Conversion of the Valence States of ^{57}Fe Atoms Produced in ^{57}Co-labelled [Co(pyridine)$_2$Ni(CN)$_4$]

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Emission Mössbauer spectra of the title compound measured below 80K consist of three components ascribed to two Fe(II) high-spin states and one Fe(III) low-spin state. It was concluded that a part of the Fe(II) high-spin species converts to an Fe(III) high-spin species above 210 K, based on the comparison of the results with temperature-depending spin-crossover transition of the isomorphous compound, [Fe(py)$_2$Ni(CN)$_4$].

The title compound is an analogue of the Fe(II)-Ni(II) coordination polymer, [Fe(py)$_2$Ni(CN)$_4$]. The Fe(II)-Ni(II) polymer complex shows thermally induced high-spin $^5T(O_h) \rightleftharpoons$ low-spin $^1A(O_h)$ transition with regard to Fe(II) atoms, and diamagnetic Ni(II) atoms (square-planar C_4 coordination) and Fe(II) atoms (octahedral N_6 coordination) are bridged by CN$^-$ ligands forming a two-dimensional network of [FeNi(CN)$_4$]$_\infty$.[1] In the present paper, we studied the chemical state of ^{57}Fe atoms produced by the EC-decay in ^{57}Co-labelled [Co(py)$_2$Ni(CN)$_4$] by means of emission Mössbauer spectroscopy. Emission Mössbauer spectroscopic studies have been reported for several ^{57}Co(II)-labelled compounds whose Fe(II) analogues are spin-crossover complexes.[2-6] In all these cases, most of the ^{57}Fe atoms formed by nuclear decay are in an Fe(II) high-spin state over the temperature regions studied, in spite of the spin-crossover behavior of the Fe(II) compounds. Gütlich et al. have proposed an interpretation that the anomalous Fe(II) high-spin state produced at lower temperature is grasped to be in the excited electronic state (^5T) formed by the NIESST (Nuclear decay Induced Excited Spin State Trapping) effect which was termed after the LIESST (Light Induced Excited Spin State Trapping) effect.[7-9] The present report will show a conversion of the valence states of produced ^{57}Fe atoms from Fe(II) to Fe(III) at higher temperature.

Figure 1 shows emission Mössbauer spectra of ^{57}Co-labelled [Co(py)$_2$Ni(CN)$_4$] obtained by using the labelled compound as a Mössbauer γ-ray source kept in a cryostat against an ^{57}Fe-enriched K$_4$[Fe(CN)$_6$]•3H$_2$O absorber moving in a constant acceleration mode at room temperature.[10] The spectra measured at 5K and 80 K are decomposed into three components ascribed to two Fe(II) high-spin states (Fe(II)HS1 and Fe(II)HS2) and one Fe(III) low-spin state (Fe(III)LS). Above 210 K, a new quadrupole doublet due to an Fe(III) high-spin state (Fe(III)HS) appears at the expense of the Fe(II)HS2 doublet. These observations are interpreted by assuming that a part of Fe(II)HS2 converts to Fe(III)HS above 210 K. Mössbauer parameters of the components are summarized in Table 1 together with their absorption peak areas. The origin of each component is interpreted as described below.

Fe(II)HS1: This component has Mössbauer parameters (δ and ΔE_Q) at 296 K and 210 K very similar to those observed in the absorption Mössbauer spectra of [Fe(py)$_2$Ni(CN)$_4$] measured at 298 K (δ = 1.06, ΔE_Q = 0.86 mm/s) and 210 K (δ = 1.13, ΔE_Q = 1.08 mm/s). It is reasonable to conclude that the produced ^{57}Fe atoms of this component are located in the original coordination environment above 210 K. Following the interpretation of Gütlich et al. ^{57}Fe atoms are assumed to be trapped in the excited electronic state (^5T) by the NIESST effect at low temperatures.

Fe(III)LS: After ^{57}Co^{2+} atoms captured an inner shell electron, Auger ionization subsequently may occur in most cases, producing ^{57}Fe atoms with a highly positive charge ranging from

Table 1. Mössbauer parameters obtained by least-squares fitting of emission Mössbauer spectra of ^{57}Co-labelled [Co(py)$_2$Ni(CN)$_4$]

	δ (mm/s)^a				ΔE_Q (mm/s)$^{b,\,c}$			
T/K	Fe(II)HS1	Fe(III)LS	Fe(II)HS2	Fe(III)HS	Fe(II)HS1	Fe(III)LS	Fe(II)HS2	Fe(III)HS
5	1.19	-0.23	1.09		1.58	0.86	2.46	
80	1.17	-0.35	1.10		1.39	0.79	2.39	
210	1.14	-0.54	1.16	0.29	1.07	0.13	2.20	0.41
296	1.07	-0.50	1.03	0.28	0.86	0.13	1.98	0.45
348	1.01	-0.48	0.89	0.21	0.76	0.13	1.78	0.41

	Γ (mm/s)^d				Area (%)			
T/K	Fe(II)HS1	Fe(III)LS	Fe(II)HS2	Fe(III)HS	Fe(II)HS1	Fe(III)LS	Fe(II)HS2	Fe(III)HS
5	0.55	0.96	0.76		71.7	10.3	18.0	
80	0.55	0.89	0.70		70.3	11.7	18.0	
210	0.53	1.45	0.51	0.53	71.2	12.0	6.0	10.8
296	0.52	1.39	0.57	0.45	70.8	11.2	6.2	11.8
348	0.47	1.26	0.42	0.42	72.0	11.5	5.7	10.8

[a] Isomer shift relative to metallic iron. [b] Quadrupole splitting. [c] ΔE_Q values of Fe(III)LS were fixed at 0.13 mm/s at and above 210 K. [d] Full linewidth at half maximum height.

