Inorg. Chem. 1985, 24, 2174–2178

Contribution from the Institut für Anorganische Chemie und Analytische Chemie, Johannes-Gutenberg-Universität, D-6500 Mainz, FRG, and Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland

Light-Induced Excited-Spin-State Trapping in Iron(II) Spin-Crossover Systems. Optical Spectroscopic and Magnetic Susceptibility Study

S. DECURTINS,[†] P. GÜTLICH,*[†] K. M. HASSELBACH,[†] A. HAUSER,[‡] and H. SPIERING[†]

Received July 24, 1984

Single-crystal optical absorption spectra of the iron(II) spin-crossover compounds $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-propyltetrazole) and $[Fe(2\text{-pic})_3]Cl_2\cdot EtOH$ (2-pic = 2-(aminomethyl)pyridine) have been measured between room temperature and 8 K. The well-established thermally induced spin transition high spin (${}^5T_{2g}$) $\rightleftharpoons$ low spin (${}^1A_{1g}$) as well as the recently discovered phenomenon of "light-induced excited-spin-state trapping (LIESST)" is followed and analyzed. A kinetic study by optical spectroscopy of the relaxation from the light-induced high-spin (HS) state to the low-spin (LS) state has been carried out for $[Fe(ptz)_6](BF_4)_2$ in the temperature range 53–61 K. The magnetic susceptibility of the light-induced HS state of this compound has also been measured.

1. Introduction

There are many iron(II) compounds that show thermally induced high-spin (HS) $\rightleftharpoons$ low-spin (LS) transitions.[1,2] Among the various physical methods used to follow the spin transition, magnetic susceptibility measurements and, for iron compounds, Mössbauer spectroscopy are the most commonly employed techniques. Only few studies made use of optical spectroscopy, because with the often deeply colored compounds having strong charge-transfer bands not much information could be gained. Despite this shortcoming with respect to general applicability, the optical method adds an inherent extension to the other techniques. Whereas the other methods are limited in the sense that they enable one to examine ground-state properties only, the optical method yields information on ground-state and excited-state properties simultaneously, which enlarges substantially the field of electron dynamics in the crossover domain.

The iron(II) complexes $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-propyltetrazole)[3,4] and $[Fe(2\text{-pic})_3]Cl_2\cdot EtOH$ (2-pic = 2-(aminomethyl)pyridine)[5,6] are well-known to exhibit a thermally induced spin transition, ${}^5T_{2g}$ $(O_h) \rightleftharpoons {}^1A_{1g}$ (O_h). The transition temperature, defined as the temperature of equal fractions of both spin states $T_c = T(\gamma_{HS} = \gamma_{LS})$, was found to lie around 130 K (with hysteresis) in the ptz complex[4] and at ca. 120 K (without hysteresis) in the pic complex.[6]

Very recently, we have observed a ligh-induced low-spin (${}^1A_{1g}$) $\rightarrow$ high-spin (${}^5T_{2g}$) conversion, during which the molecules can be quantitatively trapped in the excited HS state at sufficiently low temperatures. We call this "light-induced excited-spin-state trapping (LIESST)", and we have verified the existence of the pure light-induced HS state for several iron(II) crossover compounds with optical, Mössbauer, and magnetic susceptibility measurements. The Mössbauer results for three iron(II) compounds have recently been published.[7,8] In the present paper we report optical absorption measurments for the two spin-crossover compounds $[Fe(ptz)_6](BF_4)_2$ and $[Fe(2\text{-pic})_3]Cl_2\cdot EtOH$ in the solid state at temperatures $8 \lesssim T \lesssim 300$ K. In the same way as the thermally induced and light-induced spin transitions are followed optically, the kinetic behavior of the spin transition can be examined. In addition to the optical results, a preliminary study of the LIESST effect by the magnetic susceptibility technique down to 10 K is presented for $[Fe(ptz)_6](BF_4)_2$.

2. Experimental Section

2.1. Preparation and Structure. $[Fe(ptz)_6](BF_4)_2$ was prepared according to a procedure previously described.[3] The complexes crystallized in colorless, well-shaped hexagonal plates up to 1 mm in diameter. The spin conversion is accompanied by a drastic change in color; when the crystals are cooled with liquid nitrogen, they turn deeply violet, the typical color of the low-spin (${}^1A_{1g}$) state. A single-crystal structure determination at 140 K showed that the compound crystallizes in the rhombohedral space group $R\bar{3}$ and that the symmetry of the ligand field is nearly regular octahedral.[9] The same study revealed that the coordination site of the 1-alkyltetrazoles is the N(4) atom. A structure investigation at variable temperatures, in connection with the LIESST study, is in progress in our laboratory.

