even if the results of the COSY experiments were not known.

D. Conclusions. The present work has thus demonstrated for two representative zeolite structures that it is possible to perform reliable 2D COSY and INADEQUATE experiments in natural abundance. Although the T_2 values are of the order of seconds in these systems, and are much larger than the T_2^* values, the line widths are such that they impose no real constraints on the experiments. All of the anticipated ^{29}Si–O–^{29}Si interactions are observed, detailing the complete 3D connectivities in the two structures. In addition, the couplings, thought to be scalar in nature, between the ^{29}Si/^{29}Si spin pairs are observed and have "apparent" values of 10–15 Hz. The techniques may be considered of quite general applicability and will be useful in the investigation of other 3D-bonded solid-state structures. In this regard, it is useful to consider the information now available from the NMR studies alone. For example in the case of ZSM-12 we would know that the unit cell contained seven inequivalent T sites of equal occupancies, one of which was "buried" in the walls of the structure, and all of the connectivities given in Table I. Bearing in mind that the total of the connectivities to a given T site must be four, and that the cross-peak intensities qualitatively reflect the numbers of connections, some estimates could also be made on the numbers of the different connectivities present. Taken together with other experimental data, for example for sorption studies, these results would be very useful in discriminating between different proposed structures and, in favorable cases, might even be used to generate possible structures for comparison with experimental powder X-ray diffraction data.

The results also make it possible to predict from magnitudes of the observed scalar couplings that the simple experiments described will not be unduly constrained by T_2^* values for systems with line widths of approximately 30 Hz or less and that useful data may be obtained from COSY experiments for even broader resonances. It should be possible, for extreme cases where $T_2 \gg T_2^*$ in the solid state, to generate more efficient versions of the COSY experiment. Work in this area is currently in progress as are studies of a number of other zeolite systems.

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Thermal- and Light-Induced Spin Transition in $[Fe(mtz)_6](BF_4)_2$: First Successful Formation of a Metastable Low-Spin State by Irradiation with Light at Low Temperatures[†]

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Abstract: The iron(II) spin-crossover complex $[Fe(mtz)_6](BF_4)_2$ (mtz = 1-methyl-1*H*-tetrazole) has two different iron(II) lattice sites A and B. The ^{57}Fe Mössbauer spectra of the compound consist of only one quadrupole doublet above ~160 K, which is typical for iron(II) in the high-spin (HS) state. This indicates that the two sites A and B are indistinguishable above this temperature. Below ~160 K two different doublets are observed, both arising from iron(II) in the HS state. Several reasons for this phenomenon are discussed. Only the complex molecules, or rather the metal ions, in lattice site A undergo thermal spin transition to the low-spin (LS) state of iron(II), whereas those in lattice site B remain in the HS state down to 4.2 K. By irradiation with light of a Xe arc lamp ($\lambda \sim$ 350–650 nm) at 20 K the well-known LIESST (light-induced excited spin state trapping) effect is observed for the lattice site A ions. A metastable HS state is formed, which has a practically infinitely long lifetime below 40 K. Irradiation of $[Fe(mtz)_6](BF_4)_2$ with red light (λ > 700 nm) at 20 K causes a light-induced HS → LS conversion at lattice site B. The populated LS state is also metastable with a practically infinitely long lifetime below 50 K. This is the first example for a successful light-induced formation of a metastable LS state in an iron(II) HS complex.

1. Introduction

Temperature-dependent spin transition (spin crossover) is a well-established phenomenon in the coordination chemistry of first-row transition elements. Many examples are known, particularly for iron(II) compounds for which thermal low-spin (LS) ⇄ high-spin (HS) transition has been extensively studied, employing various techniques.[1,2]

A few years ago, Decurtins et al.[3,4] showed that in iron(II) spin-crossover complexes light-induced LS ($^1A_1$) → HS ($^5T_2$) conversion can be observed by irradiation with green light ($\lambda \sim$ 550 nm) into the $^1A_1 \rightarrow {}^1T_1$ ligand field absorption band at temperatures well below the thermal transition temperature. A mechanism for this phenomenon, denoted as "light-induced excited spin state trapping" (LIESST), was proposed.[4] Figure 1 shows the potential energy surfaces of the low-lying ligand field states for a d^6 system with ligand field strengths in the region of spin crossover.[5] The mechanism involves intersystem crossing from the excited $^1T_1$ state to an intermediate low-lying $^3T_1$ state and from there to the $^5T_2$ state, where at sufficiently low temperatures

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[†] Dedicated to Professor D. Reinen on occasion of his 60th birthday.

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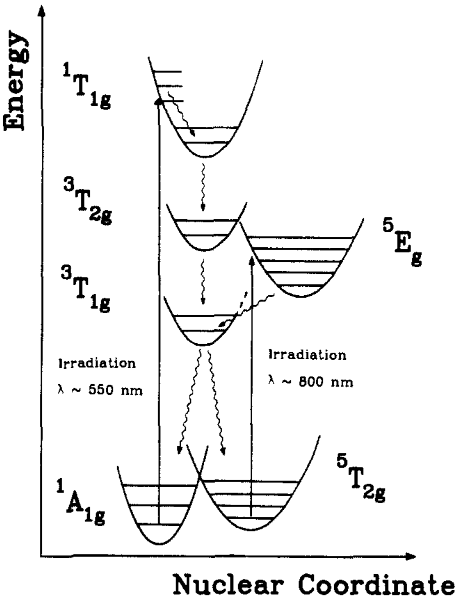

Figure 1. Schematic potential surfaces of the low-lying ligand field states for a d^6 spin-crossover complex. The arrows indicate the mechanism for LIESST(L→H) and reverse LIESST(L←H) (see text).

the HS state remains trapped. The large difference of 20 pm[1] in the equilibrium bond lengths of the two spin states separates the two potential wells and gives rise to a potential barrier between the two states. In the meantime, the LIESST effect has been observed in a number of iron(II) compounds.[6-9]

Before the observation of Decurtins et al.[3,4] McGarvey and Lawthers[10] found a rapid depopulation of the LS state upon pulsed laser excitation of iron(II) spin-crossover complexes in solution at ambient temperatures. In their case the relaxation rate back to the LS state was of the order of 10^7 s^{-1}, which made it difficult to characterize properly the metastable state. The experiments of Decurtins et al. were with crystalline material at temperatures below 50 K. The relaxation rates were less than 10^{-5} s^{-1}, and the metastable state could unambiguously be identified as the HS state.

The trapped HS state relaxes back to the LS state thermally at some higher temperatures, but it has also been shown that the system can be pumped back to the LS state by irradiating into the ${}^5T_2 \rightarrow {}^5E$ ligand field absorption band ($\lambda \sim 850$ nm).[4,11] The pathway for the relaxation back to the ${}^1A_1$ state is again a double intersystem crossing via the ${}^3T_1$ state (see Figure 1). This process was termed "reverse LIESST".

