

## Nuclear inelastic scattering studies on a dinuclear iron(II) spin crossover complex

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**Abstract** The vibrational properties of the (high-spin)-(high-spin) and the (high-spin)-(low-spin) states of the dinuclear Fe(II) spin crossover complex  $[\{\text{Fe}(\text{L}-\text{N}_4\text{Me}_2)\}_2(\text{BiBzIm})](\text{ClO}_4)_2 \cdot 2\text{EtCN}^1$  have been studied by means of nuclear inelastic scattering. At a temperature of 80 K typical low spin marker bands are detected in the region around  $400 \text{ cm}^{-1}$ , these bands almost completely disappear after increasing temperature to 190 K. Corresponding density functional theory calculations using the functional B3LYP\* and the basis set CEP-31G reproduce the experimental data and thus allow a deeper understanding of the vibrational properties of dinuclear Fe(II) spin crossover complexes.

**Keywords** Nuclear inelastic scattering · Molecular magnetism · Spin crossover · Density functional theory · Polynuclear iron complexes

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<sup>1</sup> $\text{L} - \text{N}_4\text{Me}_2$  N,N'-Dimethyl-2,11-diaza[3.3](2,6)pyridinophane  
BiBzIm 2,2'-Bibenzimidazolate

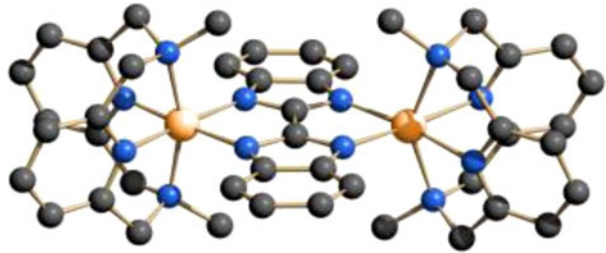
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**Fig. 1** Perspective view of  $[\{\text{Fe}(\text{L-N}_4\text{Me}_2)\}_2(\text{BiBzIm})]^{2+}$  [2]



## 1 Introduction

Iron (II) spin crossover (SCO) complexes can be switched reversibly from the low spin state (LS,  $S = 0$ ) to the high spin state (HS,  $S = 2$ ) by variation of temperature, pressure or by irradiation with light. Therefore these materials are very promising candidates for information storage [1]. Nuclear inelastic scattering (NIS) of synchrotron radiation is a powerful tool to investigate Mössbauer active isotopes like  $^{57}\text{Fe}$ . For this reason NIS is particularly suitable to study the vibrational properties of  $^{57}\text{Fe}$  containing SCO complexes. In order to study the interaction between Fe(II) centers in polynuclear complexes simulations based on density functional theory (DFT) have been performed which allow to assign all experimentally observed vibrational modes.

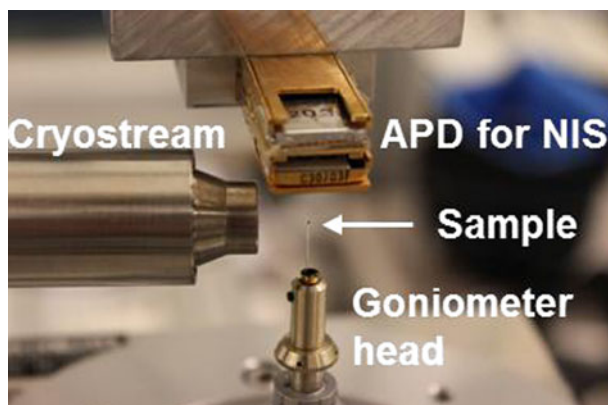
## 2 Materials and methods

NIS experiments were performed at the “Dynamics Beamline P01 at Petra III”, DESY in Hamburg, Germany under experiment No. 9777. In this study NIS was used to characterize the HS and LS states of the dinuclear SCO complex  $[\{\text{Fe}(\text{L-N}_4\text{Me}_2)\}_2(\text{BiBzIm})](\text{ClO}_4)_2 \cdot 2\text{EtCN}$  further denoted as  $[\{\text{Fe}(\text{L-N}_4\text{Me}_2)\}_2(\text{BiBzIm})]^{2+}$  [2] (see Fig. 1). The powder sample was prepared on a thin glass fiber on a goniometer head (see Fig. 2). The storage ring operated at 60 bunch mode with a bunch separation of 123 ns and 6 GeV beam energy. For taking NIS spectra the scattered radiation was detected by an avalanche photodiode (APD) mounted 1 cm above the sample (see Fig. 2). For temperature control a cryogenic  $\text{N}_2$  gas stream (Oxford Cryosystems Ltd) was used. The sample was first measured by NIS at 80 K and then at 190 K. The NIS data were collected during several scans within the energy range  $-20$  to  $70$  meV with a  $0.25$  meV step size and 3 s measuring time. The experimental energy resolution of the set-up was  $\sim 1$  meV ( $\sim 8$   $\text{cm}^{-1}$ ). The experimentally determined partial density of vibrational states (pDOS) was generated with a binning of  $0.5$  meV.

