



Spin crossover behaviour in Hofmann-like coordination polymer $\text{Fe}(\text{py})_2[\text{Pd}(\text{CN})_4]$ with ^{57}Fe Mössbauer spectra

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Abstract We have prepared the 2D spin crossover complexes $\text{Fe}(\text{L})_2\text{Pd}(\text{CN})_4$ ($\text{L} = \text{py}$: **1a**; py-D5 : **1b** and py-15N : **1c**). **1a** has been characterised by ^{57}Fe Mossbauer spectroscopic measurements, single crystal X-ray determination and SQUID measurements. The Mössbauer spectra for **1a** indicate that the iron(II) spin states are in high spin states at 298 K and are in low spin states at 77 K. The crystal structures of **1a** at 298 K and 90 K also show the high spin state and the low spin state respectively, associated with the Fe(II)-N distances. The spin transition temperature range of **1a** is higher than that of $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ since Pd(II) ions are larger and heavier than Ni(II) ions. SQUID data indicate isotope effects among **1a**, **1b** and **1c** are observed in very small shifts of the transition temperatures probably due to larger and heavier Pd(II) ions. The delicate shifts would be associated with subtle balances between different vibrations around Fe(II) atoms and electronic factors.

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

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This paper is dedicated to Prof. Rivka Bauminger and Prof. Rolfe Herber on the occasions of their 90 birthdays.

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1 Introduction

Iron(II) spin crossover (SCO) phenomena in magnetic coordination polymer complexes are interesting as ^{57}Fe Mössbauer spectroscopic researches because of the high potential for producing molecular-based devices with sensory and spintronic properties [1]. Coordination polymers built up by metal-cyanide units provide various attractive materials interesting physical and chemical properties such as mineralomimetic cadmium cyanide system [2, 3]. While Mössbauer spectroscopy is very useful tool for studying 3d-4f heterometallic cyano coordination polymer compounds [4–7], Iwamoto reported that Hofmann-like coordination polymers contain attractive properties in the clathration of various guest molecules [8, 9] and recently the various kinds of SCO investigations with valuable Hofmann-like structures have been continued extensively [9–18]. The iron(II) spin-crossover (SCO) behaviour of the original Hofmann-like coordination polymer $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ was discovered by chance by mainly ^{57}Fe Mössbauer spectroscopy and SQUID technique during the research for the correct-meaning Hofmann-type clathrates $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{G}$ (G = Guest organic molecules) which do not act as SCO compounds [19–22]. The Hofmann-type clathrates $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{G}$ system probably would have implications for potentially SCO materials associated with unexpected outstanding methods and techniques. As to the aspect of the hot atom behaviors related with radio-chemistry, the nuclear-decay-induced excited spin state trapping (NIESST) for ^{57}Co -labelled analogous $^{57}\text{Co}(\text{py})_2\text{Ni}(\text{CN})_4$ was found using the emission Mössbauer spectroscopic study [23]. Isotope effects on the spin transitions of the Hofmann-related coordination polymers have been reported [24, 25]. A brief history of Hofmann-like SCO coordination polymers was listed in connections with Iwamoto's reviews [8, 9, 26].

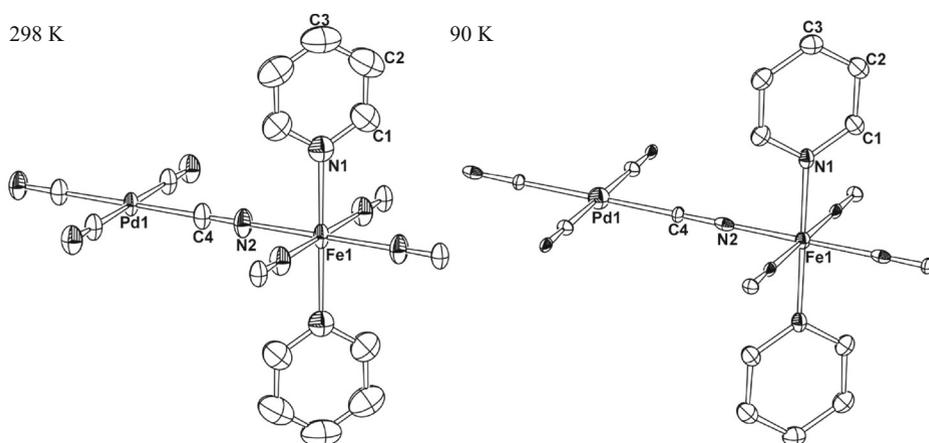
Now we have reported the 2D spin crossover complexes $\text{Fe}(\text{L})_2\text{Pd}(\text{CN})_4$ (L = py : **1a**; py-D5 : **1b** and py- ^{15}N : **1c**). **1a** has been characterized by ^{57}Fe Mossbauer spectroscopic measurements, single crystal X-ray determination and SQUID measurements.