In iron(II) spin-crossover complexes, the entropy of the HS state is much larger than that of the LS state.[2,12] Furthermore, the minimum of the ${}^1A_1$ potential lies typically ~500 cm^{-1} below that of the ${}^5T_2$ state.[2] If this difference $\Delta E = E({}^5T_2) - E({}^1A_1)$ is smaller but still positive, the compound tends to remain in the HS state because the thermodynamic equilibrium (in a rough approximation we can set ΔE to ΔH) is on the side of the LS state only at lowest temperatures, where the system is no longer able to overcome the potential barrier between the HS and the LS states. If in an iron(II) compound the potential well of the ${}^5T_2$ state lies below that of the ${}^1A_1$ state, the system remains in the HS state at all temperatures because of the larger entropy in the HS state as compared to the LS state. The excited LS state is not thermally accessible. However, if the energy difference between the ${}^1A_1$ state and the ${}^5T_2$ state is small, an appreciable potential barrier between the two states can be expected similar to that in spin-crossover complexes (see Figure 2).

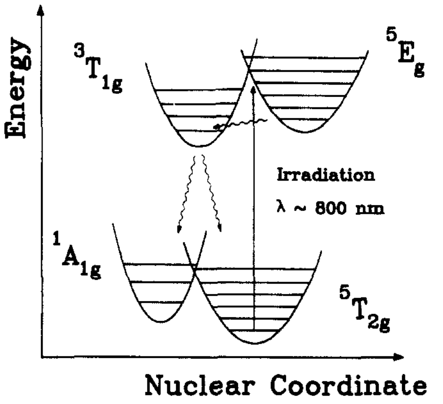

Figure 2. Schematic potential surfaces for a d^6 high-spin complex, with an appreciable potential barrier between the ${}^1A_1$ and the ${}^5T_2$ states. Arrows indicate the mechanism for LIESST(H→L).

Hauser[11] first pointed out that it may be possible to generate and trap the ${}^1A_1$ state in such systems by irradiation with red light into the ${}^5T_2 \rightarrow {}^5E$ band at low temperatures; this process would correspond to the original LIESST effect, but now in the direction HS → LS yielding a long-lived metastable LS state (see Figure 2). However, our first attempts to trap the ${}^1A_1$ state in several HS complexes failed.[8]

In the course of our studies of thermal- and light-induced spin crossover in iron(II) complexes we have investigated the compounds $[Fe(mtz)_6]X_2$, where mtz ≡ 1-methyl-1*H*-tetrazole and X ≡ BF_4^-, ClO_4^-, $CF_3SO_3^-$, and PF_6^-. The results for $[Fe(mtz)_6](PF_6)_2$ and preliminary results for $[Fe(mtz)_6](ClO_4)_2$ have already been published.[13,14] Some preliminary results from an early study of the $[Fe(mtz)_6](BF_4)_2$ complex compound have also been reported,[15] but the chemical characterization as well as the characterization of the spin transition were unsatisfactory, most likely due to preparation effects,[2] and a number of unanswered questions awaited further experiments with better material. Here we present the results from a very careful reinvestigation of the thermal spin-transition behavior in samples of $[Fe(mtz)_6](BF_4)_2$ prepared with a newly worked out synthesis procedure and employing Mössbauer spectroscopy, optical spectroscopy, and magnetic susceptibility measurements in the temperature range between 300 and 4 K. We have also studied carefully the light-induced spin-crossover behavior. The system $[Fe(mtz)_6](BF_4)_2$ turned out to become the first example of an iron(II) complex for which the formation of a metastable LS state by light was successful. Moreover, the system exhibits an unusual spin-transition behavior that was never seen before.

2. Experimental Section

Sample Preparation. 1-Methyl-1*H*-tetrazole was prepared as described earlier.[16,17] $[Fe(mtz)_6](BF_4)_2$ was obtained from equimolar concentrated aqueous solutions of $[Fe(H_2O)_6](BF_4)_2$ and the ligand under nitrogen. The volume of this solution was carefully reduced at room temperature until the complex crystallized from the solution. The raw product was filtered and dried. It was further purified by solution of the material in dry nitromethane. The volume of the saturated solution was reduced with an oxygen-free and dry-nitrogen stream. By very slow evaporation at 30 °C, single crystals of $[Fe(mtz)_6](BF_4)_2$ up to 3–5 mm in diameter were obtained within a few days. This preparation method proved to be reproducible. The physical properties of samples obtained from different preparations were identical. Anal. Found: C, 19.70; H, 3.31; N, 45.65. Calcd for $C_{12}H_{24}N_{24}B_2F_8Fe$: C, 19.64; H, 3.31; N, 45.80.

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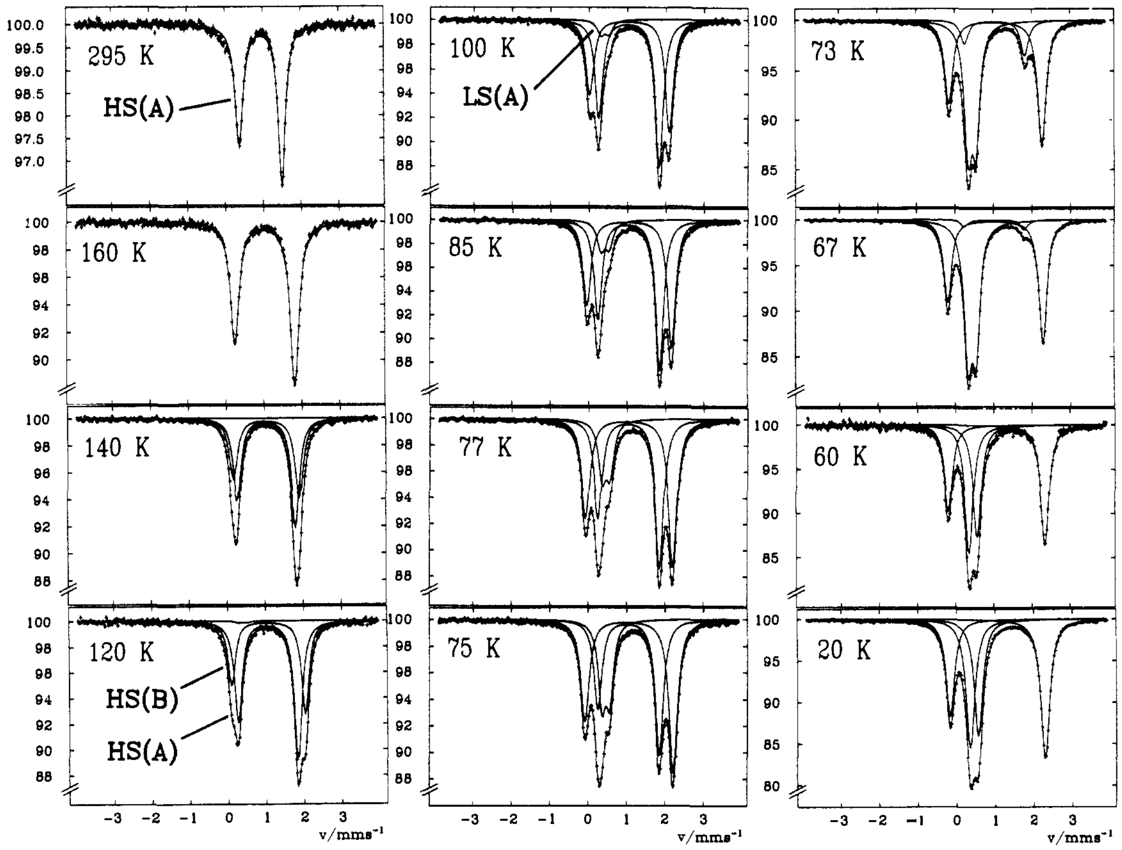

Figure 3. ^{57}Fe Mössbauer spectra of [Fe(mtz)$_6$](BF$_4$)$_2$ recorded at various temperatures (source ^{57}Co/Rh at 295 K).

