Hyperfine Interact
DOI 10.1007/s10751-011-0468-4

Crystal structure and spin state of $Fe_{0.5}Co_{0.5}(NCS)_2(bpa)_2$

Satoru Nakashima · Takaki Morita · Katsuya Inoue

Abstract $Fe(NCS)_2(bpa)_2$, $Co(NCS)_2(bpa)_2$, and $Fe_{0.5}Co_{0.5}(NCS)_2(bpa)_2$ were synthesized. X-ray structural analysis revealed that the structure was the same among the three complexes. Although the metal-ligand distance in the mixed crystals was shorter than the distance in $Fe(NCS)_2(bpa)_2$ and was similar to that in $Co(NCS)_2(bpa)_2$, the spin state remained temperature-independent Fe^{II} high-spin state in ^{57}Fe Mössbauer spectra.

Keywords Assembled complexes · Mixed crystals · X-ray structure · Mössbauer spectroscopy · Spin state

1 Introduction

Self-assembled coordination polymers containing transition metal ions and organic bridging ligands have attracted intensive interests because of their potential abilities for selective inclusion and transformation of ions and molecules [1]. It is possible to construct various structures for porous assembled iron complexes bridged by bis(4–pyridyl) type ligand. We have studied iron complexes bridged by 1,2–bis(4–pyridyl)ethane (bpa), and revealed the relation between the *anti*/*gauche* conformer for coordinated bpa and the assembled structure, and the relation between the guest molecule and the spin state of iron [2–5]. We have also studied the magnetic behaviors and structural properties for some assembled complexes with more flexible ligand, 1,3–bis(4–pyridyl)propane (bpp), which has three methylenes, by using single

S. Nakashima (✉)
Natural Science Center for Basic Research and Development, Hiroshima University,
Kagamiyama, Higashi-Hiroshima 739-8526, Japan
e-mail: snaka@hiroshima-u.ac.jp

T. Morita · K. Inoue
Graduate School of Science, Hiroshima University, Kagamiyama,
Higashi-Hiroshima 739-8526, Japan

Table 1 Crystal data

Sample	FeY[1]	$Fe_{0.5}Co_{0.5}Y$[1]	CoY[1]
a/ Å	19.7890(5)	19.775(6)	19.746(4)
b/ Å	9.9620(2)	9.948(2)	9.9444(19)
c/ Å	14.4810(5)	14.591(3)	14.571(3)
β/ °	110.156(1)	110.381(7)	110.403(3)
V/ Å^3	2679.9(1)	2690.6(11)	2681.7(9)

[1] Y=$(NCS)_2(bpa)_2$

crystal X–ray diffraction analyses, Mössbauer spectroscopy, and SQUID measurements [6, 7]. Recently, we discussed the spin state of the mixed crystals with zinc or cobalt ion both in the 2D interpenetrated and 1D chain structures for the assembled complexes bridged by bpp [8]. The chemical pressure effect was observed in NCSe complex, while the effect was not observed in NCS complex. In the present study, we obtained single crystals of $Fe(NCS)_2(bpa)_2$, $Co(NCS)_2(bpa)_2$, and $Fe_{0.5}Co_{0.5}(NCS)_2(bpa)_2$, and discussed the structure and spin state of mixed crystals.

2 Experimental

$Fe(NCS)_2(bpa)_2$, $Co(NCS)_2(bpa)_2$, and $Fe_{0.5}Co_{0.5}(NCS)_2(bpa)_2$ were obtained by diffusion method. Iron and cobalt ions (1:1) were mixed in the synthetic process to obtain mixed crystals. The structures were determined by using single-crystal X-ray diffraction analysis.

A ^{57}Co(Rh) source in a constant acceleration mode was used for ^{57}Fe Mössbauer spectroscopic measurements. ^{57}Fe Mössbauer spectra were measured at 78 K and room temperature by using a Wissel Mössbauer spectrometer and a proportional counter. The isomer shift was referred to metallic iron foil. The Mössbauer parameters were obtained by a least-squares fitting to Lorentzian peaks.

3 Results and discussion

We obtained single crystals of $Fe(NCS)_2(bpa)_2$, $Co(NCS)_2(bpa)_2$, and $Fe_{0.5}Co_{0.5}(NCS)_2(bpa)_2$. The X-ray structural analyses revealed that all the samples had 1D chain structure, although the several types of crystal structure were expected. The color of the mixed crystals is orange, which is intermediate between yellow of iron complex and red of cobalt complex. The crystal data are summarized in Table 1. The crystal parameters are similar to each other. The unit-cell volume of iron complex is slightly smaller than that of cobalt complex, although the ion radius of Fe^{2+}(HS, 92 pm) is slightly larger than that of Co^{2+}(HS, 88.5 pm), suggesting a good packing of iron complex. The unit-cell volume of mixed crystals is largest among the three complexes. This suggests a relatively bad packing of 1D chains in mixed crystals maybe due to the coexistence of iron and cobalt ions in the crystal.

