New Hofmann-like spin crossover compound with 3,5-lutidine

Takafumi Kitazawa · Miwa Takahashi

Abstract A new type III of 3,5-lutidine spin crossover coordination compound with formula $Fe(3,5\text{-lutidine})_2Ni(CN)_4 \cdot 2[(H_2O)(3,5\text{-lutidine})]$ 2c has been obtained. The ratio of the high spin state (HS) iron (II) changing to the low spin state (LS) iron (II) in 2c is higher than that of type I and type II 3,5-lutidine coordination polymer 2a and 2b previously reported. ^{57}Fe Mössbauer spectra of 2c show two different doublets which correspond to HS1 (inner doublet lines) and HS2 (outer doublet lines). The intensity of the HS1 doublet decreases on cooling to 80 K while the intensity of another component, the LS singlet, increases. The 90 % of the HS1 doublet change to the LS singlet is probably due to suitable environments of octahedral iron (II) ions coordinated by four nitrogen atoms of cyano groups and two nitrogen atoms of 3,5-lutidine ligands. We also prepared the Hofmann-like 3,5-dichloropyridine coordination compound $Fe(3,5\text{-dichloropyridine})_2Ni(CN)_4 \cdot 2[(3,5\text{-dichloropyridine})(H_2O)]$ 2d to compare it with 2c. ^{57}Fe Mössbauer spectra of 2d show that 2d is not a spin crossover coordination compound.

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

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1 Introduction

The spin crossover (SCO) phenomenon is found in first-row transition-metal complexes of d^4-d^7 configuration, the largest number of examples being available for octahedral iron(II). External stimuli, such as temperature, light, or pressure, can be used to switch between these states. SCO research areas continue to develop with the coming of new SCO materials, associated with theories and prospective applications [1].

Coordination polymer frameworks built up by self-assembly constitute a most useful and efficient process for building up nano-scale supramacromolecular architectures with unique network topologies and potentially interesting magnetic properties. Cyanometalates are useful building blocks for various dimensional coordination polymeric networks as transition metal templates. Special attention is currently paid to coordination polymer iron(II) SCO compounds acting in cooperative behaviour since they can manifest sensory and memory functions. The Hofmann pyridine coordination polymer $Fe(py)_2Ni(CN)_4$ 1 shows iron(II) SCO behaviour, as revealed by [57]Fe Mössbauer spectroscopy and the SQUID technique [2]. Pressure tuning Raman spectroscopy of 1 was reported [3] and an isotope effect of 1 was found [4]. An emission Mössbauer spectroscopic study of [57]Co-labelled analogous [57]$Co(py)_2Ni(CN)_4$ demonstrated nuclear-decay-induced excited spin state trapping (NIESST) [5].

The effect on the spin crossover of Cl and CH_3 replacements located at different positions on the pyridine ring was also studied [6, 7]. The related spin crossover coordination compounds have been developed [8–18]. Some of them contain 3D pillared Hofmann-type-organic frameworks [10–16].

We previously reported two kinds of 2D coordination polymer iron(II) spin crossover complexes containing 3,5-lutidine with formula $Fe(3,5$-lutidine$)_2Ni(CN)_4\cdot$ [n(H_2O)m$(3,5$-lutidine$)$] whose host framework is similar to that of 1 [17]. The type I material obtained from the pH 5.2 solution is $Fe(3,5$-lutidine$)_2Ni(CN)_4\cdot[0.8(H_2O)]$ 2a, in which water molecules coordinate to iron(II) ions and/or are accommodated with the host $Fe(3,5$-lutidine$)_2Ni(CN)_4$framework. The type II material obtained from the pH 8.5 solution is $Fe(3,5$-lutidine$)_2Ni(CN)_4\cdot[0.5(H_2O)(3,5$-lutidine$)]$ 2b, in which 3,5-lutidine molecules act both as ligands coordinating to octahedral Fe(II) atoms and as guest molecules accommodated with the host $Fe(3,5$-lutidine$)_2Ni(CN)_4$framework. Their SCO properties studied by temperature dependent [57]Fe Mössbauer spectroscopy indicate incomplete SCO behaviour [17]. Sometimes the SCO behaviour depends on the preparation methods and/or preparation conditions.