2 Experimental

We prepared the 2D spin crossover complexes $\text{Fe}(\text{L})_2\text{Pd}(\text{CN})_4$ (L = py : **1a**; py-D5 : **1b** and py- ^{15}N : **1c**) in the ambient atmosphere by a method similar to that for the prototype $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$. The samples of **1a**, **1b** and **1c** were prepared by the follow procedure. 34.4 mg (0.100 mmol) of $\text{K}_2[\text{Pd}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ were added into 5 ml of water. To the water solution, 39.3 mg (0.100 mmol) of Mohr's salt ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), 31.0 mg (0.161 mmol) of citric acid and 3 drops of 1,3-diaminopropane were added. Colorless crystals of the sample **1a** were formed from the mixture solution by vapor diffusion method with neat pyridine (3 drops) for a few days. White powder samples **1b** or **1c** were formed from the mixture solution by vapor diffusion method with neat pyridine-D5 or pyridine- ^{15}N (3 drops) for a few days. The sample **1a**, **1b** and **1c** were identified by SQUID, powder XRD and elemental analysis. The sample **1a** was also identified by single-crystal X-ray diffraction and ^{57}Fe Mössbauer spectroscopy. The C, H and N elemental analysis for the sample **1a**, **1b** and **1c** were carried out with a YANACO JM 10 and suggest the formation of $\text{Fe}(\text{py})_2\text{Pd}(\text{CN})_4$ (Found: C, 39.19; H, 2.49; N, 19.61. Calculated for $\text{C}_{14}\text{H}_{10}\text{FeN}_6\text{Pd}$ (424.53): C, 39.61; H, 2.37; N, 19.80.), $\text{Fe}(\text{py-D}_5)_2\text{Pd}(\text{CN})_4$ (Found: C, 37.35; H, 4.82; N, 18.99. Calculated for $\text{C}_{14}\text{D}_{10}\text{FeN}_6\text{Pd}$ (434.60): C, 36.95; H (as D), 4.77; N, 19.89.) and $\text{Fe}(\text{py-}^{15}\text{N})_2\text{Pd}(\text{CN})_4$ (Found: C, 38.96; H, 2.52; N, 19.87. Calculated for $\text{C}_{14}\text{H}_{10}\text{FeN}_5^{15}\text{NPd}$ (426.53): C, 39.42; H, 2.36; N, 20.17.).

Table 1 Crystal data for **1a**

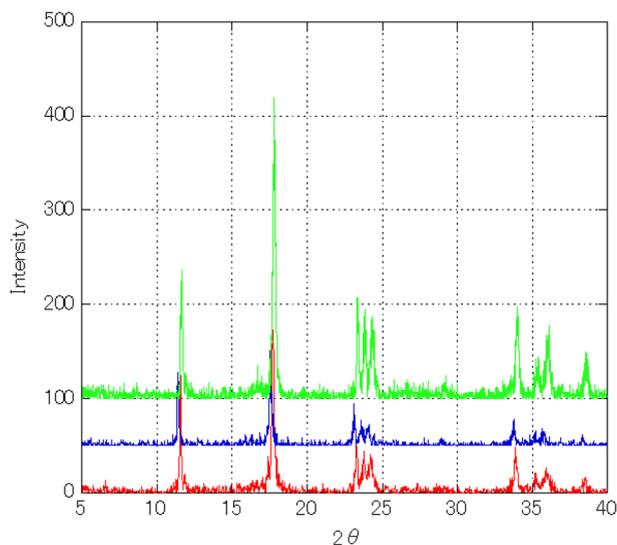
Temperature / K	298	90
Empirical formula	C ₁₄ H ₁₀ FeN ₆ Pd	C ₁₄ H ₁₀ FeN ₆ Pd
Formula weight	424.53	424.53
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Cmmm</i>	<i>Cmmm</i>
<i>a</i> / Å	7.5077(5)	7.2501(10)
<i>b</i> / Å	15.2815(11)	14.8356(19)
<i>c</i> / Å	7.4518(5)	7.1307(10)
<i>V</i> / Å ³	854.94(10)	766.98(18)
<i>Z</i>	2	2
<i>d</i> _{calc} / g cm ⁻³	1.649	1.838
μ / mm ⁻¹	1.903	2.121
F(000)	416	416
Reflections collected	3213	2656
Independent reflections	761 [<i>R</i> _{int} = 0.0163]	577 [<i>R</i> _{int} = 0.0492]
GOF	0.899	1.117
<i>R</i> , <i>R</i> _w [<i>I</i> > 2σ(<i>I</i>)]	0.0172, 0.0550	0.0894, 0.1560
<i>R</i> , <i>R</i> _w (all data)	0.0175, 0.0554	0.0903, 0.1567
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ / e.Å ⁻³	0.382, -0.278	4.476, -4.619

