2D iron(II) spin crossover complex with 3,5-lutidine

**Takafumi Kitazawa · Miwa Takahashi ·
Takeshi Kawasaki**

Abstract 2D coordination polymer iron(II) spin crossover complexes containing 3,5-lutidine with host framework $Fe(3,5\text{-lutidine})_2Ni(CN)_4$ were synthesized. Their spin crossover properties were studied by temperature dependent ^{57}Fe Mössbauer spectroscopy. Materials show gradual incomplete spin crossover with distinct thermochromism, while only 25 % of iron(II) ions are switched to the low spin state at 80 K, as determined by a detailed ^{57}Fe Mössbauer study.

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

1 Introduction

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). Transition metal complexes of first-row transition series with d^4–d^7 configuration in an octahedral crystal field have a possibility of SCO between the low-spin(LS) and the high-spin(HS) state. 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].

T. Kitazawa (✉) · M. Takahashi · T. Kawasaki
Department of Chemistry, Faculty of Science, Toho University,
2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan
e-mail: kitazawa@chem.sci.toho-u.ac.jp

T. Kitazawa
Research Centre for Materials with Integrated Properties, Toho University,
2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan

 Springer

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 block for various dimensional coordination polymeric networks as transition metal templates [2]. Special attention is currently paid to coordination polymer iron(II) SCO compounds acting 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, revealed by [57]Fe Mössbauer spectroscopy and SQUID technique [3]. Emission Mössbauer spectroscopic study [57]Co-labelled analogous [57]$Co(py)_2Ni(CN)_4$ was reported in the nuclear-decay-induced excited spin state trapping (NIESST) [4].

The effect on the spin crossover of Cl and CH_3 replacements located at different positions on the pyridine ring were also studied [5, 6]. The related spin crossover coordination compounds have been developed [7, 8]. 2D coordination polymer iron(II) spin crossover complexes containing 3,5-lutidine with ideal formula $Fe(3,5\text{-lutidine})_2Ni(CN)_4 \cdot n(H_2O)m(3,5\text{-lutidine})$, whose host framework is similar to that of **1,** have been synthesized now. Their SCO properties have been studied by temperature dependent [57]Fe Mössbauer spectroscopy.

2 Experimental

We prepared 2D spin crossover materials with 3,5-lutidine ligands in the ambient atmosphere by a method similar to that for **1**. Mohl's salt ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) 1.73 g (4.44 mmol)and 1.07 g of potassium tetracyanonickelate(II) (4.44 mmol) ($K_2[Ni(CN)_4]$) were added into 60 ml of water, and then a light blue precipitate formed immediately . The last one was dissolved by adjusting the pH of aqueous solution between 5.2 and 8.5, using citric acid and 1,3-diaminopropane. The aqueous solution was covered with a layer of neat 3,5-lutidine and kept at room temperature for a few days. Yellow fine solid particles were formed at the interface between the organic and aqueous phases or/and at the bottom of the aqueous phase. The materials **2a** and **2b** were obtained from the pH 5.2 and the pH 8.5 aqueous solution respectively. Unfortunately single crystals suitable for X-ray determination have not yet been obtained. The materials were identified by [57]Fe Mössbauer spectrosocopy, SQUID, elemental analysis, powder X-ray diffraction, and infrared spectroscopy. The elemental analysis for C, H, and N was carried out with a Perkin-Elmaer Model 2400.

[57]Fe Mössbauer spectra were obtained using an Austin Science S-600 spectrometer in connection with an EG & G Ortrec 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 room temperature. 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 α-iron foil at room temperature.

