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High-field Mössbauer spectroscopy on dinuclear iron(II) spin crossover complexes

T. O. Bauer · M. Schmitz · M. Graf · H. Kelm · H.-J. Krüger · V. Schünemann

Abstract The dinuclear complex [{Fe(L-N_4Me_2)}$_2$(BzImCOO)](ClO_4)$_2$*0.5(CH_3)$_2$CO has been investigated by Mössbauer spectroscopy carried out in the temperature range from T = 5 K up to T = 190 K with externally applied magnetic fields of up to B = 5 T. By means of a consistent simulation of all experimental data sets within the Spin Hamiltonian formalism, the zero-field splitting and the rhombicity parameter of the ferrous high-spin site could be determined to be $D = 7.2 \pm 0.5$ cm^{-1} and $E/D = 0.1 \pm 0.02$. The sign of the quadrupole splitting is positive which indicates that the ferrous high-spin site of the dinuclear complex [{Fe(L-N_4Me_2)}$_2$(BzImCOO)]-(ClO_4)$_2$*0.5(CH_3)$_2$CO has an electronic ground state with the d_{xy} orbital twofold occupied.

Keywords Mössbauer spectroscopy · Spin crossover · Molecular magnetism · Zero-field-splitting

1 Introduction

Iron (II) spin crossover (SCO) systems [1] provide interesting materials for future sensor and memory devices [2]. They can be switched reversibly from the low-spin (LS) state (S = 0) to the high-spin (HS) state (S = 2) by variation of temperature, pressure or by irradiation with light [1]. The dinuclear compound [{Fe(L-N_4Me_2)}$_2$

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T. O. Bauer (✉) · V. Schünemann
Department of Physics, University of Kaiserslautern, Erwin-Schrödinger-Str. 46, 67663 Kaiserslautern, Germany
e-mail: thbauer@rhrk.uni-kl.de

M. Schmitz · M. Graf · H. Kelm · H.-J. Krüger
Department of Chemistry, University of Kaiserslautern, Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern, Germany

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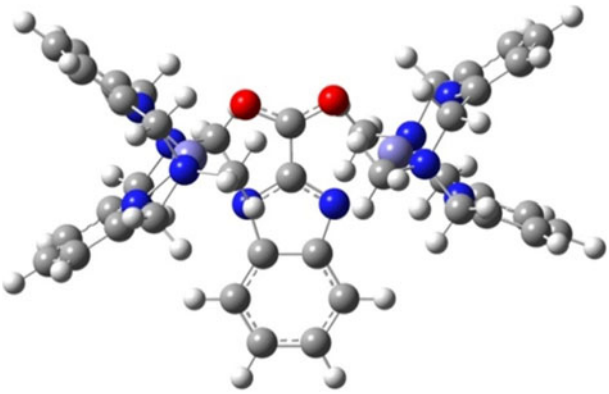

Fig. 1 Perspective view of Fe_2BzCOO [3, Krüger et al., unpublished]. The two iron centers of the complex are shown in purple

(BzImCOO)]$(ClO_4)_2$*0.5$(CH_3)_2CO$[1] (further denoted as Fe_2BzCOO) exhibits a gradual spin crossover between 175 K and 250 K with $T_{1/2} = 210$ K. Because of the intramolecular cooperativity communicated via the bridging-ligand this complex has not a LS-LS but a LS-HS ground state [3]. Here, we report on the characterization of this complex by means of temperature and field dependent Mössbauer spectroscopy. The aim of this study is to characterize the electronic ground state of the HS (S = 2) site of the dinuclear iron complex and to determine its zero field splitting D and its rhombicity parameter E/D.

2 Materials and methods

The molecular structure of Fe_2BzCOO is shown in Fig. 1. Structural details were discussed in [3, Krüger et al., unpublished]. Mössbauer spectra were recorded with a 1.85 GBq ^{57}Co(Rh) source on powder samples embedded in a sample holder made of Delrin© in transmission geometry and constant acceleration mode. The measurements obtained at high magnetic fields were performed with a closed cycle cryostat equipped with a superconducting magnet as described earlier [4]. Magnetically split spectra were simulated on the basis of the Hamiltonian approximation using Vinda Add On for Excel 2003 [5].

