High-Spin → Low-Spin Relaxation in $[Fe(bpp)_2](CF_3SO_3)_2 \cdot H_2O$ after LIESST and Thermal Spin-State Trapping—Dynamics of Spin Transition versus Dynamics of Phase Transition

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Dedicated to Professor Gerhard Herberich on the occasion of his 60th birthday

Abstract: The iron(II) complex $[Fe(bpp)_2](CF_3SO_3)_2 \cdot H_2O$ (bpp = 2,6-bis(pyrazolyl-3-yl)pyridine) shows a thermal spin transition associated with a hysteresis of approximately 140 K width. The transition temperatures $T_{1/2}$ (where the fraction of HS species $\gamma_{HS} = 0.5$) are 147 K and ≈285 K in the cooling and heating directions, respectively. The compound shows the LIESST and reverse-LIESST effects at low temperatures. The relaxation of the metastable HS states generated by LIESST was observed quantitatively at temperatures between 77.5 and 85 K by Mössbauer spectroscopy. Metastable HS states can also be generated by rapid cooling of the sample. The relaxation of the metastable HS states formed by thermal spin-state trapping was monitored at temperatures between 104 and 118 K by magnetic susceptibility measurements. The relaxation mechanisms of the HS states generated by LIESST and thermal spin-state trapping are completely different. We suggest that the HS → LS relaxation after thermal spin-state trapping is triggered by an additional structural phase transition of the system.

Keywords
iron complexes · magnetic susceptibility · Mössbauer spectroscopy · phase transitions · spin crossover

Introduction

A thermally induced low-spin (LS) → high-spin (HS) transition in complexes with $3d^4-d^7$ transition-metal ions is a well-known phenomenon in 3d transition metal chemistry. Such transitions have been extensively studied in iron(II) complexes ($3d^6$) in particular, and numerous reviews have been published.[1] Since the discovery of the LIESST (light-induced excited spin state trapping) effect in 1984 it has become widely known that metastable HS states can be formed in spin-transition compounds by irradiating the compound with light of appropriate wavelengths at temperatures well below the thermal transition temperature range.[2] For iron(II), the mechanism of the LIESST effect involves double intersystem crossing from the excited $^1T_1$, $^1T_2$ singlet states to the $^5T_2$ state via low-lying triplet states ($^3T_1$, $^3T_2$). The trapped HS state can also be pumped back to the LS state by irradiation with light into the ligand-field absorption band of the HS state (reverse LIESST).[3] The mechanisms for LIESST and reverse LIESST have been fully elucidated.[4] Applications of this effect in optical data processing have been proposed.[5]

It has become evident that the application of the LIESST and reverse-LIESST effects provide a very effective probe for study of the dynamics of spin transitions, since the generation of metastable spin states is readily achieved through these effects, and subsequent relaxation of these states can be monitored by a number of methods.[6]

According to Hauser, the HS → LS relaxation can be understood on the basis of a nonadiabatic multiphonon process in the strong vibronic coupling limit.[7] The process is characterized by thermally activated behavior at ambient temperatures and tunneling at low temperatures. The low-temperature tunneling rate correlates well with the energy difference between the lowest vibronic levels of the LS and HS states ("inverse energy gap"), which is, to a first approximation, reflected by the spin-transition temperature $T_{1/2}$ ($\gamma_{HS} = 0.5$).

Another way of trapping metastable HS states in some spin-transition compounds is by rapidly cooling the sample.[8] For example, in $[Fe(paptH)_2](NO_3)_2$ (paptH = 2-(2-pyridylamino)-4-(2-pyridyl)thiazole) a slow HS → LS relaxation over hours and days was observed at temperatures between 160 and 180 K.[8a] In this instance, the very slow decay of the metastable HS states is rather remarkable, since fast rates of the order of $10^2-10^8\ s^{-1}$ are predicted for the HS → LS transition at temperatures above 140 K.[6f] In the systems where metastable states may be thermally trapped, the thermal spin transition is associated with large hysteresis effects. This observation is

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considered to indicate the occurrence of crystallographic phase transitions in these compounds. It has been suggested that rapid cooling of the sample causes freezing-in of the high-temperature structure and that the observed HS → LS relaxation at higher temperatures actually reflects the structural relaxation of the system, that is, the electronic HS → LS transition is only a consequence of the structural phase change and is triggered by the rate of the structural phase change. Thus, it is obvious that the HS → LS relaxation mechanism may be completely different from that in those cases where the kinetics of the electronic transition only are detected (i.e., those for which there is no accompanying structural phase change).