The magnetic susceptibilities of polycrystalline forms in the materials $Fe(3,5\text{-lutidine})_2Ni(CN)_4 \cdot [n(3,5\text{-lutidine})m(H_2O)]$ **2a** and **2b** were determined with a

Fig. 1 ^{57}Fe Mössbauer spectra
of spin crossover coordination
polymer Fe(3,5-lutidine)$_2$-
[Ni(CN)$_4$]0.8(H$_2$O) **2a** at
various temperatures
on cooling
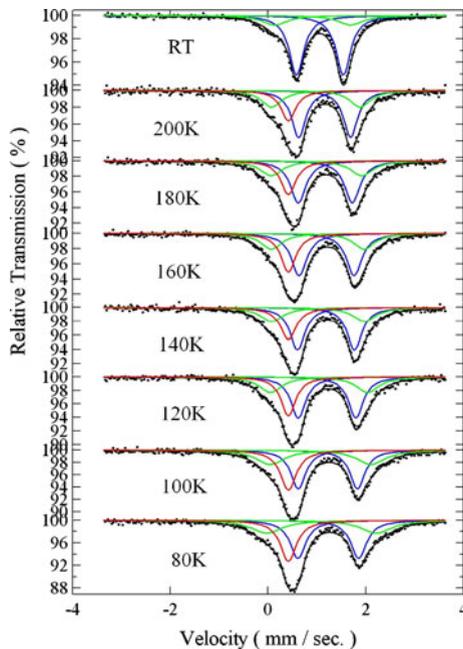
SQUID magnetometer (Quantum Design, Inc) between 2 and 290 K with magnetic
flux densities of 0.1 T.

3 Results and discussion

We prepared two types of 3,5-lutidine materials with two-dimensional layered frame-
work consisting of Fe(3,5-lutidine)$_2$Ni(CN)$_4$. The formation of the two materials
depends on the pH of the mother aqueous solution containing equimolar amounts
of Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O and K$_2$[Ni(CN)$_4$]. The material **2a** obtained from the
pH 5.2 solution is Fe(3,5-lutidine)$_2$Ni(CN)$_4$·0.8H$_2$O (Found C, 48.21; H, 3.84; N,
18.53 %. Calcd. C, 48.32; H 4.42; N 18.79 %). The material **2b** obtained from
the pH 8.5 solution is Fe(3,5-lutidine)$_2$Ni(CN)$_4$·[(3,5-lutidine)0.5H$_2$O] (Found C,
54.48; H, 4.92; N, 17.63 %. Calcd. C, 54.68; H 5.14; N 17.89 %), in which 3,5-
lutidine molecules act both ligand coordinating to octahedral Fe(II) atoms and guest
molecules accommodated with host Fe(3,5-lutidine)$_2$Ni(CN)$_4$ framework.

^{57}Fe Mössbauer spectra of material **2a** performed at various temperatures are
shown in Fig. 1. Both spectra of **2a** and **2b** indicate similar incomplete SCO
behavior as shown in Figs. 2 and 3. ^{57}Fe Mössbauer spectra of material **2b** are
slightly diffrent from those of material **2a** (supplemental information Fig. S1). High-
temperature Mössbauer spectra of materials(**2a** and **2b**) show two diffrent doublets
which correspond to the HS1 (inner doublet lines) and HS2 (outer doublet lines)
states. The intensity of the HS1 doublet decreases gradually on cooling to 80 K at
the expense of a new one featuring the LS singlet. Considering both the Mössbauer
parameters (sδ = 1.06, ΔE_Q = 0.96 mm s^{-1} at 295 K for **2a** and δ = 1.15, ΔE_Q =
1.10 mm s^{-1} at 295 K for **2b**) and the structural data for Fe(py)$_2$Ni(CN)$_4$ [3],

