Thermal and Light-Induced Spin Transition in $[\mathrm{Fe(bpen)X_2}]$ (bpen = 1,6-Bis(2-pyridyl)-2,5-diazahexane, X = $\mathrm{NCS^-}$, $\mathrm{NCSe^-}$)

T. Buchen,* H. Toftlund, and P. Gütlich

Dedicated to Professor Max Herberhold on the occasion of his 60th birthday

Abstract: The thermal and light-induced spin transitions in $[\mathrm{Fe(bpen)(NCS)_2}]$ and $[\mathrm{Fe(bpen)(NCSe)_2}]$ have been investigated by means of magnetic susceptibility and Mössbauer measurements. The HS → LS transition in $[\mathrm{Fe(bpen)(NCS)_2}]$ is detected at temperatures below 120 K ($T_{1/2}$ [when the fraction of high-spin species $\gamma_{HS} = 0.5$] = 68 K) with a residual HS fraction of 8% at 20 K. The transition is fairly abrupt and no hysteresis is observed, in contrast to earlier studies (ref. [8]). The generation of metastable HS states in $[\mathrm{Fe(bpen)(NCS)_2}]$ is achieved by rapid cooling of the sample and by irradiating the compound at low temperatures with light of appropriate wavelengths (LIESST). The HS → LS relaxation of the metastable spin states after rapid cooling is observed at temperatures between 35 and 42.5 K and shows strong deviations from single exponential behavior. The spin-transition behavior changes drastically on substitution of the thiocyanate ions by $\mathrm{NCSe^-}$. In $[\mathrm{Fe(bpen)(NCSe)_2}]$ a gradual and complete spin transition between 140 and 250 K is observed ($T_{1/2} = 181$ K). Irradiation of the compound with green light at low temperatures does not result in formation of long-lived metastable HS states. The spin-transition curves derived from magnetic susceptibility and Mössbauer studies show good agreement for each compound, and no hints of significantly different Lamb–Mössbauer factors for the HS and LS states are observed.

Keywords
iron complexes · kinetics · magnetic susceptibility · Mössbauer spectroscopy · spin crossover

Introduction

Thermal and light-induced high-spin (HS) → low-spin (LS) crossover is a well-known phenomenon in $3d^4$–d^7 transition-metal chemistry.[1] Complexes with 1,10-phenanthroline (phen) ligands have been studied in particular detail.[2] It is well known that substitution of the hydrogen atoms in the 2- and/or 9-position of the phen molecule in the diamagnetic LS complex $[\mathrm{Fe(phen)_3}]^{2+}$ changes the magnetic behavior of the compound dramatically. Instructive examples are also available for the effect of ligand replacement on the magnetic behavior of $[\mathrm{Fe(phen)_3}]^{2+}$. For instance it has been shown that replacing one phenanthroline molecule by two $\mathrm{NCS^-}$ ions forms the spin-crossover compound $[\mathrm{Fe(phen)_2(NCS)_2}]$, which has been the subject of several investigations.[3]

Toftlund suggested that a decrease in the number of chelate rings in the iron(II) complex will also influence the spin-transition behavior.[1a] In fact, replacing the two phen molecules in $[\mathrm{Fe(phen)_2(NCS)_2}]$ by a tetradentate ligand of the bispyridyldiamine or trispyridylamine type yielded a new class of spin-crossover compounds that have received considerable attention. For example, the comparison of the spin-transition curves, that is, the HS fraction γ_{HS} as a function of temperature derived from Mössbauer and magnetic susceptibility measurements, in the complexes $[\mathrm{Fe(tpa)(NCS)_2}]$ (tpa = tris(2-pyridylmethyl)amine) and $[\mathrm{Fe(bptn)(NCS)_2}]$ (bptn = 1,7-bis(2-pyridyl)-2,6-diazaheptane) has led to a heated discussion about the implications of different Lamb–Mössbauer factors for HS and LS species for the evaluation of the spin-transition curve.[4–6] This topic was also the main concern of a careful study of the spin-crossover system $[\mathrm{Fe_xZn_{1-x}(ptz)_6](BF_4)_2}$ ($0 < x \leq 1$; ptz = 1*n*-propyl-1H-tetrazole).[7]