$[Fe(2\text{-pic})_3]Cl_2\cdot EtOH$ was prepared as described in a previous publication.[6] The raw material was recrystallized from an ethanol solution at 45 °C to obtain yellow-brown prismatic crystals of up to 1 mm in length. In correspondence with the spin crossover, the color changes from yellow-brown at room temperature to red at liquid-nitrogen temperature. The compound crystallizes in the monoclinic space group $P2_1/c$ for both the HS and the LS state.[10,11]

2.2. Optical Measurements. Single-crystal absorption spectra were recorded on a Cary 17 spectrometer equipped with a red-sensitive GaAs photodetector and a PbS cell. The samples were cooled by the helium gas flow-tube technique, and the temperature was measured with a gold–iron/chromel thermocouple. For the measurements of smaller crystals, a condensing optic consisting of a pair of reflecting objectives (Ealing Beck) was introduced into the sample beam. During the LIESST experiments the crystals were illuminated with the light of a 150-W xenon arc lamp.

Typical irradiation times until complete conversion from red (low-spin state) to white (high-spin state) were on the order of 10 min. Any possible uncontrolled heating of the sample was definitely lower than the deactivation temperature, where the light-induced metastable high-spin state noticeably relaxes back to the low-spin state.

2.3. Magnetic Susceptibility Measurements. The measurement was performed on a polycrystalline sample of $[Fe(ptz)_6](BF_4)_2$ of ca. 15 mg, in the temperature range 180–10 K, by using a Faraday type magnetometer equipped with a continuous-flow cryostat. The temperature was measured with a gold–iron/chromel thermocouple. $Hg[Co(NCS)_4]$ was used as a susceptibility standard. Effective magnetic moments were calculated from $\mu_{eff} = 2.828(\chi_m T)^{1/2}$, where χ_m is the corrected molar susceptibility. The diamagnetic corrections were calculated from Pascal's constants (503×10^{-6} cm^3 mol^{-1}). For the LIESST experiment the sample was excited with the light of an argon laser with a multiline power of 40 mW (λ = 514.5, 488.0, 476.5 nm).

Our Faraday balance is constructed such that the sample can be observed through a window above the balance. The laser beam was deflected by a mirror and guided through this window. The sample was illuminated with the multiline laser beam sufficiently long (approximately 30 min) until the material had adopted the white color that is characteristic of the high-spin state.

3. Results and Discussion

3.1. Optical Absorption Spectra of $[Fe(ptz)_6](BF)_2$. According to the Tanabe–Sugano diagram[12] for an ion with a d^6 electronic

---

[†] Johannes-Gutenberg-Universität.

[‡] Universität Bern.

(1) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293.
(2) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83.
(3) Franke, P. L.; Haasnoot, J. G.; Zuur, A. P. *Inorg. Chim. Acta* **1982**, *59*, 5.
(4) Müller, E. W.; Ensling, J.; Spiering, H.; Gütlich, P. *Inorg. Chem.* **1983**, *22*, 2074.
(5) Renovitch, G. A.; Baker, W. A., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 6377.
(6) Sorai, M.; Ensling, J.; Gütlich, P. *Chem. Phys.* **1976**, *18*, 199.
(7) Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, *105*, 1.
(8) Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H. *J. Chem. Soc., Chem. Commun.* **1985**, 430.
(9) Franke, P. L. Doctoral Thesis, Rijksuniversiteit Leiden, 1982.
(10) Katz, B. A.; Strouse, C. E. *J. Am. Chem. Soc.* **1979**, *101*, 6214.
(11) Mikami, M.; Konno, M.; Saito, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 275.
(12) Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753.

0020-1669/85/1324-2174$01.50/0 © 1985 American Chemical Society

Table I. Calculated and Experimental Energies of Electronically Excited States of $[Fe(ptz)_6](BF_4)_2$

LS state			HS state			
	energies, cm^{-1}			energies, cm^{-1}		
electronic state notation (O_h)	exptl	calcd^a	electronic state notation (O_h)	exptl	calcd^b	calcd^c
$^1A_{1g}$		0	$^5T_{2g}$		0	0
$^3T_{1g}$		13 020	$^1A_{1g}$		2 640	5 900
$^3T_{2g}$		17 090	$^3T_{1g}$		6 130	8 330
$^5T_{2g}$		18 300	$^3T_{2g}$		10 150	12 590
$^1T_{1g}$	18 400	18 420	^5E_g	12 250	12 250	12 250
$^1T_{2g}$	26 650	26 640	$^1T_{1g}$		13 240	16 360
			$^1T_{2g}$		21 080	24 510

^{a} $C/B = 4$, $B = 625$ cm^{-1}, $Dq = 2005$ cm^{-1}. ^{b} $C/B = 4$, $B = 800$ cm^{-1}, $Dq = 1225$ cm^{-1}. ^{c} $C/B = 4$, $B = 900$ cm^{-1}, $Dq = 1225$ cm^{-1}.

