



Characterization of the light induced excited spin state of a heterometallic FePt₂ complex by high-field Mössbauer spectroscopy

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Abstract In order to study the interaction of light with iron containing complexes we have built a dedicated sample holder based on fiber optics, which allows exposing iron containing samples with external light sources during Mössbauer spectroscopic experiments both at low temperatures down to $T = 4.2$ K and high fields up to $B = 5$ T. With this set-up it was possible to study light induced spin state trapping (LIESST) of a heterometallic trinuclear FePt₂ spin crossover (SCO) complex. The analysis of the field dependent Mössbauer spectra obtained at 4.2 K under illumination with red laser light at 635 nm shows the presence of a LIESST state with a zero field splitting of $D = 5.3$ cm⁻¹ and a rhombicity parameter of $E/D = 0.14$.

Keywords Mössbauer spectroscopy · LIESST · High magnetic fields · Spin crossover complexes

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1 Introduction

The spin state of iron(II) containing spin crossover (SCO) complexes can be switched reversibly between the iron's low spin ($S = 0$, LS) and its high spin ($S = 2$, HS) state by variation of temperature, and external pressure but also under light irradiation [1]. Some SCO complexes have the intriguing propensity that irradiation with light at low temperatures of typically <40 K lead to a light excited spin state trapping, a phenomenon which is called LIESST effect [2]. This effect has been studied for a variety of systems but only recently novel SCO systems occurred which have in addition to SCO active iron centers optically active components which may act even as optical spin state reporters. Very recently, the Ruben group developed a heterometallic trinuclear FePt_2 spin crossover (SCO) complex which contains a photoactive Pt ligand system in combination with an SCO active iron center [3]. In the solid state this compound has two conformations: A slightly bent molecular conformation which hinders SCO of the central iron(II) and an almost linear conformation which shows reversible SCO with a transition temperature of 268 K. Using Mössbauer spectroscopy it has been found that the linear conformation of FePt_2 is also LIESST active [3]. Here we report on the electronic properties of the LIESST state of this compound using field dependent Mössbauer spectroscopy. For that purpose we have built a dedicated sample holder based on fiber optics, which allows exposing iron containing samples with external light sources during Mössbauer spectroscopic experiments both at low temperatures down to $T = 4.2$ K and high fields of up to $B = 5$ T.

2 Materials and methods

The FePt_2 complex ($\text{C}_{80}\text{H}_{86}\text{B}_4\text{F}_{16}\text{FeN}_{16}\text{Pt}_2$) **1** was prepared according to the protocol given in [3]. A structural view of the straight **1^L** and of the bent conformation **1^H** of the molecule is shown in Fig. 1. The complex was prepared using metallic ^{57}Fe in powder form which enabled us to prepare a sufficiently thin sample which was embedded in between two polyethylene foils glued together with polyacrylate glue in order to reach optimal optical excitation. The sample was mounted in a specially designed sample holder for optical experiments. A schematic sketch of the design of the sample holder including sample rod and optical components is shown in Fig. 2. The sample rod is equipped with a DN50 flange and has four vacuum tight feedthroughs which have multimode (MM) FC/PC connectors with a numerical aperture of 0.22. This enables mounting of fiber coupled lasers and/or LEDs in a range of 190–1100 nm. The fiber coming from the light source is split into 4 and all four ports have been used for the experiment. In order to allow sufficient illumination of the whole sample from both sides 4 MM fibers were chosen which have a high numerical aperture of 0.39 and a core diameter of 400 μm . Fibers were purchased from Thorlabs®. Illumination in this study was performed with a continuous wave diode laser (CLDT-635-50G-SMA, TOPAG®) the optical power of which was determined with a power meter to 81 mW. The sample rod was mounted into a closed-cycle cryostat equipped with a superconducting magnet the details of which have been published earlier [4].

The Mössbauer spectra presented in this study were analyzed by means of the spin Hamiltonian formalism describing a paramagnetic iron with spin $S = 2$ according to the following electronic spin Hamiltonian which is used to calculate spin expectation values $\langle \hat{S} \rangle$ [5]:

$$\hat{H}_S = D[\hat{S}_z^2 - S(S+1)/3] + E[\hat{S}_x^2 - \hat{S}_y^2] + \mu_B \vec{S} \cdot \vec{g} \cdot \vec{B}. \quad (1)$$