In contrast to the above-mentioned complexes, which show gradual transitions at relatively high temperatures [$T_{1/2}$ ($\gamma_{HS} = 0.5$) > 150 K], $[\mathrm{Fe(bpen)(NCS)_2}]$ (bpen = 1,6-bis(2-pyridyl)-2,5-diazahexane) was found to undergo a fairly abrupt spin transition with hysteresis at temperatures below 100 K.[8] In this compound, however, the spin conversion shows a distinct time dependence; this permits the HS state to be trapped by rapid cooling of the sample. Therefore, it is questionable whether the observed hysteresis in the spin-transition curve really reflects the equilibrium of the system. The hysteresis may also be caused by the freezing-in of part of the HS fraction. In addition, neither a quantitative investigation and analysis of the HS → LS relaxation behavior nor an investigation of the light-induced spin-

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transition behavior has been performed. Moreover, no Mössbauer measurements have been used to study and characterize the system. All this has motivated us to reexanine the spin-transition behavior in [Fe(bpen)(NCS)$_2$].

In this paper we present a careful reinvestigation of the thermal spin transition in [Fe(bpen)(NCS)$_2$] by means of magnetic susceptibility and Mössbauer measurements. We also report on the light-induced spin-transition behavior in this compound and the HS → LS relaxation behavior after thermal spin-state trapping. Furthermore, we report the synthesis and spectral and magnetic characterization of the new spin-crossover compound [Fe(bpen)(NCSe)$_2$].

Results and Discussion

[Fe(bpen)(NCS)$_2$]: Temperature-dependent Mössbauer spectra of [Fe(bpen)(NCS)$_2$] are shown in Figure 1. Down to about 150 K the spectrum is dominated by an iron(II) HS doublet with an isomer shift δ(150 K) of 0.963 mm s^{-1} and a quadrupole splitting ΔE_Q(150 K) of 1.355 mm s^{-1} (see Table 1). Another iron(II) HS doublet with very weak intensity ($\delta = 0.75$ mm s^{-1}, $\Delta E_Q = 2.81$ mm s^{-1}) is also present and presumably originates from small traces of the precursor $FeSO_4 \cdot 7H_2O$. At $T \leq 110$ K an additional doublet appears with parameters typical for an iron(II) LS state ($\delta = 0.32$ mm s^{-1}, $\Delta E_Q = 0.34$ mm s^{-1} at 110 K). The intensity of this doublet increases with decreasing temperature, documenting a thermal spin transition of the iron(II) molecules. The HS fraction derived from the Mössbauer spectra decreases from 68.5% at 70 K to only 14.4% at 65 K. At 20 K a residual HS fraction of 8% is detected in the Mössbauer spectrum.

The drastic change in the spin state of more than 50% of the molecules in a temperature interval of only 5 K is also reflected in the Mössbauer parameters of the molecules. The isomer shift increases with decreasing temperature as expected.[9] However, near the transition temperature of 68 K, it passes through a maximum and then decreases on further lowering the temperature. This $\delta(T)$ dependence is unusual and is presumably due to the enormous internal pressure caused by the very abrupt spin transition in the present case. The pressure dependence of the isomer shift was treated by Williamson and explains, at least qualitatively, this observation.[10] In fact, similar observations have been made earlier.[11] The sudden increase in the quadrupole splitting seen in the region near the transition temperature is also a consequence of the abrupt spin transition and the accompanying changes in the lattice.

