Spin state of mixed crystals of iron with zinc or cobalt for the assembled complexes bridged by 1,3–bis(4–pyridyl)propanes

S Nakashima¹, T Dote², M Atsuchi² and K Inoue²

¹ Natural Science Center for Basic Research and Development, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526, Japan
² Graduate School of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526, Japan

E-mail: snaka@hiroshima-u.ac.jp

Abstract. Mixed crystals, [Fe₁₋ₓMₓ(NCX)₂(bpp)₂] (M=Zn, Co; X=S, Se; bpp= 1,3–bis(4–pyridyl)propane), had a similar structure with 2D interpenetrated structure of [Fe(NCX)₂(bpp)₂]. The proportion of Fe II low-spin state in the mixed crystals of NCSe complex increased compared with that of the corresponding Fe complex, while such change in the Mössbauer spectra was not observed in the NCS complex.

1. Introduction

The design and construction of various structures for assembled complexes have attracted great interest to many chemists because of their potential abilities for selective inclusion and transformation of ions and molecules [1–3]. Especially, the assembled complexes including the transition metal ions with the 3dn (4 ≤ n ≤ 7) electron configuration attract attention to know the relation between assembled structures and their spin states [4–10].

Recently, we have synthesized assembled the iron complex [Fe(NCS)₂(bpp)₂] (bpp = 1,3–bis(4–pyridyl)propane) [11]. This bridging–ligand bpp has three methylenes, and this is a flexible ligand. We revealed that [Fe(NCS)₂(bpp)₂] consisted of the heap of 2D interpenetrated sheets. The sheet consisted of two separated grids. And [Fe(NCBH₃)₂(bpp)₂], having 2D interpenetrated structure, shows the spin-crossover phenomenon.

In the present study, we synthesized mixed crystals of [Fe₁₋ₓMₓ(NCX)₂(bpp)₂] (M=Zn, Co; X=S, Se; bpp=1,3–bis(4–pyridyl)propane). The aim of the present study is to know the dilution effect by Zn²⁺ or Co²⁺ ion which has a smaller ion radius compared with Fe²⁺(HS) ion. We studied the spin state of the mixed crystals in the 2D interpenetrated structure and we discussed the effect of the formation of mixed crystals on the spin state of iron ion.

2. Experimental

All complexes were prepared by the diffusion method under the argon atmosphere in order to prevent oxidation of Fe II. The same amounts of iron ions and cobalt or zinc ions were dissolved with the anion into water, while the bpp ligand was dissolved in EtOH. By diffusing the solutions slowly, mixed crystals were obtained for several days. The structures of the mixed crystals were checked by
comparing the powder X-ray diffraction patterns with those of the corresponding iron, zinc, or cobalt complex.

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

The magnetic susceptibilities were obtained on a SQUID magnetometer.

3. Results and discussion

$[\text{Fe}(\text{NCS})_2(\text{bpp})_2]$ has a novel 2D interpenetrated structure [11]. Powder X-ray diffraction patterns showed that $[\text{Co}(\text{NCS})_2(\text{bpp})_2]$ has a similar structure with the corresponding Fe complex, while $[\text{Zn}(\text{NCS})_2(\text{bpp})_2]$ has a different structure from the corresponding Fe complex. The powder X-ray diffraction pattern of the mixed crystals, $[\text{Fe}_{1-x}\text{Zn}_x(\text{NCS})_2(\text{bpp})_2]$, is not a superposition of those of the corresponding Fe and Zn complexes, but similar to that of the Fe complex. The color of the crystals was different from the corresponding Fe complex, suggesting the formation of mixed crystals. The powder X-ray diffraction pattern of the mixed crystals, $[\text{Fe}_{1-x}\text{Co}_x(\text{NCS})_2(\text{bpp})_2]$, is similar to those of the corresponding Fe and Co complexes. In this case, it is not easy to judge whether the crystals are mixed crystals or not. But, we judged that the obtained crystals are mixed crystals because of the color change from the corresponding Fe or Co complex. Although it is not easy to determine the value of x, we judged from the results of magnetic susceptibilities that the x does not differ much from 0.5.

Figure 1. Mössbauer spectra of (a) $[\text{Fe}(\text{NCS})_2(\text{bpp})_2]$, (b) $[\text{Fe}_{1-x}\text{Zn}_x(\text{NCS})_2(\text{bpp})_2]$, and (c) $[\text{Fe}_{1-x}\text{Co}_x(\text{NCS})_2(\text{bpp})_2]$ at 78 K.

Figure 2. Mössbauer spectra of (a) $[\text{Fe}(\text{NCSe})_2(\text{bpp})_2]$, (b) $[\text{Fe}_{1-x}\text{Zn}_x(\text{NCSe})_2(\text{bpp})_2]$, and (c) $[\text{Fe}_{1-x}\text{Co}_x(\text{NCSe})_2(\text{bpp})_2]$ at 78 K.
doublets. The results show that the cobalt or zinc atoms were introduced into the two iron sites randomly. Although the effect of mixed crystals were not observed on the spin state, the Mössbauer parameters slightly changed by forming mixed crystals. The QS value of the inner doublet decreased by forming mixed crystals, while the outer doublet did not change. This slight change might be an effect of the formation of mixed crystals.