Susceptibility Measurements. The magnetic susceptibilities $\chi(T)$ for [Fe(mtz)$_6$](BF$_4$)$_2$ between 20 and 295 K were measured with a Foner-type magnetometer, equipped with a helium-flow cryostat, in an external field of 1 T. The diamagnetic correction for the ferrous complex was determined from a measurement of χ at room temperature of the diamagnetic [Zn(mtz)$_6$](BF$_4$)$_2$ complex ($\chi = -406 \times 10^{-6}$ cm^3 mol^{-1}), which was prepared in the same manner as the iron complex with [Zn(H$_2$O)$_6$](BF$_4$)$_2$. Effective moments were calculated from $\mu_{\rm eff} = 2.828(\chi T)^{1/2}$, where $\chi_{\rm m}$ is the corrected molar susceptibility.

Mössbauer Spectroscopy. Mössbauer spectra of [Fe(mtz)$_6$](BF$_4$)$_2$ between 5 and 295 K were recorded with a conventional Mössbauer spectrometer. The source was ^{57}Co/Rh at room temperature. All isomer shifts in this work refer to the source. To convert to the metallic iron scale, 0.112 mm/s was added. The samples were sealed in polished Plexiglass containers (3 cm^2, ~7 mg of Fe cm^{-2}) and mounted in a helium-flow cryostat (CF 506, Oxford Instruments). The cryostat was equipped with windows of transparent Mylar foils. The samples were irradiated with a Xe arc lamp with a water bath as an IR filter. For LIESST experiments, a filter with a maximum transmission between 350 and 650 nm was used, for reverse LIESST experiments a filter transparent for $\lambda > 700$ nm. A carbon/glass resistance was directly mounted at the sample holder to control the temperature during irradiation.

Most of the Mössbauer spectra were fitted to Lorentzians with the program MOSFUN,[18] but some of them were fitted with the transmission integral[19] with a program of Adler.[20] The parameters of the source were determined from a spectrum of sodium nitroprusside of known effective thickness.

Optical Spectroscopy. Variable-temperature absorption spectra were recorded with an Omega 10 UV/vis/near-infrared absorption spectrometer (Bruins Instruments) equipped with a flow tube cryostat for temperatures down to 8 K.

3. Results

Thermal Spin Transition of [Fe(mtz)$_6$](BF$_4$)$_2$. The crystal structure of [Fe(mtz)$_6$](BF$_4$)$_2$ was determined by X-ray diffraction at 157 and 113 K and that of the isomorphous [Fe(mtz)$_6$](ClO$_4$)$_2$ at 298 K. The whole structure analysis will be published separately.[21] Some essential results are summarized as follows: The space group is $P2_1/n$ ($Z = 4$) with iron atoms in spatial positions (Fe1 in [0,0,0], [$^1/_2$,$^1/_2$,$^1/_2$] and Fe2 in [$^1/_2$,0,0], [0,$^1/_2$,$^1/_2$]). Thus, there are two inequivalent iron(II) complex molecules A and B with equal amounts. They are related to each other by a pseudomirror plane, and the geometries of the two molecules A and B are nearly identical down to 113 K. There is, however, a clear distinction between A and B molecules in the magnitude of the temperature factors. Despite the presence of two inequivalent iron(II) ions, it is surprising that the ^{57}Fe Mössbauer spectra of [Fe(mtz)$_6$](BF$_4$)$_2$ consist of only one quadrupole doublet between 295 and 160 K, with typical parameters for Fe(II) in the HS state (see Figure 3; for parameters of the spectra see Table I). The different intensities of the two lines are due to texture caused by the flat monoclinic crystals. Around 160 K, the resonance lines begin to broaden and the doublet splits up into two quadrupole doublets with nearly the same isomer shift but different quadrupole splittings, which are still characteristic of iron(II) in the HS state. In the following the doublet with the smaller quadrupole splitting is denoted as HS(A) and the one with the larger quadrupole splitting as HS(B). Obviously, at higher temperatures the two lattice sites are so similar that they cannot be distinguished by Mössbauer spectroscopy. This will be discussed later.

The temperature dependence of the quadrupole splitting $\Delta E_{\rm Q}$ of HS(A) and of HS(B) is quite different. $\Delta E_{\rm Q}$ of HS(A) is nearly temperature independent. It varies from ~1.48 mm/s at 160 K to ~1.6 mm/s at 75 K. In contrast, $\Delta E_{\rm Q}$ of HS(B) varies very strongly with temperature. It increases from ~1.65 mm/s at 160 K to 2.5 mm/s at 20 K (see Figure 4).

Between 110 and 60 K only the complex cations at lattice site A undergo a thermal HS → LS transition. The intensity of HS(A) decreases, and a new doublet with parameters typical for iron(II) in the LS state appears in the spectrum (see Table I and Figure 3). This doublet will be denoted as LS(A). At ~60 K the HS(A)

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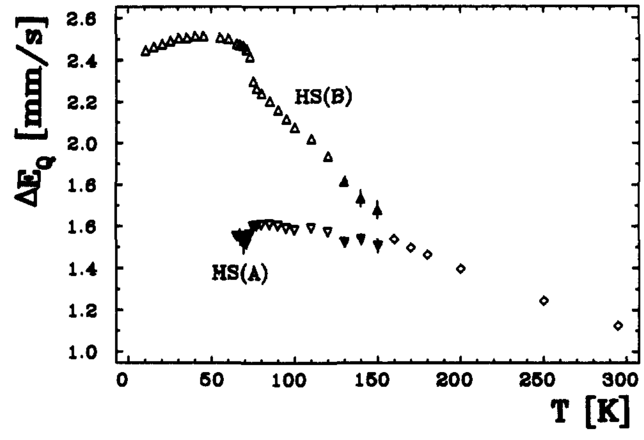

Figure 4. Quadrupole splitting ΔE_Q of the HS(A) doublet and the HS(B) doublet of $[Fe(mtz)_6](BF_4)_2$ as a function of temperature.

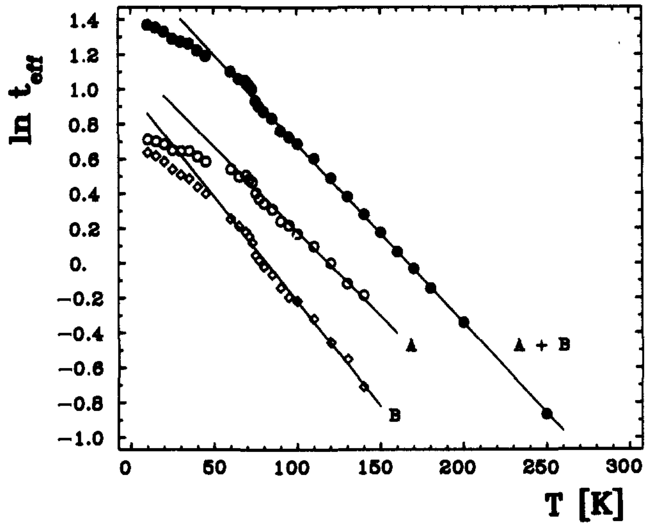

Figure 5. Natural logarithm of the effective thicknesses of the iron(II) ions at lattice sites A and B of $[Fe(mtz)_6](BF_4)_2$ separately and for the total absorber. The effective thicknesses were obtained from a fit with the transmission integral.

