

## Multistep Spin-Crossover Complex : $\text{Fe}(\text{4-methylpyrimidine})_2[\text{Au}(\text{CN})_2]_2$

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Hofmann-type complexes octahedrally coordinated by  $\text{Fe}^{\text{II}}$  ( $3d^6$ ) central ion are bridged by ligand  $[\text{M}^{\text{I}}(\text{CN})_2]^-$  or  $[\text{M}^{\text{II}}(\text{CN})_4]^{2-}$  equatorially and axially by pyridine-like ligands, and forming the metal organic framework. Some of these compounds exhibit spin-crossover (SCO) phenomena, which switches between high spin (HS) and low spin (LS) states reversibly. Especially, since SCO complexes in  $3d^6$  transition metals show LS state in diamagnetism whereas HS state in paramagnetism, these have potentials for use in spin on-off devices. Many kinds of SCO complexes have been reported, and some of these display multistep SCO. For example, Real and co-workers reported the two step SCO complex using 3-fluoropyridine [1], Kosone and co-workers reported the three step SCO complex using 4-methylpyridine [2] and recently the four step SCO complex has been reported by Kepert group [3]. Okabayashi and co-authors reported the EXAFS investigations on some SCO Hofmann-like Coordination polymers [4]. However, the general rules for multistep SCO have not been clarified yet. We focus on 4-methylpyrimidine introducing into axial ligand molecule because the methyl molecule promotes the disorder for nitrogen bonding in pyrimidine, which might become a driving force for the multistep SCO.

We synthesized novel SCO complex using 4-methylpyrimidine ligands into the Fe-Au based networks  $\text{Fe}(\text{4-methylpyrimidine})_2[\text{Au}(\text{CN})_2]_2$  by liquid reaction using Mohr's salt of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , L-ascorbic acid,  $\text{K}[\text{Au}(\text{CN})_2]$  and 4-methylpyrimidine, which were mixed with all reagents together. The microcrystals were obtained after a few days through the ligand-ligand interfacial reaction.

Temperature-dependent X-ray absorption fine structure (XAFS) and extended XAFS (EXAFS) were performed at BL-9C, Photon Factory (KEK). The sample used for XAFS measurements were diluted by BN powder and formed into pellets. The samples were cooled by the conventional closed Helium cryostat from room temperature to 15 K.

Crystal structure of  $\text{Fe}(\text{4-methylpyrimidine})_2[\text{Au}(\text{CN})_2]_2$  was determined by single-crystal X-ray diffraction (XRD). As shown in Fig. 1 with the space group of  $Pbcm$ . The magnetic susceptibility was measured by superconducting quantum interference device (SQUID) as shown in Fig.1. This complex exhibits two-step transition. The critical temperatures for the first and the second steps are 202 K ( $T_{\text{c}}^{11}$ ) and 186 K ( $T_{\text{c}}^{21}$ ), respectively. The temperature hysteresis of 1 K between cooling and heating processes was

estimated and the magnetic susceptibility is nearly half at 190 K.

Temperature-dependent Fe  $K$ -edge XAFS spectra of  $\text{Fe}(\text{4-methylpyrimidine})_2[\text{Au}(\text{CN})_2]_2$  are shown in Fig. 2. We measured the spectra from 205 to 165 K at intervals of 5 K on cooling. Peak shift was observed only at Fe  $K$ -edge absorption spectra, which suggests that SCO occurs only at the  $\text{Fe}^{2+}$  sites. Peak energy is shifted from 7125.2 eV at 230 K to 7127.2 eV at 165 K, which accounts for the HS-LS spin transition through the changes of the crystal field strength by temperature. We successfully detected the spectrum at intermediate temperature range at 190 K. Peak width becomes broad, which can be explained by the combination of both HS and LS states. Therefore, the HS-LS co-existing states are stabilized by the effect of the ligand molecule in 4-methylpyrimidine.

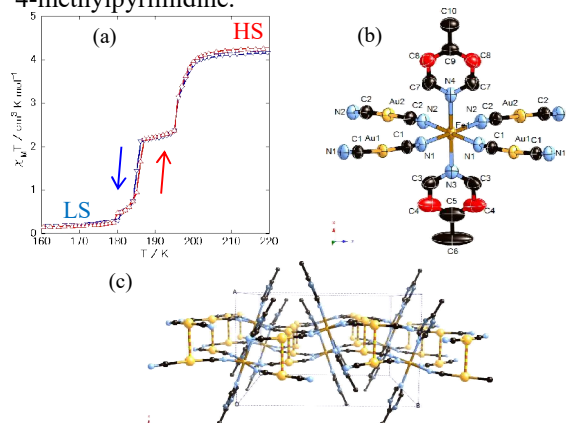


Fig. 1. (a): Magnetic property of  $\text{Fe}(\text{4-methylpyrimidine})_2[\text{Au}(\text{CN})_2]_2$  measured by SQUID. (b): Crystal structure determined by XRD. (Black: C, Aqua: N, Brown: Fe, Yellow: Au, Red: disordered between C and N). (c): Packing structure along the [001] direction.

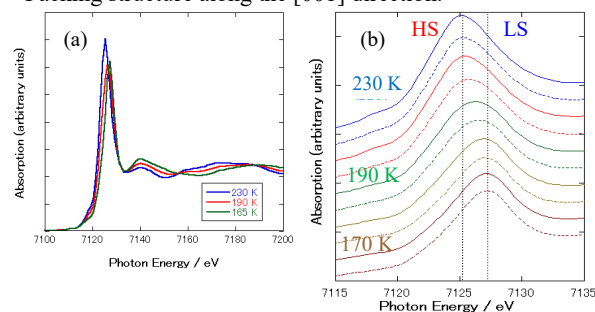


Fig.2 Temperature-dependent Fe  $K$ -edge XAFS spectra of  $\text{Fe}(\text{4-methylpyrimidine})_2[\text{Au}(\text{CN})_2]_2$ .(a): Fe  $K$ -edge EXAFS spectra,(b): Fe  $K$ -edge XANES spectra.

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