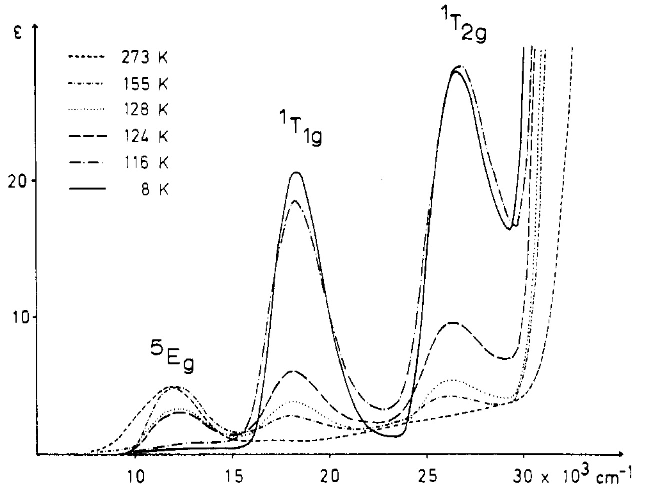

Figure 1. Single-crystal absorption spectra (unpolarized) of $[Fe(ptz)_6](BF_4)_2$ at variable temperatures.

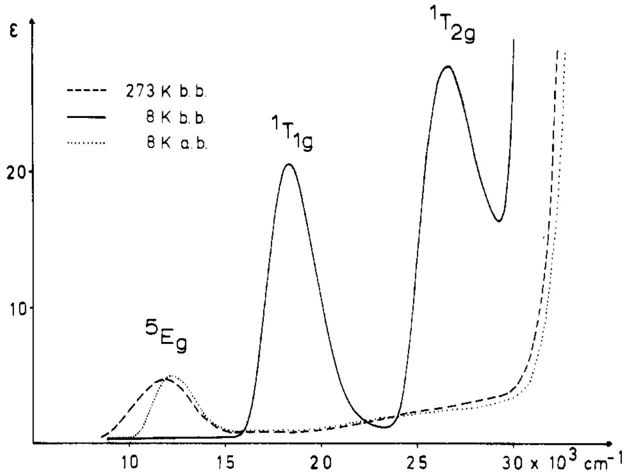

Figure 2. Single-crystal absorption spectra (unpolarized) of $[Fe(ptz)_6](BF_4)_2$ before bleaching (b.b.) and after bleaching (a.b.) at 8 K for 2 min with white light.

configuration in an octahedral ligand field, one can expect quite different absorption spectra for high-spin or low-spin complexes. In the former case there will be only one spin-allowed absorption band corresponding to the $^5T_{2g} \rightarrow {}^5E_g$ transition, whereas for the latter case two spin-allowed absorption bands corresponding to the $^1A_{1g} \rightarrow {}^1T_{1g}$, $^1T_{2g}$ transition should be encountered. Therefore, the absorption spectra of a spin-crossover compound taken at temperatures above and below the spin-transition temperature T_c should clearly reflect a thermally induced spin transition. This is demonstrated in Figure 1, which shows the single-crystal absorption spectra of $[Fe(ptz)_6](BF_4)_2$ at different temperatures. The light was unpolarized and propagated perpendicularly to the hexagonal crystal plate. At 273 K one sees only one absorption band centered at 12 250 cm^{-1}, corresponding to the quintet transition, $^5T_{2g} \rightarrow {}^5E_g$, of the molecules in the HS state. At 8 K this absorption band has completely disappeared, and two new absorption bands at 18 400 and 26 650 cm^{-1}, corresponding to the singlet transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ of the molecules in the LS state, have appeared. The spectra at intermediate temperatures demonstrate that the spin transition from HS to LS begins gradually already above 155 K and appears to be abruptly complete around 120 K. The magnetic susceptibility measurement reveals this temperature to be 123.5 (5) K in the cooling direction and 131.0 (5) K in the heating direction (see Figure 8).

There is a slight asymmetry in the lowest energy band, which is probably caused by a Jahn–Teller splitting of the excited E term. One might expect some weak absorption bands from the spin-forbidden transitions to the excited triplet states. Since their electronic configurations differ also from that of the ground state, the bands will not be sharp and will hardly be detectable. We could not identify any transition to a triplet state in these spectra.

$[Fe(ptz)_6](BF_4)_2$ can be diluted in the isomorphic $[Zn(ptz)_6](BF_4)_2$, which proves to be a transparent host compound up to 47 000 cm^{-1}. Preliminary absorption measurements with a single crystal of $[Fe_xZn_{1-x}(ptz)_6](BF_4)_2$ ($x \approx 0.02$) revealed a strong absorption band at 40 000 cm^{-1}, but its exact temperature dependence and assignment are not yet clear.

