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Nuclear inelastic scattering studies of a 1D- polynuclear spin crossover complex of Fe(II) urea-triazoles

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Abstract The partial density of vibrational states (pDOS) of the low-spin isomer of the tosylate salt of $[\mathrm{Fe}\{(\text{N-Propyl})\text{-N}'\text{-}(1,2,4\text{-triazole-4-yl-urea})\}_3]^{2+}$ was determined by nuclear inelastic scattering experiments performed at 8 K. The pDOS features a rich band structure from 320 to 500 cm^{-1}, characteristic of the low spin state of the complex. Density functional theory calculations (B3LYP/CEP-31G) were used to assign molecular modes to the experimentally observed peak in the pDOS.

Keywords Nuclear inelastic scattering · Spin crossover · Molecular magnetism · Density functional theory

1 Introduction

The cooperativity of the spin transition in spin crossover (SCO) materials, which determines the strength of hysteresis during SCO [1–3], is a key property required for their application in future electronics [4]. The established theoretical models of the SCO phenomenon

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[5, 7] underline the importance of the elastic properties of the spin crossover materials, that themselves are related to far ranging elastic interactions. Therefore, as first proposed by Kahn et al. [8], polynuclear spin crossover systems, in which the spin switching iron atoms are linked by a system of covalent bonds are of special interest. In this regard, the following question arises: How do the vibrational properties of a given spin crossover material depend on its dimensionality? A strategy to answer this question, is to study both one-dimensional (1D) and three-dimensional (3D) networks for the same coordination core of a SCO complex. This is a synthetic challenge, but nevertheless Rentschler and Malotki [9] reported that by using differently N-urea substituted triazoles it is possible to obtain not only the 1D chains, typical for the triazole Fe(II) systems, but also 3D networks. Here, we report first results of the study of the vibrational properties of the 1D complex [Fe{ (N-Propyl)-N′-(1,2,4-triazole-4-yl-urea)}$_3$](tosylate)$_2$ (denoted as [Fe(n-Protrzu)$_3$](tos)$_2$, (**1**)) using nuclear inelastic scattering and density functional theory calculations.

2 Materials and methods

The complex under study was prepared with 98% ^{57}Fe enrichment, following the method described in ref [9]. Nuclear inelastic scattering (NIS) and nuclear forward scattering (NFS) spectra were recorded at the Dynamics Beamline P01 at Petra III, DESY in Hamburg, Germany [6]. This beamline has a two-step monochromatisation. The first step is performed with a Si(111) double-crystal monochromator which renders a bandwidth of approximately 2 eV to the incident beam. The following high-resolution monochromator (HRM) decreases the bandwidth of the incident beam down to 1 meV. This beam is used to excite the 14.4125 keV level of the ^{57}Fe nuclei in the sample. The excited nuclear state decays with a lifetime of 141 ns to the ground state by emitting conversion electrons with a probability of 90%. The subsequent 6.4 keV K-fluorescence radiation, which is delayed compared to electronic scattering, is measured with fast avalanche photodiodes (APD) with a time-resolution of 1 ns. NIS and NFS measurements of the sample were taken at 8 K using a helium closed-cycle-cryostat. The NFS data was collected only from 25 ns on wards due to the use of the veto signal (from 0 up to 25 ns), which is needed to suppress the prompt electronic scattering signal. The granular powder-like sample used for NIS/NFS was embedded in between two Kapton® foils and was oriented in a way that the surface of the foils was almost parallel to the synchrotron beam in order to maximize the NIS signal.

Mössbauer spectra were measured in the 77–320 K area by means of an Oxford cryostat and a Wissel Electronics spectrometer. The sample (32 mg of compound) used for conventional Mössbauer spectroscopy was embedded inside a conventional Mössbauer cup made of Delrin©. Density functional theory (DFT) calculations were performed with the Gaussian 09 software using the ONIOM method, in which in which the vibrations of most of the atoms are calculated with the functional B3LYP and the basis set CEP-31G. The n-propyl groups on urea fragments were modelled via MM2 molecular mechanics using the Universal Force Field method (see the ref [10] for more detailed discussion). Similar to our previous studies ([11] and references therein), the low-spin 1D chain was modelled with a heptanuclear molecule [(OH$_2$)$_3$ Fe(n-Protrzu)$_3$(Fe(n-Protrzu)$_3$)$_5$(n-Protrzu)$_3$Fe(H$_2$O)$_3$](BF$_4$)$_{14}$, shown in Fig. 1. The geometry of the molecule was optimized and the normal coordinate analysis was performed, which was used for calculation of the phonon density of states (pDOS).