We report here the preparation of the new type III material of Hofmann-like 3,5-lutidine spin crossover coordination compound with formula $Fe(3,5$-lutidine$)_2Ni(CN)_4\cdot2[(H_2O)(3,5$-lutidine$)]$ 2c. We also prepared the Hofmann-like 3,5-dichloropyridine coordination compound $Fe(3,5$-dichloropyridine$)_2Ni(CN)_4\cdot2[(3,5$-dichloropyridine$)(H_2O)]$ 2d to compare to 2c. [57]Fe Mössbauer data indicate that 2c is spin crossover compound, while 2d does not have SCO behaviour.

Table 1 Types of Fe(3,5-lutidine)$_2$Ni(CN)$_4$·[n (H$_2$O) m(3,5-lutidine)]

	Guest ratio	Abb.	Preparation condition	SCO behaviour
Type I	$n = 0.8, m = 0$	2a	pH = 5.2 (direct method)	incomplete (36 %)
Type II	$n = 0.5, m = 1$	2b	pH = 8.5 (direct method)	incomplete (27 %)
Type III	$n = 2, m = 2$	2c	pH = 5.2 (vapor method)	Almost (90 %) complete

Type I, Type II ref. [17]; Type III [This work]

2 Experimental

Although we previously prepared 2a and 2b using direct contact methods with the aqueous solution containing Mohr's salt (Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O) and potassium tetracyanonickelate(II) to neat 3,5-lutidine [17], we prepared the new type III Fe(3,5-lutidine)$_2$Ni(CN)$_4$·2[(H$_2$O)(3,5-lutidine)] 2c using by vial-in-vial slow diffusion methods with aqueous solutions and 3,5-lutidine vapors. 3.14 g (8.80 mmol) of Mohr's salt (Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O) and 2.12 g (8.80 mmol) of potassium tetracyanonickelate(II) (K$_2$[Ni(CN)$_4$]) were added into 120 ml of water, and then a light blue precipitate formed immediately. The last one was dissolved by adjusting the pH 5.2 of an aqueous solution, using 4.79 g of citric acid and 2.2 ml of 1,3-diaminopropane. The aqueous solution was located in a small vial. The small vial was put in a large vial with 5 ml of 3,5-lutidine. After standing for a few days at room temperature (RT), yellow solid particles 2c were formed at the interface between the organic and aqueous phases or/and at the bottom of the aqueous phase. Fe(3,5-dichloropyridine)$_2$Ni(CN)$_4$· 2[(3,5-dichloropyridine)(H$_2$O)] 2d was obtained by a similar method for 2c. Unfortunately single crystals suitable for X-ray determination have not yet been obtained. The materials were identified by [57]Fe Mössbauer spectroscopy, elemental analysis, powder X-ray diffraction, and infrared spectroscopy. The elemental analysis for C, H, and N was carried out with a Perkin-Elmer Model 2400.

[57]Fe Mössbauer spectra were obtained using an Austin Science S-600 spectrometer in connection with an EG & G Ortec Model 5500 multichannel analyzer. The temperature dependence of the spectra in the range of 80–295 K were measured by keeping the sample in a gas-flow type cryostat (Oxford Instrument CF1104) and the source was kept at RT. The temperature of the sample was controlled by a DTC2 digital temperature controller from Oxford Instruments. A platinum resistor was used to measure the temperature. The spectra were computer-fitted to Lorentzian lines. The values of the isomer shift are given relative to an α-iron foil at RT.

3 Results and discussion

We prepared type III of 3,5-lutidine materials with the majority of two-dimensional layered framework consisting of Fe(3,5-lutidine)$_2$Ni(CN)$_4$. The formation of the three materials type I, II and III in Table 1 depends on the pH of the mother aqueous solution containing equimolar amounts of