Complementary to the optical measurements, we calculated the term energies using the matrices of Tanabe and Sugano.[12] From the relation $C = 4B$ between the electron repulsion parameters and the experimental energies for the excited $^1T_{1g}$ and $^1T_{2g}$ states, values of $B = 625$ cm^{-1} and $10Dq = 20\,050$ cm^{-1} are obtained, which refer to the complexes in their LS state. The spectra of the complexes in their HS state do not provide data from which B can be derived, but this value will lie between 1058 and 760 cm^{-1}, the free-ion value and the crossover value ($10Dq/B \approx 16.1$), respectively. The octahedral ligand field parameter $10Dq$ corresponds to the energy of the observed $^5T_{2g} \rightarrow {}^5E_g$ transition at 12 250 cm^{-1}. Table I shows the energies of the excited states for the LS and HS complexes.

3.2. Optical Investigation of the LIESST Effect in $[Fe(ptz)_6](BF_4)_2$. If the crystals of $[Fe(ptz)_6](BF_4)_2$ are illuminated at temperatures below ≈50 K with white light or with laser light within the singlet absorption regions, their deeply red color is totally "bleaching", and they stay colorless as long as the temperature is kept below ≈50 K. Figure 2 shows the corresponding single-crystal absorption spectrum before and after bleaching with white light, and it clearly demonstrates that the light-induced and trapped spin state corresponds to the high-temperature HS state. Figure 3 demonstrates that, at a temperature around 50 K, the light-induced HS state relaxes back to the normal LS state. In contrast to other compounds (see below), we noticed no shattering of the single crystals during the light-induced spin conversion. Our interpretation of the mechanism of the LIESST effect is sketched in Figure 4, which shows a diagram of the electronic potential wells for the relevant ground and excited spin states. The excitation with light of the LS complexes leads to a population of the excited singlet states. These states are very short-lived and will mainly decay rapidly back to the $^1A_{1g}$ ground state. But, initiated by spin–orbit coupling, there is an alternative decay path to the lowest spin triplet state (intersystem crossing) and from there either to the $^1A_{1g}$ ground state or to the excited $^5T_{2g}$ state. The molecules will remain trapped in this excited HS state if the temperature is sufficiently low, so that the energy barrier between the HS and

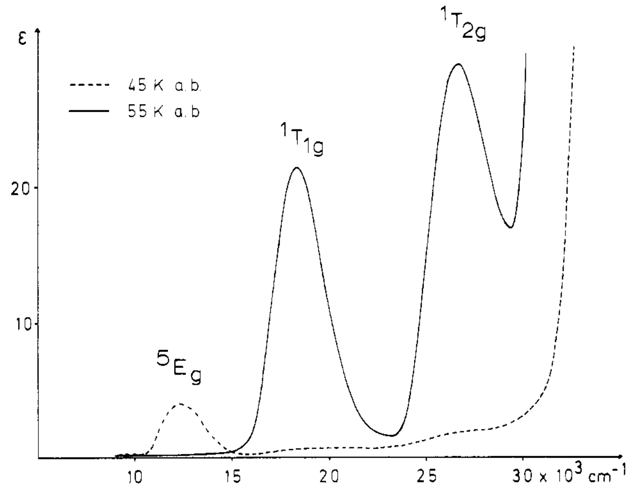

Figure 3. Single-crystal absorption spectra (unpolarized) of $[Fe(ptz)_6](BF_4)_2$ after bleaching (a.b.) at 8 K with white light and warming to 45 and 55 K, respectively.

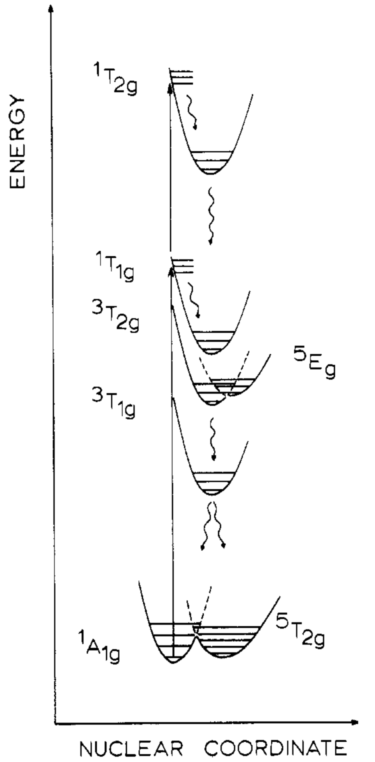

Figure 4. Potential surface diagram drawn according to the energy values listed in Table I.

the LS potential minima is not thermally overcome.