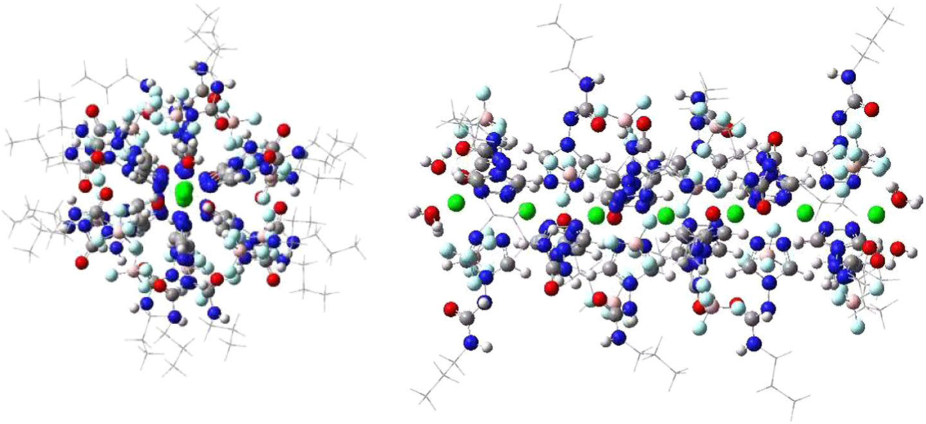

Fig. 1 Model molecule of the complex **1** used in DFT calculations shown along the 1D axis (left) and perpendicular to it (right). For the simulations shown in Fig. 3 the atoms depicted as coloured balls were treated with DFT. The n-propyl groups shown as framework were calculated with Molecular Mechanics. Fe atoms are shown in green, N atoms in dark blue, O in red, C in dark grey and H in pale grey

3 Results and discussion

Mössbauer spectra of **1** are shown in Fig. 2. The physical thickness of ^{57}Fe in the enriched sample was about 1.9 mg/cm^2. Therefore, the analysis of the spectra was performed by means of the transmission integral formalism using the software WinNormos [14]. The analysis shows that in addition to the major low-spin (LS) isomer with $\delta^{\mathrm{LS}} = 0.51$ mm/s, some residual high-spin (HS) isomer with $\delta^{\mathrm{HS}} = 1.17$ mm/s is present at 78 K (for further parameters, see Table 1). The HS fraction shows an increase with increasing temperature, with a rapid increase above 270 K. Therefore, the NIS experiments were performed at 8 K in order to have the sample in a predominantly low-spin (LS) state. The NFS spectrum shows a complicated beat pattern caused by the superposition of elastically scattered 14.4 keV radiation from the major LS and the minor HS phases as well as by dynamical beats. The simulation of the NFS spectrum presented in Fig. 2 has been performed with CONUSS [15] and yields about 4.5% contribution from HS isomer at 8 K. It should be noted that the NFS spectrum has been simulated by taking into account an effective thickness distribution centered at 72 with a full width at half maximum of 33. This was needed because the NFS spectra were taken immediately after the NIS scans with the surface of the Kapton® foil holding the sample being almost parallel to the propagation of the synchrotron beam, which lead to an ill-defined sample thickness distribution in the forward scattering direction. The Lamb-Mössbauer factor for the spectrum measured at 8 K used in the CONUSS simulations was f $= 0.87$. It was obtained through an evaluation of the NIS data at 8 K (Fig. 3b) and corresponds to that of nearly fully low-spin form at this temperature.

The results of the NIS experiments are shown in Fig. 3. The first inspection of the experimental pDOS of **1** (Fig. 3b) reveals a clear difference compared to the pDOS of the related $[\mathrm{Fe(trzH)_2(trz^-)}](\mathrm{BF_4})_2$complex (Fig. 3a). The spectra indicate that the substitution of triazole with N-substituted urea brings about the distribution of the normal vibrations involving