**Fig. 1** ORTEP drawing of Fe(py)₂Pd(CN)₄ **1a** at 298 K (left) and 90 K (right) (50% probability level)

Structural characterization for **1a** was determined by the single-crystal X-ray diffraction using BRUKER APEXII SMART (at 298 K) and BRUKER SMART (at 90 K) CCD area-detector diffractometer with monochromated Mo-K α ($\lambda = 0.71073$ Å) under the temperature controlled N₂ gas flow. The diffraction data were treated SAINT. Absorption correction were performed using SADABS. Their structures were solved by direct method, expanded using Fourier techniques, and refined by full-matrix least square refinement. All H atoms were placed at calculated position, and allowed ride on the parent atom. CCDC for **1a** are 1558389 for 298 K and 1558390 for 90 K.

Table 2 Selected bond lengths [Å] for **1a**

	298 K	90 K
Fe1-N1	2.211(3)	2.005(14)
Fe1-N2	2.160(2)	1.948(9)
Pd1-C4	1.995(2)	1.982(10)

**Fig. 2** X-ray Powder diffraction for $\text{Fe}(\text{L})_2\text{Pd}(\text{CN})_4$: L = py (red); **1a**, py- D_5 (blue); **1b**, py- ^{15}N (green); **1c**

Powder X-ray diffraction (PXRD) patterns for **1a**, **1b** and **1c** were obtained using Rigaku RAD-IIB with monochromated $\text{Cu-K}\alpha$.

^{57}Fe Mössbauer spectra were obtained using a WissEl Mössbauer system consisting of MVT-1000, MR-260A, DFG-500 and CMCA-550. The temperature dependence of the spectra at the 77 and 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 **1a** 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.

Measurements of the temperature dependence of the magnetic susceptibility of the complexes in the temperature range of 2–300 K with cooling and heating were measured on a MPMS-XL Quantum Design SQUID magnetometer.

3 Results and discussion

Crystal data for **1a** at 298 and 90 K are listed in Table 1. Figure 1 shows crystal structure for **1a**. Crystal structure of **1a** is same crystal system, space group and structure for the $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ [19] and $\text{Fe}(\text{py})_2\text{Pt}(\text{CN})_4$, [11] and is a typical 2-D Hofmann-like sheet structure. The Fe-N bond lengths in **1a** at 297 K indicate HS d^6 states for Fe^{II} ions, and

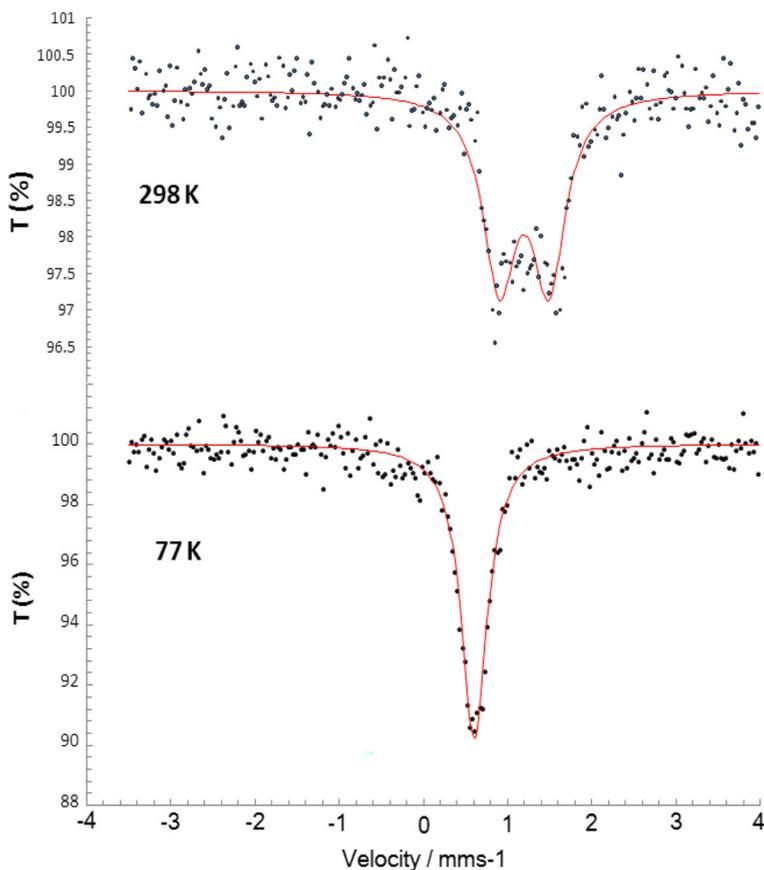


Fig. 3 Mössbauer spectra for Fe(py)₂[Pd(CN)₄] **1a** at 298 K (top) and 77 K (bottom)