Experimental evidence for this working hypothesis may be provided by studying spin-transition compounds in which metastable spin states can be generated both by LIESST and by rapidly cooling the sample. A comparison of the subsequent HS → LS relaxation behavior after LIESST and after rapid cooling should reveal the differences in the relaxation mechanisms.

A first attempt towards this goal was made with the complex $[Fe(bpp)_2](BF_4)_2$ (bpp = 2,6-bis(pyrazolyl-3-yl)pyridine).[8c] In this case, however, the relaxation of the metastable HS state generated by LIESST occurs in two steps. A small fraction of the HS state relaxes to the LS state within minutes between 60 and 70 K; in the second step a complete relaxation to the LS state was observed over hours and days at temperatures between 90 and 100 K. The HS → LS relaxation behavior of this second step turned out to be the same as the one observed in the relaxation process of the metastable HS states formed by rapid cooling of the sample.

In the course of our work on iron(II) spin-crossover systems with the complex cation $[Fe(bpp)_2]^{2+}$[9] we found that the formation of metastable spin states in $[Fe(bpp)_2](CF_3SO_3)_2 \cdot H_2O$ is possible by rapid cooling of the sample as well as by application of the LIESST effect. In this report we present the results from investigations of the thermal spin-transition behavior and the HS → LS relaxation behavior after LIESST and thermal spin-state trapping. The relaxation of the metastable LIESST states was followed quantitatively by Mössbauer spectroscopy between 77.5 and 85 K. The HS → LS relaxation after thermal spin-state trapping was monitored by magnetic susceptibility measurements. The results demonstrate that the relaxation mechanism depends heavily on the method used to generate the metastable HS states.

Results and Discussion

Thermal spin transition: Some representative Mössbauer spectra of $[Fe(bpp)_2](CF_3SO_3)_2 \cdot H_2O$ recorded in the cooling direction are reproduced in Figure 1. At 292 K the Mössbauer spectrum is dominated by a doublet with an isomer shift of $\delta = 0.865(4)\ \mathrm{mm\,s^{-1}}$ (relative to the $^{57}Co/Rh$ source at 292 K) and a quadrupole splitting of $\Delta E_Q = 2.280(8)\ \mathrm{mm\,s^{-1}}$; these values are typical for iron(II) HS compounds. A doublet with very low intensity and $\delta = -0.04(6)\ \mathrm{mm\,s^{-1}}$, $\Delta E_Q = 0.4\ \mathrm{mm\,s^{-1}}$ is also present and presumably originates from small amounts of an iron(III) impurity. An additional doublet with $\delta \approx 0.3\ \mathrm{mm\,s^{-1}}$, $\Delta E_Q \approx 0.55\ \mathrm{mm\,s^{-1}}$ and very low intensity (ca. 2% area fraction) is detected in the Mössbauer spectra at 200 K. The parameters of this doublet are typical for iron(II) LS compounds. The appearance of this doublet indicates the onset of a thermally induced HS → LS transition. On further cooling the spectra remain essentially unchanged down to temperatures of about 150 K. The quadrupole splitting of the iron(II) HS state increases from $2.280(8)\ \mathrm{mm\,s^{-1}}$ at 292 K to $2.862(2)\ \mathrm{mm\,s^{-1}}$ at 150 K; this is due to the increasing population of lower-valence electron levels contributing to the electric field gradient with decreasing temperature. The area fraction of the LS doublet increases very slightly to about 4% at 150 K. A drastic change in the Mössbauer spectra appears between 150 and 140 K. The iron(II) LS doublet with $\delta = 0.286\ \mathrm{mm\,s^{-1}}$ and $\Delta E_Q = 0.685\ \mathrm{mm\,s^{-1}}$ dominates in intensity now, while the iron(II) HS doublet has decreased in intensity to only about 5%. Thus, the HS → LS transition is very sharp between 150 and 140 K in the cooling direction. At temperatures below 140 K no more changes in the area fractions are observed; the residual HS fraction of ≈5% remains unchanged down to around 20 K.

