

Mössbauer spectroscopic study on spin crossover coordination polymer $\text{Fe}(\text{3-Clpy})_2[\text{Pd}(\text{CN})_4]$

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Abstract ^{57}Fe Mössbauer spectroscopic results on the alternatively prepared spin crossover coordination polymer $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ sample **I** agree with those of SQUID data. Mössbauer spectrum at RT shows two different doublets which correspond to the HS1 (inner doublet) and HS2 (outer doublet). The intensity of the HS1 doublet decreases on cooling to 78 K at the expense of a new one featuring the LS singlet. Almost 100 % of HS1 change to LS singlet due to iron(II) ions coordinated by four N atoms of cyano groups and two N atoms of 3-Clpy ligand in the sample **I**. The SQUID data of the sample **I** prepared by a new direct contact method are different from those of the already reported $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ sample. The differences of the SQUID data are associated with particle size effects in molecule spin crossover samples.

Keywords ^{57}Fe Mössbauer spectroscopy · Coordination polymer · Spin crossover

1 Introduction

Special attention is currently much paid to Hofmann-like coordination polymer iron(II) SCO compounds acting cooperative behaviour because they can manifest sensory and

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memory functions [1]. Recently ^{57}Fe Mössbauer spectroscopy has provided very powerful information on re-appearance of cooperativity in ultra-small spin crossover Hofmann-type $\text{Fe}(\text{pz})[\text{Ni}(\text{CN})_4]$ nanoparticles [2]. The original Hofmann pyridine coordination polymer $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ shows iron(II) SCO behaviour, revealed by ^{57}Fe Mössbauer spectroscopy and SQUID technique [3]. Pressure tuning Raman spectroscopy of the prototype compound $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ has been reported [4]. Emission Mössbauer spectroscopic study ^{57}Co -labelled analogous $^{57}\text{Co}(\text{py})_2\text{Ni}(\text{CN})_4$ was carried out in the nuclear-decay-induced excited spin state trapping (NIESST) [5]. Temperature-dependent EXAFS study for $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ has also been reported [6]. The effect on the SCO behavior of Cl and CH_3 replacements located at different positions on the pyridine ring were also studied [7, 8]. ^{57}Fe Mössbauer spectroscopic study of the spin crossover polymer complex, $\text{Fe}(\text{3-Clpy})_2\text{Ni}(\text{CN})_4$ was reported [7]. The related SCO coordination compounds have been developed [9–29]. Some of them contain 3D pillared Hofmann-type-organic frameworks [16–22]. Recently Kosone et al. have reported an interconversion of nuclear-spin isomers for hydrogen molecule H_2 adsorbed in a Hofmann-type porous coordination polymers (PCPs), by the temperature dependence of Raman spectra [27].

We previously reported three kinds of 2D coordination polymer iron(II) spin crossover complexes containing 3,5-lutidine with general formula $\text{Fe}(\text{3,5-lutidine})_2\text{Ni}(\text{CN})_4 \cdot n(\text{H}_2\text{O})/m(\text{3,5-lutidine})$, whose host framework is similar to that of $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ [9, 10]. Thermal-, pressure and light-induced spin crossover behavior in Hofmann-like spin crossover coordination compound $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ have been described in details [11, 12].

We report here ^{57}Fe Mössbauer spectroscopic study on the spin crossover coordination polymer $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ sample **I** prepared by an alternative method. Mössbauer spectrum at RT shows two different doublets which correspond to the HS1 (inner doublet lines) and HS2 (outer doublet lines). The intensity of the HS1 doublet decreases on cooling to 78 K at the expense of a new one featuring the LS singlet. Almost 100 % of HS1 change to LS singlet due to iron(II) ions coordinated by four N atoms of cyano groups and two N atoms of 3-Clpy ligand. The SQUID data for the sample **I** agree with the Mössbauer data for the same sample **I**. The SQUID data of the sample **I** prepared by a direct contact method are different from those of the already reported $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ sample by the other method [11, 12]. The differences of the SQUID data are associated with particle size effects in molecule SCO samples [2].