at 90 K indicate LS states (Table 2). For **1b** and **1c**, the suitable crystals for single-crystal X-ray diffraction couldn't be obtained. Therefore, structural analysis for **1b** and **1c** were performed by comparison between these complexes PXRD patterns and **1a**. The PXRD pattern of **1a**, **1b** and **1c** are shown in Fig. 2. The PXRD patterns of **1b** and **1c** are the same patterns of **1a**, indicating that **1b** and **1c** are the same crystal structures as **1a**.

⁵⁷Fe Mössbauer spectra of **1a** at 298 and 77 K are shown in Fig. 3. At 298 K, doublet peak of HS with $\delta = 1.23 \text{ mm s}^{-1}$ and $\Delta E_Q = 0.59 \text{ mm s}^{-1}$ and $\Gamma_{\text{exp}} = 0.50 \text{ mm s}^{-1}$ is only observed. On the other hand, at 77 K, singlet peak of LS with $\delta = 0.60 \text{ mm s}^{-1}$ and $\Gamma_{\text{exp}} = 0.38 \text{ mm s}^{-1}$ is only observed. This suggest that all Fe^{II} are transition from HS at 298 K to LS at 77 K. The ΔE_Q value at 298 K is smaller than that of Fe(py)₂Ni(CN)₄ (0.86 mm s⁻¹) because the space group of **1a** is Cmmm and that of Fe(py)₂Ni(CN)₄ is C2/m [19]. The higher symmetry around the Fe(II) ions allow the smaller ΔE_Q value of **1a**. The δ value at 298 K for **1a** is higher than that for Fe(py)₂Ni(CN)₄ (1.06 mm s⁻¹) [19] probably due to the chemical property differences between [Pd(CN)₄]²⁻ and [Ni(CN)₄]²⁻ accompanied with 3d⁸ and 4d⁸ electron environments making shielding effects by the d electrons to the s densities of the iron(II) atoms. The shielding effects might increase slightly in **1a**. The

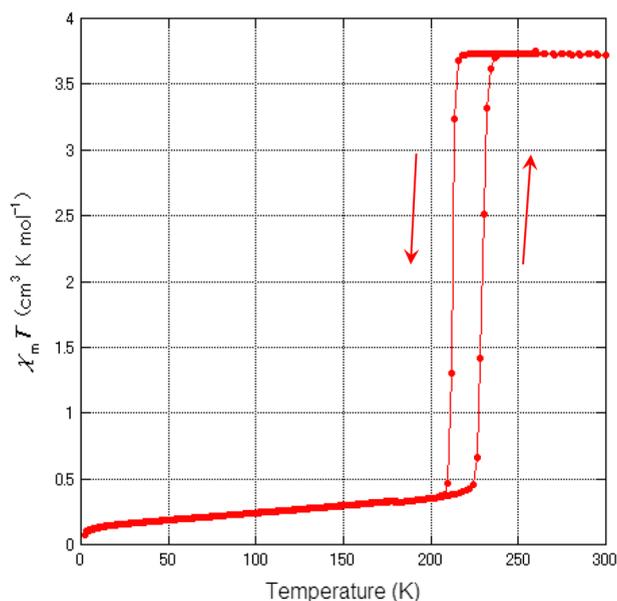


Fig. 4 χ_{MT} vs T plot of $\text{Fe}(\text{py})_2[\text{Pd}(\text{CN})_4]$ **1a**

s densities of **1a** might decrease by the indirect influence associated with the shielding by the d-electrons which would take part in chemical bonds between the iron(II) ions and the $[\text{Pd}(\text{CN})_4]^{2-}$ ligands as the balance between the donation and the back donation.