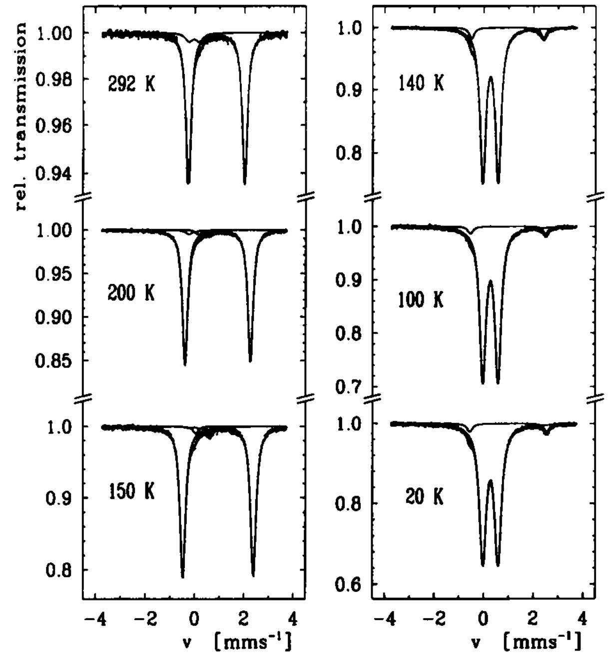

Fig. 1. Mössbauer spectra of $[Fe(bpp)_2](CF_3SO_3)_2 \cdot H_2O$ recorded in the cooling direction. At 292 K the spectrum is dominated by an iron(II) HS doublet. The HS → LS transition is observed between 150 and 140 K. At temperatures below 140 K a residual HS fraction of ca. 5% is observed.

A series of temperature-dependent Mössbauer spectra recorded in the heating direction are presented in Figure 2. Between 20 and 160 K no changes in the area fractions of the HS and LS doublets are detected; again, a residual HS fraction of about 5% remains present over this interval. At 190 K the intensity of the iron(II) HS doublet has increased to about 33%. It remains approximately the same up to 225 K and then increases, on further heating, to around 45% at 260 K. Above 260 K the HS doublet intensity increases sharply, whereas the LS resonances disappear entirely at 304 K. The Mössbauer spectrum recorded at 292 K and above in the heating direction again reveals a small amount of an iron(III) impurity.

Magnetic susceptibility measurements agree well with the results from the Mössbauer investigations. The spin-transition curves derived from both techniques are shown in Figure 3. The spin transition occurs very abruptly at $T_{1/2} = 147$ K in the cooling direction. Below 140 K, a residual HS fraction of about 5% is detected. In the heating direction no change in the HS fraction is observed over the temperature range 20–≈150 K. An increase of the HS fraction is seen only at temperatures higher than 150 K, leading to a plateau of about 33% HS fraction at 190 K which stays constant up to around 250 K. A further increase of γ_{HS} occurs at temperatures higher than this. A HS fraction of about 90% is still apparent around room tempera-