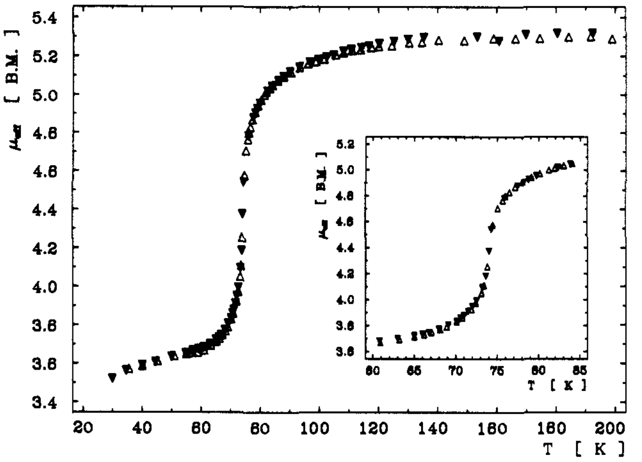

Figure 6. Effective magnetic moment of $[Fe(mtz)_6](BF_4)_2$ as a function of temperature calculated from the magnetic susceptibilities: Δ, increasing temperature; ∇, decreasing temperature.

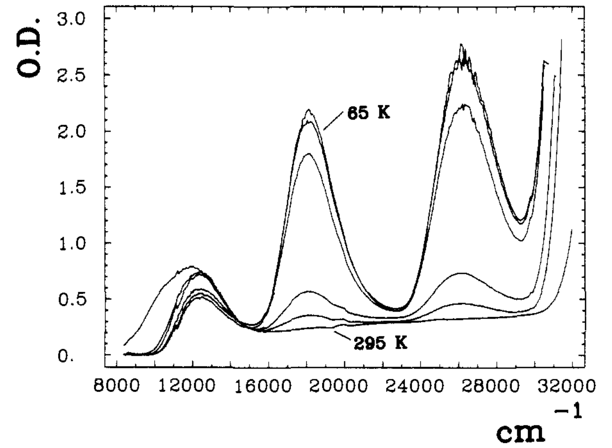

Figure 7. Optical absorption spectra of a single crystal of $[Fe(mtz)_6](BF_4)_2$ at 295, 100, 80, 72, 69, and 65 K. The band at 12300 cm^{-1} originates from the $^5T_2 \rightarrow {}^5E$ transition of the HS complex. The bands at 18200 and 26400 cm^{-1} arise from the $^1A_1 \rightarrow {}^1T_1$ and the $^1A_1 \rightarrow {}^1T_2$ transitions of the LS complex.

resonance lines have disappeared; the spin transition at lattice site A is complete. In contrast to lattice site A the complex ions at lattice site B stay in the HS state at all temperatures under study down to 5 K.

Provided that the Debye–Waller factors for HS(A), LS(A), and HS(B) are equal, the proportion of the resonance line intensities of HS(A) and LS(A) to that of HS(B) should be 1. This is in fact only the case at very low temperatures, whereas at higher temperatures the proportion is larger than 1 (up to 1.6 at 120 K). This implies that the Debye–Waller factors of the iron(II) ions at lattice sites A and B cannot be taken the same in the whole temperature range. To demonstrate this, we fitted the Mössbauer spectra with the full transmission integral theory, in order to evaluate the effective thickness $t_{eff} = n\sigma_0 f$, where n is the number of resonating atoms per centimeter squared, σ_0 the absorption cross section per iron atom, and f the Debye–Waller factor of the resonating nucleus.[19,22] Figure 5 shows the logarithm of the effective thicknesses of the whole absorber (sum of all resonance lines) and those of HS(A) + LS(A) and of HS(B) separately. In agreement with the theory of the Debye–Waller factor (high-temperature limit)[22] there is a linear relationship between ln t_{eff} and T above ~60 K. The slope of ln t_{eff} vs T of the ions at lattice site A remains constant during the HS(A) → LS(A) spin transition. Therefore, the Debye–Waller factors of HS(A) and LS(A) are practically the same. The Debye–Waller factor of HS(B), however, is smaller than that of the sum of LS(A) and HS(A) at higher temperatures, but it shows a more pronounced temperature dependence, eventually leading to nearly the same Debye–Waller factors of A and B at low temperatures. It is also noteworthy that no deviation from the linear behavior is observed not even at ~160 K, the temperature at which a splitting into two doublets is observed.

Figure 6 shows the effective magnetic moment of $[Fe(mtz)_6](BF_4)_2$ calculated from the susceptibilities measured with a Foner magnetometer. The moment of 5.32 μ_B at ~200 K is considerably larger than the spin-only value of 4.9 μ_B because of an orbital moment contribution, due to the fact that the complex molecules are nearly octahedral. The moment drops to 3.68 μ_B at ~60 K as expected from the fact that only 50% of the complexes undergo thermal spin transition. The further decrease of the moment of 3.52 μ_B at ~30 K may be due to a decrease of the orbital momentum contribution. Figure 6 also shows that the values obtained with decreasing temperature match those obtained with increasing temperature; no hysteresis is observed. From the susceptibilities a critical temperature T_c for the spin transition (i.e., the temperature at which the HS(A) fraction is 0.5) of 74.5 K is calculated. This is in accordance with the value of 74 K obtained from ^{57}Fe Mössbauer spectra.

Optical absorption spectra of $[Fe(mtz)_6](BF_4)_2$ were measured between 295 and 20 K with a single crystal (see Figure 7). The spectrum at 295 K consists only of the $^5T_2 \rightarrow {}^5E$ band of the HS state (~12300 cm^{-1}). The band is rather broad, and it is not possible to distinguish between the lattice sites A and B. Above 30000 cm^{-1} one sees the rise of the MLCT bands. Upon cooling

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Table I. Parameters of the ^{57}Fe Mössbauer Spectra of $[Fe(mtz)_6](BF_4)_2$ (Thermal Spin Transition) Obtained from a Fit with Lorentzian Lines. (Most of the Spectra Fitted with Only 1 Half-Width for Both Resonances of a Doublet[a])