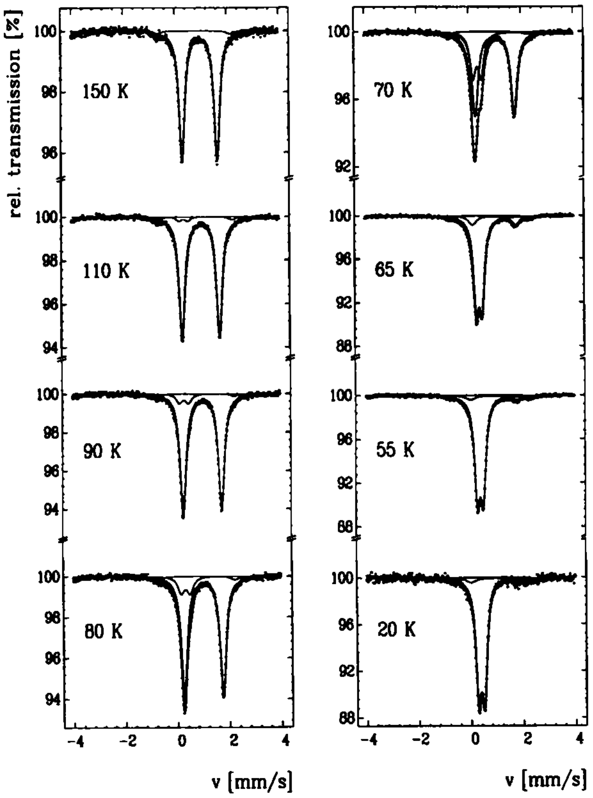

Fig. 1. Mössbauer spectra of [Fe(bpen)(NCS)$_2$] recorded between 150 and 20 K. At 150 K only a HS doublet with typical parameters for iron(II) HS is detected. At temperatures below 110 K a resonance doublet typical for iron(II) LS is observed, which increases in intensity with decreasing temperatures. At $T \leq 20$ K the Mössbauer spectrum is dominated by the iron(II) LS doublet, and a residual HS fraction of only ca. 8% (area fraction) is detected by Mössbauer spectroscopy.

The Mössbauer investigations were supported by measurements of the magnetic susceptibility. The derived spin-transition curve, together with the results of the Mössbauer investigations, is plotted in Figure 2. The spin transition is centered around 65 K. Within the temperature interval of 65 ± 5 K, approximately 55% of the molecules change their spin state. The transition temperature $T_{1/2}$ has been determined as 68 K. No hysteresis could be observed, which contradicts results reported earlier.[8] As already noticed by Toftlund et al., the rate of the spin transition is comparatively slow. This may have led to the observation of hysteresis by Toftlund and coworkers. We assume that some metastable HS fraction has been frozen in by

Table 1. Mössbauer parameters in [Fe(bpen)(NCS)$_2$].

		HS			LS		
T (K)	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	$\Gamma/2$ (mm s^{-1})	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	$\Gamma/2$ (mm s^{-1})	γ_{HS}
150	0.963(1)	1.355(3)	0.131(2)	–	–	–	100
120	0.978(1)	1.421(2)	0.133(2)	0.32 [a]	0.34 [a]	0.13 [a]	98.2(0.6)
110	0.983(1)	1.44(2)	0.135(2)	0.32 [a]	0.34 [a]	0.13 [a]	97.0(0.5)
100	0.988(1)	1.464(1)	0.135(2)	0.24(2)	0.40(4)	0.15(3)	94.7(0.8)
90	0.995(1)	1.481(2)	0.136(2)	0.30(15)	0.35(3)	0.14(2)	92.9(0.7)
80	1.003(1)	1.499(1)	0.136(2)	0.32(1)	0.35(2)	0.144(14)	87.7(0.7)
70	1.020(1)	1.495(3)	0.140(2)	0.348(3)	0.313(6)	0.130(4)	68.5(0.7)
65	0.966(1)	1.64(2)	0.14 [a]	0.394(1)	0.227(1)	0.125(1)	14.4(1.0)
60	0.969(15)	1.67(29)	0.14 [a]	0.396(1)	0.225(1)	0.122(1)	11.7(1.2)
55	0.922(23)	1.766(44)	0.14 [a]	0.395(1)	0.226(1)	0.124(1)	8.5(1.2)
40	0.926(63)	2.01(12)	0.14 [a]	0.395(1)	0.229(2)	0.126(2)	7.2(2.7)
20	0.94(5)	1.83(11)	0.14 [a]	0.400(1)	0.230(3)	0.120(3)	8.1(2.6)

[a] Parameter fixed.