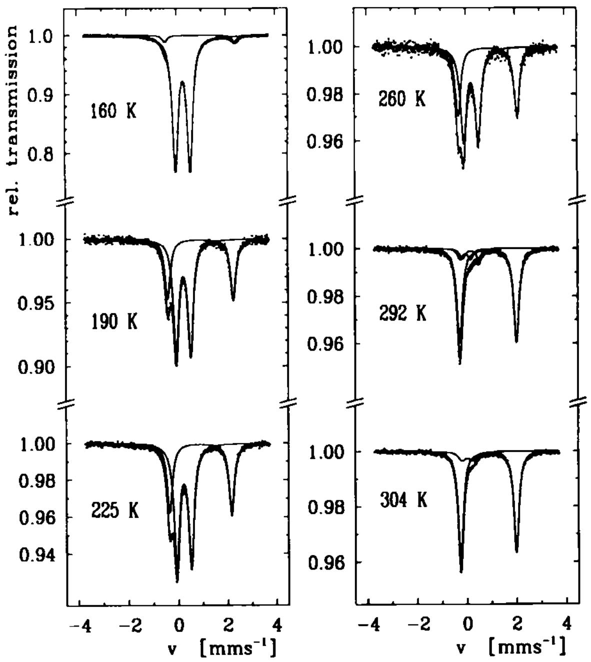

Fig. 2. Mössbauer spectra of [Fe(bpp)$_2$](CF$_3$SO$_3$)$_2$·H$_2$O recorded in the heating direction. At 160 K the Mössbauer spectrum is very similar to the one recorded at 20 K. The same residual HS fraction of ca. 5% is detected. An increase in the HS fraction to ca. 33% is observed between 160 and 190 K. This HS fraction stays constant up to about 260 K and then increases further. The LS doublet is no longer observed in the Mössbauer spectra at temperatures ≥304 K.

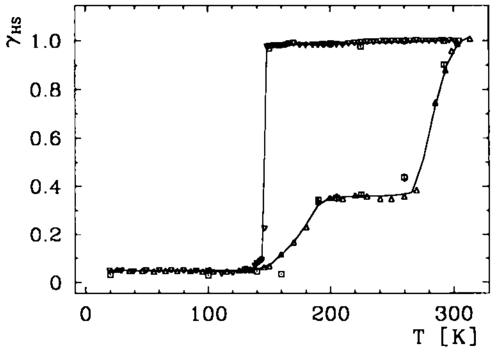

Fig. 3. HS fraction γ_{HS} as a function of temperature in [Fe(bpp)$_2$](CF$_3$SO$_3$)$_2$·H$_2$O derived from magnetic susceptibility (▽ for decreasing temperatures and △ for increasing temperatures; - guide for the eye) and Mössbauer investigations (□). The thermal spin-transition behavior of the complex is characterized by a hysteresis of ca. 140 K width. The transition temperatures $T_{1/2}$ ($\gamma_{HS} = 0.5$) are 147 and 285 K for the cooling and heating directions, respectively. At temperatures below 140 K a residual HS fraction of ca. 5% is detected.

ture. The transition temperature for the second step of the spin transition in the heating direction may be derived as about 285 K. For this compound, then, measurements through the cooling/heating cycle reveal a very broad and unsymmetrical hysteresis loop, the width being estimated as ≈140 K.

HS → LS relaxation: Long-lived metastable HS states can be formed at low temperatures by means of the LIESST effect. In Figure 4 the Mössbauer spectra at 20 K before (A) and after (B) irradiation with green light are shown. The spectra clearly demonstrate a nearly quantitative light-induced conversion of the LS state to the metastable HS state. After about 45 min irradiation, more than 95% of the LS molecules are converted to the HS state. The HS state is represented by two doublets with slightly different quadrupole splittings. These metastable HS states can be partially transformed back to the original LS state by irradiation of the complex with red light. The increase in the LS fraction is only ≈10% in the present experiment. The incompleteness of the HS → LS back-transformation is probably due to the broad-band excitation by a Xe arc lamp with filters and was discussed in detail in ref. [10]. It is important to mention that the present irradiation experiments were performed after cooling the compound from 300 K to 130 K, then heating up to about 150 K, and finally cooling down to 20 K, where the LIESST experiments were performed. The LIESST effect is also observed when the sample is cooled from room temperature to 20 K, but in this case only one HS doublet after LIESST is detected; the one with the slightly smaller quadrupole splitting in Figure 4 is no longer detected. This may be because of the existence of two different lattice sites for the molecules; this fact may also account for the observed two-step transition in the heating direction. However, one HS doublet only is detected in the course of the thermal spin transition.

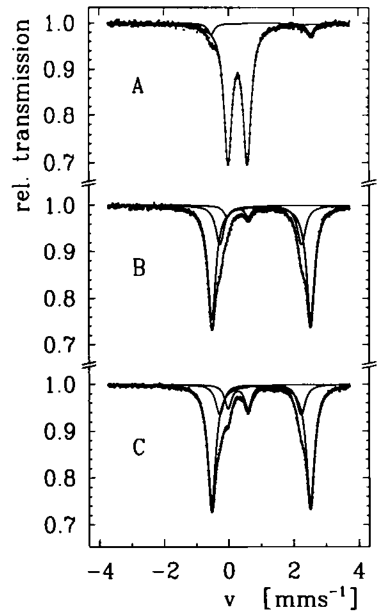

Fig. 4. Mössbauer spectra at 20 K before (A) and after (B) irradiation with green light. The compound shows the LIESST effect. Irradiation with green light converts the LS state into two different HS doublets with slightly different quadrupole splittings. After irradiation with red light (after LIESST) a back-transformation of ca. 10% of the molecules is observed (spectrum C), proving that the complex also undergoes the reverse-LIESST effect.

