

XAFS study of novel spin crossover complex  $\text{Fe}(\text{ethyl-nicotinate})_2[\text{Au}(\text{CN})_2]_2$ Jun Okabayashi,<sup>1\*</sup> Shoutaro Ueno,<sup>2</sup> and Takafumi Kitazawa<sup>2</sup><sup>1</sup>Research Center for Spectrochemistry, The University of Tokyo, Bunkyo, Tokyo 113-0033, Japan<sup>2</sup>Department of Chemistry, Toho University, Funabashi, Chiba 274-8510, Japan

### 1 Introduction

Spin crossover (SCO) phenomena is one of the interesting topics in the research of coordinated magnetic complexes because of their high potentials for utilizing as the molecular-based devices possessing the sensing and spintronic properties. In the SCO phenomena using the magnetic complexes, the relationship between structural and magnetic properties has to be clarified explicitly. However, because of the difficulty to synthesize the single-crystal compounds, the synthesis of complex molecules are limited only for the specific ones, and little works have been performed for the investigation of the relationship between structural and magnetic properties.

Hofmann-type molecular complexes possessing the two-dimensional layers, where the Fe centres are bridged by the cyano along the in-plane directions, have been investigated. In the past, the Hofmann-type two-dimensional layers have been realized using the Fe-Ni combinations as the host site atoms [1]. Recently, the complexes including the Fe-Au compounds exhibiting the SCO transition have been investigated because they can be synthesized easily as the single crystals [2]. Furthermore, because Au atoms are introduced into each layer of the Hofmann-type molecular complexes, an aurophilic interaction between interlayer Au atoms through the layers can be expected [3]. It is believed that the SCO phenomena occurs at the Fe sites of the  $3d^6$  systems by the transitions between high-spin (HS) and low-spin (LS) states. Therefore, we report the site-specific chemical states across the SCO transition measured by x-ray absorption fine structure (XAFS) in  $\text{Fe}(\text{ethyl-nicotinate})_2[\text{Au}(\text{CN})_2]_2$  (**1**).

### 2 Experiment

Single crystal of **1** was prepared by the slow diffusion of solutions,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , ascorbic acid, and  $\text{K}[\text{Au}(\text{CN})_2]$  in 10 ml water using a small vial.

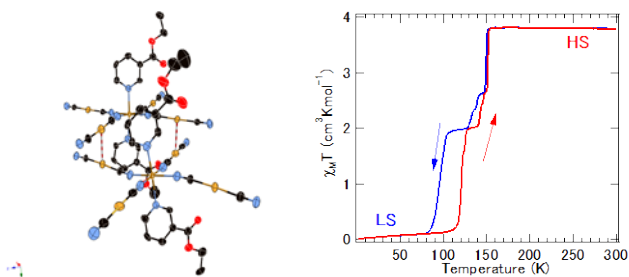
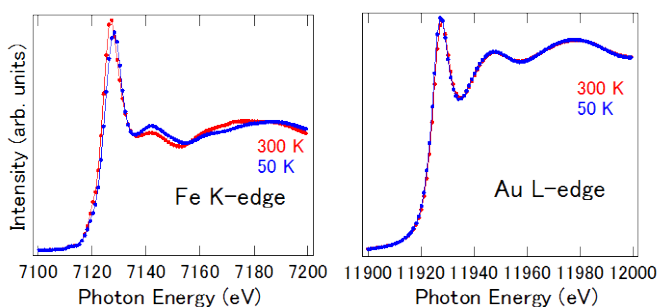
For the XAFS measurements, the sample was diluted with BN powders and was formed to pellets for the measurements in the transmission mode at KEK-PF BL-9C. The sample was cooled to 50 K using a conventional He cryostat. Transmitted X-rays were detected by the ionization chamber filled by Ar gas.

### 3 Results and Discussion

The crystal structure of **1** was revealed by the single-crystal X-ray diffraction at 100 K as shown in Fig. 1. The Hofmann-type two-dimensional layer and the dimerized bilayers are observed [3]. It is derived from the aurophilic interaction between the interlayer Au-Au atoms. The

temperature dependence of the magnetic susceptibility measured by SQUID for **1** reveals the multiple SCO between HS and LS states. These novel phenomena might be related to the aurophilic interaction between Au-Au atoms and the ligand size effects of ethyl-nicotinate.

The temperature dependence of XAFS spectra of Fe *K*-edges and Au *L*-edges for **1** is shown in Fig. 2. The main peak positions in Fe *K*-edge XAFS spectra are shifted to the higher energy side with decreasing the temperature, which is originated to the HS-LS transitions. On the other hand, spectral line shapes of Au *L*-edges remained unchanged across the SCO transition. These results suggest that the SCO occurs only at the Fe sites and the aurophilic interactions remain unchanged across the SCO transition although they contribute to the multiple SCO.

Fig. 1: Crystal structure and SQUID data of **1**.Fig. 2: XAFS spectra of Fe *K*-edge and Au *L*-edges measured at 300 K (HS) and 50 K (LS) for **1**.

### References

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