An inspection of Figure 4 reveals also a possible mechanism by which the molecules of the trapped HS state ($^5T_{2g}$) could eventually be "pumped" back to the LS ground state ($^1A_{1g}$). Through excitation of the molecules from the $^5T_{2g}$ state exclusively to the ^5E_g state with light of $\bar{\nu} \lesssim 15\,000$ cm^{-1} (see Figure 1), one opens a decay path (intersystem crossing) to the $^3T_{1g}$ state and finally to the $^1A_{1g}$ state, from where no absorption to the excited singlet states occurs by using light of the above energy conditions. A preliminary measurment proved this to be the case. A single crystal of $[Fe(ptz)_6](BF_4)_2$, which was quantitatively trapped in the HS state, was excited at $T = 10$ K with light of $\lambda > 700$ nm and thereafter exhibited again the typical LS absorption spectrum. Further studies in this field, especially for a comparison of the two alternative light-induced spin conversions, are in progress.

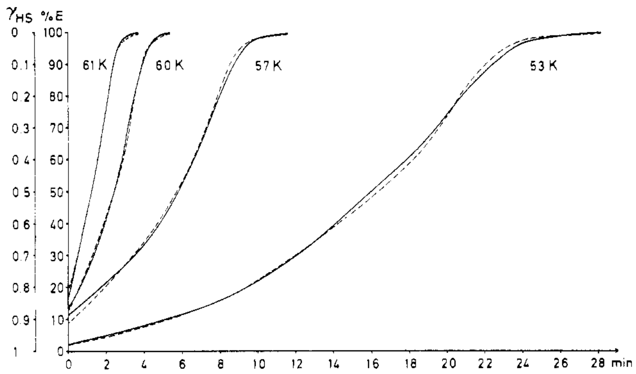

Figure 5. Optical extinction (%E) as a function of time at 545 nm after the quantitative light-induced spin conversion LS → HS at 8 K in a single crystal of $[Fe(ptz)_6](BF_4)_2$ and warming to the temperatures indicated: (—) measured function of $\gamma_{HS}(T)$; (---) calculated HS fraction as a function of time, $\gamma_{HS}(T)$, from eq 1 with $A = 670$ s^{-1} and E_γ taken from Figure 6.

We have measured the rate of the relaxation from the light-induced excited HS state to the LS ground state at four temperatures above 50 K. This was done by recording the time-dependent increase of the optical extinction of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition at the fixed wavelength of 545 nm at constant temperatures. We thereby followed the concentration of the absorbing LS complexes, and the crystal thickness was chosen such that the range of the optical absorbance was less than 1. Figure 5 shows the experimental curves of the optical extinction (%E) vs. time for the temperatures 53, 57, 60, and 61 K. Since they exhibit sigmoidal characteristics, they do not represent a simple first-order law. The transition rates appear to depend on the amount of complexes that are already converted to the low-spin state.

We shall first attempt to analyze these data in the frame of the "elastic interaction and lattice expansion" model.[13] This model is based on the assumption that the complex molecules couple with each other by cooperative elastic interactions. These elastic interactions are considered to be caused by the image pressure p_{im}, which in turn arises from the different sizes of the HS and LS complexes ($V_{HS} > V_{LS}$).[11] The interaction is of infinite range and increases with each volume change from the larger HS to the smaller LS spheres. Furthermore, we assume that the rate depends on the elastic interactions between the HS and LS complexes. This infinite range interaction is considered to be the only interaction operative between the HS and LS complexes, so that cluster formation should not occur. The image pressure p_{im}, which acts on each complex molecule, increases linearly with increasing fraction of the LS complexes, $p_{im} \sim (1 - \gamma)$, so that the energy difference $p_{im}(V_{HS} - V_{LS})$ between the HS and LS states also increases with increasing LS fraction. To explain the observed change of the transition rates as a function of the LS fraction, the energy barrier between the two states is also assumed to depend on the pressure $p_{im} \sim (1 - \gamma)$ on the complex molecule. As a consequence, a decrease of the energy barrier with increasing LS fraction is anticipated. In addition the barrier should be independent of temperature within this small temperature range of 8 K under study.

Correspondingly, we have expanded the energy of the barrier in a polynomial function of γ_{HS} and fitted the experimental curves of Figure 5 with the equation

$$\gamma_{HS}(t) = \gamma_{HS}(t = 0)\exp(-At\exp(-E(\gamma_{HS})/kT)) \qquad \gamma_{HS}(t = 0) = 1 \tag{1}$$

where A is the preexponential ("frequency") factor of the Arrhenius equation.

A simultaneous fit of the curves recorded at four different temperatures was carried out with the computer program MINUIT.[14] The fits were achieved with values for the energy barrier on the order of a few hundred wavenumbers and for the A factor on the order of 10^3 s^{-1}. Figure 6 shows the variation of the barrier energy

---

(13) Spiering, H.; Meissner, E.; Köppen, H.; Müller, E. W.; Gütlich, P. *Chem. Phys.* **1982**, *68*, 65.

(14) James, F.; Roos, M. *Comput. Phys. Commun.* **1975**, *10*, 343.