After subsequent heating to temperatures within the interval 77.5–85 K, relaxation curves of the metastable HS state generated by LIESST were determined by Mössbauer spectroscopy. At the end of the relaxation process, a residual HS fraction corresponding to the HS fraction at low temperatures in the course of the thermal spin transition is detected. If we substract this residual HS fraction and consider only the molecules showing spin transition we obtain the relaxation curves presented in Figure 5, where each point represents the HS fraction derived

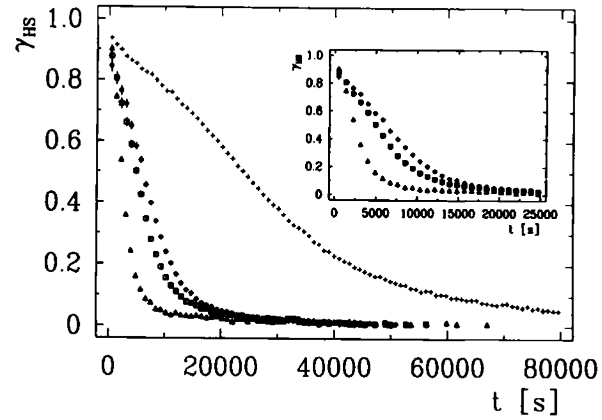

Fig. 5. Relaxation curves $\gamma_{HS}(t)$ after LIESST at temperatures of 77.5 (+), 80 (◇), 82.5 (□), and 85 K (△), with each data point representing the HS fraction derived from a single Mössbauer spectrum.

from a single Mössbauer spectrum recorded for 15 min. The HS → LS relaxation is quite fast in the beginning, but slows down towards the end of the relaxation process.

Metastable HS states can also be formed by rapid cooling of the sample. Figure 6 shows the spectrum at 20 K after slow cooling (spectrum A). An almost complete HS → LS transition has occurred and a residual HS fraction of only about 5% is detected in the spectrum at 20 K. After the compound was suspended in liquid nitrogen and then quickly transferred to the cryostat, spectrum B was recorded at 20 K. This spectrum clearly shows that more than 90% of the HS molecules can be trapped by rapid cooling. After thermal spin-state trapping and subsequent heating to a temperature within the interval 104–118 K, the HS → LS relaxation behavior of the thermally trapped HS molecules was studied by means of magnetic susceptibility measurements. The HS → LS relaxation curves derived from these experiments are depicted in Figure 7. Large deviations from simple exponential behavior are clearly visible.

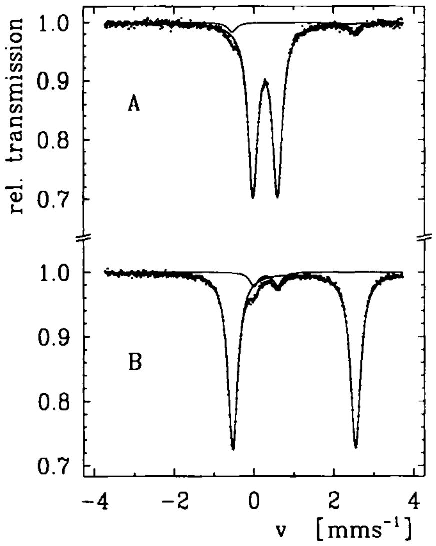

Fig. 6. Mössbauer spectra at 20 K after slow cooling of the sample (spectrum A). After suspending the compound in liquid nitrogen and subsequent transfer to a cryostat, spectrum B was recorded at 20 K. The Mössbauer spectrum clearly shows that more than 90% of the HS molecules can be trapped by rapidly cooling the sample.