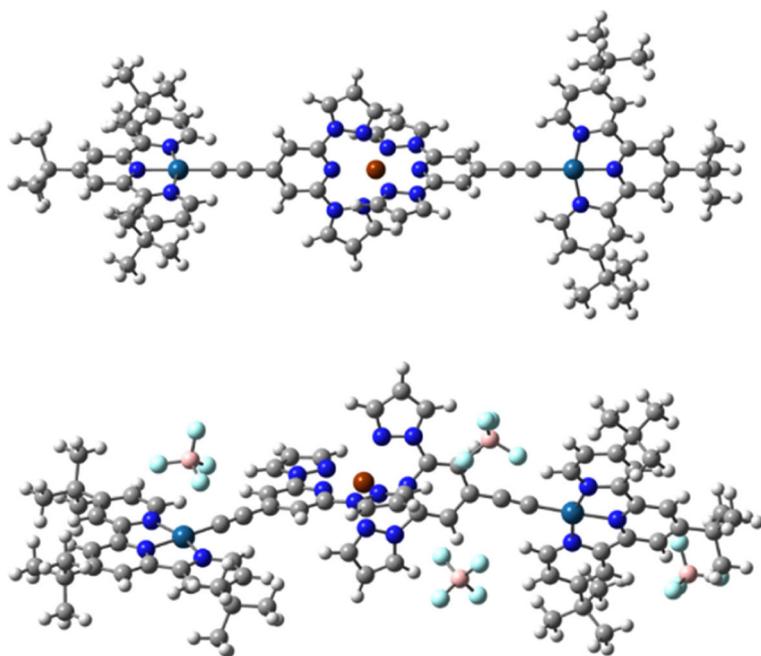


Fig. 1 Structural view of the straight conformation 1^L that is SCO active and shows LIESST after irradiation with red light (top) in comparison to the bend conformation 1^H which only shows a HS state (below) taken from [3]

Here D is the zero field splitting and E/D the rhombicity parameter. Mössbauer spectra were simulated using (1) together with the nuclear Hamiltonian:

$$\hat{H}_N = \frac{eQV_{zz}}{4I(2I-1)} \left[3\hat{I}_z^2 - I(I+1) + \eta \left(\hat{I}_x^2 - \hat{I}_y^2 \right) \right] - g_N \mu_N \vec{I} \cdot \vec{B} + \langle \vec{S} \rangle \cdot \vec{A} \cdot \vec{I} \quad (2)$$

Here I denotes the spin quantum number of the nuclear states, Q the nuclear quadrupole moment, V_{zz} the z -component of the electric-field gradient (efg) tensor, $\eta = (V_{xx} - V_{yy})/V_{zz}$ the asymmetry parameter of the efg, \vec{A} the hyperfine coupling tensor which couples $\langle \vec{S} \rangle$ to the nuclear spin \vec{I} and g_N the nuclear g -factor.

3 Results and discussion

The Mössbauer spectra of **1** obtained at $T = 4.2$ K in various external magnetic field up to $B = 5$ T applied parallel to the to the γ -beam are shown in Fig. 3. The Mössbauer spectrum obtained in a field of 200 mT has been analyzed using three components (Fig. 3a). Component 1 with 7% rel. area which has $\delta = 0.40$ mms $^{-1}$ and $\Delta E_Q = 0.75$ mms $^{-1}$ represents iron(II) centers which remained in their LS state during illumination. The Mössbauer parameters of component 1 correspond to those of the LS iron(II) in the 1^L conformation of the molecule as has shown previously [3]. Component 2 contributes with 50% relative area to the spectrum and has been fixed in the simulation with $\delta = 1.11$ mms $^{-1}$ and $\Delta E_Q = 3.43$ mms $^{-1}$. These parameters reflect HS iron(II) centers in the bend conformation