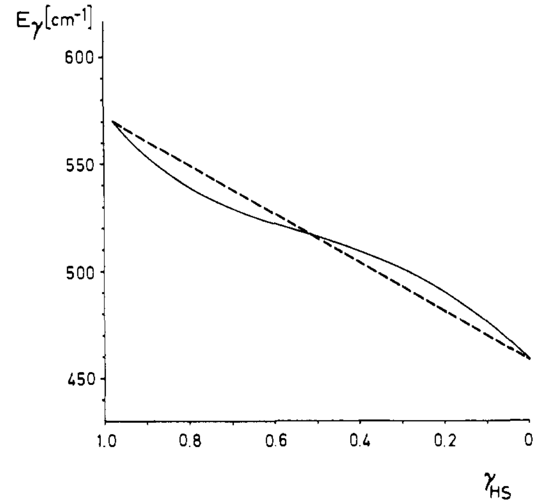

Figure 6. Variation of the HS/LS ($^5T_{2g}/^1A_{1g}$) barrier energy E_γ as a function of the HS fraction γ_{HS} as it enters into the graphs of γ_{HS} vs. time shown in Figure 5. The function $E_\gamma(\gamma_{HS})$ deviates only slightly from linearity.

as a function of the HS fraction γ_{HS}, which, together with an A factor of 670 s^{-1}, produces the graphs for $\gamma_{HS}(t)$ depicted in Figure 5.

The preexponential factor A in this case turns out to be unusually small. In relaxation studies on spin-crossover systems in solution, where the relaxation rates are much larger (10^5–10^7 s^{-1}) A is at least 3–4 orders of magnitude larger,[15,16] whereas the energy barrier between the HS and the LS states is of comparable magnitude, as in the present case.

There is a similar kinetic study on a spin-crossover system in the solid state, where the back-relaxation rate of the $^5T_{2g} \rightarrow {}^1A_{1g}$ conversion after trapping the HS state by rapidly cooling the sample down has been measured by Mössbauer spectroscopy.[17] The relaxation rates are similar, as in our case. The decay shows a first-order behavior, but the energy barrier for the HS → LS spin-state conversion is about 7 times larger and their preexponential factor is 3–4 orders of magnitude higher than in our analysis. The reason that they do not observe a deviation from a first-order transition may be the fact that the relative change of the barrier by the image pressure is too small to be observed (the relative change in our case is ca. 100 cm^{-1} in 550 cm^{-1}; their barrier height is about 7 times larger with presumably the same change of ca. 100 cm^{-1}).

The variation of the potential barrier with γ_{HS} shows an interesting feature. The leading term in the expansion of $E(\gamma_{HS})$ is the linear term shown as the dotted line in Figure 6. The potential barrier decreases essentially proportionally to the image pressure of the low-spin complexes. The small deviation of $E(\gamma_{HS})$ from linearity may be a hint for the presence of a short-range interaction between the complex molecules, which usually gives rise to cluster formation. Since we cannot exclude the occurrence of cluster formation, we shall try now another approach and consider the kinetics of the HS → LS transition to be determined by a nucleation and growth mechanism (with short interaction being dominant). The rate equation

$$x = 1 - \exp(-kt^n) \qquad (2)$$

frequently referred to as the Avrami equation,[18] combines the nucleation and the growth rates for a phase transition. $x = 1 - \gamma_{HS}$ represents the fraction of the final phase formed during time t, and k is a rate constant parameter that takes on positive values.

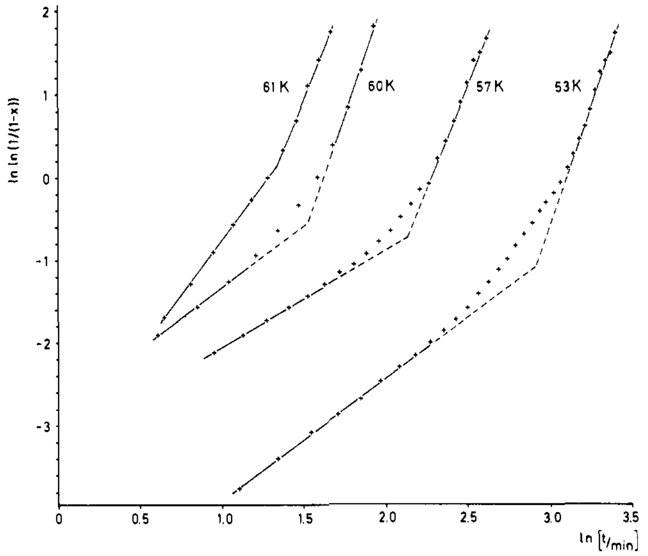

Figure 7. Avrami plots for the HS → LS transition of a single crystal of $[Fe(ptz)_6](BF_4)_2$.