DFT calculations including normal mode calculations were performed with Gaussian09 for the previously optimized structure of  $[\{\text{Fe}(\text{L-N}_4\text{Me}_2)\}_2(\text{BiBzIm})]^{2+}$  using the B3LYP\* functional and the CEP-31G basis set.

## 3 Results and discussion

$[\{\text{Fe}(\text{L-N}_4\text{Me}_2)\}_2(\text{BiBzIm})]^{2+}$  shows thermally induced spin switching from the HS-LS state at 80 K to the HS-HS state at 190 K [2]. Figure 3c shows the experimentally determined partial density of vibrational states (pDOS) obtained at 80 K which shows two distinct peaks with maxima at  $197$  and  $225$   $\text{cm}^{-1}$ . Additionally the PDOS reveals a number of

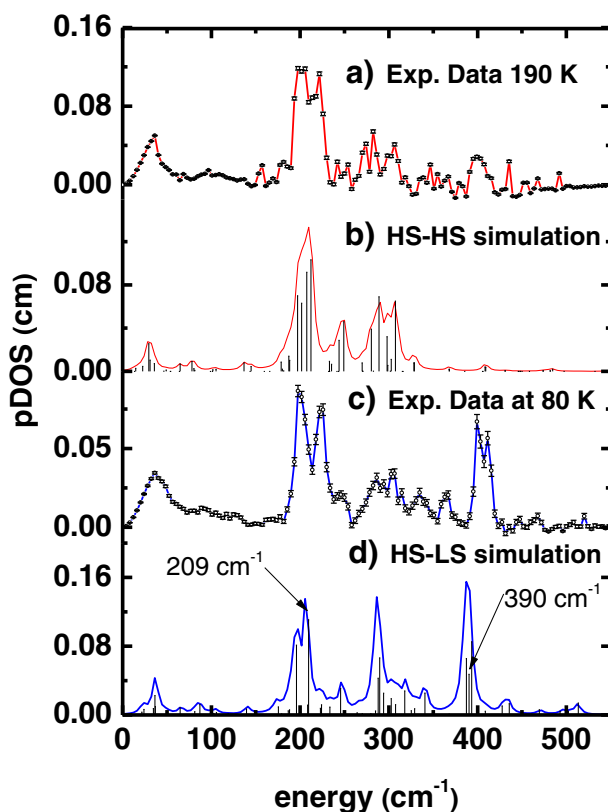


**Fig. 2** Experimental setup for sample cooling used in this study

smaller bands between 280 and 360  $\text{cm}^{-1}$ . Furthermore two prominent bands are observable at about 400  $\text{cm}^{-1}$ . The maxima are at 399 and 411  $\text{cm}^{-1}$ . The latter peaks are nearly extinct in the PDOS after increasing the sample temperature to 190 K (see Fig. 3a). Therefore these bands are assigned as typical low spin marker bands. The HS-HS state also shows two prominent bands at 202 and 222  $\text{cm}^{-1}$ , leading to the conclusion that this spectral area is not influenced by the spin state conversion.

