Hyperfine Interact
DOI 10.1007/s10751-012-0562-2

Crystal structure and spin state of mixed-crystals of iron with zinc and cobalt for the assembled complexes bridged by 1,3-bis(4-pyridyl)propanes

Haruka Dote · Satoru Nakashima

Abstract Mixed crystals of cobalt and zinc were synthesized using 1,3–bis(4–pyridyl)propane (bpp) as bridging ligand and NCS^- as anion. Red crystals and blue crystals were obtained. Powder X-ray diffraction patterns showed that the former is in 2D interpenetrated structure, while the latter has the same structure with $Zn(NCS)_2$(bpp). Iron ion was introduced both into the red crystals and blue crystals of the mixed crystals of cobalt with zinc. ^{57}Fe Mössbauer spectrum of the red crystals showed a main doublet of Fe^{II} high-spin state at 78 K, while the spectrum of blue crystals did not show Fe^{II} high-spin state at 78 K.

Keywords Assembled complexes · Mixed crystals · 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

H. Dote
Graduate School of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima, 739–8526, Japan

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

Published online: 17 January 2012

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–crystal X–ray diffraction analysis, Mössbauer spectroscopy, and SQUID measurements [6, 7]. $Fe(NCX)_2(bpp)_2$ (X = S, Se, and BH_3) had a 2D interpenetrated structure and the $NCBH_3$ complex showed a spin–crossover phenomenon. We also synthesized $Fe(NCX)_2(bpp)_2{\cdot}2(benzene)$ (X = S, Se, and BH_3). They had a 1D structure and were in temperature-independent Fe^{II} high-spin state. Both 2D interpenetrated and 1D structures were converted to each other by desorption and adsorption of benzene molecules [7]. Recently, we discussed the spin state of the mixed crystals with zinc or cobalt ion both in the 2D interpenetrated and 1D structures for the assembled complexes bridged by bpp [8]. In the present study, we discussed the structure of the mixed crystals of zinc and cobalt ions for the assembled complexes bridged by bpp, and then we discussed the spin state of the mixed crystals of iron ion with zinc and cobalt ions for the assembled complexes bridged by bpp.

2 Experimental

Mixed crystals were obtained by diffusion method. Bottom layer; metals, NCS^-, and ascorbic acid in H_2O. Middle layer; H_2O and cyclohexane. Upper layer; bpp in EtOH and cyclohexane. Found for Zn complex: C, 47.28; H, 3.89; N, 14.90; S, 16.98%. Calcd for $Zn(NCS)_2bpp$: C, 47.43; H, 3.72; N, 14.75; S, 16.89%. Found for red crystals of $Fe_{0.14}Zn_{0.17}Co_{0.69}(NCS)_2bpp_2$: C, 58.78; H, 4.66; N, 14.74; S,11.19%. Calcd for $Fe_{0.14}Zn_{0.17}Co_{0.69}(NCS)_2bpp_2$: C, 58.76; H, 4.93; N, 14.69; S, 11.21%. Found for blue crystals of $Fe_{0.20}Zn_{0.63}Co_{0.17}(NCS)_2bpp$: C, 45.18; H, 3.45; N, 16.06; S, 17.43%. Calcd for $Fe_{0.20}Zn_{0.63}Co_{0.17}$ $(NCS)_2bpp$: C, 47.80; H, 3.75; N, 14.87; S, 17.02%. The relative contents of metals were determined by ICP-OES.

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 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 discussions

3.1 Mixed crystals of zinc and cobalt complexes

Zinc and cobalt ions were mixed in the synthetic process. From the solution, red crystals and blue crystals were obtained. The relative contents of metals were determined by ICP-OES, which revealed that red crystals have relatively larger cobalt content, while blue crystals have larger zinc content. Powder X-ray diffraction patterns (Fig. 1) showed that the red crystals are in the 2D interpenetrated structure like $Fe(NCS)_2bpp_2$ [6]. The patterns for red crystals and $Fe(NCS)_2bpp_2$ revealed a preferred orientation. On the other hand, the structure of blue crystals is similar to that of $Zn(NCS)_2bpp$. Although the structure of $Zn(NCS)_2bpp$ is unknown, there are two possibilities from the results of elemental analysis and powder X-ray diffraction

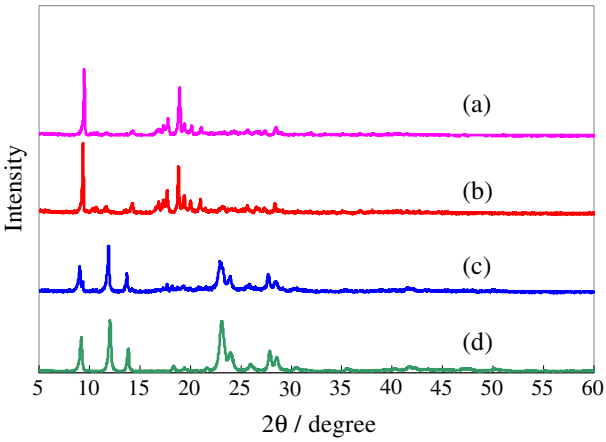

Fig. 1 Powder X-ray diffraction patterns of **a** $Fe(NCS)_2bpp_2$, **b** $Zn_{0.29}Co_{0.71}(NCS)_2bpp_2$ (*red crystals*), **c** $Zn_{0.89}Co_{0.11}(NCS)_2bpp$ (*blue crystals*), and **d** $Zn(NCS)_2bpp$