It is well known that the HS → LS relaxation in solid spin-transition compounds is strongly influenced by cooperative effects.[11] The consequence is that the rate constant k of the relaxation process is no longer independent of the γ_{HS} fraction and therefore sigmoidal HS → LS relaxation curves are observed in concentrated spin-crossover materials. Only in highly diluted mixed crystals, where these cooperative interactions disappear, has single exponential decay of the metastable HS states been detected. The HS → LS relaxation curves after LIESST in $[Fe(ptz)_6](BF_4)_2$ (ptz = 1*n*-propyl-1 H-tetrazole) could be described well if a linear dependence of the activation energy on the γ_{HS} fraction was assumed [Equation (1), where E_A^+ incorporates an additional activation energy owing to the cooperativity of the HS → LS conversion]. The same equation holds true for the HS → LS relaxation after thermal spin-state trapping in $[Fe(bpen)(NCS)_2]$ (bpen = 1,6-bis(2-pyridyl)-2,5-diazahexane).[12] There are, however, reports of other compounds where the dependence of the rate constant k on the HS fraction is more complex.

$$k = k_0 \exp\left(\frac{-E_A^+}{k_B T} \cdot \gamma_{HS}\right) \qquad (1)$$

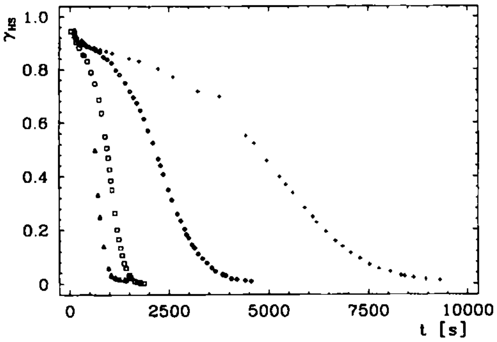

Fig. 7. Relaxation curves $\gamma_{HS}(t)$ after thermal spin-state trapping at temperatures of 104 (+), 108 (◇), 113 (□), and 118 K (△). The HS fraction was determined from magnetic susceptibility measurements. The relaxation curves show strong deviations from single exponential behavior.

A comparison of Figures 5 and 7 shows that the decay of the metastable HS states formed by LIESST at 85 K is nearly as fast as the relaxation of the metastable HS states generated by thermal spin-state trapping at 104 K. At any particular temperature the relaxation of the thermally generated HS state is slower than that of the LIESST-generated metastable HS state. This observation points to a different relaxation mechanism for the decay of the differently produced metastable HS states. This becomes more evident from a comparison of the dependence of the rate constant k on the HS fraction γ_{HS} for the HS → LS relaxation after LIESST and thermal spin-state trapping, respectively. Plots of ln(k) vs. γ_{HS} representing the relaxation of the metastable HS states after LIESST (above) and thermal spin-state trapping (below) are shown in Figure 8. The relaxation

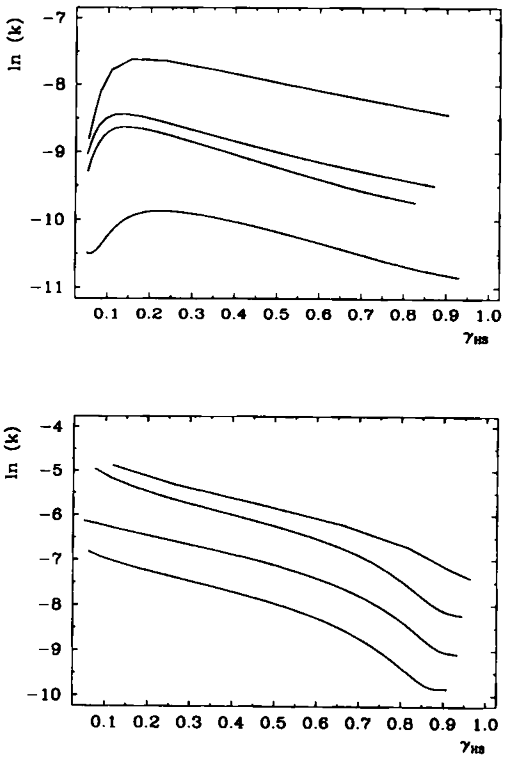

Fig. 8. ln(k) vs. γ_{HS} plots after LIESST (above) and thermal spin-state trapping (below). After LIESST the rate constant of the relaxation process is a linear function in γ_{HS} for $\gamma_{HS} \geq 0.2$ and then slows down towards the end of the relaxation process. After thermal spin-state trapping the rate of the HS → LS relaxation increases at the beginning of the relaxation process and then for $\gamma_{HS} \leq 0.7$ is linear with respect to γ_{HS}.

