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Ligand 4-X pyridine (X=Cl, Br, I) dependence in spin crossover complexes: Fe(4-Xpyridine)$_2$[Au(CN)$_2$]$_2$

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Spin crossover (SCO) properties have a high potential for the development of molecular switching and memory devices using the flexibilities of designed organic frameworks. Especially, the reversible changes using the transition between high-spin (HS) and low-spin (LS) states in Fe^{2+} (3d^6) configurations become key technologies with the external perturbations such as temperature, light, pressure, magnetic or electric fields. Two-dimensional Hofmann-type layers were successfully synthesized using pyridine (py) ligands in Fe(pyridine)$_2$Ni(CN)$_4$ and further developments have been performed for cyanide-bridged SCO complex analogs [1]. Recently, the SCO complexes linking between Fe and Au ions bridged by cyanides have attracted much attention because the single crystals can be easily synthesized and aurophilic interactions between interlayer Au ions can be expected. We focus on the systematic investigations of the relationship between structure, electronic states, and magnetic properties of Fe(4-Xpy)$_2$[Au(CN)$_2$]$_2$. By introducing the 4-Xpy ligands in the axial sites, drastic changes in SCO and aurophilic interactions can be expected. Here, we aim to clarify the relationship between structural and magnetic properties in Fe(4-Xpy)$_2$[Au(CN)$_2$]$_2$ (X=Cl, Br, I) depending on the ligand molecules X by using X-ray absorption fine structure (XAFS) measurements.

The complexes were synthesized by a slow diffusion method for the preparation of single crystals. The reaction with an aqueous mixture of FeSO$_4$(NH$_4$)2SO$_4$·6H$_2$O (0.11 mmol) and 4X-py (0.10 mmol) in 10 mL of water, which contained K[Au(CN)$_2$] (0.20 mmol) in 10 mL of water at room temperature. The single crystals were obtained by crystallization after more than 2 days.

XAFS measurements in Fe K-edges and Au L-edges were performed at KEK-PF BL-9C. The samples were diluted with BN powder and scrapped to pellet shapes for the measurements in transmission mode. The transmitted XAFS signals were detected by the ion chamber in Ar and N$_2$ mixed gases. The measurement temperatures were controlled by the conventional closed Helium gas cryostat and heating system. Extended XAFS (EXAFS) analyses were performed by using the conventional FEFF8 code.

The inset of Fig. 1 (a) shows the sample structure determined by the single-crystal X-ray diffraction. The magnetization data in Fig. 1 (b) reveals the SCO transition at 200 K for decreasing temperature and 223 K for increasing temperature.

Figure 1 (c) shows the temperature-dependent XAFS spectra of Fe(4-Clpy)$_2$[Au(CN)$_2$]$_2$, for Fe K-edge and Au L-edges. In the Fe K-edge XAFS spectra, the shifts in the main peaks originating from 1s to 4p electric dipole transitions can be clearly observed. The main peak positions correspond to the Fe^{2+} states. At temperatures less than 200 K, the peak positions shift to higher photon energies, which can be explained by the decreased nearest-neighbor distance and the shift of unoccupied states toward higher energies through the increase of the crystal field strength, which induces the transition to the LS states.

Figure 1 (d) displays the Au L-edge XAFS spectra of HS and LS states. Contrary to those of Fe, the peak positions of the Au L-edges remain unchanged across the SCO transition. These results demonstrate the well-known property that the SCO occurs only at Fe^{2+} sites. This behavior suggests that the total volume in this compound remains unchanged across the SCO transition and the local distortion only near the Fe sites brings the SCO phenomena [2].
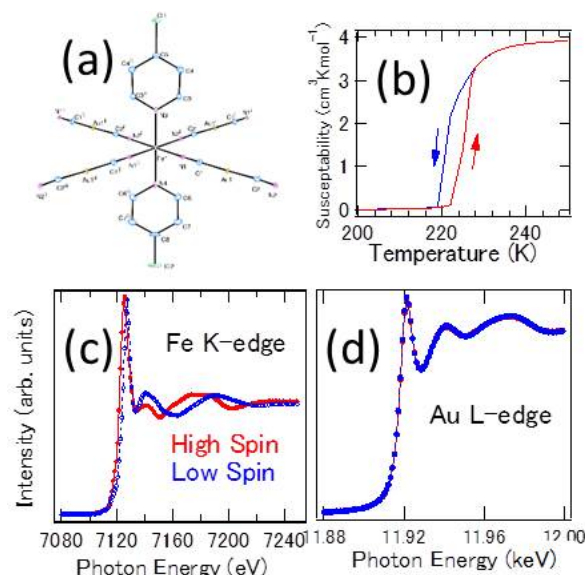

Fig. 1, (a) Crystal structure, (b) Magnetic susceptability, (c) Fe K-edge XAFS, and (d) Au L-edge XAFS of Fe(4-Clpy)$_2$[Au(CN)$_2$]$_2$.

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