Figure 2 shows the Mössbauer spectra of [Fe(NCSe)\(_2\)(bpp)\(_2\)], [Fe\(_{1-x}\)Zn\(_x\)(NCSe)\(_2\)(bpp)\(_2\)], and [Fe\(_{1-x}\)Co\(_x\)(NCSe)\(_2\)(bpp)\(_2\)] at 78 K. The Mössbauer parameters are summarized in Table 1. [Fe(NCSe)\(_2\)(bpp)\(_2\)] showed a slight Fe\(^{II}\) low-spin (LS) state in addition to the two Fe\(^{II}\) HS states. The small amount of Fe\(^{II}\) LS state agreed with the result of magnetic susceptibility. [Fe\(_{1-x}\)Zn\(_x\)(NCSe)\(_2\)(bpp)\(_2\)] and [Fe\(_{1-x}\)Co\(_x\)(NCSe)\(_2\)(bpp)\(_2\)] show the two doublets of the Fe\(^{II}\) HS state and one singlet of the Fe\(^{II}\) LS state. The difference was observed in the proportion of the LS state between mixed crystals and the corresponding Fe complex. The proportion of the LS state increased by forming the mixed crystals. In this case also, the QS values of the two doublets of the HS state slightly changed by forming mixed crystals. That is, the QS value of the outer doublet increased and the QS value of the inner doublet decreased by forming mixed crystals. SQUID measurement showed that the \(\chi T\) value of [Fe\(_{1-x}\)Zn\(_x\)(NCSe)\(_2\)(bpp)\(_2\)] is less than half the \(\chi T\) value of the corresponding iron complex. The smaller value of [Fe\(_{1-x}\)Zn\(_x\)(NCSe)\(_2\)(bpp)\(_2\)] was explained by the increase of the Fe\(^{II}\) LS state.

| Sample | IS/ mm s\(^{-1}\) | QS/ mm s\(^{-1}\) | Area/ % |
|--------|-----------------|-----------------|--------|
| Fe(NCS)\(_2\)(bpp)\(_2\) | 1.14 | 2.72 | 34 |
| | 1.15 | 2.13 | 66 |
| Fe\(_{1-x}\)Zn\(_x\)(NCS)\(_2\)(bpp)\(_2\) | 1.17 | 2.71 | 33 |
| | 1.20 | 1.99 | 67 |
| Fe\(_{1-x}\)Co\(_x\)(NCS)\(_2\)(bpp)\(_2\) | 1.17 | 2.71 | 32 |
| | 1.20 | 1.99 | 68 |
| Fe(NCSe)\(_2\)(bpp)\(_2\) | 1.16 | 1.73 | 55 |
| | 1.19 | 1.23 | 35 |
| | 0.46 | 0 | 10 |
| Fe\(_{1-x}\)Zn\(_x\)(NCSe)\(_2\)(bpp)\(_2\) | 1.10 | 1.84 | 50 |
| | 1.17 | 1.05 | 21 |
| | 0.48 | 0 | 29 |
| Fe\(_{1-x}\)Co\(_x\)(NCSe)\(_2\)(bpp)\(_2\) | 1.22 | 2.08 | 37 |
| | 1.19 | 1.19 | 22 |
| | 0.41 | 0 | 41 |

a) Relative to iron foil

The ligand field of [Fe(NCX)\(_2\)(bpp)\(_2\)] in the 2D interpenetrated structure is close to the spin-crossover point, because [Fe(NCBH\(_3\))\(_2\)(bpp)\(_2\)] shows the spin-crossover phenomenon [11]. In this situation, such a small change by forming mixed crystals has affected the spin state. The ion radii for Zn\(^{2+}\) and Co\(^{2+}\) (HS) were 89pm and 88.5pm, respectively, which are smaller than that of Fe\(^{2+}\) (HS, 92pm). Zn or Co ions are connected with Fe ion by bpp in the present mixed crystals. Introduced small metal ions are thought to enforce the reduction of iron ion radius; i.e., the proportion of Fe\(^{II}\) LS state increases. This means that the chemical pressure effect worked by forming the mixed crystals with the metal ion having smaller ion radii than Fe\(^{2+}\). Gütlich et al. already reported the dilution effect by using mixed crystals such as [Fe\(_{1-x}\)Co\(_x\)(NCS)\(_2\)(phen)\(_2\)] [12]. They showed that the Fe\(^{2+}\) (HS) complex molecules embedded in the cobalt host lattice feels like being exposed to pressure. The
present results do not contradict the results by Gütlich et al. The remarkable effect was observed in the NCSe complex compared with the NCS complex in the present study. This may be due to the softness of Se atom compared with S atom.

References
[1] Moulton B and Zaworotko M J 2001 Chem. Rev. 101 1629
[2] Gütlich P, Garcia Y and Goodwin H A 2000 Chem. Soc. Rev. 29 419
[3] Batten S R and Robson R 1998 Angew. Chem. Int. Ed. 37 1460
[4] Real J A, Andrés E, Muñoz, M C, Julve M, Granier T, Bousseksou A and Varret F 1995 Science 268 265
[5] Halder G J, Kepert C J, Moubaraki B, Murray K S and Cashion J D 2002 Science 298 1762
[6] Kahn O and Martinez C J 1998 Science 297 44
[7] Moliner N, Muñoz M C, Létard S, Salmon L, Tuchgues J–P, Bousseksou A and Real J A 2002 Inorg. Chem. 41 6997
[8] Morita T, Nakashima S, Yamada K and Inoue K 2006 Chem. Lett. 35 1042
[9] Agustí G, Muñoz M C, Gaspar A B and Real J A 2008 Inorg. Chem. 47 2552
[10] Quesada M, Prins F, Roubeau O, Gomez P, Teat S J, Koningsbruggen P J, Haasnoot J G and Reedijk J 2007 J. Inorg. Chem. Acta 3787
[11] Atsuchi M, Higashikawa H, Yoshida Y, Nakashima S and Inoue K 2007 Chem. Lett. 36 1064
[12] Ganguli P, Gütlich P and Müller E W 1982 Inorg. Chem. 21 3429