Hyperfine Interact
DOI 10.1007/s10751-011-0406-5

Study on the ferromagnetic state in iron mixed-valence complexes, $A[Fe^{II}Fe^{III}(dto)_3]$ ($A = (n\text{-}C_nH_{2n+1})_4N$; $dto = C_2S_2O_2$) by means of Mössbauer spectroscopy

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Abstract We have investigated the ferromagnetic states for $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ (n = 3–6; dto = $C_2O_2S_2$) by means of ^{57}Fe Mössbauer spectroscopy. The major component of the spin configuration in the ferromagnetic states for n = 3 and 4 is the low-temperature phase (LTP) with the Fe^{III} (S = 5/2) and Fe^{II} (S = 0) states. The high-temperature phase (HTP) of n = 4 remains by more than 20%, which is consistent with two ferromagnetic transitions (T_C = 7 & 13 K). Moreover, it was revealed that the Mössbauer spectra in the ferromagnetic states for n = 5 and 6 correspond to the HTP consisting of the Fe^{II} (S = 2) and Fe^{III} (S = 1/2) states.

Keywords Mixed-valence complex · Dithiooxalato · Ferromagnetism · Mössbauer spectroscopy

1 Introduction

The mixed-valence iron complex $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ (dto = $C_2O_2S_2$) is an intriguing material showing a new type of first-order phase transition around 120 K, where the thermally induced charge transfer between the Fe^{II} and Fe^{III} sites occurs

Electronic supplementary material The online version of this article (doi:10.1007/s10751-011-0406-5) contains supplementary material, which is available to authorized users.

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Published online: 28 October 2011

reversibly [1]. The complex has a two-dimensional honeycomb network structure and the $(n\text{-}C_3H_7)_4N$ cations are intercalated between $[Fe^{II}Fe^{III}(dto)_3]_\infty$ layers [2]. The spin states of the iron sites change between $Fe^{III}S_6$ ($S = 1/2$)-$Fe^{II}O_6$ ($S = 2$) and $Fe^{II}S_6$ ($S = 0$)-$Fe^{III}O_6$ ($S = 5/2$) corresponding to the high-temperature phase (HTP) and low-temperature phase (LTP), respectively, due to the charge transfer phase transition (CTPT). The CTPT also occurs in $(n\text{-}C_4H_9)_4N[Fe^{II}Fe^{III}(dto)_3]$, while the CTPT does not occur in $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ (n = 5 and 6) [3, 4]. Moreover, $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ (n = 3–6) show the ferromagnetic phase transitions [3]. The Curie temperatures, T_C, for n = 3 and 4 are 7 K and 7 & 13 K, respectively, while those for n = 5 and 6 are 19.5 K and 22 K, respectively [3]. In this paper, we report the detailed analysis of the Mössbauer spectra in the ferromagnetic states of $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ (n = 3–6).

2 Experimental

$(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ were prepared according to a similar way of the previous report [3] at the synthesis temperature of 10°C. For ^{57}Fe Mössbauer measurement, ^{57}Co in Rh was used as a Mössbauer source. The spectra were calibrated by the six lines of α-Fe, the center of which was taken as zero isomer shift. Mössbauer spectra have been fitted with a MossWinn 3.0 program [5]. The model was calculated by solving the exact Hamiltonian for mixed magnetic and quadrupole interaction with arbitrary relative orientation, where the following parameters are included; the isomer shift δ, the internal magnetic field H_n, the quadrupole splitting ΔE_Q, the angle θ between the principle axis of the electric field gradient (EFG) and the magnetization direction, the line width Γ, and the component V_{zz} of the EFG. The V_{zz} has the unit: 10^{21} V/m^2. The asymmetry parameter η of the EFG is herein zero.

3 Results and discussion

The parameters of the Mössbauer spectra in the ferromagnetic states for n = 3–6 are listed in Table 1.