In order to calculate spin expectation values $< \vec{S} >$ the following Hamiltonian was used [6, 7]:

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

where S is the spin quantum number of the electronic ground state, D the zero field splitting, E/D the rhombicity parameter, μ_B the bohr magneton and $< \overleftrightarrow{A} >$ the hyperfine coupling tensor which couples $< \vec{S} >$ to the nuclear spin $< \vec{I} >$ according to the nuclear Hamiltonian [6, 7]:

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

[1] L-N_4Me_2 N,N′-Dimethyl-2,11-diaza[3.3](2,6)pyridinophane BzImCOO Benzimidazole-2-carboxylate.

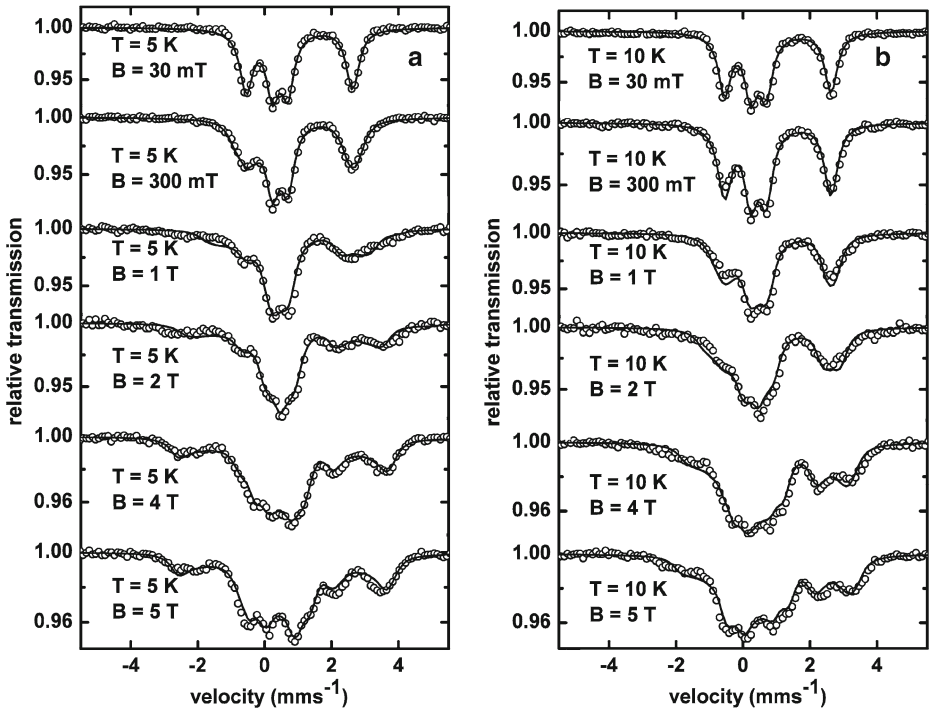

Fig. 2 Field dependent Mössbauer spectra of Fe_2BzCOO taken at T = 5 K (**a**) and at T = 10 K (**b**) with indicated external fields varied from 30 mT to 5 T applied perpendicular to the γ-beam. The *solid lines* are the result of a spin-Hamilton analysis including simultaneous fitting of all displayed data sets. The resulting parameters are given in Table 1. The simulations given for the data obtained at 5 K in (**a**) were obtained in the slow-relaxation limit and those given for the data obtained at 10 K in the fast relaxation limit

Here I denotes the spin quantum number of the nuclear ground and excited states, Q the nuclear quadrupole moment, V_{zz} the z-component of the electric-field gradient (efg) tensor, $\eta = \left(V_{xx} - V_{yy}\right)/V_{zz}$, the asymmetry parameter of the efg, and g_N the nuclear g-factor.

3 Results and discussion

Figure 2 a shows the Mössbauer spectra of Fe_2BzCOO taken at T = 5 K in magnetic fields of up to B = 5 T perpendicular to the γ-beam. The spectrum obtained at a small applied field of 30 mT shows two components with a relative area of 1:1. Component 1 has a small quadrupole splitting ($\Delta E_{Q1} = 0.45(3)$ mms^{-1}) and arises from the diamagnetic ferrous LS site of the complex.