Fig. 2 Temperature dependence of the HS fraction $\gamma_{HS}(T)$, determined from the ^{57}Fe Mössbauer spectra of Fe(3,5-lutidine)$_2$Ni(CN)$_4$· 0.8(H$_2$O)**2a**. The HS fraction $\gamma_{HS}(T)$ is HS1/(HS1+LS). *Blue* is cooling mode and *red* is warming mode
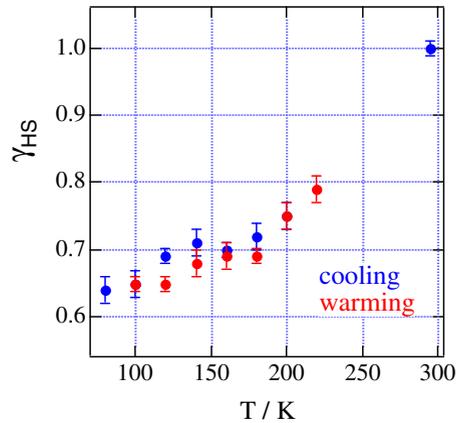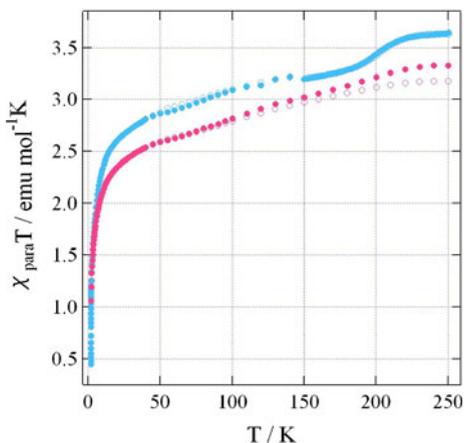

Fig. 3 Temperature dependence of the HS fraction $\gamma_{HS}(T)$, determined from the ^{57}Fe Mössbauer spectra of Fe(3,5-lutidine)$_2$Ni(CN)$_4$· [(3,5-lutidine)0.5H$_2$O] **2b**. The HS fraction $\gamma_{HS}(T)$ is HS1/(HS1+LS). *Blue* is cooling mode and *red* is warming mode
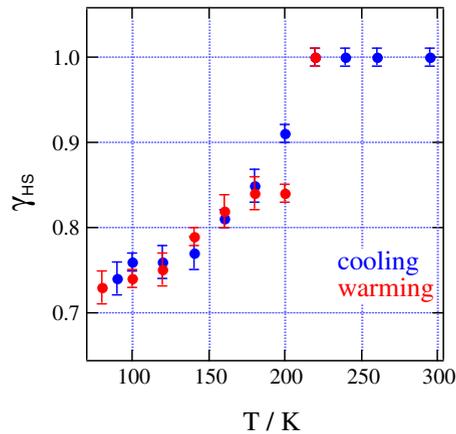
Fe(3-Cl-py)$_2$Ni(CN)$_4$ [5], Fe(3-Methyl-py)$_2$Ni(CN)$_4$ [6], and Fe(3-F-py)$_2$Ni(CN)$_4$ [7, 8], the iron(II) atoms in HS1 of **2a** and **2b** have six coordination with four nitrogen atoms of cyano groups and two nitrogen of 3,5-lutidine. A part of HS1 site changes to the singlet LS state due to the FeN$_6$ environment. The Mössbauer parameters of LS at 80 K are $\delta = 0.42$, $\Delta E_Q = 0.00$ mm s^{-1} for **2a** and $\delta = 0.42$, $\Delta E_Q = 0.00$ mm s^{-1} for **2b** respectively.

The minor HS2 site with a large ΔE_Q value (1.55 mms^{-1} for **2a** and 2.28 mm s^{-1} for **2b** at 295 K) 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 4 nitrogen atoms of cyano group, one nitrogen atom of the 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 of particle sizes of **2**, the HS2 doublet may ascribed to the iron(II) uints 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.[8]

Fig. 4 SQUID data for
Fe(3,5-lutidine)$_2$Ni(CN)$_4$·
0.8(H$_2$O)**2a** (*red*) and
Fe(3,5-lutidine)$_2$Ni(CN)$_4$·
[(3,5-lutidine)0.5H$_2$O]
2b (*blue*)

The temperature dependence of the HS1 fraction $\gamma_{HS}(T)$, where $\gamma_{HS}(T)$ is HS1/(HS1+LS), also shows that the 64 % and 73 % of HS1 sites still remains unchanged at 80 K for **2a** and **2b** respectively (Figs. 2 and 3). The SCO transition of the HS1 site occurs over the temperature range of 220 K to 80 K (or below 80 K) with a vanishingly small hysteresis. SQUID data support the SCO behavior of **2a** and **2b** (Fig. 4). While even at 80 K the spin transition is incomplete, distinct thermochromism from yellow to purple occurs. 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.