Fig. 1 ^{57}Fe Mössbauer spectra of spin crossover coordination polymer Fe(3,5-lutidine)$_2$Ni(CN)$_4$· 2[(H$_2$O)(3,5-lutidine)] 2c at RT and 80 K
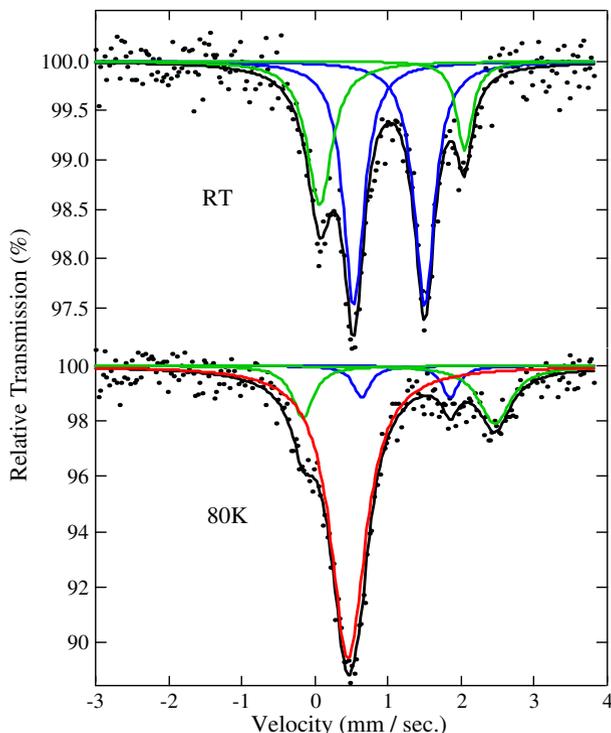
Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O and K$_2$[Ni(CN)$_4$], and preparation methods with or without using the vial-in-vial slow diffusion method. The material 2c obtained by using the vial-in-vial slow diffusion method is Fe(3,5-lutidine)$_2$Ni(CN)$_4$·2[(H$_2$O)(3,5-lutidine)] (Found C, 55.89; H, 5.49; N, 16.28 %. Calcd. C, 56.24; H, 5.90; N, 16.40 %), in which 3,5-lutidine molecules act both as ligand coordinating to octahedral Fe(II) atoms and as guest molecules accommodated with the majority of the host Fe(3,5-lutidine)$_2$Ni(CN)$_4$framework. The material 2d by using the vial-in-vial slow diffusion method is Fe(3,5-dichloropyridine)$_2$Ni(CN)$_4$·2[(3,5-dichloropyridine)(H$_2$O)] (Found C, 33.19; H, 3.21; N, 13.15 %. Calcd. C, 34.02; H, 1.89; N, 13.23 %), in which 3,5-dichloropyridine molecules act both as ligand coordinating to octahedral Fe(II) atoms and as guest molecules accommodated with the host Fe(3,5-dichloropyridine)$_2$Ni(CN)$_4$framework.

^{57}Fe Mössbauer spectra of material 2c and 2d performed at 80 K and RT are shown in Figs. 1 and 2. ^{57}Fe Mössbauer parameters for 2c and 2d are listed in Tables 2 and 3. Spectra of 2c indicate SCO behavior with 90 % inner HS sites changing to LS sites, while the percentage of HS changing to LS (90 %) in 2c is higher than those of the type I and the type II 3,5-lutidine coordination polymer 2a (36 %) and 2b (27 %) previously reported [17]. Spectra of 2d do not show SCO behaviour. ^{57}Fe Mössbauer spectra parameters for 2d ($\delta = 1.11(2)$, $\Delta E_Q = 1.68(2)$ mm s^{-1} for RT and $\delta = 1.22(2)$, $\Delta E_Q = 2.19(2)$ mm s^{-1} for 80 K) indicate that iron(II) sites at both 80 K and RT are high spin states.

Fig. 2 ^{57}Fe Mössbauer spectra of Fe(3,5-dichloropyridine)$_2$Ni(CN)$_4\cdot$2[(3,5-dichloropyridine)(H$_2$O)] 2d at RT and 80 K
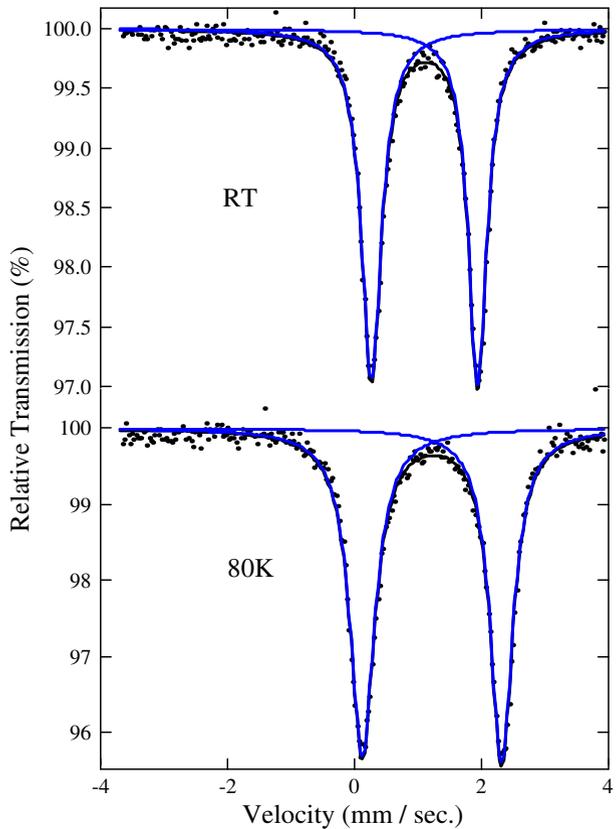
Table 2 ^{57}Fe Mössbauer parameters of Fe(3,5-lutidine)$_2$Ni(CN)$_4\cdot$2[(H$_2$O)(3,5-lutidine)] 2c