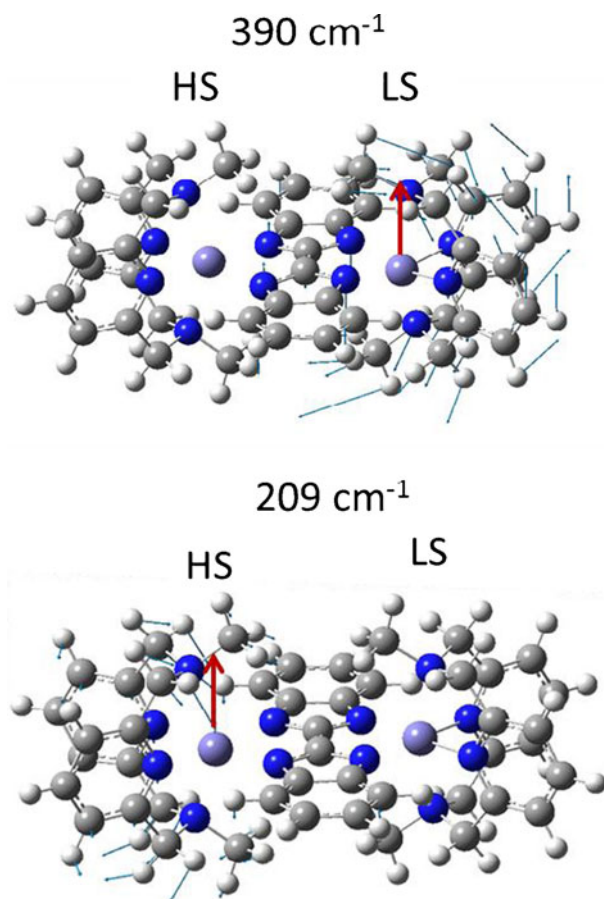
The corresponding simulations of the NIS data which are obtained by DFT calculations and subsequent normal mode analysis using Gaussian 09 (B3LYP\*/CEP31-G) are shown in Fig. 3b and d. The simulation for the HS-LS state shows two bands at around 200  $\text{cm}^{-1}$ . The vertical lines in the simulation demonstrate the quadratic displacement of the iron atoms as a function of the energy of the corresponding vibrations. The simulation fits the experimental data very well and confirms that the experimentally observed bands at 197 and 225  $\text{cm}^{-1}$  are almost completely caused by two vibrational modes calculated to occur at 196 and 209  $\text{cm}^{-1}$ . Both modes display a vibration of the HS irons only. At 196  $\text{cm}^{-1}$  the HS iron moves in the plane of the bridging ligand, vertical to the iron-iron axis. At 209  $\text{cm}^{-1}$  the iron moves instead perpendicular to the plane of the bridging ligand (see also Fig. 4). Furthermore there are three bands in the region of 280 to 350  $\text{cm}^{-1}$ . One band at 290  $\text{cm}^{-1}$  with large iron displacements at 288 and 290  $\text{cm}^{-1}$ , the former caused by the movement of the LS iron in the plane of the bridging ligand, vertical to the iron-iron axis, the latter caused by the movement of the HS iron along the iron-iron axis. The two bands with smaller intensity are due to two modes with smaller iron displacements (319 und 339  $\text{cm}^{-1}$ ), both display movement of the LS iron only. All three bands correspond to the experimentally observed bands in the region around 300  $\text{cm}^{-1}$ . In addition the simulation also yields an intense band at 391  $\text{cm}^{-1}$  which is formed by three overlapping modes at 387, 390 and 393  $\text{cm}^{-1}$  which are all caused by the solely movement of the LS iron. At 387  $\text{cm}^{-1}$  the LS iron moves in the plane of the bridging ligand, vertical to the iron-iron-axis. The mode at 390  $\text{cm}^{-1}$  shows the LS iron moving perpendicular to the plane of the bridging ligand (see also Fig. 4). At 393  $\text{cm}^{-1}$  the LS iron moves along the iron-iron axis with a stretching of the iron- pyridinophane bond. This finding concerning the three modes is consistent with the experimental NIS data around 400  $\text{cm}^{-1}$ . Altogether the calculated HS-LS simulation fits very well to the experimentally determined pDOS obtained at 80 K.

The HS-HS simulation (Fig. 3b) displays one prominent band at 210  $\text{cm}^{-1}$  which corresponds to the two bands at 202 and 222  $\text{cm}^{-1}$  in the experimental data (Fig. 3c). The



**Fig. 3** **a** Experimentally determined pDOS of  $[\{\text{Fe}(\text{L-N}_4\text{Me}_2)_2(\text{BiBzIm})\}^{2+}]$  obtained at 190 K; **b** DFT simulation for the HS-HS state (*nonet*); **c** experimentally determined pDOS obtained at 80 K and **d** DFT simulation for the HS-LS state (*quintet*) state of  $[\{\text{Fe}(\text{L-N}_4\text{Me}_2)_2(\text{BiBzIm})\}^{2+}]$  based on density functional calculations using Gaussian 09 (B3LYP\*/CEP31-G). The vertical lines highlight the quadratic displacement of the iron atoms as a function of the energy of the corresponding vibrations