2 Experimental

The preparation method of the $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ sample **I** using a direct contact method is different from that reported by Real and coauthors [11]. We prepared the 2D spin crossover $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ sample **I** in the ambient atmosphere by a method similar to that for the prototype $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$. 138.5 mg (0.404 mmol) of $\text{K}_2[\text{Pd}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ were added into 10 ml of water. To the water solution, Mohr's salt ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) 186.4 mg (0.475 mmol), and 362.9 mg (1.889 mmol) citric acid were added. Then a light blue precipitate formed immediately. The precipitate was dissolved by adding 1,3-diaminopropane dropwise. 98.0 mg (0.863 mmol) neat 3-Clpyridine were added to the mixture solution. Pale light yellow fine solid particles were formed immediately as the sample **I**. The sample **I** was identified by ^{57}Fe Mössbauer spectroscopy, SQUID, powder XRD and elemental analysis. The C, H and N elemental analysis for the sample **I** was carried

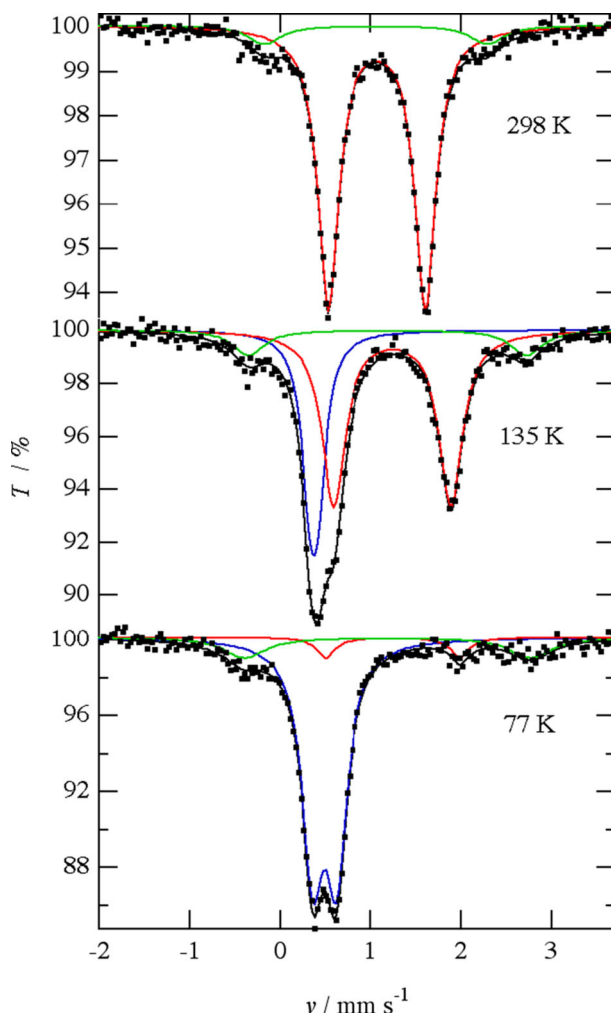


Fig. 1 ^{57}Fe Mössbauer spectra of the $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ sample **I** at 77, 135 and 298 K

out with a **YANACO JM 10** and suggest the formation of $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ (Found C, 33.37; H, 2.06; N, 16.66. Calcd. C, 34.08; H, 1.63; N, 17.33), though small amounts of water molecules are suggested.

^{57}Fe Mössbauer spectra were obtained using a WissEl Mossbauer system consisting of MVT-1000, MR-260A, DFG-500 and CMCA-550. The temperature dependence of the spectra in the range of 80–298 K were measured by keeping the sample in a gas-flow type cryostat (Advanced Reserach System LT-3-100 Helitran System) and the source was kept at room temperature. The temperature of the sample **I** was controlled by a 9620-1 digital temperature controller from Scientific Instruments. A silicon diode was used to measure the temperature. The spectra were computer-fitted to Lorentzian lines using a MossWinn 3.0i software. The values of the isomer shift are given relative to α -iron foil at room temperature.

Table 1 ^{57}Fe Mössbauer parameters for the $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ sample **I**

		δ mm s^{-1}	ΔE_Q mm s^{-1}	Γ mm s^{-1}	Area %
298 K	HS1	1.070(1)	1.077(2)	0.280(4)	91(2)
	HS2	1.06(2)	2.46(5)	0.45(8)	9(2)
135 K	HS1	1.240(2)	1.299(5)	0.316(7)	58(2)
	HS2	1.19(2)	3.07(3)	0.42(6)	11(2)
	LS	0.370(2)	0.09(1)	0.22(1)	31(2)
77 K	HS1	1.24(1)	1.48(3)	0.24(6)	6(2)
	HS2	1.18(2)	3.16(4)	0.56(8)	14(2)
	LS	0.489(2)	0.266(3)	0.285(5)	79(2)