	HS(A)				HS(B)				LS(A)			
T (K)	δ_{IS} (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	int (%)	δ_{IS} (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	int (%)	δ_{IS} (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	int (%)
295	0.940 (2)	1.125 (4)	0.224 (8)/0.254 (8)	100								
250	0.975 (1)	1.245 (4)	0.230 (6)/0.250 (8)	100								
200	1.004 (1)	1.397 (1)	0.232 (2)/0.240 (4)	100								
180	1.017 (1)	1.464 (2)	0.246 (4)/0.266 (6)	100								
170	1.025 (1)	1.497 (2)	0.250 (4)/0.254 (6)	100								
160	1.032 (1)	1.538 (6)	0.262 (4)/0.266 (6)	100								
150	1.036 (8)[b]	1.506 (30)	0.246 (3)[b]	57.6 (6.9)	1.036 (8)[b]	1.679 (40)	0.246 (6)[b]					
140	1.030 (2)	1.537 (25)	0.246 (18)	55.8 (18.1)	1.043 (3)	1.735 (40)	0.264 (20)					
130	1.034 (2)	1.523 (21)	0.252 (8)[b]	55.3 (2.7)	1.047 (3)	1.816 (22)	0.252 (8)[b]					
120	1.037 (2)	1.574 (6)	0.242(8)	60.5 (3.0)	1.047 (2)	1.939 (9)	0.234 (12)	38.7 (3.0)	0.40[c]	0.211[c]	0.115[c]	0.8[c]
110	1.039 (2)	1.592 (5)	0.244 (8)	55.7 (2.1)	1.049 (2)	2.021 (7)	0.246 (10)	41.3 (2.1)	0.40[c]	0.211[c]	0.115[c]	3.0 (1)
100	1.039 (2)	1.582 (6)	0.236 (4)	52.9 (1.1)	1.050 (4)	2.076 (8)	0.244 (6)	41.5 (1.0)	0.402[c]	0.211[c]	0.23[c]	5.6 (3)
95	1.041 (2)	1.591 (3)	0.236 (4)	52.1 (9)	1.051 (1)	2.119 (3)	0.242 (4)	41.4 (9)	0.402 (11)	0.211 (18)	0.23[c]	6.5 (3)
90	1.047 (2)	1.603 (4)	0.236 (4)	49.5 (1.0)	1.057 (2)	2.161 (4)	0.238 (6)	42.0 (1.0)	0.416 (10)	0.206 (17)	0.252 (17)	8.5 (5)
85	1.049 (1)	1.609 (3)	0.240 (4)	48.1 (7)	1.059 (1)	2.205 (3)	0.246 (4)	41.9 (6)	0.430 (6)	0.214 (9)	0.240 (18)	10.0 (3)
80	1.050 (2)	1.608 (3)	0.246 (4)	44.7 (8)	1.062 (1)	2.242 (3)	0.254 (4)	42.3 (7)	0.441 (5)	0.199 (8)	0.238 (16)	13.0 (4)
77	1.051 (2)	1.604 (2)	0.246 (4)	40.8 (6)	1.062 (1)	2.267 (3)	0.258 (2)	42.7 (6)	0.450 (3)	0.200 (5)	0.234 (10)	16.4 (3)
75	1.049 (2)	1.600 (4)	0.246 (4)	35.5 (6)	1.061 (1)	2.301 (1)	0.262 (2)	42.6 (6)	0.456 (2)	0.200 (4)	0.226 (8)	21.9 (3)
73	1.042 (5)	1.561 (20)	0.240 (12)	11.5 (5)	1.062 (1)	2.418 (2)	0.254 (4)	43.5 (4)	0.457 (1)	0.204 (2)	0.234 (4)	45.0 (3)
71	1.062 (16)	1.527 (32)	0.274 (30)	7.9 (7)	1.061 (1)	2.451 (3)	0.242 (4)	42.7 (5)	0.454 (2)	0.207 (3)	0.246 (6)	49.4 (5)
69	1.022 (26)	1.514 (52)	0.238 (32)	5.0 (1.0)	1.061 (2)	2.468 (4)	0.242 (6)	43.6 (8)	0.453 (2)	0.208 (3)	0.244 (8)	51.4 (8)
67	1.031 (12)	1.548 (36)	0.224 (32)	3.2 (4)	1.059 (1)	2.471 (2)	0.242 (2)	44.3 (3)	0.452 (1)	0.208 (1)	0.238 (2)	52.5 (3)
65	1.029 (14)	1.552 (38)	0.246 (36)	3.1 (4)	1.056 (1)	2.476 (2)	0.240 (2)	44.5 (3)	0.452 (1)	0.208 (1)	0.238 (2)	52.4 (3)
60					1.062 (2)	2.501 (4)	0.236 (10)	45.8 (6)	0.456 (4)	0.213 (3)	0.248 (12)	54.2 (6)
55					1.065 (1)	2.507 (3)	0.258 (8)	45.9 (5)	0.459 (4)	0.210 (1)	0.262 (10)	54.1 (5)
45					1.065 (2)	2.523 (4)	0.258 (10)	46.8 (9)	0.460 (6)	0.216 (4)	0.256 (8)	53.2 (8)
40					1.066 (2)	2.518 (5)	0.254 (8)	47.5 (8)	0.459 (5)	0.217 (4)	0.258 (8)	52.5 (8)
35					1.067 (2)	2.510 (4)	0.254 (6)	48.4 (7)	0.458 (5)	0.222 (4)	0.268 (8)	51.6 (7)
30					1.070 (1)	2.508 (2)	0.242 (6)	48.1 (3)	0.458 (2)	0.216 (2)	0.256 (6)	51.9 (3)
25					1.069 (2)	2.494 (4)	0.243 (6)	48.5 (9)	0.463 (6)	0.213 (4)	0.258 (4)	51.5 (8)
20					1.069 (2)	2.479 (2)	0.260 (6)	49.2 (3)	0.465 (2)	0.214 (2)	0.262 (6)	50.8 (6)
15					1.069 (2)	2.466 (4)	0.262 (8)	49.6 (8)	0.462 (5)	0.212 (4)	0.248 (16)	50.4 (8)
10					1.069 (2)	2.449 (4)	0.260 (6)	49.8 (7)	0.461 (5)	0.207 (4)	0.260 (14)	50.2 (7)

[a] If two values are given, the first corresponds to the high-velocity component of a doublet and the second corresponds to the low-velocity component. Intensities were evaluated from the areas of the Lorentzian lines. [b] Only one parameter for HS(A) and HS(B). [c] Parameter was not varied.

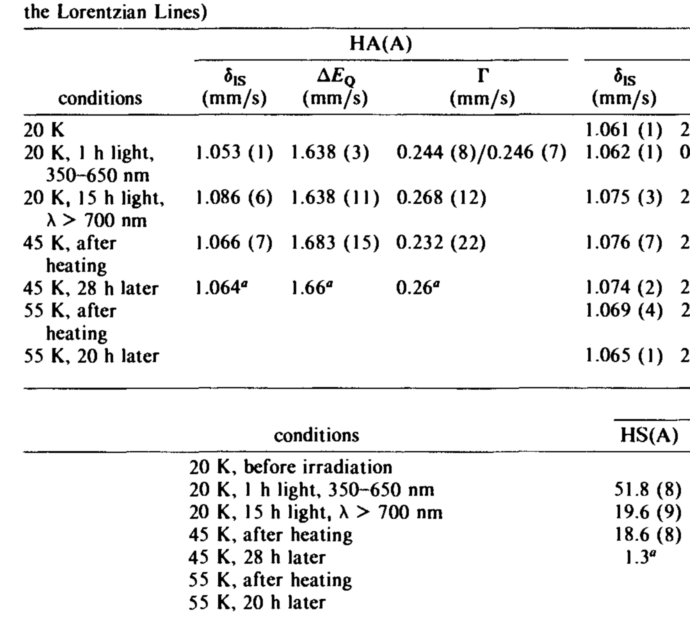

Figure 8. ^{57}Fe Mössbauer spectra of $[Fe(mtz)_6](BF_4)_2$ after various irradiation experiments (see text). The 20 K spectrum on top was obtained after slow cooling from 295 K.

below ~120 K, one can observe in addition the $^1A_1 \rightarrow {}^1T_1$ band (~18 200 cm^{-1}) and the $^1A_1 \rightarrow {}^1T_2$ band (~26 200 cm^{-1}) of the LS state. 10*Dq* for the HS state can be directly obtained from the maximum of the $^5T_2 \rightarrow {}^5E$ band as 12 300 cm^{-1}. 10*Dq* for the LS can be estimated using the following expression:[23]

$$10Dq(\mathrm{LS}) = E(^1T_{1g}) + \frac{E(^1T_{2g}) - E(^1T_{1g})}{4}$$

This way one finds a value of 20 200 cm^{-1}.