T K	Site	δ (mm s^{-1})	ΔE_Q (mms^{-1})	Γ_{exp} (mm s^{-1})	A %
RT	HS1	1.02(2)	0.97(1)	0.34(2) 0.34(2)	67(2)
	HS2	1.06(2)	1.98(2)	0.41(2) 0.26(2)	33(2)
80	HS1	1.24(2)	1.21(1)	0.27(2)	7 (2)
	HS2	1.15(2)	2.63(2)	0.35(2) 0.52(3)	21(3)
	LS	0.45(2)	0.00(1)	0.57(3)	72(3)

Γ_{exp}: The full experimental linewidth at half maximum height

As shown in Fig. 1, the ^{57}Fe Mössbauer spectrum of material 2c at RT shows two different doublets which correspond to the HS1(inner doublet lines: blue lines) and HS2(outer doublet lines: green lines) states. The intensity of the HS1 doublet decreases gradually on cooling to 80K while a new spectrum component, the LS singlet(red lines), increases in intensity. As listed in Table 2, the ratio of HS1 to HS2 at RT is 67(2): 33(2), and that of HS1 and HS2 to LS at 80 K is 7(2): 21(3): 72(3). The recoil-free fraction of HS1 is different of that of HS2 due to different octahedral iron(II) enviroments. Considering both the Mössbauer parameters of 2c ($\delta = 1.02(2)$, $\Delta E_Q = 0.97(1)$ mm s^{-1} at RT and $\delta = 1.24(2)$, $\Delta E_Q = 1.21(1)$ mm s^{-1} at 80 K) and the structural and Mössbauer data for Fe(py)$_2$Ni(CN)$_4$ [2], Fe(3-Cl-py)$_2$Ni(CN)$_4$ [6],

Table 3 ^{57}Fe Mössbauer parameters of Fe(3,5-dichloropyridine)$_2$Ni(CN)$_4 \cdot$ 2[(3,5-dichloropyridine)(H$_2$O)] 2d

T K	Site	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ_{exp} (mm s^{-1})	A %
RT	HS	1.11(2)	1.68 (2)	0.39(2) 0.35(2)	100(2)
80	HS	1.22 (2)	2.19 (2)	0.47(2) 0.44(2)	100(2)

Γ_{exp}: The full experimental linewidth at half maximum height

Fe(3-Methyl-py)$_2$Ni(CN)$_4$ [7], and Fe(3-F-py)$_2$Ni(CN)$_4$ [8, 9], the iron(II) atoms in HS1 of 2c have six coordinations with four nitrogen atoms of cyano groups and two nitrogens of 3,5-lutidine. 90 % of HS1 sites change to the singlet LS state due to the suitable FeN$_6$ environment for SCO behaviour. The Mössbauer parameters of LS at 80 K is $\delta = 0.45(2)$, $\Delta E_Q = 0.00(1)$ mm s^{-1} for 2c.

The minor HS2 parameters ($\delta = 1.06(2)$, $\Delta E_Q = 1.98(2)$ mm s^{-1} at RT and $\delta = 1.15(2)$, $\Delta E_Q = 2.63(2)$ mm s^{-1} at 80 K) with a large ΔE_Q value is probably due to the FeN$_5$(OH$_2$) or FeN$_4$(OH$_2$)$_2$ environment. The FeN$_5$O core consists of an octahedral iron(II) atom coordinated by four nitrogen atoms of the cyano group, one nitrogen atom of the 3,5-lutidine and one oxygen atom of the water ligand. The FeN$_4$O$_2$ core completes an octahedral iron(II) atom by coordinating two water molecules at the axial position. Taking into account the particle sizes of 2c, 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, cannot exhibit spin crossover [9].

