrow {}^1MLCT$ transition, produced no effect other than laser scatter. In these experiments the monitoring wavelengths covered the range 370–560 nm, spanning both the LF and MLCT absorption regions. In contrast to these observations, when the irradiation wavelength was altered to 532 nm, near the maximum of the lowest energy LF band of the singlet isomer, rapid ground-state depletion of the sample absorbance occurred within the laser pulse duration followed by recovery, to the original absorbance level with a time constant of 25 ± 5 ns at room temperature. The transient depletion spectrum recorded with a gated multichannel detector 15 ns after the laser pulse is shown in the lower trace in Figure 3. The abrupt cutoff on the long-wavelength side of trace B is due to the onset of laser scatter, which saturates the detector. By moving to a longer irradiation wavelength (637 nm; vide infra), one could observe the depletion of the ground-state absorption to wavelengths beyond 550 nm.

Traces showing the transient depletion and decay recorded in the spectrophotometric studies at individual monitoring wavelengths are displayed in Figure 4. Such transients were observed at several monitoring wavelengths over the same range as employed in the experiments using 355-nm irradiation. The effect was investigated over the temperature range from +23 to −42 °C (the lower limit being set by the freezing point of the solvent MeCN). As the traces in Figure 4 show, some improvement was observed with decreasing temperature in the signal:noise ratio of the transient absorbance depletion traces but the time constant for recovery of the absorbance was independent of temperature over this range, within experimental error.[17] Confirmation that irradiation within the MLCT band of **1** did *not* result in transient depletion and recovery was demonstrated by further experiments carried out at an excitation wavelength of 416 nm. This gave the same result as already recorded following 355-nm irradiation; i.e., no transient signal could be detected other than that due to laser scatter at monitoring wavelengths close to the excitation laser line. On reverting to an irradiation wavelength of 532 nm however, we again observed a transient absorbance depletion signal, confirming the findings from previous experiments at this wavelength. Irradiation experiments at 637 nm, generated by stimulated Raman scattering from H_2 of the third harmonic from the Nd/YAG laser, provided additional confirmation.[18] A transient depletion was clearly evident, as in the irradiation experiments at 532 nm. Thus when the same gas (H_2) was used in the Raman cell, it proved possible (with appropriate adjustment of the cell pressure to optimize the output) to generate either an irradiation wavelength (637 nm, third Stokes line from H_2) which caused perturbation of the spin equilibrium or a wavelength (416 nm, first Stokes from H_2 at the same input wavelength, 354.7 nm) which did not.

Discussion

The magnetic susceptibility studies on **1** in the solid state show that the complex exhibits singlet–quintet spin-crossover behavior with the singlet spin state strongly favored at room temperature. In solution, the variable-temperature absorption spectra show that the proportion of high-spin species increases significantly with increasing temperature, being almost 30% at room temperature. The transient depletion and recovery of absorbance following pulsed laser irradiation of **1** in solution are ascribed to photoinduced perturbation and subsequent thermal relaxation of the $^1A_1 \rightleftharpoons {}^5T_2$ spin equilibrium. The improvement in the signal:noise ratio of the transient traces at lower temperatures (Figure 4), where the low-spin isomer is more favored, is qualitatively in accord with this proposal. The ground-state recovery time corresponding to the relaxation of the spin-state equilibrium is comparable to the reported[15] value in THF solution for spin crossover in the closely related complex $[Fe(HB(pz)_3)_2]$.

In the majority of examples in solution reported previously where the photoperturbation method has been successfully employed, the absorption spectrum in the visible region is dominated by the intense metal–ligand charge-transfer transition of the low-spin isomer and irradiation into this transition results in population of the lowest MLCT state of the low-spin isomer. In most cases, as the schematic energy level diagram in Figure 1 shows, the LF states lie below but near the initially populated MLCT state so that interstate communication is efficient and the photophysical relaxation terminates partly in the potential

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(17) It has been suggested by a reviewer that heating of the sample by the laser pulse should be considered. At the laser pulse energies and sample absorbances used in the present work, heating effects will be negligible. Furthermore, we have not observed them in experiments very similar to those reported here carried out on other spin-crossover systems under conditions of significantly higher pulse energies and sample absorption cross sections.