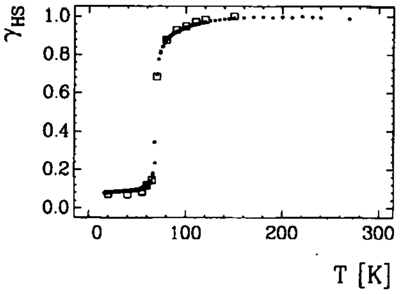

Fig. 2. The HS fraction $\gamma_{HS}(T)$ determined by Mössbauer spectroscopy (□) and magnetic susceptibility measurements (•) in [Fe(bpen)(NCS)$_2$]. A thermal spin transition is observed below 110 K. The transition is relatively abrupt, without hysteresis, and a residual HS fraction of ca. 8% is detected at $T \leq 20$ K.

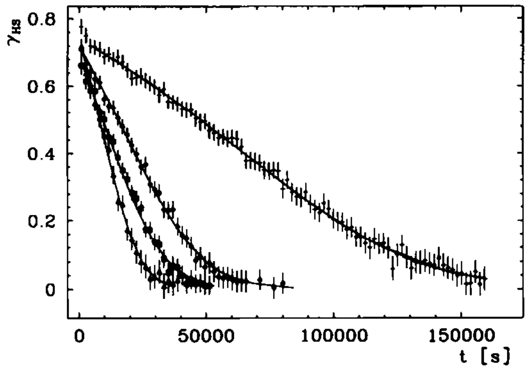

Fig. 4. HS → LS relaxation curves for [Fe(bpen)(NCS)$_2$] recorded at 35 (+), 37.5 (◇), 40 (□), and 42.5 K (△) after thermal trapping of the HS state. Each point represents the HS fraction derived from a single Mössbauer spectrum recorded for 30 min. The relaxation curves were corrected by subtracting the residual HS fraction of 8%, which is also seen in the Mössbauer low-temperature spectra. The relaxation curves deviate considerably from single exponential behavior and were fitted according to Equation (3).

cooling the sample too fast and that the reported magnetic susceptibility data of Toftlund et al. are not the thermodynamic equilibrium values. Another hint at this interpretation is the fact that we observed a residual HS fraction of only 8% whereas Toftlund et al. found a residual HS fraction of ca. 30% at 20 K. The spin-transition curves derived from Mössbauer and magnetic susceptibility investigations are identical. Thus our assumption of equal Lamb–Mössbauer factors for the HS and LS isomers in [Fe(bpen)(NCS)$_2$] is justified.

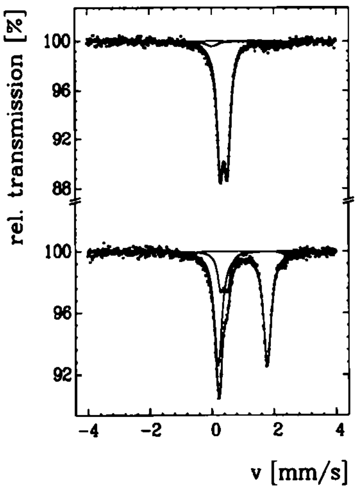

Fig. 3. Mössbauer spectra of [Fe(bpen)(NCS)$_2$] at 20 K after slow and rapid (from 150 to 20 K within ca. 2 min) cooling of the sample to 20 K (above and below, respectively). A large proportion of HS species can be frozen in owing to the slow kinetics of the spin transition. Over several runs the HS fraction detected at 20 K after rapid cooling was always greater than 70%.