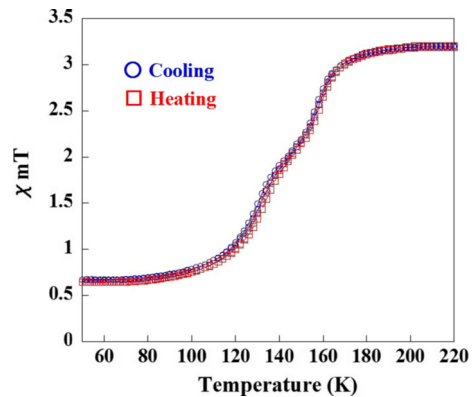
3 Results and discussion

In the present preparation of $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ sample **I**, citric and 1,3-diamonopropane were used to adjust pH of the mother aqueous solution containing $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{K}_2[\text{Pd}(\text{CN})_4]$. The precipitation rate of the sample **I** depends on the pH of the mother aqueous solution, and fine particles were precipitated due to the direct contact method. The powder XRD patterns of the sample **I** at RT were almost similar to those simulated from the reported single crystal data in the high spin state phase at 170 K in ref. [11].

^{57}Fe Mössbauer spectra of the sample **I** obtained at 77, 135 and 298 K are shown in Fig. 1. ^{57}Fe Mössbauer parameters for **I** are listed in Table 1. Spectra of **I** indicate SCO behavior with one of the high spin sites, i.e. inner HS1 sites changing to LS state. 93.4 % of HS sites in **I** were changed to LS at 77 K. As shown in Fig. 1, ^{57}Fe Mössbauer spectrum of the sample **I** at 298 K shows two different doublets which correspond to the HS1(inner doublet lines :red lines) and HS2(outer doublet lines : green lines) states. The intensity of the HS1 doublet decreases gradually on cooling to 77K at the expense of a new one featuring the LS singlet(blue lines). As listed in Table 1, the ratio of HS1 to HS2 at 298 K is 91 :9, that of HS1 and HS2 to LS at 135 K is 58 :11 :31, and at 77 K is 6 :14 :79 respectively. The recoil-free fraction of HS1 is different of that of HS2 due to different octahedral iron(II) environments. Considering both the Mössbauer parameters and/or the structural data for $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ [3, 13], $\text{Fe}(\text{3-Cl-py})_2\text{Ni}(\text{CN})_4$ [7], $\text{Fe}(\text{3-Methyl-py})_2\text{Ni}(\text{CN})_4$ [8], $\text{Fe}(\text{3-F-py})_2\text{Ni}(\text{CN})_4$ [11, 14] and other related compounds [2, 15, 21, 25, 26], the iron(II) ions in HS1 of the sample **I** have six coordination with four nitrogen atoms of cyano groups and two nitrogen of 3-Cl-pyridine ligands. 93.4 % of HS1 sites change to the singlet LS state due to the suitable FeN_6 environment for SCO behavior. The Mössbauer parameters of LS at 78 K is $\delta = 0.489(2)$, $\Delta E_Q = 0.266(3)$ mm s^{-1} for **I**.

The HS2 species in **I** with a large quadrupole splitting can be also explained by the presence of defects in the coordination polymer frameworks [2]. The minor HS2 parameters with a large ΔE_Q value as 2.46(5) mm s^{-1} at 298 K is also probably due to the $\text{FeN}_5(\text{OH}_2)$ or $\text{FeN}_4(\text{OH}_2)_2$ environment. The FeN_5O core consists of an octahedral iron(II) atom coordinated by four nitrogen atoms of cyano group, one nitrogen atom of the lutidine and one oxygen atom of the water ligand. The FeN_4O_2 core completes an octahedral iron(II) atom by coordinating two water molecules at the axial position. The Mössbauer parameters for $\text{Fe}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ which contains the $\text{FeN}_4(\text{OH}_2)_2$ environment ($\delta = 1.16$, $\Delta E_Q = 2.56$ mm s^{-1} at RT and $\delta = 1.28$, $\Delta E_Q = 3.30$ mm s^{-1} at 80 K) are similar to those of the HS2 site [30].