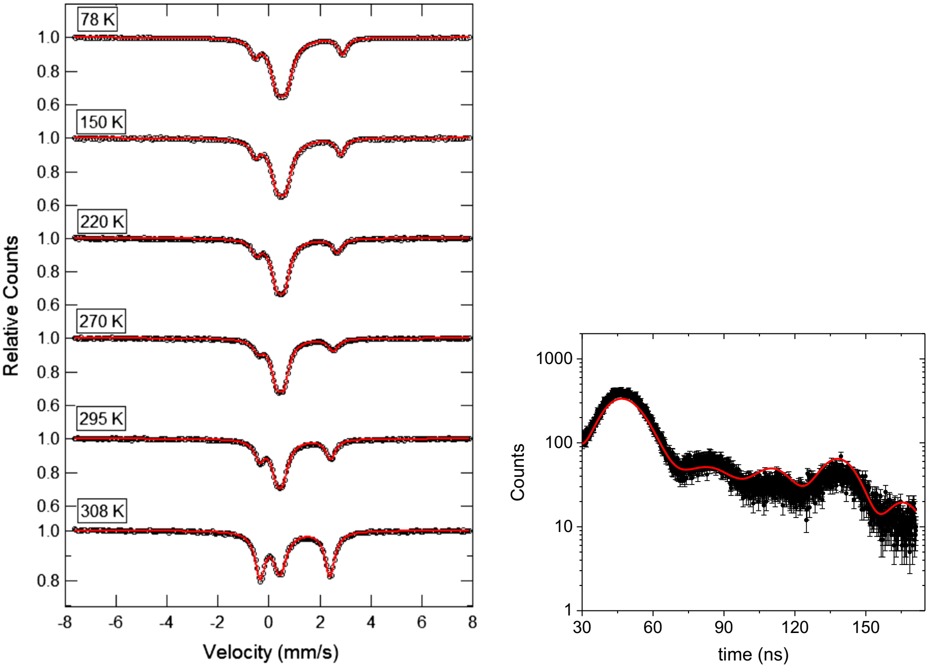

Fig. 2 Left: Mössbauer spectra of 1 obtained at $T = 78$, 150, 220, 270, 298 and 308 K. The solid lines represent transmission integral fits generated using the WinNormos program with parameters listed in Table 1. Right: NFS spectrum of the complex 1 at 8 K (black spheres) and simulation (red line) performed using the CONUSS program, yielding a HS contribution of 4.5 ± 0.3%. Further parameters: $\delta^{\mathrm{HS}} - \delta^{\mathrm{LS}} = 0.66 \pm 0.03$ mm/s; $\Delta E_{\mathrm{Q}}^{\mathrm{HS}} = 3.45 \pm 0.03$ mm/s; $\Delta E_{\mathrm{Q}}^{\mathrm{LS}} = 0.35 \pm 0.03$ mm/s

Table 1 Parameters obtained from the transmission integral analysis shown as red solid lines in Fig. 2 (left)

T (K)	δ^{LS} (mm/s)	δ^{HS} (mm/s)	ΔE_Q^{LS} (mm/s)	ΔE_Q^{HS} (mm/s)	HS fraction (%)	f
78	0.51	1.17	0.22	3.45	9	0.26
150	0.49	1.14	0.21	3.35	11	0.25
220	0.47	1.10	0.22	3.16	13	0.16
270	0.45	1.06	0.22	2.93	15	0.13
298	0.43	1.03	0.17	2.78	29	0.11
308	0.43	1.03	0.10	2.74	63	0.09

The superscripts refer to the LS and HS phases. The effective HS thicknesses were 1.13, 1.09, 1.05, 0.97, 1.62 and 2.79 at 78, 150, 220, 270, 298 and 308 K, Uncertainties for δ, ΔE_{Q}, HS fraction and the Lamb-Mössbauer factor are ± 0.03 mm/s, ± 0.03 mm/s, ± 1% and ± 0.1, respectively

Fe movement to a significantly broader area along with a concomitant shift of the maximum of the pDOS band structure towards lower frequencies. The influence of the n-propyl chains on the vibrational pattern is also seen in the results of the DFT modelling. The calculated pDOS (Fig. 3c) for the model shown in Fig. 1 yields a much different pattern of the Fe-involving vibrations compared to the smaller model in which no n-propyl groups were modelled (Fig. 3d). In the following, we discuss the experimentally obtained vibrational