Component 2 has a significantly larger quadrupole splitting ($\Delta E_{Q2} = 3.18(3)$ mms^{-1}) and represents the contribution from paramagnetic ferrous HS site of the complex. In order to reproduce the field dependent Mössbauer spectra obtained at T = 5 K (Fig. 2a) and at T = 10 K (Fig. 2b) spin Hamilton simulations have been performed, the result of which are displayed as solid lines in Fig. 2 with

Table 1 Parameters obtained by the spin Hamilton simulations (solid lines)[1] shown in Fig. 1

Comp.	S	δ /mms^{-1}	ΔE_Q/mms^{-1}	D /cm^{-1}	E/D	$A_{xx,yy,zz}/\mu_N g_N$/T
1	0	0.46(3)	±0.45(3)	—	—	—
2	2	1.04(3)	+3.18(3)	+7.2(5)	0.10(2)	−3.0(15), −11.0(5), −26.0(30)

[1]The exp. area of the two components was set 1:1, the line width was $\Gamma = 0.45$ mms^{-1} and the asymmetry parameter was obtained to be $\eta = 1$ for iron(II) low-spin and $\eta = 0$ for iron(II) high-spin

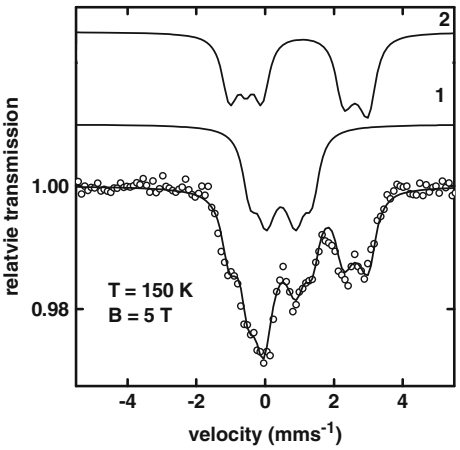

Fig. 3 Mössbauer spectrum of Fe_2BzCOO taken at T = 150 K with an external field of B = 5 T applied perpendicular to the γ-beam. The *solid line* is a result of a spin-Hamilton simulation, representing the diamagnetic LS site 1 and the paramagnetic HS site 2 in a relative ratio of 1:1. The spin Hamilton simulation has been performed with the parameters shown in Table 1 using the fast relaxation limit

the parameters given in Table 1. The diamagnetic ferrous LS site 1 of the complex renders $\delta_1 = 0.46(3)$ mms^{-1}, an asymmetry parameter of $\eta = 1$ and therefore the sign of the electric field gradient is not defined ($\Delta E_{Q1} = (\pm)0.45(3)$ mms^{-1}). The zero field splitting and the rhombicity parameter of the paramagnetic HS site 2 has been determined to $D = +\ 7.2(5)$ cm^{-1} and $E/D = 0.10(2)$. Furthermore site 2 yields $\delta_2 = 1.04(3)$ mms^{-1}, $\eta = 0$ and $\Delta E_{Q2} = +3.18(3)$ mms^{-1} and an anisotropic hyperfine coupling tensor $A/\mu_N g_N = (-3.0(15), -11{,}0(5), -26.0(30))$ T.

It should be noted that A_{xx} and A_{zz} could be determined only with a lower accuracy than A_{yy}. This originates from the fact that in the case of a positive D and a rhombicity of ∼0.1, the largest component of $<\vec{S}>$ is orientated along the y-direction. The value of the zero field splitting is among those found for other ferrous high-spin complexes [7, 8].

In order to confirm the positive sign of the electric field gradient for the HS site 2 a Mössbauer spectrum was measured at T = 150 K in an applied field of 5 T. At such a temperature the fine structure levels of the HS site are almost equally populated and fast spin relaxation between the sublevels leads to a quasi diamagnetic Mössbauer pattern [8] as can be seen in Fig. 3. Also here the experimental data could be very well reproduced with the data set given in Table 1 which confirms the positive sign of the quadrupole splitting for the HS site of the complex.

Under the assumption that the electronic contribution to the electric field gradient dominates, the Townes-Daily approximation [9, 10] indicates that a ferrous HS site with a positive ΔE_Q value has an electronic ground state with a doubly occupied

d_{xy} orbital. In order to confirm this finding quantum mechanical density functional theory calculations are currently undertaken in our laboratory.

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