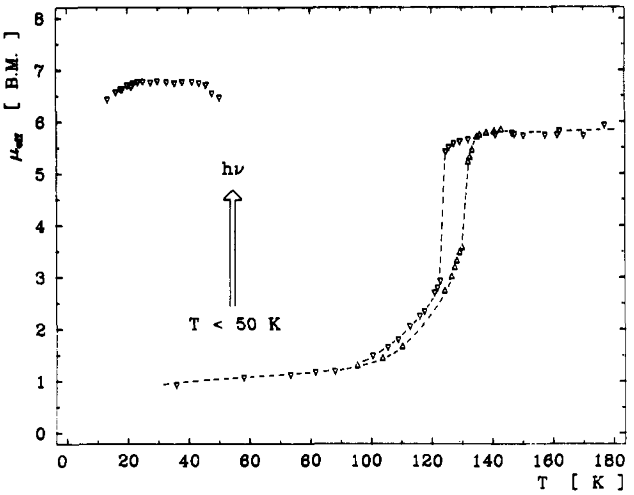

Figure 8. Effective magnetic moment of a polycrystalline sample of $[Fe(ptz)_6](BF_4)_2$ as a function of temperature and excitation with laser light.

The time exponent n adapts different values for different nucleation rates. Figure 7 represents a plot of ln [ln (1/(1 − x))] vs. ln t for the HS → LS back-relaxation at four temperatures. The exponent n is represented by the slope, and k is deduced from the intercept ln k = ln [ln(1/(1 − x))] at t = 1 of a straight line. It is seen, that eq 2 does not describe the transitions over the whole time range under study but only in the ranges where a majority of HS or LS molecules is present. The HS and LS ranges produce time exponents n of ca. 1.5 and of 5–6, respectively. n values of 1 and 2 are characteristic of transformations with nucleation in the beginning plus continuing nucleation at grain boundaries and grain edges, whereas n values >4 describe a nucleation at increasing rate.[18] The existence of linear regions in the Avrami plots for the investigated transition suggests that clustering effects caused by short-range interactions will occur. A decisive experiment will be a kinetic study on mixed crystals $[Fe_xZn_{1-x}(ptz)_6](BF_4)_2$ with decreasing x values, where short-range interactions are successively suppressed and the image pressure decreases linearly with decreasing x, so that the rates can be predicted in the framework of the lattice-expansion model.

3.3. Magnetic Susceptibility Study of the LIESST Effect in $[Fe(ptz)_6](BF_4)_2$. A magnetic susceptibility measurement should reflect the light-induced LS to HS conversion as clearly as the Mössbauer and the optical measurements. Figure 8 shows the values of μ_{eff} as a function of temperature for a polycrystalline sample of $[Fe(ptz)_6](BF_4)_2$. The thermally induced spin transition

---

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

(16) Beattie, J. K.; Binstead, R. A.; West, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 3044.

(17) Ritter, G.; König, E.; Irler, W.; Goodwin, H. A. *Inorg. Chem.* **1978**, *17*, 224.

(18) Rao, C. N. R.; Rao, K. J. "Phase Transitions in Solids"; McGraw-Hill: New York, 1978.

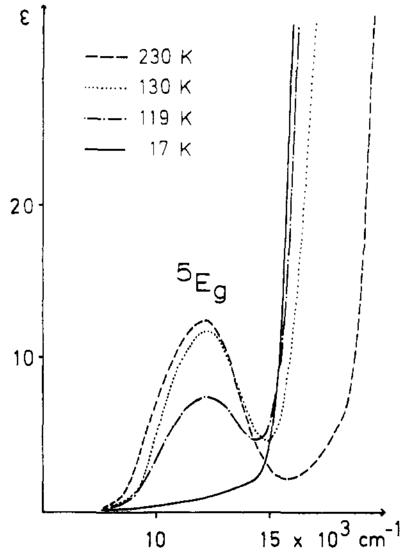

Figure 9. Single-crystal absorption spectra (unpolarized) of $[Fe(2\text{-}pic)_3]Cl_2{\cdot}EtOH$ as a function of temperature.

appears to be complete and rather abrupt, and it shows a hysteresis with transition temperatures at $T_c{\downarrow}$ (cooling) = 123.5 (5) K and $T_c{\uparrow}$ (heating) = 131.0 (5) K. The characteristics of this spin transition have already been discussed.[4] The excitation with the green-blue laser light within the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption band at $T < 50$ K initiates the light-induced spin conversion, which results in a rise of μ_{eff} from 1.0 to 6.5–7.0 μ_B in the temperature range 10–50 K. It should be noted that these μ_{eff} values do not correspond to real average magnetic moments (powder moments) since, due to the laminar crystal habit, a polycrystalline sample will exhibit orientation effects. Grinding the crystals is not recommended, because, as is known from separate studies, the crystal quality influences the spin-crossover properties.[19,20]