Because of the slow kinetics of the HS → LS transition it is possible to trap the HS state by rapidly cooling the sample. Figure 3 presents the spectra obtained at 20 K after very slow and rapid (from ca. 150 K to 20 K within about 2 min) cooling. It is obvious that a large proportion of HS molecules can be frozen in. In several runs the metastable HS fraction obtained by rapid cooling of the sample was always greater than ca. 70%. After subsequent heating to a temperature range of 35–42.5 K the HS → LS relaxation behavior of the metastable HS states can be followed by Mössbauer spectroscopy. At the end of the relaxation process a constant HS fraction of around 8% is observed, which corresponds to the residual HS fraction at low temperatures detected in the course of the thermal spin transition. If we substract the fraction of residual HS molecules and consider only the fraction of molecules showing thermal spin transition in [Fe(bpen)(NCS)$_2$] we obtain the HS → LS relaxation curves, that is, the HS fraction γ_{HS} as a function of time, presented in Figure 4. Each data point represents the HS fraction derived from a single Mössbauer spectrum recorded for 30 min. The relaxation curves show large deviations from single exponential behavior; this is caused by the cooperativity of the spin transition. The HS → LS relaxation behavior after LIESST (light-induced excited spin state trapping) in [Fe(ptz)$_6$](BF$_4$)$_2$ was studied in detail by Hauser. He observed sigmoidal HS → LS relaxation curves that could be explained phenomenologically by assuming a linear dependence of the activation energy on the HS fraction.[12] Equations (1)–(3) were proposed by Hauser to

$$\frac{-d\gamma_{HS}}{dt} = k(\gamma_{HS})\cdot\gamma_{HS} \tag{1}$$

$$k(\gamma_{HS}) = A\exp\left(\frac{-E_a(\gamma_{HS})}{k_BT}\right) = A\exp\left(\frac{-(Ea+\gamma_{HS}E_a^*)}{k_BT}\right) \tag{2}$$

$$k(\gamma_{HS}) = k_0\exp\left(\frac{-E_a^*}{k_BT}\cdot\gamma_{HS}\right) \tag{3}$$

describe the HS → LS relaxation in this spin-crossover system. From a least-squares fit of the experimental data with the free parameters k_0 and E_a^* we obtain the theoretical relaxation curves (solid lines in Fig. 4), which fit the experimental curves quite well. The rate constants k_0 are 4.04×10^{-5}, 9.06×10^{-5}, 1.17×10^{-4}, and $1.84\times10^{-4}\,s^{-1}$ at 35, 37.5, 40, and 42.5 K, respectively.

The ln(k_0) data derived from the relaxation curves and plotted against $1/T$ yield a nearly straight line. However, the derived preexponential factor A (of less than 10 s^{-1}) is unreasonably small for a thermally activated spin transition. Therefore we suggest that tunneling is the predominant mechanism for the HS → LS relaxation in the temperature range under investigation. Similar behavior has been observed for the spin-crossover complex [Fe(otz)$_6$](BF$_4$)$_2$ (otz = 1*n*-octyl-1 H-tetrazole).[13]

The additional activation energy E_a^* reflects the cooperativity of the spin transition. From our fits of the experimental relaxation curves we obtain a mean value of $E_a^* = 60$ cm^{-1} (fit parameter $E_a^* = 62$, 57, 57, and 63 cm^{-1} at 35, 37.5, 40, and 42.5 K). This is only ≈35% of the value derived for the spin-crossover system [Fe(ptz)$_6$](BF$_4$)$_2$[12b] and is probably caused by the low cooperativity of the spin transition in [Fe(bpen)(NCS)$_2$] compared with the [Fe(ptz)$_6$](BF$_4$)$_2$ system. It is important to mention that the abruptness of the spin transition at relatively low temperatures is no hint at large interactions between the spin-changing molecules.[14]

The generation of metastable spin states can also be achieved by irradiating the sample with green light (LIESST). Figure 5 shows the Mössbauer spectra recorded at 10 K before and after irradiation. A metastable HS fraction of about 40% could be obtained. The incompleteness of the HS → LS conversion is most probably due to the fact that we used a broad-band excita-