The Mössbauer spectra of n = 3 at 4.2 K are shown in Fig. 1a and the fitting parameters are listed in Table S1 given in Online Resource. Mainly, a central doublet ($\delta = 0.43$ mm/s, $\Delta E_Q = 0.39$ mm/s) and a sextet with a large hyperfine field ($H_n =$ 447 kOe) from -8 to 8 mm/s were observed. The former can be assigned to the non-magnetic state of Fe^{II} ($S = 0$) and the latter is typical of the magnetically ordered state of Fe^{III} ($S = 5/2$). The Mössbauer parameters are similar to those in the ferromagnetic state of the LTP for $(SP)[Fe^{II}Fe^{III}(dto)_3]$ (SP = spiropyran) [6]. The sextets of the Fe^{II} ($S = 2$) and Fe^{III} ($S = 1/2$) sites, which correspond to the HTP, are also required to fit the spectra with ca. 15%. The θ value was estimated by the following equation for axial symmetry; $\Delta\varepsilon_1 - \Delta\varepsilon_2 = -1/2eV_{zz}\left(3\cos^2\theta - 1\right)$ (Fig. 1a). On the assumption of positive and negative V_{zz}, θ are estimated at 90° and 40°, respectively. Here, θ can be recognized as 90°, because the principal axis of V_{zz} lies along the D_3 axis of the $[Fe^{II}Fe^{III}(dto)_3]_\infty$ layer and H_n lies in

Table 1 The selected Mössbauer spectral hyperfine parameters in the ferromagnetic ordered states at 4 or 4.5 K for $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ (n = 3–6)

		n = 3			n = 4			n = 5			n = 6		
		δ[a]	ΔE_Q[b]	H_n[c]	δ	ΔE_Q	H_n	δ	ΔE_Q	H_n	δ	ΔE_Q	H_n
LTP	Fe^{II} ($S = 0$)	0.43	0.39	–	0.46	0.46	–	–	–	–	–	–	–
	Fe^{III} ($S = 5/2$)	0.55[d]	0.90[d]	448	0.55[d]	0.95[d]	448	–	–	–	–	–	–
HTP	Fe^{II} ($S = 2$)	1.26[d]	1.41[d]	102	1.26[d]	1.41[d]	100	1.24	1.84	73	1.26[d]	1.37[d]	99
	Fe^{III} ($S = 1/2$)	0.33[d]	0.55[d]	234	0.33[d]	0.51[d]	241	0.40[d]	0.73[d]	246	0.42[d]	0.71[d]	248

[a] Isomer shift (mm/s)
[b] Quadrupole splitting (mm/s)
[c] Internal magnetic field (kOe)
[d] Parameter constrained to the given value

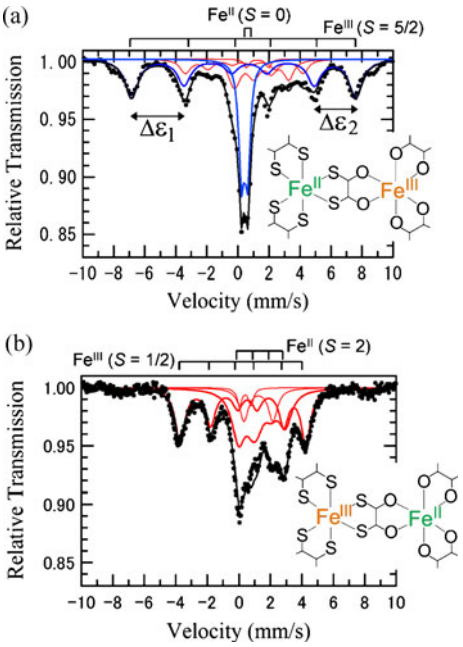

Fig. 1 Magnetically ordered Mössbauer spectra of **a** $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ at 4.2 K and **b** $(n\text{-}C_5H_{11})_4N[Fe^{II}Fe^{III}(dto)_3]$ at 4 K

the $[Fe^{II}Fe^{III}(dto)_3]_\infty$ layer according to the anisotropic magnetization measurement [7].