3.4. Optical Investigations of the LIESST Effect in $[Fe(2\text{-}pic)_3]Cl_2{\cdot}EtOH$. $[Fe(2\text{-}pic)_3]Cl_2{\cdot}EtOH$ produces a thermally induced spin transition within two steps at $T_c = 121$ K and $T_c = 114$ K.[21] As this compound exhibits energetically low-lying charge-transfer transitions, only the energy range below 19 000 cm^{-1} is accessible for an optical investigation. Figure 9 shows the unpolarized single-crystal absorption spectrum of $[Fe(2\text{-}pic)_3]Cl_2{\cdot}EtOH$, whereby the light propagated perpendicularly to a well-developed pinacoid. At 230 K one sees around 12 000 cm^{-1} the broad, asymmetric absorption band that corresponds to the quintet transition, $^5T_{2g} \rightarrow {}^5E_g$, of the molecules in the HS state. According to the well-established and thoroughly studied thermally induced spin transition,[6] this absorption band decreases in intensity with decreasing temperature until it disappears completely at 17 K. If the crystals are illuminated with light at temperatures below ≈25 K, their color changes from red ($^1A_{1g}$ state) to yellow ($^5T_{2g}$ state), indicating the occurrence of the LIESST effect. Figure 10 shows the relevant absorption spectra before and after the excitation with light. At a temperature around 25–30 K the trapped excited HS state is noticeably relaxing back to the LS ground state within 1 h. Additional kinetic measurements are needed to reveal the detailed temperature dependence of the relaxation rate. In contrast to the $[Fe(ptz)_6](BF_4)_2$ crystals, the $[Fe(2\text{-}pic)_3]Cl_2{\cdot}EtOH$ crystals showed some cracks after they were illuminated with light at a temperature below 25 K. Apparently, the volume change that accompanies the light-induced LS → HS conversion causes the crystal to shatter. In view of the fact that the volume change due to the spin transition is much larger than the change due to the thermal lattice expansion,[22] this observation is not unexpected. In addition, the shattering of the crystals may also have an influence on the lifetime of the trapped excited HS state.

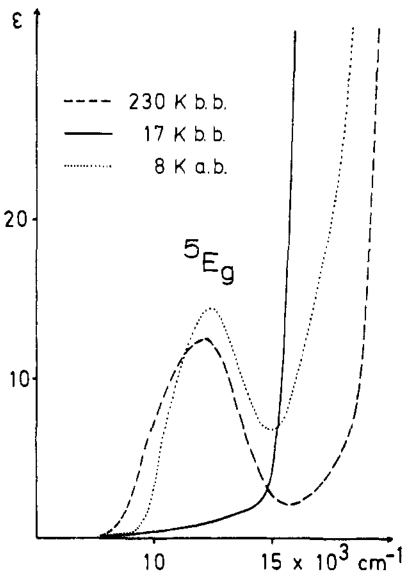

Figure 10. Single-crystal absorption spectra (unpolarized) of $[Fe(2\text{-}pic)_3]Cl_2{\cdot}EtOH$ before bleaching (b.b.) and after bleaching (a.b.) at 8 K for 2 min with white light.

It is known that the methanol adduct $[Fe(2\text{-}pic)_3]Cl_2{\cdot}MeOH$ undergoes a destructive phase transition during the thermally induced spin transition.[10] We have observed that, after excitation with light at 8 K, these crystallites changed their color completely from red to yellow, but with the temperature kept at 8 K, they turned red again within about 30 s. In addition, we have observed the LIESST effect also in $[Fe(2\text{-}pic)_3]Br_2{\cdot}EtOH$ at temperatures below ≈20 K, and the experiment caused some cracks in these crystals, too.

In further studies, we shall focus our attention on the question of what kind of chemical and crystallographic factors play an important role in determining the lifetime of the trapped excited HS state at a given temperature.

Acknowledgment. S.D. wishes to thank the Alexander von Humboldt Foundation for the award of a fellowship. We also wish to thank the Deutsche Forschungsgemeinschaft, the Stiftung Volkswagenwerk, and the Fonds der Chemischen Industrie for financial support.

Registry No. $[Fe(ptz)_6](BF_4)_2$, 82285-70-9; $[Fe(2\text{-}pic)_3]Cl_2$, 18433-69-7.

---

(19) Haddad, M. S.; Federer, W. D.; Lynch, M. W.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 131.

(20) Müller, E. W.; Spiering, H.; Gütlich, P. *Chem. Phys. Lett.* **1982**, *93*, 567.

(21) Köppen, H.; Müller, E. W.; Köhler, C. P.; Spiering, H.; Meissner, E.; Gütlich, P. *Chem. Phys. Lett.* **1982**, *91*, 348.

(22) Meissner, E.; Köppen, H.; Spiering, H.; Gütlich, P. *Chem. Phys. Lett.* **1983**, *95*, 163.