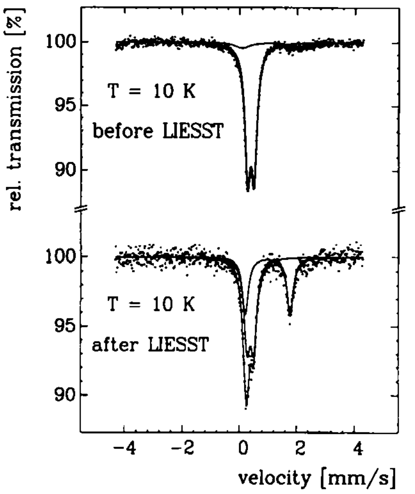

Fig. 5. Mössbauer spectra of [Fe(bpen)(NCS)$_2$] recorded at 10 K before (above) and after (below) irradiation with green light. It is obvious that a partial LS → HS conversion has resulted from irradiation of the sample.

tion of the LS state, whereby partial backconversion HS → LS is effected by hitting the $^5T_2 \rightarrow {}^5E$ absorption band. This effect has been discussed in detail in ref. [11]. Unfortunately, a quantitative investigation of the HS → LS relaxation after LIESST at 10 K turned out not to be very promising because of the low proportion of the HS species. Therefore, only a minor part of the relaxation curve at higher temperatures is accessible. At any rate, the observed deviation from single-exponential relaxation of the thermally trapped HS molecules, that is, the dependence of activation energy on the γ_{HS} fraction, which is indicative of a self-acceleration process, provides evidence for the existence of cooperative interactions during the HS → LS relaxation. There is no doubt that this applies also to the relaxation processes after LIESST.

[Fe(bpen)(NCSe)$_2$]: The thermal spin transition in [Fe(bpen)(NCSe)$_2$] was also investigated by Mössbauer and magnetic susceptibility measurements. Some representative Mössbauer spectra as a function of temperature are shown in Figure 6. At 260 K the spectrum consists of an iron(II) HS doublet ($\delta = 0.902$ mm s^{-1}, $\Delta E_Q = 0.916$ mm s^{-1}, see Table 2), and a doublet originating from some iron(III) impurities. At 230 K an additional doublet with $\delta = 0.39$ mm s^{-1} and $\Delta E_Q = 0.2$ mm s^{-1} (typical for iron(II) in the LS state) is observed. The intensity of this doublet increases with decreasing temperature at the expense of the Fe(II) HS doublet. The iron(II) HS doublet is no longer observed in the Mössbauer spectra at $T \leq 100$ K; only the doublet of the small fraction of an iron(III) HS impurity remains next to the dominant iron(II) LS doublet. Thus, the Mössbauer spectra prove the occurrence of a gradual and complete $^5T_2 \rightarrow {}^1A_1$ spin transition in [Fe(bpen)(NCSe)$_2$]. Again, the Mössbauer measurements were supported by magnetic susceptibility measurements. Since the Mössbauer spectra revealed that there are also iron(III) impurities present in the sample under study, the magnetic data were corrected for the iron(III) species by substracting from the measured magnetic susceptibility data the contribution $\chi(T)$ arising from the iron(III) species, which was extrapolated from the magnetism below 100 K, where $\chi(T)$ results only from the iron(II) LS and the impurity. The derived spin-transition curve is plotted in Figure 7. This correction pro-