Figure 1 shows the crystal structure of $Fe_{0.5}Co_{0.5}(NCS)_2(bpa)_2$. It can be seen that the structure is 1D chain one. Metal ion showed a distorted octahedral geometry by coordination of four N atoms of bpa and two N atoms of NCS in the *trans* position. The bpa ligand is in *gauche* conformer. The average distance between metal and nitrogen atoms of ligand is 2.192(1), 2.161(3), and 2.165(1) Å for $Fe(NCS)_2(bpa)_2$, $Co(NCS)_2(bpa)_2$, and $Fe_xCo_{1-x}(NCS)_2(bpa)_2$, respectively. The distance in cobalt

Fig. 1 Crystal structure of $Fe_{0.5}Co_{0.5}(NCS)_2(bpa)_2$

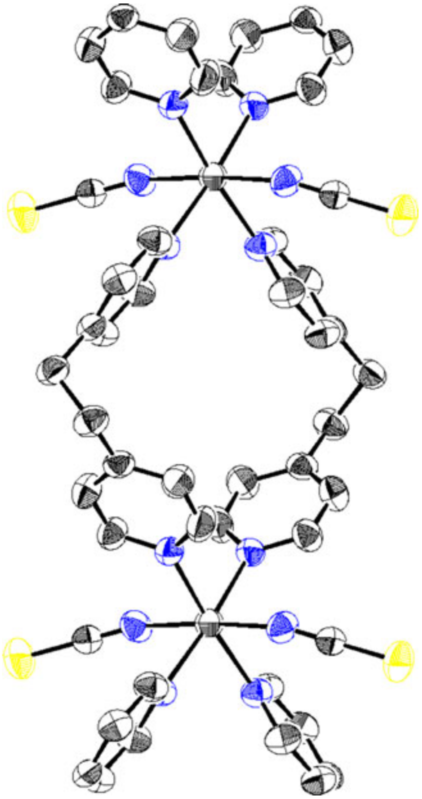
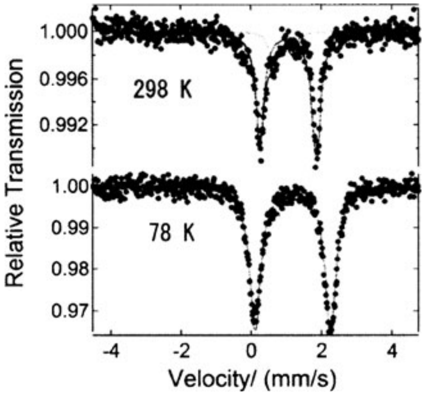


Fig. 2 ^{57}Fe Mössbauer spectra of $Fe_{0.5}Co_{0.5}(NCS)_2(bpa)_2$



complex is shorter than that of iron complex, because the ion radius for Co^{2+}(HS, 88.5 pm) is shorter than that of Fe^{2+}(HS, 92 pm), which shows the opposite trend observed in the unit-cell volume. The distance in mixed crystals is similar to that of cobalt complex. One of the explanations is that the chemical pressure effect worked on the iron ion by making the mixed crystals with the ion having smaller ion radius than Fe^{2+}.

Figure 2 shows the Mössbauer spectra of $Fe_{0.5}Co_{0.5}(NCS)_2(bpa)_2$ at 78 and 298 K. Mössbauer parameters (IS = 1.05 mm s^{-1}, QS = 1.60 mm s^{-1} at 298 K and IS = 1.18 mm s^{-1}, QS = 2.14 mm s^{-1} at 78 K) reveal a temperature-independent Fe^{II} high-spin state. Mixed crystals showed almost the same Mössbauer spectra with the corresponding pure iron complex in the 1D structure. No significant differences in Mössbauer parameters were observed between the pure iron complex [3] and mixed crystals. Line width, however, is somewhat larger at 78 K. One of the possibilities is that the coordination circumstances around iron ion have distribution because the coexisting cobalt ions affect the coordination circumstances around iron ion. The distribution will be averaged by the thermal vibration at room temperature, which results in the narrow line width at 298 K. The present spectra mean that the spin state of the mixed crystals is the same with $Fe(NCS)_2(bpa)_2$, although the chemical pressure effect was expected from the results of X-ray structural analyses.

In conclusion, the average distance between metal and nitrogen atoms in mixed crystals approached the distance in $Co(NCS)_2(bpa)_2$. The spin state, however, remained the temperature-independent high-spin type.

References

1. Moulton, B., Zaworotko, M.J.: Chem. Rev. **101**, 1629 (2001)
2. Nakashima, S., Morita, T., Yamada, K., Inoue, K.: Hyperfine Interact. **166**, 469 (2005)
3. Morita, T., Asada, Y., Okuda, T., Nakashima, S.: Bull. Chem. Soc. Jpn. **79**, 738 (2006)
4. Morita, T., Nakashima, S., Yamada, K., Inoue, K.: Chem. Lett. **35**, 1042 (2006)
5. Nakashima, S., Morita, T., Inoue, K.: Hyperfine Interact. **188**, 107 (2009)
6. Atsuchi, M., Higashikawa, H., Yoshida, Y., Nakashima, S., Inoue, K.: Chem. Lett. **36**, 1064 (2007)
7. Atsuchi, M., Inoue, K., Nakashima, S.: Inorg. Chim. Acta **370**, 82 (2011)
8. Nakashima, S., Dote, T., Atsuchi, M., Inoue, K.: J. Phys. **C217**, 012035 (2010)