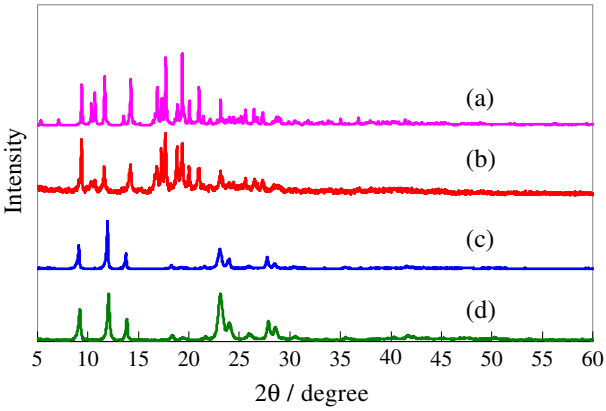

Fig. 2 Powder X-ray diffraction patterns of **a** $Fe(NCS)_2bpp_2$ (simulation), **b** $Fe_{0.14}Zn_{0.17}Co_{0.69}(NCS)_2bpp_2$ (*red crystals*), **c** $Fe_{0.20}Zn_{0.63}Co_{0.17}(NCS)_2bpp$ (*blue crystals*), and **d** $Zn(NCS)_2bpp$

patterns (Fig. 1). One is tetrahedral coordination around metals, and the other is octahedral coordination around metals whose NCS^- is used as bridging ligand.

3.2 Iron in mixed crystals of zinc and cobalt complexes

Iron, zinc, and cobalt ions were mixed in the synthetic process. From the solution, red crystals and blue crystals were obtained. Elemental analysis showed that red crystals have two bpp in their molecule, while blue crystals have one bpp in their molecule. Powder X-ray diffraction patterns (Fig. 2) showed that the red crystals are in the 2D interpenetrated structure like $Fe(NCS)_2bpp_2$ [6]. The pattern of red crystals did not reveal a preferred orientation. Therefore, the pattern is compared with a simulation pattern of $Fe(NCS)_2bpp_2$ from a result of single-crystal X-ray diffraction analysis. On the other hand, the structure of blue crystals is similar to that of $Zn(NCS)_2bpp$. In this case also, the structure of $Zn(NCS)_2bpp$ is unknown, and there are two possibilities of tetrahedral coordination around metals and octahedral coordination around metals whose NCS^- is used as bridging ligand. ICP-OES revealed that red

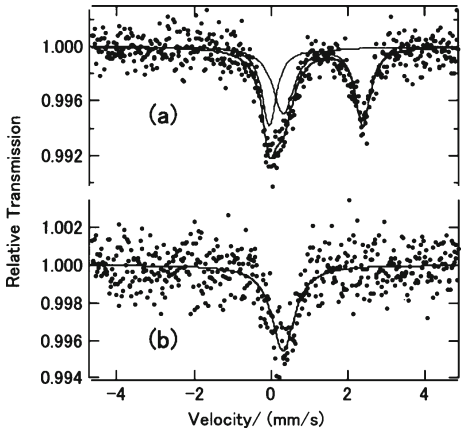

Fig. 3 ^{57}Fe Mössbauer spectra at 78 K of **a** $Fe_{0.14}Zn_{0.17}Co_{0.69}(NCS)_2bpp_2$ (*red crystals*) and **b** $Fe_{0.20}Zn_{0.63}Co_{0.17}(NCS)_2bpp$ (*blue crystals*)

crystals have larger cobalt content, while blue crystals have larger zinc content. And ICP-OES also revealed that the content of iron is relatively low both in red and blue crystals.

Figure 3 shows the ^{57}Fe Mössbauer spectrum of the red crystals of $Fe_{0.14}Zn_{0.17}Co_{0.69}(NCS)_2bpp_2$ at 78 K and the ^{57}Fe Mössbauer spectrum of the blue crystals of $Fe_{0.20}Zn_{0.63}Co_{0.17}(NCS)_2bpp$ at 78 K. There are two components in the spectrum of red crystals. Main component (IS = 1.16 mm/s, QS = 2.43 mm/s) is Fe^{II} high-spin state and minor component is singlet (IS = 0.31 mm/s). On the other hand, Fe^{II} high-spin state is not observed for blue crystals. Instead of Fe^{II} high-spin doublet, singlet (IS = 0.23 mm/s) is observed, which has a similar parameter with the minor component in the red crystals.

4 Conclusion

Different colored complexes were obtained by using zinc and cobalt ions (and iron ion) with NCS^- and bpp. It was shown from powder X-ray diffraction patterns that blue complexes have the same structure with pure zinc complex, while red crystals are in the 2D interpenetrated structure. The difference in structure affected the spin state of iron ion in the mixed crystals with zinc and cobalt.

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, H., Atsuchi, M., Inoue, K.: J. Phys. **C217**, 012035 (2010)