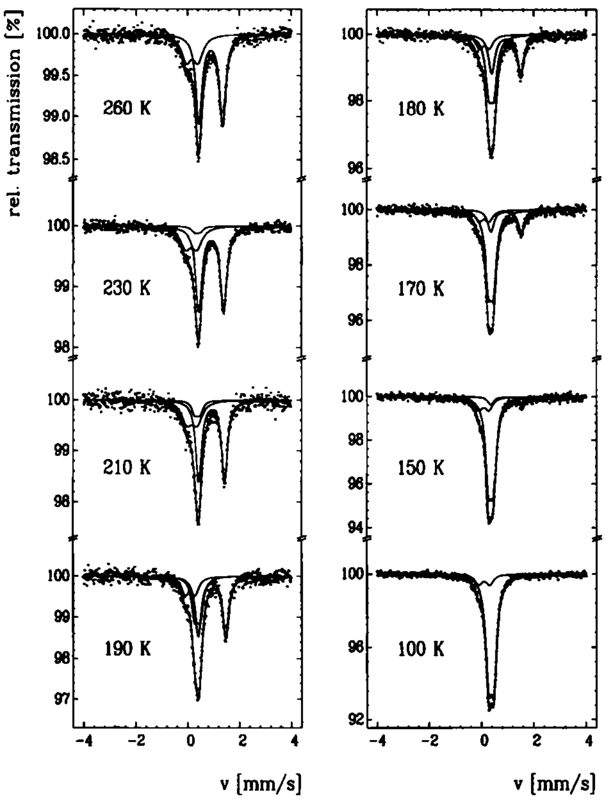

Fig. 6. Mössbauer spectra of [Fe(bpen)(NCSe)$_2$] measured in the temperature range 260–100 K. At 260 K the spectrum is dominated by a doublet corresponding to iron(II) HS ($\delta \approx 1$ mm s^{-1}; $\Delta E_Q \approx 1.5$ mm s^{-1}). A doublet with a small quadrupole splitting and an isomer shift typical for iron(III) HS is also present. The doublet at 230 K has parameters typical for iron(II) LS. The intensity of this doublet increases with decreasing temperature until at 100 K only the resonances of the iron(II) LS state and the doublet originating from the iron(III) impurities are observed.

Table 2. Mössbauer parameters in [Fe(bpen)(NCSe)$_2$].

	HS			LS			
T(K)	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	$\Gamma/2$ (mm s^{-1})	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	$\Gamma/2$ (mm s^{-1})	γ_{HS}
260	0.902(8)	0.916(16)	0.147(8)	–	–	–	100
240	0.913(6)	0.956(13)	0.146(6)	0.39 [a]	0.2 [a]	0.13 [a]	95.4(3.5)
230	0.928(5)	0.96(1)	0.146(6)	0.39 [a]	0.2 [a]	0.13 [a]	94.0(3.1)
220	0.935(6)	0.99(1)	0.143(7)	0.39 [a]	0.2 [a]	0.13 [a]	89.2(3.5)
210	0.940(7)	1.00(1)	0.137(8)	0.39 [a]	0.2 [a]	0.13 [a]	86.5(4.4)
200	0.947(6)	1.02(1)	0.137(8)	0.39 [a]	0.2 [a]	0.13 [a]	82.9(4.5)
190	0.955(7)	1.060(14)	0.13(1)	0.393(14)	0.210(26)	0.12(4)	62.1(2.4)
180	0.956(8)	1.11(2)	0.13(1)	0.387(8)	0.195(14)	0.12(1)	44.2(1.7)
170	0.956(11)	1.157(22)	0.13(2)	0.379(5)	0.187(8)	0.12(1)	25.3(1.6)
150	0.977(23)	1.206(47)	0.13 [a]	0.385(3)	0.188(5)	0.12(1)	9.3(1.3)
100	–	–	–	0.393(3)	0.199(3)	0.134(4)	0

[a] Parameter fixed.

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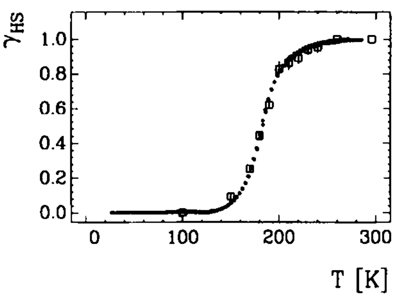

Fig. 7. The HS fraction $\gamma_{HS}(T)$ in [Fe(bpen)(NCSe)$_2$] derived from Mössbauer (□) and magnetic susceptibility measurements (•). A gradual and complete HS → LS transition is detected in the temperature range from ca. 250 to 140 K.

cedure affects the spin-transition curve by only about 2% in the HS fraction, thus implying that the amount of iron(III) impurity is very small. The fact that the area ratio of the iron(III) impurity and the iron(II) spin-crossover system in the Mössbauer spectra is larger than 2% is probably caused by the correspondingly different Lamb–Mössbauer factors. The spin transition in [Fe(bpen)(NCSe)$_2$] occurs at temperatures between approximately 250 and 140 K. It is of the gradual type ($T_{1/2} = 181$ K) and is complete at 140 K; no hysteresis is observed.