Light-Induced Spin Transition. Irradition experiments with light of different wavelengths regions from a Xe arc lamp with filters were carried out on crystals of $[Fe(mtz)_6](BF_4)_2$ that were first slowly cooled to ~20 K. The corresponding Mössbauer spectrum is depicted on top of Figure 8 (for parameters see Table II). It contains the two doublets arising from LS(A) and HS(B). If the crystals are irradiated with light of ~350–650 nm at 20 K, one observes a quantitative conversion of the LS(A) state into HS(A), which is known as the normal LIESST effect. The Mössbauer spectrum (see Figure 8, right branch) now contains the same two quadrupole doublets as those originating from the iron(II) HS(B) and HS(A) states in the temperature region between ~60 and ~160 K, and the quadrupole doublet of the LS(A) state has disappeared. The metastable HS(A) state has a practically infinitely long lifetime. Two Mössbauer spectra recorded within 24 h were identical within the errors. It relaxes back to the thermodynamically stable LS(A) state if the crystals are warmed to ≥45 K (within 4 days at 46 K). The kinetics of the HS(A) → LS(A) relaxation strongly deviates from simple exponential behavior, the rate constant increasing with increasing LS fraction. This well-known behavior is due to cooperative effects; it was discussed in detail in ref 24. Detailed kinetic investigations are in progress. The Mössbauer spectrum taken at 55 K (Figure 8,

Table II. Parameters of the ^{57}Fe Mössbauer Spectra of $[Fe(mtz)_6](BF_4)_2$ (Irradiation Experiments) Obtained from a Fit with Lorentzian Lines (Intensities Evaluated from the Areas of the Lorentzian Lines)

	HA(A)			HS(B)			LS(B)			LS(B)		
conditions	δ_{IS} (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	δ_{IS} (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	δ_{IS} (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	δ_{IS} (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)
20 K				1.061 (1)	2.463 (2)	0.260 (4)/0.273 (3)	0.457 (2)	0.209 (2)	0.262 (6)/0.271 (7)			
20 K, 1 h light, 350–650 nm	1.053 (1)	1.638 (3)	0.244 (8)/0.246 (7)	1.062 (1)	0.277 (3)	0.257 (6)/0.245 (7)						
20 K, 15 h light, λ > 700 nm	1.086 (6)	1.638 (11)	0.268 (12)	1.075 (3)	2.261 (7)	0.264 (6)	0.461 (10)	0.208 (56)	0.26 (6)	0.47 (1)	0.10 (6)	0.27 (6)
45 K, after heating	1.066 (7)	1.683 (15)	0.232 (22)	1.076 (7)	2.300 (15)	0.281 (28)	0.472 (5)	0.208^a	0.26^a	0.47^a	0.1^a	0.26^a
45 K, 28 h later	1.064^a	1.66^a	0.26^a	1.074 (2)	2.362 (2)	0.264 (6)	0.453^a	0.208^a	0.26^a	0.47^a	0.1^a	0.26^a
55 K, after heating				1.069 (4)	2.394 (9)	0.242 (12)	0.453^a	0.216^a	0.26^a	0.47^a	0.1^a	0.26^a
55 K, 20 h later				1.065 (1)	2.505 (5)	0.254 (6)	0.453^a	0.216^a	0.26^a			

	intensities			
conditions	HS(A)	HS(B)	LS(A)	LS(B)
20 K, before irradiation		49.1 (3)	50.9 (3)	
20 K, 1 h light, 350–650 nm	51.8 (8)	48.2 (8)		
20 K, 15 h light, λ > 700 nm	19.6 (9)	18.4 (8)	31.2 (42.0)	30.8 (42.3)
45 K, after heating	18.6 (8)	17.7 (6)	32.9 (2.2)	31.8 (2.0)
45 K, 28 h later	1.3^a	17.5 (3)	49.6 (7)	31.4 (6)
55 K, after heating		17.2 (6)	50.6 (1.4)	32.2 (1.3)
55 K, 20 h later		46.1 (5)	53.9 (5)	

[a] Parameter was not varied.

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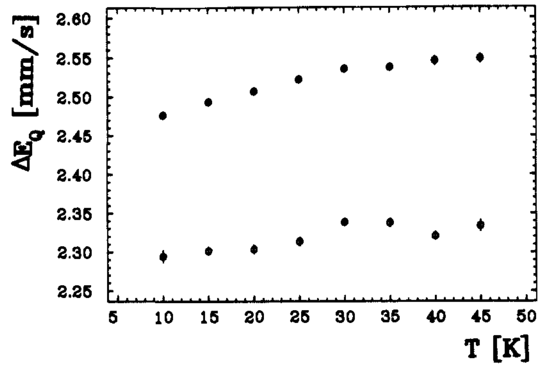

Figure 9. Quadrupole splitting ΔE_Q of the HS(B) doublet as a function of temperature: ●, before LIESST(L→H) (A molecules in the LS state); ϕ, after LIESST(L→H) (A molecules in the HS state).

Table III. Quadrupole Splitting ΔE_Q of the HS(B) Doublet before LIESST (L→H) (A Molecules in the LS State) and after LIESST (L→H) (A Molecules in the HS State)

	ΔE_Q (mm/s)		
T (K)	before LIESST	after LIESST	$\Delta(\Delta E_Q)$
10	2.477 (4)	2.295 (8)	0.182 (12)
15	2.494 (4)	2.302 (4)	0.192 (8)
20	2.507 (4)	2.304 (4)	0.203 (8)
25	2.522 (5)	2.314 (5)	0.208 (10)
30	2.536 (2)	2.339 (4)	0.197 (6)
35	2.538 (4)	2.338 (5)	0.200 (9)
40	2.546 (5)	2.321 (5)	0.225 (5)
45	2.549 (5)	2.334 (7)	0.215 (12)

bottom on the right) is identical with the one we started out with at 20 K (top of Figure 8).

As the iron–ligand bond length increases drastically (by ~20 pm[2]) in the course of the LS → HS transition, the crystal lattice will be strongly influenced, even if the spin transition is not accompanied by a crystallographic phase transition. The influence of the thermal spin transition on Mössbauer parameters, especially the quadrupole splitting, has been studied in detail in the past.[25] In $[Fe(mtz)_6](BF_4)_2$, the B-site molecules serve as a probe and ΔE_Q of HS(B) can be studied for the case that all A-site molecules are in the LS state as well as for the case that all are in the HS state without changing the temperature. It is therefore possible to distinguish between lattice contributions to the electric field gradient and temperature-dependent effects. At all temperatures between 10 and 45 K the quadrupole splitting ΔE_Q of HS(B) is around 0.2 mm/s larger if all A-site molecules are in the LS state rather than in the HS state (see Table III and Figure 9). Obviously only the (nearly temperature independent) lattice contribution of the electric field gradient of the B-molecules is changed, whereas the (temperature dependent) valence contribution remains unchanged.