process of the thermally trapped HS molecules has increasing $\ln(k)$ values at the beginning of the relaxation process, but for γ_{HS} values ≤ 0.7, $\ln(k)$ is a linear function of the HS fraction γ_{HS}. The relaxation mechanism of metastable HS states generated by LIESST in $[Fe(bpp)_2](CF_3SO_3)_2 \cdot H_2O$ is different. At the beginning $\ln(k)$ depends linearly on the HS fraction γ_{HS}, and only towards the end of the relaxation process does the rate slow down somewhat. Therefore, it is obvious that the relaxation mechanism for the metastable HS states does indeed depend on the process of their formation. The relaxation behavior after thermal spin-state trapping is quite similar to that observed in $[Fe(bpp)_2](BF_4)_2$, where the HS → LS relaxation is influenced by an additional structural phase transition of the system.[8c] We therefore conclude that the HS → LS relaxation in $[Fe(bpp)_2](CF_3SO_3)_2 \cdot H_2O$ after thermal spin-state trapping is also triggered by an additional phase transition of the compound, that is, the HS → LS relaxation actually reflects the rate of the structural phase transition. The relaxation mechanism after LIESST differs from the one observed after thermal spin-state trapping. We suggest that the decay of the metastable HS states after LIESST is determined primarily by the HS → LS electronic conversion.

Experimental Section

Preparation: The ligand 2,6-bis(pyrazol-3-yl)pyridine (bpp) was prepared following Lin and Lang [13]. The complex $[Fe(bpp)_2](CF_3SO_3)_2 \cdot 3H_2O$ was obtained by reaction of the ligand with iron(II) chloride tetrahydrate in hot water under a nitrogen atmosphere. After the reaction was complete the mixture was filtered and an aqueous solution of sodium triflate was added to the filtrate, upon which the deep red-brown complex triflate crystallized as a trihydrate. This was converted to the bright yellow monohydrate by heating at 60–70 °C in a N_2 atmosphere for several hours. Both hydrates were characterized by elemental analysis. The samples used in the present study were enriched in ^{57}Fe to 30%. This enabled us to record the Mössbauer spectra at much shorter time intervals than on samples with natural iron content.

Susceptibility measurements: The magnetic susceptibilities $\chi(T)$ were measured between 20 and 300 K with a Foner magnetometer equipped with a helium flow cryostat. The applied external field was 1 T. The HS fraction $\gamma_{HS}(T)$ was calculated from the measured susceptibilities with the assumptions that i) the iron complex in the HS state shows Curie behavior, and ii) the LS state shows temperature-independent paramagnetism. The diamagnetic correction for the ferrous complex was determined from Pascal's constants. The HS → LS relaxation after thermal spin-state trapping was followed with a Newport variable-temperature Gouy balance calibrated with $[CoHg(NCS)_4]$.

Mössbauer measurements: Mössbauer spectra were recorded between 10 and 300 K in transmission geometry. The source was $^{57}Co/Rh$ kept at room temperature. All isomer shift values are given relative to the source. The samples were sealed in polished plexiglass containers and mounted in a He-flow cryostat (CF506, Oxford Instruments) equipped with windows of transparent mylar foil to allow irradiation of the sample with light. LIESST experiments with green light yielding metastable light-induced HS states were performed with a Xe arc lamp and appropriate filters. For reverse-LIESST experiments a cut-off filter was used to afford essentially red light with $\lambda \geq 690$ nm.

The Mössbauer spectra were fitted by use of the transmission integral with the program MOSFUN [14]. The HS → LS relaxation after LIESST was followed by monitoring the HS fraction derived from the Mössbauer spectra in the temperature interval 77.5–85 K. Spectra were recorded every 15 min.

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