The formation of long-lived metastable HS states by irradiation of the complex with green light at low temperatures failed in this case. This is explained on the basis of the model developed by Hauser, who studied the HS → LS relaxation kinetics after laser excitation in a series of iron(II) complexes with Fe–N$_6$ cores.[15–17] He observed a thermally activated relaxation behavior at elevated temperatures and a nearly temperature-independent tunneling mechanism for the HS → LS relaxation at low temperatures. The low-temperature tunneling rate depends, on the one hand, on the so-called Huang–Rhys factor,[1e] which is a measure of the horizontal displacement of the potentials of the HS and LS states, and, on the other hand, on the energy gap between the HS and LS states, which is the crucial paramater for the low-temperature tunneling rate and is reflected by the spin-transition temperature $T_{1/2}$. Hauser observed an increase in the low-temperature tunneling rate with increasing $T_{1/2}$ (inverse energy-gap law). In [Fe(bpen)(NCSe)$_2$] the energy gap estimated from the thermal spin-transition temperature is quite large and therefore a fast relaxation of the metastable spin states is expected to take place at low temperatures. In fact, no long-lived metastable HS states can be observed by Mössbauer spectroscopy in [Fe(bpen)(NCSe)$_2$].

The observation of the long-lived metastable HS states in [Fe(bpen)(NCS)$_2$] after LIESST and thermal trapping is in good agreement with this model. The energy gap between the LS and HS states is considerably smaller than for [Fe(bpen)(NCSe)$_2$] (estimated from the low thermal transition temperature $T_{1/2} = 68$ K), and this accounts for the observed slow relaxation at low temperatures.

Experimental Procedure

Susceptibility measurements: The magnetic susceptibility $\chi(T)$ of [Fe(bpen)(NCS)$_2$] and [Fe(bpen)(NCSe)$_2$] between 20 K and 295 K was measured with a Foner magnetometer equipped with a helium flow cryostat in an external field of 1 T. The diamagnetic corrections for the ligands were obtained from Pascal constants. The HS fraction as a function of temperature was calculated from the measured susceptibilities, assuming Curie behavior for the pure compound in the HS state and temperature-independent paramagnetism for the LS state (400×10^{-6} cm^3 mol^{-1}).

Mössbauer spectroscopy: Mössbauer spectra of [Fe(bpen)(NCS)$_2$] and [Fe(bpen)(NCSe)$_2$] were recorded between 10 and 295 K with a conventional Mössbauer spectrometer. The ^{57}Co/Rh source was kept at room temperature. All isomer shifts are given with respect to the source. The samples were sealed into polished plexiglass containers (3 cm^2, ca. 7 mg Fe cm^{-2}) and mounted in a helium flow cryostat (CF 506, Oxford Instruments) equipped with windows of transparent mylar foil. The samples were irradiated by a Xe arc lamp, with a water bath as IR filter. For LIESST experiments a filter with maximum transmission between 350 and 650 nm was used. The Mössbauer spectra were fitted to Lorentzians by the program MOSFUN [18], assuming equal Lamb–Mössbauer factors for the HS and LS states. The lines of the quadrupole doublets were fitted with equal intensities and no texture effects were considered.

Sample preparation: The ligand 1,6-bispyridyl-2,5-diazahexane (bpen) was prepared following the procedure described by Newkome et al. [19]. [Fe(bpen)(NCS)$_2$] and [Fe(bpen)(NCSe)$_2$] were synthesized as in ref. [8]. The purity of the complexes was checked by elemental analysis. [Fe(bpen)(NCS)$_2$], found (calcd.): C 46.06 (46.38), H 4.46 (4.38), N 20.19 (20.28); [Fe(bpen)(NCSe)$_2$]: C 38.35 (37.82), H 3.61 (3.57), N 16.51 (16.54).

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