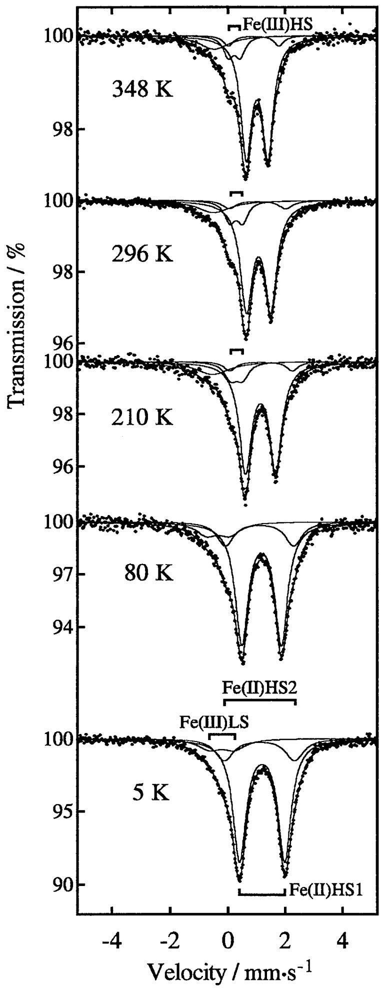

Figure 1. Emission Mössbauer spectra of ^{57}Co-labelled [Co(py)$_2$Ni(CN)$_4$]. Solid lines indicate the results of least-squares fitting using a Lorentzian line shape.

3+ to 7+.[11] Most of the highly charged atoms are supposed to be neutralized in a very short time in solid, and the Fe(III)LS species may be produced due to the incomplete neutralization.

Fe(II)HS2 and Fe(III)HS: The Fe(II)HS2 component has a larger quadrupole splitting compared with the Fe(II)HS1 component. This indicates that the coordination environment of the ^{57}Fe atoms produced is distorted from O_h symmetry. We propose two possibilities to explain the distortion and the conversion from Fe(II)HS2 to Fe(III)HS at higher temperatures. First, a local radiolytic process caused by emitted Auger electrons produces an electron defect on pyridine and/or CN ligands. For example, below 80 K, the defect on a pyridine ligand produces [Fe(II)(py)$^+$(py)Ni(II)(CN)$_4$] which has a lifetime comparable to or longer than the Mössbauer time window. Electron transfer takes place from the Fe(II) atom to a cationic ligand above 210 K, thus forming [Fe(III)(py)$_2$Ni(II)(CN)$_4$]. Second, the excited electronic state of $^5E(O_h)$ (probably being subjected to Jahn-Teller distortion) above $^5T(O_h)$ has a lifetime of at least several hundreds nano seconds below 80 K. The lifetime decreases with increasing temperature, and an electron is transferred to one of the ligands or a nickel atom in the deexcitation process. For example, this process forms [Fe(III)(py)$^-$(py)Ni(II)(CN)$_4$] above 210 K and thus the quadrupole splitting of this Fe(III)HS component is ascribed to the negative charge of one of the py ligands. It may be concluded that the Fe(II)HS2 component below 80 K is composed of two components, and one of them shows the temperature-dependent conversion of the valence states and the other does not.

Spiering et al. pointed out two possibilities (an electron defect and a long lifetime ^5E state) in their explanation for the production of an Fe(II) high-spin species in a distorted environment of an isolated complex, ^{57}Co-labelled [Co(phen)$_3$]ClO$_4$ (phen = 1, 10-phenanthroline).[12] As they suggested, emission Mössbauer spectroscopy using a γ-X-ray coincidence technique will give more detailed information for our system. If the Fe(III)HS species found in this study has a sufficiently long lifetime, this species might be produced and detected by the excitation of ^5T to ^5E by visible light and the subsequent decay of the ^5E state.

References and Notes

1 T. Kitazawa, Y. Gomi, M. Takahashi, M. Takeda, M. Enomoto, A. Miyazaki, and T. Enoki, *J. Mater. Chem.*, **6**, 119 (1996).
2 J. Ensling, P. Gütlich, and K. M. Hasselbach, *Chem. Phys. Lett.*, **42**, 232 (1976).
3 J. Fleisch and P. Gütlich, *Chem. Phys. Lett.*, **42**, 237 (1976).
4 J. Fleisch and P. Gütlich, *Chem. Phys. Lett.*, **45**, 29 (1976).
5 J. Fleisch, P. Gütlich, and H. Köppen, *Radiochem. Radioanal. Lett.*, **42**, 279 (1980).
6 P. Gütlich and H. Köppen, *J. Physique.*, **41**, C1-311 (1980).
7 P. Gütlich, A. Hauser, and H. Spiering, *Angew. Chem. Int. Ed. Engl.*, **33**, 2024 (1994).
8 P. Gütlich, J. Ensling, and F. Tuczek, *Hyperfine Interactions*, **84**, 447 (1994).
9 P. Gütlich and J. Jung, *Nuovo Cimento D*, **18**, 107 (1996).
10 The labelled compound was synthesized by following the procedure reported for [Fe(py)$_2$Ni(CN)$_4$], with some modifications.[1] We used cobalt(II) chloride containing ca. 74 MBq of ^{57}Co instead of iron(II) sulfate.
11 H. Pollak, *Phys. Stat. Sol.*, **2**, 720 (1962).
12 H. Spiering, M. Alflen, P. Gütlich, A. Hauser, C. Hennen, U. Manthe, and F. Tuczek, *Hyperfine Interactions*, **53**, 113 (1990).