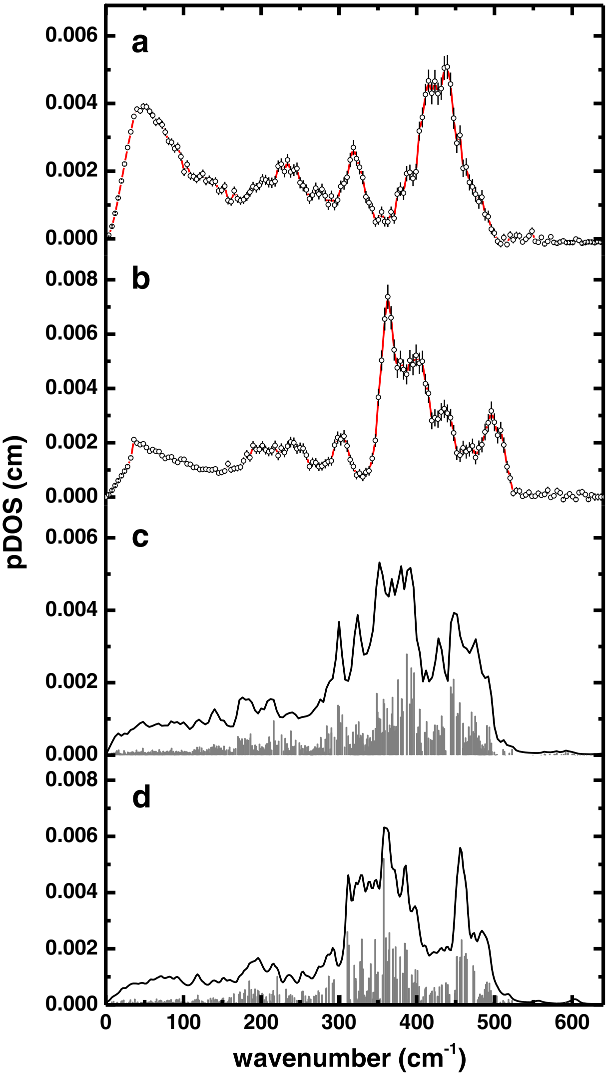

Fig. 3 Experimental pDOS of **1** at 8 K (**b**) shown in comparison with the experimental pDOS of the related $[Fe(trzH)_2(trz^-)](BF_4)_2$ triazole complex (**a**) [11–13]. **c** pDOS calculated by DFT for the model molecule using the ONIOM method. **d** pDOS calculated using a model molecule in which the n-propyl substituents on urea were replaced with hydrogen. It should be noted that for the simulations only the five inner iron centres were taken into account

pattern with respect to DFT calculations for the model involving the n-propyl groups. The band in the experimental pDOS with maxima at ca. 360 and 405 cm^{-1} may be ascribed to the vibrational modes predicted to occur in the 350–395 cm^{-1} region. The predicted maxima around 380 and 395 cm^{-1} are due to vibrations that involve the Fe-N stretching along and normal to the long axis of the molecule, coupled with the movement of triazole rings and stretching and bending of the urea fragment (see Fig. 4a and b, respectively). A significant admixture of the movements of some n-propyl groups as a whole is also observed. The

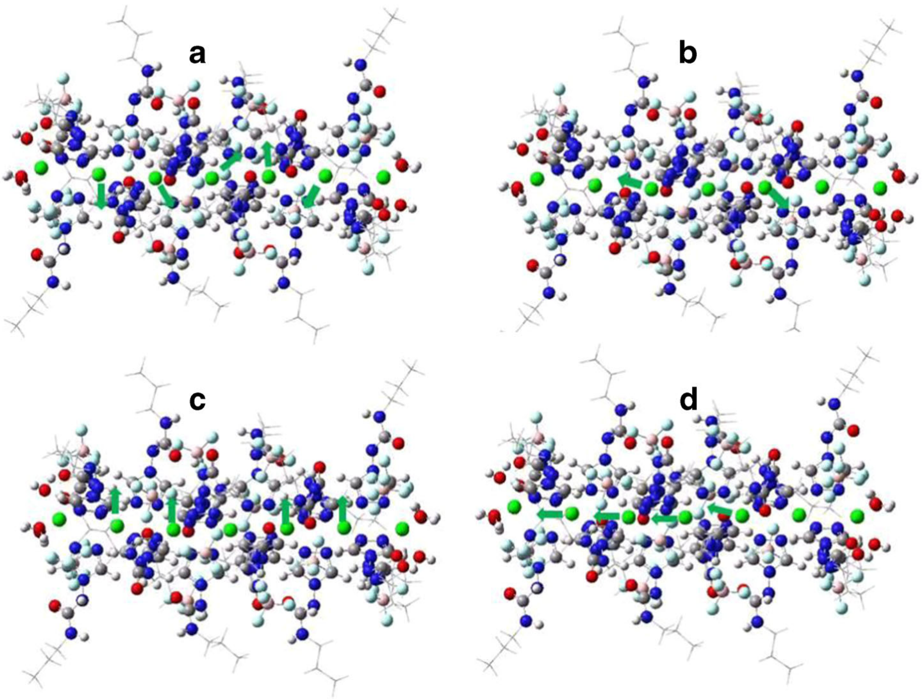

Fig. 4 Calculated (ONIOM:B3LYP/CEP-31G/UFF) vibrations of the model molecule of (**1**), predicted at 382 (**a**), 391 (**b**), 447 (**c**) and 493 (**d**) cm^{-1}, respectively. The green arrows depict the mode of movement of iron atoms of significant amplitude. The GIF movies of the vibrations are given as Supplementary Materials)

band at 438 cm^{-1} may be assigned to the modes predicted at 430–450 cm^{-1} that are similar to those described above with the iron atoms moving only normal to the long axis of the molecule (see Fig. 4c). The band observed at 497 cm^{-1} may be due to vibrations predicted at 470–498 cm^{-1} which involve Fe-N stretching along the long axis of the chains, again coupled to the above-mentioned vibrations of the triazole and deformation of the urea fragments (see Fig. 4d).

In summary this study shows that in iron(II) azole containing SCO polymers the substitution of the N-4 triazole atom with a long n-propyl-urea chain has an effect on the vibrational bands involving iron ligand modes.

Supplementary materials GIF movies showing the characteristic vibrations for **1**. Gaussian 09 reference.

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