In contrast to the 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. For material 2c with guest 3,5-lutidine species, another explanation about the outer high spin state sites may be possible such as $\pi - \pi$ interactions between the ligands of 3,5-lutidine coordinated to iron(II) atoms and the guest molecules of 3,5-lutidine in 2D and 3D Hofmann-like coordination polymer compounds [10–16]. While 2c has the 2D host framework, guest 3,5-lutidine molecules probably have $\pi - \pi$ interactions with ligand 3,5-lutidine species. At RT, the Mössbauer spectrum is composed of two different doublets that can be attributed to iron(II) in the HS state. The low 0.97(1) mm s^{-1} value of ΔE_Q in HS1 indicates that local symmetry is lower than cubic and the ground orbital state is rather a doublet, which corresponds to an axial elongation of the octahedral environment around the iron(II) ion centre. Conversely, the large 1.98(2) mm s^{-1} value of ΔE_Q in HS2 indicates a local symmetry lower than cubic, but with a rather well-isolated ground orbital singlet, which corresponds to an axial compression of the octahedral structure. When decreasing the temperature to 80 K, the doublet with smaller quadrupole splitting HS1 was transformed into the LS state, while the second doublet HS2 was not affected by the spin crossover behaviour.

The large amount of the accommodated guest 3,5-lutidine molecules in the network involved in $\pi - \pi$ stacking interactions with the coordinated 3,5-lutidine molecules in the type III decreases the electron density of the ligand molecule and thus explains the elongation of almost all the axial Fe(II)-N bonds, which represent the SCO-active Fe(II) ion centers [15]. By contrast, only a small amount of guest 3,5-

lutidine molecules in the type I and II are included within the network; a proportion of iron(II) ion centers in which the coordinated 3,5-lutidine is not involved in $\pi - \pi$ stacking interactions conserves an axial compression agreeing with the inactive iron(II) ion centers. Moreover, the important variation in the value of ΔE_{Q} of HS2 $(1.98(2) -2.63(2)$ mm s^{-1}) of the non-active HS doublet between RT and 80 K is due to a strongly distorted equatorial environment associated with a small energy gap between the d$_{xy}$ orbital and the thermally accessible d$_{xz}$ or d$_{yz}$ orbitals [15].

Water molecules can act both as ligands coordinating to iron(II) ions and as guest molecules in the Fe(3,5-lutidine)$_2$Ni(CN)$_4$ host framework in 2c. Water molecules accommodated with the Fe(3,5-lutidine)$_2$Ni(CN)$_4$ 2D framework may be associated with subtle coordination environments of iron(II) ions. The residual fractions of the high spin HS1 molecules in the low temperature range may be related to the packing mode of 3,5-lutidine in 2c. While a favorable $\pi - \pi$ interaction between the 3,5-lutidine ligands of the host frameworks and the guest 3,5-lutidine molecules in 2c may be associated with a nature of spin transition which acts as 90 % HS1 transferring to LS, subtle environments around Fe(II)N$_6$ coordinated by two pyridine ligands and four nitrogen atoms of cyano groups in 2c induce that 90 % of HS1 change to the LS singlet.

We have obtained the new type III of 3,5-lutidine Hofmann spin crossover coordination compound 2c. The spin crossover behaviour of type III is different from that of type I and II. Contents of 3,5-lutidine and water molecules are linked to differences of SCO behaviours in 2a, 2b and 2c. Chemical pressure of 3,5-lutidine and water molecules are associated with different SCO rate of HS1 to LS in 2a, 2b and 2c. Guest water molecules in 2c are key to active SCO behaviour. Figures 1 and 2 also indicate that using 3,5-lutidine molecules may induce water molecules coordinating to iron(II) atoms. Probably water molecules in 2d may be guest molecules in the host framework Fe(3,5-dichloropyridine)$_2$Ni(CN)$_4$.

Both 3-methyl-pyridine Hofmann complex Fe(3-Methyl-py)$_2$Ni(CN)$_4$ and 3-chloro-pyridine Hofmann complex Fe(3-Cl-py)$_2$Ni(CN)$_4$ act as incomplete spin crossover behaviour [6, 7]. The position-3 substituent of the pyridine ring may be associated with spin crossover behaviour in Fe(3-Cl-py)$_2$Ni(CN)$_4$, Fe(3-Methyl-py)$_2$Ni(CN)$_4$. Although the shape and the size of 3,5-lutidine are almost the same as those of 3,5-dichloropyridine, the 3,5-lutidine complex occurs in spin crossover while the 3,5-dichloropyridine complex does not. The effects of position-3,5 substituent to SCO behaviour are different from those of position-3.

The existence of three kinds of 3,5-lutidine Hofmann-like spin crossover compounds may promise a new way of Hofmann-like spin crossover coordination compounds using linear [Au(CN)$_2$]$^-$ ligands [16, 18, 19] and [Ag(CN)$_2$]$^-$ ligands [20, 21].

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