Temperature dependent magnetic susceptibilities of **1a**, **1b** and **1c** were measured in the 2–300 K temperature range. The χ_{MT} vs T plot of **1a** is shown in Fig. 4. The χ_{MT} value of **1a**, **1b** and **1c** at 300 K is $3.72 \text{ cm}^3 \text{ K mol}^{-1}$. The value consists of the HS Fe(II) state. The χ_{MT} vs T plot of **1a** shows spin-crossover phenomena with one hysteresis loop. The critical temperature for the cooling (T_c^\downarrow) and heating processes (T_c^\uparrow) are 212.8 and 229.6 K, respectively, while Niel *et al.* are reported that the critical temperatures of $\text{Fe}(\text{py})_2\text{Pd}(\text{CN})_4$ [13] were $T_c^\downarrow = 208$ and $T_c^\uparrow = 213$ K. The differences in the transition temperatures would be related to those in the preparation methods and the particle sizes depending on the preparation methods. The PXRD data in Fig. 2 indicate the particle sizes of **1a**, **1b** and **1c** are almost same. The χ_{MT} values of **1b** and **1c** at 300 K are 3.80 and $3.90 \text{ cm}^3 \text{ K mol}^{-1}$, respectively. The values also consist of the HS Fe(II) states. The χ_{MT} vs T plot of **1b** and **1c** show spin-crossover phenomena with one hysteresis loop, like as **1a** (Fig. 5). Their critical temperature of **1b** and **1c** for the cooling (T_c^\downarrow) and heating processes (T_c^\uparrow) are 214.5 and 230.8 K (**1b**), and 212.9 and 228.5 (**1c**), respectively (Table 3). While the $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ system and the $\text{Fe}(\text{py})_2[\text{Au}(\text{CN})_2]_2$ system have the delicate isotope effects associated with the vibration modes of the Fe-N bonds [24, 25], SQUID data indicate isotope effects among **1a**, **1b** and **1c** may be very delicate due to larger and heavy Pd(II) ions. The delicate shifts of the isotope effects would be related with subtle balances between different vibrations around Fe(II) atoms and electronic factors. Raman and calorimetric techniques will be helpful better understanding the isotope effects in these compounds. It also should be noted that factors such as pH on the preparation method, particle sizes, defects in the polymer structures and

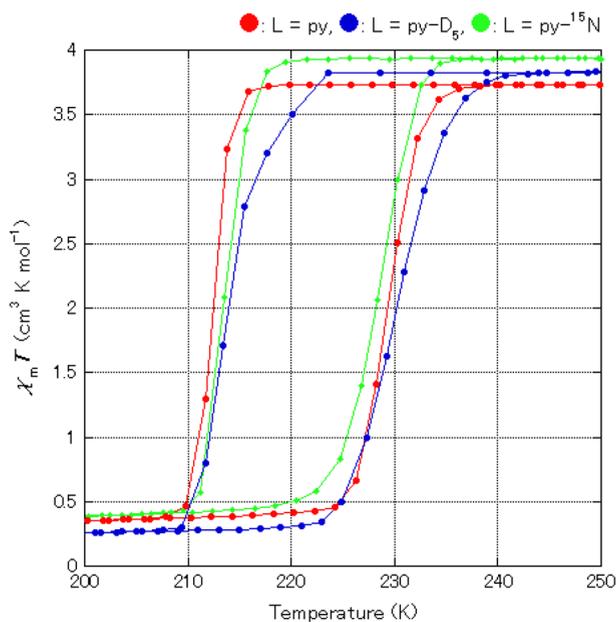


Fig. 5 $\chi_M T$ vs T plot in temperature range 200–250 K of $\text{Fe}(\text{L})_2\text{Pd}(\text{CN})_4$: $\text{L} = \text{py}$ (red); **1a**, py-D_5 (blue); **1b**, $\text{py-}^{15}\text{N}$ (green); **1c**

Table 3 Critical temperature for cooling (T_c^\downarrow) and heating (T_c^\uparrow) processes of complexes **1a**, **1b** and **1c**

Complex	Ligand	T_c^\downarrow [K]	T_c^\uparrow [K]	Hysteresis [K]
1a	py	212.8	229.6	16.8
1b	py-D ₅	214.5	230.8	16.3
1c	py- ¹⁵ N	212.9	228.5	15.6

treatment processes before SQUID measurements may be associated with the subtle shifts of the spin transition temperatures.

The spin transition temperatures of **1** are higher than those of $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ [13, 19], because the size of Pd(II) is larger than that of Ni(II). Chemical pressure effects associated with the size of Pd(II) allow the higher shift of the transition temperatures. The shift of the transition temperatures between **1** and $\text{Fe}(\text{py})_2\text{Pt}(\text{CN})_4$ is relatively small [13], since the size of Pt(II) ion is almost same as that of Pd(II), being associated with $4d^8$ and $5d^8$ electron properties. Pressure experiments [27, 28] also will be helpful for understanding spin transition temperatures in polymeric systems.

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