We measured ^{57}Fe Mössbauer spectroscopy for n = 4 between 25 and 4.5 K (Fig. S1 and Table S2). The spectrum in the ferromagnetic state at 4.5 K for n = 4 is mainly similar to that for n = 3. The central doublet (δ = 0.45 mm/s, ΔE_Q = 0.46 mm/s) of the Fe^{II} ($S = 0$) site and the sextet ($H_n = 448$) of the Fe^{III} ($S = 5/2$) site of the LTP were mainly observed. For n = 4, it should be note that two ferromagnetic transitions coexist with $T_C = 7$ and $T_C = 13$ K in the magnetic measurements [3]. Broad components of the spectra, which are not observed in n = 3, appeared above $T_C = 7$ K, indicating the development of the magnetic ordering in the HTP. The H_n values at 4.5 K corresponding to the Fe^{II} ($S = 2$) and Fe^{III} ($S = 1/2$) sites are estimated at 100 kOe and 241 kOe, respectively (see below). The component of the HTP for n = 4 are about 30%, therefore not only the LTP but also the HTP of n = 4 show the ferromagnetic phase transitions.

The Mössbauer spectra in the ferromagnetic states for n = 5 and 6 (Fig. S2, Table S3 and S4) considerably differ from those for n = 3 and 4. Figure 1b shows the spectrum for n = 5 at 4 K. In the cases of n = 5 and 6, the CTPT do not occur, therefore the spin configuration can be assigned to the Fe^{II} ($S = 2$) and the Fe^{III} ($S = 1/2$) corresponding to the HTP. The Mössbauer spectra were reasonably fitted with two sextets of the magnetically ordered HTP and additionally two doublets derived from their residual paramagnetic components (below ca. 10%). The sextets of the Fe^{III} ($S = 1/2$) sites have large H_n of 246 kOe (n = 5) and 248 kOe (n = 6) at 4 K. The Fe^{II} ($S = 2$) sites, on the other hand, have relatively small H_n of 73 kOe (n = 5) and 99 kOe (n = 6).

4 Conclusion

^{57}Fe Mössbauer spectroscopy is the most powerful tool to investigate the spin configurations in the magnetically ordered states for (n-$C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$. The Fe^{III} ($S = 5/2$) and Fe^{II} ($S = 0$) states dominate below the ferromagnetic transition temperatures for $n = 3$ and 4. In the case of $n = 4$, the ^{57}Fe Mossbauer spectra revealed the development of the magnetic ordering in the HTP. This is consistent with the result of the magnetic measurements. For $n = 5$ and 6, the spin configurations in the ferromagnetic states were assigned to the Fe^{III} ($S = 1/2$) and Fe^{II} ($S = 2$) states.

Acknowledgements This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Educational Science, Sports and Culture, Japan.

References

1. Kojima, N., Aoki, W., Itoi, M., Ono, Y., Seto, M., Kobayashi, Y., Maeda, Yu.: Solid State Commun. **120**, 165 (2001)
2. Itoi, M., Taira, A., Enomoto, M., Matsushita, N., Kojima, N., Kobayshi, Y., Asai, K., Koyama, K., Nakano, T., Uwatoko, Y., Yamaura, J.: Solid State Commun. **130**, 415 (2004)
3. Itoi, M., Ono, Y., Kojima, N., Kato, K., Osaka, K., Takata, M.: Eur. J. Inorg. Chem. **2006**, 1198 (2006)
4. Kojima, N., Ono, Y., Kobayashi, Y., Seto, M.: Hyperfine Interact. **175**, 156–157 (2004)
5. Klencsár, Z., Kuzmann, E., Vértes, A.: J. Radioanal. Nucl. Chem. **210**, 105 (1996)
6. Kida, N., Hikita, M., Kashima, I., Enomoto, M., Itoi, M., Kojima, N.: Polyhedron **28**, 1694 (2004)
7. Itoi, M., Enomoto, M., Kojima, N.: J. Magn. Magn. Mater. **272**, 1093 (2004)