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Effect of intermolecular interaction on the spin state of iron(II) assembled complexes using bis(pyridyl) type ligand

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Introduction

Iron (II) octahedral assembled complexes using bis(pyridyl) type bridging ligands can take two spin states (high spin and low spin) in intermediate ligand field. They may show a spin-crossover (SCO) phenomenon by external stimuli. These complexes are expected to be applied as switching materials but the way to control the transition temperature is not clear. Then, it is considered that the intermolecular interactions influence the temperature of spin transition. In this research, iron (II) assembled complexes were synthesized using 9,10-bis(4-pyridyl)anthracene (bpanth) which has many π electrons on the bridging ligand. We expected to reveal the relation between intermolecular interactions (π - π or CH- π) and SCO phenomenon.

Experimental

The bpanth was synthesized by Suzuki-Miyaura cross coupling reaction. The iron (II) complexes were synthesized by direct mixing and diffusion method using bpanth, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and KNCS, KNCS_e, or NaNCBH₃. These products were characterized by XRD, elemental analysis, ⁵⁷Fe Mössbauer spectroscopy and magnetic susceptibility measurements.

Results and Discussion

Results of elemental analysis and XRD revealed that the chemical formula was $[\text{Fe}(\text{bpanth})_2(\text{NCX})_2]_n$ (X = S, Se, BH₃), the structure was interpenetrated type and the CH- π interaction was suggested. (Fig. 1) These products show high spin state at 5-300K by ⁵⁷Fe Mössbauer spectroscopy and magnetic susceptibility measurements. (Fig. 2) And the local structure around iron atom was shown to be a parallel type by XRD, which was also in accordance with the results investigated by DFT calculation.^{[1][2]} CH- π interactions between the H atom of coordinated pyridine and the neighboring anthracene of the other 2D grid. It was suggested that the interpenetrated structure was supported by the stabilization of CH- π interaction, and this interaction forced the unstable parallel structure which takes high spin state.

Then, three complexes using 1,4-bis(4-pyridyl)naphthalene (bpna) which are expected to have flexible body than bpanth were synthesized. And they show SCO behavior.

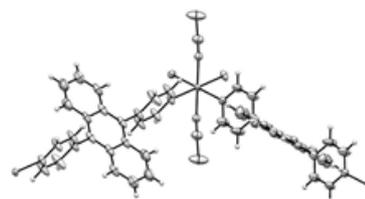


Figure 1. ORTEP for $[\text{Fe}(\text{bpanth})_2(\text{NCS})_2]_n$

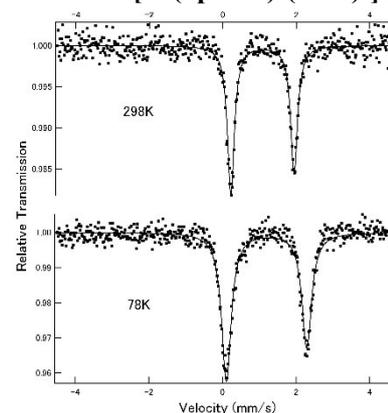


Figure 2. ⁵⁷Fe Mössbauer spectra for $[\text{Fe}(\text{bpanth})_2(\text{NCS})_2]_n$

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