quadratic displacement of the iron atoms illustrates that the simulated band at  $210\text{ cm}^{-1}$  is due to four modes between  $197$  and  $212\text{ cm}^{-1}$ . The modes at  $197$  and  $202\text{ cm}^{-1}$  show an analog movement of both HS iron atoms in the plane of the bridging ligand, vertical to the iron-iron axis. At  $197\text{ cm}^{-1}$  the irons move in opposite directions, at  $202\text{ cm}^{-1}$  however in the same direction. This analysis indicates an analogy with the HS-LS simulation in the same region. The mode at  $196\text{ cm}^{-1}$  in the HS-LS simulation displays the same kind of movement with only one iron moving. On the other hand the modes at  $208$  and  $212\text{ cm}^{-1}$  display a movement of both iron atoms perpendicular to the plane of the bridging ligand. In the former mode the irons move in the opposite direction, in the latter mode they move in the same direction. As discussed before the mode at  $209\text{ cm}^{-1}$  of the HS-LS simulation shows the same movement but with one HS iron only. Accordingly, in this case the frequencies of the modes are not influenced by the number of the moving irons. Furthermore the HS-HS simulation shows one band at  $246\text{ cm}^{-1}$  consisting of two modes at  $244$  and  $249\text{ cm}^{-1}$ . Both modes show a movement of both HS iron atoms in the plane of the bridging ligand, vertical to the iron-iron axis. In the former mode both irons move in the same direction in the latter one they move in the opposite direction. Besides there are three bands in this area from  $280$



**Fig. 4** Exemplary vibrations as obtained from the HS-LS simulation of  $[\{\text{Fe}(\text{LN}_4\text{Me}_2)\}_2(\text{BiBzIm})]^{2+}$  at  $390\text{ cm}^{-1}$  (top) and  $209\text{ cm}^{-1}$  (bottom). The mode at  $390\text{ cm}^{-1}$  shows a movement of the LS iron perpendicular to the plane of the bridging ligand (red arrow). The mode at  $209\text{ cm}^{-1}$  displays a comparable movement of the HS iron

to  $310\text{ cm}^{-1}$  each consisting of several modes. Together with the band at  $246\text{ cm}^{-1}$  these bands also reproduce the experimental NIS data in this energy region very well, as displayed in Fig. 3a. The experimentally obtained pDOS at 190 K shows a band at  $400\text{ cm}^{-1}$ . In the HS-HS simulation only a very weak band at  $407\text{ cm}^{-1}$  occurs in the area of the LS marker bands. This rather unexpected observation can be explained by the fact that the sample was first measured at 80 K and then the temperature was increased to 190 K. Depending on the crystallinity of the sample the spin crossover can be abrupt or more gradual. The additional band at about  $400\text{ cm}^{-1}$  indicates some residual HS-LS state. Nevertheless also the HS-HS simulation forecasts the experimental data at 190 K very well.

Figure 4 shows two exemplary normal modes of the HS-LS simulation at 390 and  $209\text{ cm}^{-1}$ . At  $390\text{ cm}^{-1}$  the LS iron moves perpendicular to the plane of the bridging ligand, whereas the HS iron displays a similar vibration but downshifted to  $209\text{ cm}^{-1}$ . Both modes show a comparable movement of not only the iron atoms but of all atoms in the

**Table 1** Bond length between the iron and the nitrogen atoms for the HS-LS and the HS-HS state determined by the simulations presented here (bold) in comparison with the x-ray structure analysis (italic) [2, 3]

Distances (Å)			
B3LYP*/CEP-31G	HS-LS		HS-HS
Fe-N <sub>bridge</sub>	<b>2.200,</b> <i>2.175, 2.182</i>	<b>2.075,</b> <i>2.044, 2.045</i>	<b>2.179, 2.182,</b> <i>2.139, 2.135</i>
Fe-N <sub>amin</sub>	<b>2.306,</b> <i>2.286, 2.261</i>	<b>2.124,</b> <i>2.080, 2.095</i>	<b>2.306, 2.304,</b> <i>2.238, 2.262</i>
Fe-N <sub>py</sub>	<b>2.139,</b> <i>2.128, 2.151</i>	<b>1.919,</b> <i>1.905, 1.908</i>	<b>2.137, 2.138,</b> <i>2.133, 2.116</i>

complex. The downshift is based on the different bond strength as displayed by the different bond length between the iron and the nitrogen atoms for the HS and the LS state (see also Table 1). The stronger iron-nitrogen bond of the LS iron causes the observable shift to higher frequencies.

Table 1 comprises the bond lengths between the iron and the nitrogen atoms for the HS-LS and the HS-HS state as determined by the DFT simulations (bold) and by the corresponding x-ray structure analysis (italic). The HS-HS simulation yields nearly equal bond length to the nitrogen atoms for both HS iron sites. In the case of the HS-LS simulation the HS iron has similar bond length compared to both irons in the HS-HS simulation.

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## References

1. Gütllich, P., Goodwin, H.A.: Top. Curr. Chem. **233**, 1–47 (2004)
2. Krüger, H.-J.: Coord. Chem. Rev. **253**, 2450–2459 (2009)
3. Krüger, H.-J. et al. to be published