Fig. 2 SQUID data of the $\text{Fe}(\text{3-Cl-py})_2\text{Pd}(\text{CN})_4$ sample **I**



Taking into account of particle sizes of **I**, the HS2 doublet may be ascribed to the iron(II) units located at the nanocrystals edge as they must have coordinative defects, that is, coordinatively unsaturated sites or coordinated terminal water molecules and, consequently, can not exhibit spin crossover [14]. In contrast to HS1 site, the relative area of the HS2 site does not change over the temperature range measured, suggesting that the HS2 site does not participate in the SCO behaviour as would be expected from the suggested coordination environment.

The Mössbauer data for the sample **I** agree with the SQUID data for the same sample **I**. As shown in Fig. 2 about the SQUID data for **I**, in the temperature range 300–180 K, the value of $\chi_m T$ is $3.18 \text{ cm}^3 \text{ K mol}^{-1}$, which lies in the range of values expected for an iron(II) ion in the high spin states. On the cooling mode, $\chi_m T$ decreases in unclear two steps with transition temperatures $T_{c1}^\downarrow = 157.7 \text{ K}$ and $T_{c2}^\downarrow = 127.8 \text{ K}$. The $\chi_m T$ product at 77 K is $0.67 \text{ cm}^3 \text{ K mol}^{-1}$, which corresponds to the iron(II) ion in the low spin states. The residual paramagnetism at low temperatures indicates the presence of a small amount of HS iron(II) sites. The non-zero value of $\chi_m T$ is also associated with the presence of HS2 sites which do not act as SCO behavior and the coordination polymer structure. In the warming mode, $\chi_m T$ versus T curve is not equal to that of the cooling mode, which contains the existence of very small hysteresis behavior, with transition temperatures $T_{c2}^\uparrow = 130.3 \text{ K}$ and $T_{c1}^\uparrow = 160.3 \text{ K}$, and with hysteresis width 2.6 K. These data are different from those already reported [11, 12]. The curve of the sample **I** is more gradual than that of data in ref. [11] and ref. [12]. The temperatures of the spin crossover in the sample **I** are slightly shifted to low temperatures ($\Delta T = \text{ca. } 15 \text{ K}$). These differences in SQUID data are probably due to particle size effects on spin crossover behavior. The particle sizes in the materials for the sample **I** are maybe smaller than that already reported because the methods of preparation are different. The direct contact method for the sample **I** probably provides smaller particle sizes than those reported. Finite size effects are found in spin crossover $\text{Fe}(\text{pz})[\text{Ni}(\text{CN})_4]$ nanoparticles [2].

As to $\text{Fe}(\text{3-Cl-py})_2\text{Ni}(\text{CN})_4$, the SQUID data in ref. [7] are different from those in ref. [11]. The preparation methods of $\text{Fe}(\text{3-Clpy})_2\text{Ni}(\text{CN})_4$ are different between ref. [7] and ref. [11]. The preparation method of $\text{Fe}(\text{3-Clpy})_2\text{Ni}(\text{CN})_4$ in ref. [7] is similar to that of the $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ sample **I**. While many examples for differences in SCO behavior due to different treatments including preparation methods have been found, differences in the SQUID data are probably due to nanoparticle size effects on SCO behavior. Particle sizes in the $\text{Fe}(\text{3-Clpy})_2\text{Ni}(\text{CN})_4$ in ref. [7] may be smaller than those in ref. [11] and ref. [12].

Mössbauer and SQUID data for the sample **I** indicate $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ has almost complete spin crossover behaviour, while both 3-methyl-pyridine Hofmann complex $\text{Fe}(\text{3-Methyl-py})_2\text{Ni}(\text{CN})_4$ and 3-chloro-pyridine Hofmann complex $\text{Fe}(\text{3-Clpy})_2\text{Ni}(\text{CN})_4$ show incomplete spin crossover behavior [7, 8]. The position-3 substituent of pyridine ring is associated with SCO behavior, while the position-4 substituents of pyridine ring do not allow SCO behavior. Effects of $[\text{Pd}(\text{CN})_4]^{2-}$ link to a chemical pressure effect in the spin crossover behavior in the sample **I** because transition temperatures in the sample **I** are higher than that of $\text{Fe}(\text{3-Clpy})_2\text{Ni}(\text{CN})_4$.

This study also suggests differences in SCO behavior in $\text{Fe}(\text{3-Clpy})\text{Pd}(\text{CN})_4$ system are found due to different treatments associated with particle sizes.

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