

1D5b Effect of methyl group on the spin crossover behavior for iron (II) assembled complex

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Iron (II) octahedral complex can take two spin ground states, high spin (HS) and low spin (LS), in the intermediate ligand field. It shows a spin crossover (SCO) phenomenon, in which the spin state converts to each other by external stimuli. It has been revealed by computational chemistry that the dihedral angle between two coordinating pyridines across the iron atom affects the SCO phenomenon for iron (II) assembled complex bridged with 4,4'-bipyridine type ligands. ^{[1][2]} Furthermore, Wu and co-workers have reported the iron assembled SCO complex bridged with 1,4-bis(4-pyridyl)benzene. ^[3] In this conference, we report the iron assembled complexes using 1,4-dimethyl-2,5-bis(4-pyridyl)benzene (dmbpb) and 1,2,4,5-tetramethyl-3,6-bis(4-pyridyl)benzene (tmbpb) and discuss the effect of methyl group on SCO behavior.

The bridging ligands were prepared by Suzuki coupling reaction. The iron assembled complexes were synthesized by direct mixing and diffusion method using FeSO₄·7H₂O, each bridging ligand and RNCX salt (R=K, X=Se and R=N(C(CH₃)₃)₄, X=S, BH₃) in a 1:2:2 ratio. The products from direct mixing were characterized by elemental analysis, PXRD, ⁵⁷Fe Mössbauer spectroscopy and magnetic susceptibility measurement. The structures of complexes (dmbpb: S; tmbpb: S, Se and BH₃) were determined by single crystal XRD using single crystal obtained from diffusion method.

Assembled structures of dmbpb and tmbpb complexes were 2D grid type. The diffraction patterns of complexes were the same for each bridging ligand independent of anionic ligands. The ⁵⁷Fe Mössbauer spectra showed spin state change depending on anionic ligand NCSe and NCBH₃ for the complex with bridging ligand dmbpb. As the result of magnetic susceptibility measurement, transition temperature was 128 K for NCBH₃. On the other hand, the complexes bridged with tmbpb did not show the spin state change. Therefore, the number of methyl substituent on bridging ligand affected SCO behavior. It is thought that there are some differences in local structure around iron due to steric hindrance of methyl substituent in crystal structure and LS state becomes more unstable than HS state.

[1] M. Kaneko, et al., *Chem. Lett.*, **2013**, 42, 1432-1434.

[2] M. Kaneko and S. Nakashima, *Bull. Chem. Soc. Jpn.*, **2015**, 88, 1164-1170.

[3] Xue-Ru Wu, et al, *Inorg. Chem.*, **2015**, 54, 3773-3780.

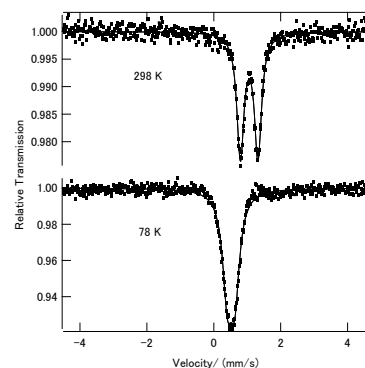


Figure 1 Mössbauer spectra for X=BH₃ (dmbpb).

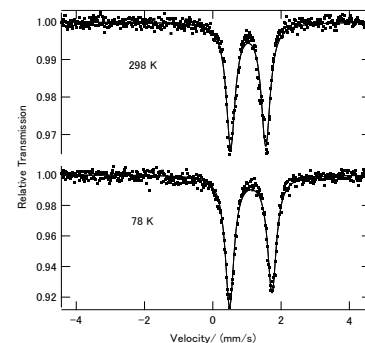


Figure 2 Mössbauer spectra for X=BH₃ (tmbpb).