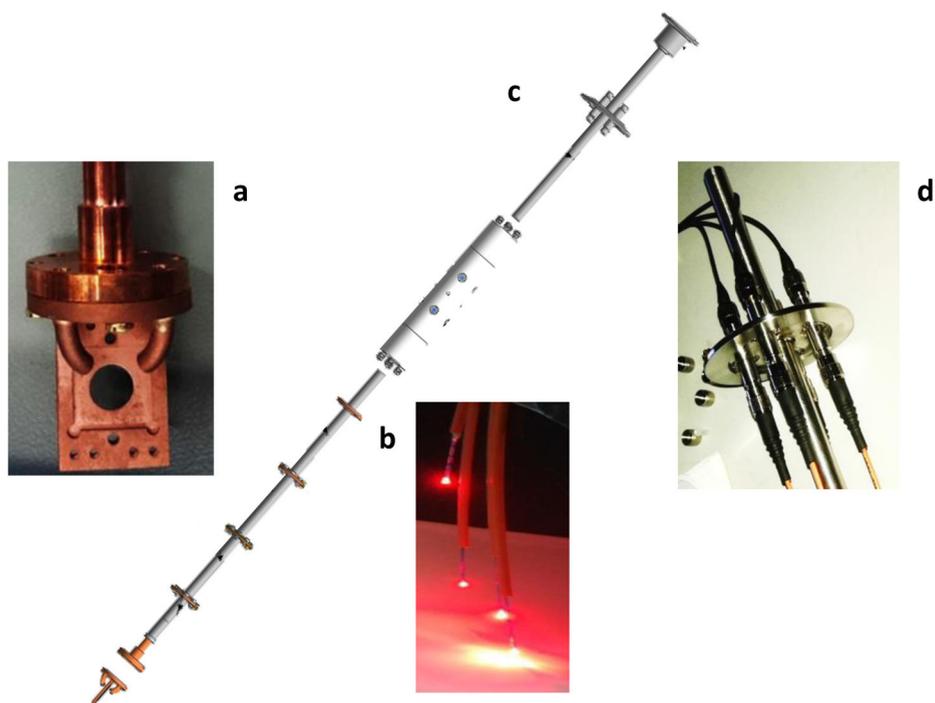


Fig. 2 Sample holder which shows copper tubing (a) which during the experiment contain scissor cut optical fibers (b) illuminating the sample. The sample rod (c) is equipped with four special optical feed-throughs (d)

of the complex which have been shown not to be SCO active. Both isomer shift and quadrupole splitting are identical to the ones reported for the iron(II) in the 1^H conformation of the molecule [3]. This strategy allowed to analyze the whole set of field dependent Mössbauer spectra displayed in Fig. 3a–h with one consistent data set representing 7% diamagnetic ($S = 0$) iron(II) in the 1^L conformation, 50% HS iron(II) in the non SCO active 1^H conformation and the remaining 43% representing HS iron(II) in its LIESST state. The LIESST state (comp. 3) shows $\delta = 1.03 \text{ mms}^{-1}$, a slightly lower value than HS iron(II) in the 1^H conformation (Table 1).

Increasing the external magnetic field leads to an increase in the magnetic splitting of the Mössbauer spectra which is typical for integer spin species. In order to reproduce their field dependency the Mössbauer spectra have been analyzed by means of the spin-Hamiltonian formalism using $S = 0$ for comp. 1 and $S = 2$ for comp. 2 and 3, respectively. The zero field splitting D of the HS iron(II) in the non SCO active 1^H conformation has been determined to $D = 2.1 \text{ cm}^{-1}$ previously by field and temperature dependent Mössbauer spectroscopy. The same holds for its rhombicity parameter $E/D = 0.23$ [3]. Therefore, we have fixed the corresponding parameters (see Table 1) including the hyperfine coupling tensor in the simulations for comp. 2. In this way the number of free parameters have been reduced considerably and the whole data sets shown in Fig. 3 have been fitted simultaneously by only letting the parameters of comp. 3 free. In this way a unique set of Mössbauer parameters of the LIESST state of 1^L could be determined. A zero field splitting parameter of $D = 5.3 \text{ cm}^{-1}$ and a rhombicity parameter $E/D = 0.14$ show that the LIESST state of 1^L is not electronically equivalent to the iron(II) $S = 2$ state of 1^H which has $D = 2.1 \text{ cm}^{-1}$ and