In another series of irradiation experiments we again started out with crystals cooled to 20 K. After irradiating the crystals with red light ($\lambda \geq 700$ nm) at 20 K, we have obtained the Mössbauer spectrum as shown in Figure 8, left branch (middle). In fact, one recognizes that a partial conversion from HS(B) to LS(B) has taken place. The HS(B) quadrupole doublet has been diminished considerably in favor of a newly formed LS(B) doublet with a splitting of only ~0.1 mm/s, which overlaps heavily with the doublet of the LS(A) state because of their similar parameter values (see Table II).

This is the first time that such a spin-state conversion from the thermodynamically stable HS state to a metastable LS state by light has been observed. We shall refer to this phenomenon as LIESST (H → L) and the "normal" LIESST effect dealt with so far, viz. the spin-state conversion from the thermodynamically stable LS state to the metastable HS state, as LIESST (L → H).

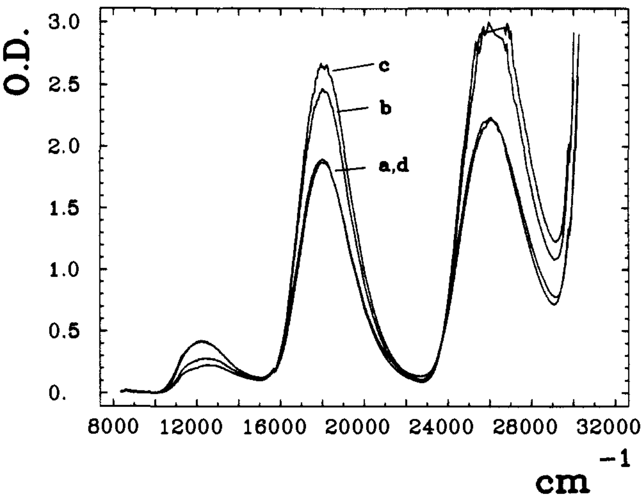

Figure 10. Single-crystal optical spectra of $[Fe(mtz)_6](BF_4)_2$: (a) at 20 K before irradiation, (b) after 20 min of irradiation with Xe arc lamp, filter, $\lambda > 700$ nm, (c) after 50 min of irradiation with Xe arc lamp, filter, $\lambda > 700$ nm, and (d) after warming to 65 K.

It was not possible under these irradiation conditions to achieve a complete HS(B) → LS(B) conversion, not even after 15 h of irradiation time with red light ($\lambda \geq 700$ nm) at 20 K. One notices also from the same Mössbauer spectrum (Figure 8, left, middle) that simultaneously with the HS(B) → LS(B) conversion a partial transformation of LS(A) → HS(A) (normal LIESST effect) has occurred as indicated by the reduced intensity of the LS(A) quadrupole doublet and the reappearance of the HS(A) quadrupole doublet (parameter values see Table II). The reason why LIESST (H → L) on lattice site B is not complete on the one hand, and why LIESST (L → H) simultaneously occurs partially in lattice site A with red light, is the following: The $^1A_1 \rightarrow {}^1T_1$ band of the LS state overlaps to some extent with the $^5T_2 \rightarrow {}^5E$ band of the HS state (see Figure 10). When irradiating with red light with such a broad wavelength region as in the present experiment, into the HS band causing LIESST (H → L), it is unavoidable to also excite (though only to a minor extent) the LS band causing LIESST (L → H). It was shown earlier that the quantum yield for LIESST (L → H) with green light is much larger than that for reverse LIESST with red light,[11] and we assume that this is similar in the present case. We tried to use filters that were transparent only for $\lambda > 780$ nm, but with no better results because too much intensity of the Xe arc lamp was lost. Undoubtly, further experiments with tunable lasers are needed for these photophysical experiments.

If, after irradiation with red light the crystals are warmed, the metastable HS(A) state relaxes back thermally to the LS(A) state at ~45 K, as seen from the Mössbauer spectrum on the bottom left of Figure 8, and in agreement with the annealing experiment described above (yielding the change in the Mössbauer spectra on going from Figure 8 right, middle to bottom). The metastable LS(B) state generated by LIESST (H → L) relaxes thermally back to HS(B) at temperatures above 55 K, as indicated by the change in the Mössbauer spectra on going from the bottom left to bottom right of Figure 8.

The LIESST (H → L) process in lattice site B could be confirmed by optical spectroscopy. Figure 10 shows optical spectra of $[Fe(mtz)_6](BF_4)_2$ recorded at 20 K. After 50 min of irradiation with light of $\lambda > 700$ nm (Xe arc lamp, filter) an increased LS fraction of 72% was obtained (50% before irradiation), but again it was not possible to convert the compound quantitatively to LS for the same reason as indicated above. After heating the crystal to ~65 K, we have measured again a HS fraction of 50% as before the irradiation.

4. Discussion

Electric Quadrupole Interaction at Lattice Sites A and B. One of the most interesting features of $[Fe(mtz)_6](BF_4)_2$ is the observation of only one quadrupole doublet above ~160 K, although

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[25] Köppen, H.; Meissner, E.; Wiehl, L.; Spiering, H.; Gütlich, P. *Hyperfine Interact.* **1989**, *52*, 29.

it is known from a crystal structure analysis[21] that the compound has two different lattice sites A and B for the iron(II) ions. Other Mössbauer investigations of compounds with different lattice sites for iron were done earlier, e.g., of $[Fe(HCOO)_2]\cdot 2H_2O$[26] or $[Fe(H_2O)_6]SO_4\cdot H_2O$,[27] but in those cases different resonance lines arising from the crystallographically inequivalent ions, at least broadened resonance lines, are observed. In $[Fe(mtz)_6](BF_4)_2$, however, the resonance lines are not broadened at all at temperatures above ~160 K. Therefore, the isomer shift and quadrupole splitting values and their temperature dependences must be *exactly* the same for the lattice sites A and B, and the question arises which mechanism could be considered responsible for this congruency of the quadrupole doublets in the temperature region above ~160 K.

Whatever the lattice process behind this phenomenon is, it does not appear to be caused by cooperative interactions between iron complex ions because the zinc-diluted complex $[Fe_{0.02}Zn_{0.98}(mtz)_6](BF_4)_2$ shows also only one doublet at elevated temperatures and two quadrupole doublets at lower temperatures. The same behavior was found in $[Fe_xZn_{1-x}(mtz)_6](ClO_4)_2$ ($0.005 \le x \le 0.8$), which was studied in more detail.[28] Furthermore, a crystallographic phase transition of first order can be ruled out. The structure of the compound remains unchanged down to 110 K, and the lattice constants *a*, *b*, and *c* shorten continuously with decreasing temperature.[21] This is in agreement with the temperature dependence of the effective thickness of the absorber (see above), which shows no deviation from linearity around 160 K. A phase change usually is accompanied by a discontinuity in the temperature dependence of the effective thickness or at least by a variation of the slope of $\ln (t_{eff}/T)$.[29,30] It should also be pointed out that the one doublet observed above ~160 K is not just an averaged doublet of the two doublets observed at lower temperatures. The HS(A) doublet has about the same quadrupole splitting as the one doublet at 160 K whereas ΔE_Q of HS(B) becomes much larger with decreasing temperature (see Figure 4). A relaxation process that just averages the hyperfine fields of A and B at elevated temperatures can, therefore, also be ruled out. The nature of the anion, however, affects the temperature at which the splitting into two doublets occurs. It is ~160 K for $[Fe(mtz)_6](BF_4)_2$ but ~130 K for the isomorphous compound $[Fe(mtz)_6](ClO_4)_2$, which behaves quite similar,[28] whereas it remains unchanged around ~130 K in mixed crystals of $[Fe_xZn_{1-x}(mtz)_6](ClO_4)_2$ ($0.005 \le x \le 0.84$)[28] even at lowest iron concentrations. Therefore, it seems to have no influence whether the complex cation is Fe^{2+} or Zn^{2+}, but it has an influence whether the anion is BF_4^- or ClO_4^-. It is known from crystal structure analysis of $[Fe(mtz)_6](ClO_4)_2$[21] and $[Zn(mtz)_6](BF_4)_2$[31] that the anions are disordered at room temperature. Therefore, it is possible that an order/disorder transition of BF_4^- or ClO_4^- is responsible for the splitting of the lines. Order/disorder transitions were considered responsible for line splittings and phase transitions in other systems investigated with the help of ^{57}Fe Moössbauer spectroscopy.[29,30,32] Unfortunately, no crystallographic investigations, neither at room temperature nor at lower temperatures, were carried out by these authors. However, the temperature-dependent Mössbauer studies clearly showed that the processes in those cases were first-order phase transitions, but this can definitely be ruled out for $[Fe(mtz)_6](BF_4)_2$.