For material **2b**, another explanation may be existed because guest molecules of 3,5-lutidine and water species probably are accommodated in the host layer of Fe(3,5-lutidine)$_2$Ni(CN)$_4$. At 295 K, the Mössbauer spectrum is composed of two different doublet that can be attribute to iron(II) in the HS state. The low 1.10 mm/s 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 2.28 mm/s 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, at 80 K, the doublet with smaller quadrupole splitting in HS1 was transformed into the LS state, where the second doublet in HS2 was not affected by the spin crossover behavior.

The large amount of the accommodated guest 3,5-lutidine molecules in the network involved in π–π stacking interactions with the coordinated 3,5-lutidine molecules decreases the electron density of the ligand and thus explains the elongation of almost all the axial Fe-N bonds, which represent the SCO-active Fe(II) centers. By contrast, only a small amount of guest 3,5-lutidine molecules are included within the network; a proportion of iron(II) centers in which the coordinated 3,5-lutidine is not involved in π–π stacking interactions conserves an axial compression consistent with the inactive iron(II) centers. Moreover, important ΔE_Q in HS2 variation (2.28–3.09 mm s^{-1}) of the non-active HS doublet between 295 and 80 K is characteristic

of 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.

Water molecules can act as both ligands coordinating to iron(II) ions and guest molecules in the $Fe(3,5\text{-lutidine})_2Ni(CN)_4$ host framework. Water molecules accommodated with the $Fe(3,5\text{-lutidine})_2Ni(CN)_4$ 2D framework may be associated with coordination environments of iron(II) ions. The residual fractions of the high spin HS1 molecules in low temperature range may be related to the packing mode of 3,5-lutidine. A favorable $\pi-\pi$ interaction of the 3,5-lutidine ligands may be associated with a nature of spin transition which is incomplete.

References

1. Gütlich, P., Goodwin, H.A. (eds.): Spin crossover in transition metal compounds, topics in current chemistry, vols. 233–235. Springer Verlag, Berlin (2004)
2. Garcia, Y., Niel, V., Muñoz, M.C., Real, J.A.: Top. Curr. Chem. **233**, 229 (2004)
3. Kitazawa, T., Gomi, Y., Takahashi, M., Takeda, M., Enomoto, M., Miyazaki, A., Enoki, T.: J. Mater. Chem. **6**, 119 (1996)
4. Sato, T., Ambe, F., Kitazawa, T., Sano, H., Takeda, M.: Chem. Lett. **1287** (1997)
5. Kitazawa, T., Takahashi, Mi., Takahashi, Ma., Enomoto, M., Miyazaki, A., Enoki, T., Takeda, M.: J. Radio. Nucl. Chem. **239**, 285 (1999)
6. Molnár, G., Guillon, T., Moussa, N.O., Rechignat, L., Kitazawa, T., Nardone, M., Bousseksou, A.: Chem. Phys. Lett. **423**, 152 (2006)
7. Martínez, V., Gaspar, A.B., Muñoz, M.C., Bukin, G.V., Levchenko, G., Real, J.A.: Chem. Eur. J. **15**, 10960 (2009)
8. Martínez, V., Boldog, I., Gaspar, A.B., Ksenofontov, V., Bhattacharjee, A., Gütlich, P., Real, J.A.: Chem. Mater. **22**, 4271 (2010)