(18) Further independent confirmation came from a picosecond pump and probe experiment in which a sample of **1** in MeCN was irradiated at 532 nm and the absorbance changes were monitored at 415 nm. A fast bleach of the absorbance at this wavelength was observed, followed by a gradual recovery, just discernible on the 1–2-ns time range over which the signal could be monitored by the optically delayed probe pulse. We are grateful to Prof. J. D. Simon and his group at the University of California, La Jolla, for carrying out this experiment.

well of the high-spin $^5T_2$ isomer, the net outcome being perturbation of the singlet–quintet spin equilibrium. In effect, what amounts to a concentration-jump perturbation of this equilibrium is brought about via charge-transfer photoexcitation and subsequent photophysical relaxation. As was made clear in our first report[2] of the phenomenon, photoinduced spin crossover in these systems in solution implies very fast intersystem crossing between CT and LF states. The feature of central interest in the system reported here is that the perturbation can only be effected via irradiation into the LF band of the complex. In this complex there is a large energy gap between the lowest singlet MLCT state and the underlying LF states. Selective irradiation into the $^1A_1 \rightarrow {}^1T_1$ LF transition leads directly to population of a LF state from which fast decay to the potential well of the high-spin isomer evidently takes place. The absence of relaxation and hence of perturbation of spin equilibrium when the irradiation falls within the MLCT absorption region, as demonstrated by the results of the irradiation experiments at 355 and 416 nm, points to an inefficient relaxation from the MLCT state to the underlying LF states because of the large energy gap referred to above. In the solid state, the phenomenon of light-induced spin-state trapping[19] in Fe(II) complexes is well established, and examples are known where irradiation in either LF or MLCT absorption bands of the LS isomer results in formation of the HS isomer. The example reported in the present work however is the first that we are aware of in solution in which the perturbation occurs exclusively via a LF state.

The lack of any appreciable temperature dependence in the spin-relaxation time is unexpected and unlike any of the previously reported cases where a genuine spin-crossover situation prevails in solution. Apart from the spectral evidence in solution that we are dealing with, additional indications of spin crossover are provided by Mossbauer studies[8] of the complex which reveal an unusually high rate for the spin crossover in the solid state, indicating a very low activation barrier. In most Fe(II) systems exhibiting spin crossover, the interconversion rate is quite slow on the Mossbauer time scale. The present case and the previously reported example[20] of $Fe(tpen)^{2+}$ (tpen = *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-1,2-ethylenediamine) are the only instances so far where the rate is faster. A further example very much related to the present one has also been shown to be very fast on the Mossbauer time scale but at higher temperatures.[11]

The distinction between the radiationless process of intersystem crossing between states of singlet and quintet multiplicities and that of thermal relaxation of the singlet–quintet spin equilibrium following photoperturbation is largely a question of semantics. In the situation where the gap between the potential minima of the singlet and quintet surfaces is sufficiently large that thermal population of the quintet state from the singlet is effectively impossible, we are in the realm of photophysics. This is the situation in the case of the low-spin complex $[Fe(bipy)_3]^{2+}$, although in this instance Hauser has demonstrated[21] that the high-spin quintet state can be populated via excitation into the lowest energy MCLT transition, just as for a complex exhibiting normal spin-crossover behavior. In the $[Fe(bipy)_3]^{2+}$ example, the excited-state relaxation changes from being activated to nearly nonactivated below about 50 K, behavior which has been rationalized in terms of nonadiabatic multiphoton relaxation theory.[22] In the case reported in the present work however, we have been unable to detect any temperature dependence for the relaxation time. Such behavior cannot be fitted to this theory for any realistic set of parameters.

Acknowledgment. We thank the SERC for support (Grants GR/F82672 and GR/F42980). We also wish to thank Professor J. D. Simon and his group for carrying out picosecond pump and probe experiments on $[Fe(tpm)_2](ClO_4)_2$.

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