Thermal- and Light-Induced Spin Transition at Lattice Site A. The absence of a hysteresis and the linearity of $\ln t_{eff}$ vs T in the course of the HS(A) $\rightleftarrows$ LS(A) spin transition indicate quite clearly that the thermal spin transition in $[Fe(mtz)_6](BF_4)_2$ is not accompanied by a crystallographic phase change.

Compared with other spin-crossover systems[2] the thermal spin transition of $[Fe(mtz)_6](BF_4)_2$ occurs at relatively low temperatures. As the entropy difference between the two spin states is of the same order (~40–50 J/K mol)[12,33] for most spin-crossover systems in the solid state, it can be concluded that the energy difference between the $^1A_1$ and the $^5T_2$ state is small in $[Fe(mtz)_6](BF_4)_2$ compared with other spin-crossover systems and that, therefore, the potential barrier between the two states is relatively high. Indeed the thermal spin transition is time dependent. Between 75 and 65 K it took always a few minutes until the system was in thermodynamic equilibrium, as found by optical spectroscopy. By rapid cooling notable HS fractions could be frozen in.

$[Fe(mtz)_6](BF_4)_2$ is another example of a spin-crossover compound exhibiting the LIESST effect in addition to those that have already been reported.[3,4,6-8,11] In principle iron(II) spin-crossover compounds can be switched between HS and LS by the LIESST effect and the reverse LIESST effect, respectively. This was discussed as a possible basis for the application of such materials for optical storage devices.[34] For this purpose, however, it is desirable to dispose of compounds in which the HS state is metastable at higher temperatures, at least above 77 K (liquid N_2). Although we have not yet reached this goal with the present system, the lifetimes of the excited HS(A) state of $[Fe(mtz)_6](BF_4)_2$ are longer than in all other pure iron(II) systems exhibiting the LIESST effect studied earlier. Even at 64 K it takes around 1 h until the HS(A) state has completely decayed, whereas in the $[Fe(ptz)_6](BF_4)_2$ complex investigated earlier it took only 5 min for the HS state to disappear at the same temperature.[35] Detailed kinetic studies of the HS(A) → LS(A) relaxation process in $[Fe(mtz)_6](BF_4)_2$ and mixed crystals thereof are in progress.

Light-Induced Spin Transition at Lattice Site B. The "normal" LIESST effect, which has so far been observed with iron(II) compounds exhibiting thermal spin crossover,[3,4,6-8] converts the LS state to the metastable HS state upon irradiation with green light into the spin singlet bands; we have symbolized this process by LIESST (L → H). A corresponding conversion of the thermodynamically stable HS state into the long-lived metastable LS state by light, denoted as LIESST(H→L), has been observed in the present work for the first time. Two requirements have to be fulfilled for this process to be successful:

(i) An appreciable potential barrier between the $^1A_1$ and the $^5T_2$ state must exist as shown in Figure 2. This is only the case, if the energy difference between the two states is not too large. Unfortunately this difference cannot be measured directly in HS complexes, but it can only be estimated for a certain iron complex.

(ii) The crucial point for LIESST(H→L) is the intersystem crossing process from the ^5E state, populated first by irradiation with red light, to the $^3T_1$ state, which is only possible if the $^3T_1$ state lies at lower energy than the ^5E state (see Figures 1 and 2). The energy of the $^3T_1$ state can also not be measured directly. Neither are there electronic transitions from the $^1A_1$ or $^5T_2$ states to the $^3T_1$ state in the absorption spectra nor emission from the $^3T_1$ state observed. For this reason only qualitative arguments can be used. An inspection of the Tanabe–Sugano diagram for d^6 complexes[5] leads to the following prediction: The weaker the ligand field (the more stable the $^5T_2$ state), the lower is the energy of the ^5E state and the higher is the energy of the $^3T_1$ state. For a rough qualitative consideration one can say that the probability for intersystem crossing from the ^5E state to the $^3T_1$ state is higher the larger the energy difference between the two states is. If the ligand field strength is weaker than a critical ligand field strength, the $^3T_1$ state is at higher energy than the ^5E state and intersystem crossing from the ^5E to the $^3T_1$ state is no longer possible. Consequently, a population of the $^1A_1$ state would also be impossible. Thus, for a successful demonstration of LIESST(H→L)

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in a HS complex the ligand field strength must be larger than that of the crossing point of $^3T_1$ with ^5E, but smaller of course, than the critical field strength for $^1A_f \rightleftharpoons {}^5T_2$ to occur.

Obviously, the B-site molecules of $[Fe(mtz)_6](BF_4)_2$ appear to fulfill both requirements, so that the formation of a metastable LS state could be demonstrated successfully for the first time. The fact that the HS(B) → LS(B) conversion was not quantitative in the present experiment is not frustrating at all. We know the reason, namely broad-band irradiation with the Xe arc lamp as already mentioned above, and we are convinced that the problem can be overcome by the use of a dye laser and irradiation at lower energies ($\lambda > 800$ nm). The lower the energy of excitation is, the less light is irradiated into the $^1A_1 \rightarrow {}^1T_1$ band and, therefore, the smaller will be the probability for LIESST(L→H). The fact that LIESST(L→H) was observed after irradiation with red light is indicative of a very low quantum yield for LIESST (H→L). Following the argumentation above the energy difference between the ^5E and the $^3T_1$ state must be small in $[Fe(mtz)_6](BF_4)_2$, and the ligand field of the B-molecules is close to the critical ligand field strength for intersystem crossing.

Noticeable thermal LS(B) → HS(B) relaxation is observed only above ~50 K, whereas the HS(A) → LS(A) relaxation is observed already at ~45 K. Therefore, the activation energy for the first process seems to be larger than that for the second process, but this is to be interpreted carefully because surely cooperative effects are also present. Only detailed kinetic measurements can lead to a reliable answer to the question whether the LS(B) → HS(B) relaxation process is influenced by cooperative effects or not. Also, kinetic measurements will yield the activation energy of the process, which is very important for the characterization of the potential barrier between the two states. We shall carry out such kinetic measurements as soon as the irradiation conditions have been optimized after installing a suitable laser source, which will yield a much higher population of the metastable LS(B) state after the LIESST(H→L) process.

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