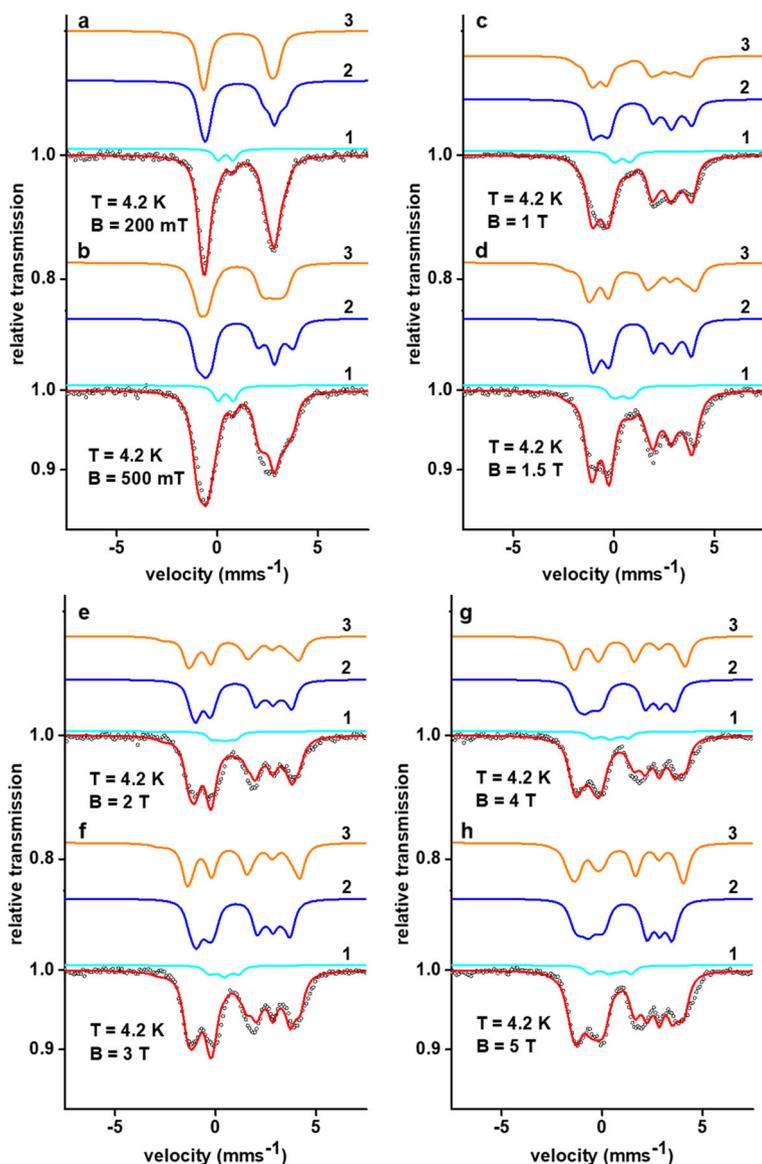


Fig. 3 Mössbauer spectra of **1** obtained at $T = 4.2$ K and the indicated external fields. The simulations (red solid lines) have been obtained by a spin-Hamiltonian analysis employing simultaneous fitting of all displayed data sets. For parameters see Table 1; each simulated spectrum consists of three components (cyan 1, blue 2 and yellow 3). All spectra were taken with fields applied parallel to the γ -beam

$E/D = 0.23$. Interestingly also the isomer shift is about 0.1 mms^{-1} smaller in the LIESST state than in the 1^{H} conformation of the molecule.

The isomer shift scales with the iron ligand distances, the higher the distances the lower the isomer shift due to increasing s -electron density at the ^{57}Fe nucleus. This indicates that some if not all iron(II) ligand distances of the LIESST state of 1^{L} are larger than those of 1^{H} .

Table 1 Mössbauer and spin Hamiltonian parameters of **1** as obtained from the spin-Hamiltonian simulations shown in Fig. 3

Component	1	2	3
spin S	0	2	2
δ (mms ⁻¹)	0.40 ± 0.03	1.11 ± 0.03	1.03 ± 0.03
ΔE_Q (mms ⁻¹)	-0.75 ± 0.03	-3.43 ± 0.03	-3.43 ± 0.03
η	0.0	0.0	0.0
Γ (mms ⁻¹)	0.48	0.48	0.48
D (cm ⁻¹)	/	2.1 ± 0.7	5.3 ± 0.5
E/D	/	0.23 ± 0.05	0.14 ± 0.05
$g_{xx,yy,zz}$	/	2.0	2.0
$A_{xx}/\mu_N g_N$	/	-2.0 ± 1.5	-7.8 ± 0.7
$A_{yy}/\mu_N g_N$	/	-4.9 ± 0.3	-7.8 ± 0.3
$A_{zz}/\mu_N g_N$	/	-0.2 ± 1.2	-22.4 ± 2.4
Relative area (%)	6.7	50.0	43.3

It would be tempting to assume that the coordination of the iron has changed from six fold in the LS **1^L** conformation to five fold in the HS LIESST **1^L** confirmation. Such a Ligand-Driven Light-Induced Spin Change (LD-LISC) was observed e.g. for Fe^{II}(t-msbpy)₂(NCS)₂ (t-msbpy = 4-methyl-4'-trans-styryl-2,2'-bipyridine) [6]. This however we consider as not likely because **1^L** and **1^H** have different conformations. Alternatively, ultrafast UV-vis spectroscopy of FePt₂ in solution [3] indicated that an energy transfer from the two photoexcited Pt units to the Fe-moiety might take place. This could induce a conformational change in the molecule explaining not only the photoexcitation to the LIESST state, but also the observation of a lower isomer shift under irradiation. This however has to be confirmed by future studies like crystal structure analysis at temperature below 40 K under light irradiation.

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