A Two-step and Hysteretic Spin-crossover Transition in New Cyano-bridged Hetero-metal $Fe^{II}Au^{I}$ 2-Dimensional Assemblage

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A new hetero-metal 2-dimensional (2D) spin-crossover complex, $\{[Fe^{II}(3\text{-Fpy})_2][Au^{I}(CN)_2]_2\}_n$ (3-Fpy = 3-fluoropyridine) has been synthesized and characterized crystallographically and magnetically. The complex consists of an octahedral Fe^{II} ion and a mononuclear $[Au^{I}(CN)_2]^-$ unit with a linear coordination geometry which combine to form an infinite 2D structure. The spin transition observed for this complex is accompanied by a drastic and reversible change of color from blue to purple.

Development of inorganic supramolecular architectures is a rapidly evolving area of research that has implications for the rational design of functional materials.[1] High-dimensionality coordination polymer systems may possess useful physical and/or chemical properties, including magnetic, nonlinear optical, conducting, catalytic, gas storage, and ion exchange.[2] In particular, their phase transitions have always interested the scientific community from a fundamental point of view, but they have also been of interest because of their possible applications.

In the field of molecular magnetism, spin-crossover complexes constitute a unique kind of switchable material.[3] On external stimulation, such as heat or light, spin-crossover complexes change between the low-spin (LS) and high-spin (HS) ground state because the strength of the ligand field in the complexes is at the borderline between the low- and high-spin states.[4] Such complexes provide a fascinating example of electronically dependent effects in transition-metal compounds. Measurements of magnetic susceptibility, heat capacity, and structural analysis by X-ray diffraction, have been carried out on spin-crossover complexes. For complexes containing the Fe^{II} ion, detailed investigations using ^{57}Fe Mössbauer spectroscopy have also been carried out.[5] Such complexes are particularly suitable for investigating spin characteristics since the spin transitions occur with distinct behavior: gradually, or rapidly, or step-wise, and with hysteresis.

Hofmann-like structures containing Fe^{II} ions have afforded a number of 2-dimensional[6] and 3-dimensional[7] spin-crossover polymers. We have developed a synthetic route to prepare several hetero-metal 2-dimensional coordination polymers with the mononuclear $[Au^{I}(CN)_2]^-$ unit.

In this paper, we report the synthesis, magnetic properties, and X-ray crystal structure of a new hetero-metal $Fe^{II}Au^{I}$ 2-dimensional complex, $\{[Fe^{II}(3\text{-Fpy})_2][Au^{I}(CN)_2]_2\}_n$ (3-Fpy = 3-fluoropyridine) (shown in Figure 1).

The complex, $\{[Fe^{II}(3\text{-Fpy})_2][Au^{I}(CN)_2]_2\}_n$ was synthesized by reaction of an aqueous mixture of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (0.25 mmol, 98 mg) and 3-Fpy (0.5 mmol, 48.5 mg) in 10 mL of water, with an aqueous solution of $K[Au^{I}(CN)_2]$ (0.25 mmol, 72 mg) at room temperature. The two solutions were communicated. Blue single crystals suitable for X-ray diffraction were obtained from the mixture by crystallization in a glass tube over a period of more than 2 days. Elemental analysis confirmed the organic content (found: C, 22.36; H, 1.28; N, 10.79%. Calcd for $C_{14}H_8N_6F_2FeAu_2$: C, 22.48; H, 1.08; N, 11.23%).

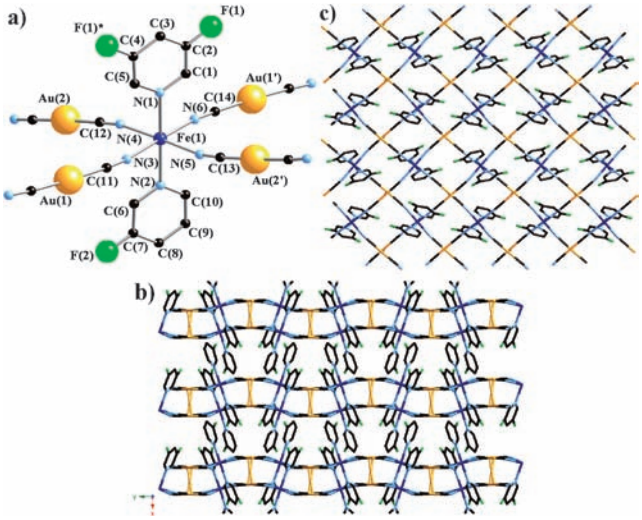

Figure 1. Drawing showing a $[Fe^{II}(3\text{-Fpy})_2][Au^{I}(CN)_2]_2$ fragment. The hetero-metals $Fe^{II}Au^{I}$ are linked in an infinite 2-D lattice structure (a). Stacking of six consecutive layers of $\{[Fe^{II}(3\text{-Fpy})_2][Au^{I}(CN)_2]_2\}_n$ along the [001] direction, yellow lines are Au^{I} aurophilic interactions (b), and the cylinder drawing, 2-D structure of $\{[Fe^{II}(3\text{-Fpy})_2][Au^{I}(CN)_2]_2\}_n$ (c). In this picture, hydrogen atoms are omitted for clarity.

The crystal structure was analyzed by single-crystal X-ray diffraction at 223 K.[8,10] The asymmetric unit of the complex consists of the mixed-metal $Fe^{II}Au^{I}$ unit of $[Fe^{II}(3\text{-Fpy})_2]$-$[Au^{I}(CN)_2]_2$ (shown in Figure 1). The Fe^{II} ion in $[Fe^{II}(3\text{-Fpy})_2][Au^{I}(CN)_2]_2$ is octahedrally coordinated by six nitrogen atoms. All Au^{I} atoms have linear coordination geometries with the cyano substituents binding to the Fe^{II} ions. While the F(1) in the 3-Fpy ligand is disordered, F(2) in the other 3-Fpy ligand is not disordered. Thus, the two 3-Fpy ligands in $[Fe^{II}(3\text{-Fpy})_2][Au^{I}(CN)_2]_2$ are not equivalent and coexist in transoid and cisoid conformations for Fe(1). The structure comprises a corrugated 2-D cyano-bridged array. Interestingly, the layers interact by pairs defining bilayers (shown in Figure 1). The cohesive force in the bilayers stems from strong aurophilic interactions. The average Au···Au distance in the bilayers is 3.152 Å, less than the sum of the van der Waals radii of Au (3.60 Å).

Magnetic measurements were performed on a powder sam-

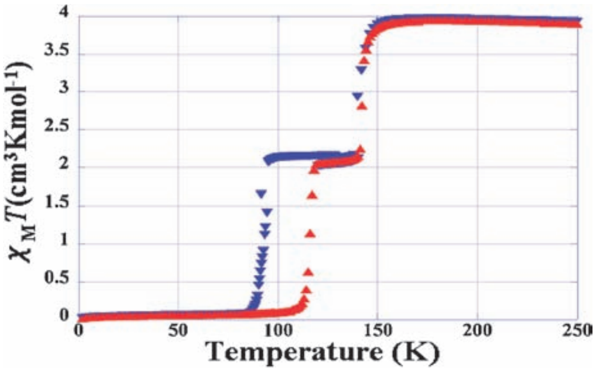

Figure 2. Thermal dependence of $\chi_M T$ for $\{[Fe^{II}(3\text{-}Fpy)_2][Au^I(CN)_2]_2\}_n$. The sample was cooled from 300 to 2 K (▼ blue) and then warmed from 2 to 300 K (▲ red).

ple, in the cooling mode at rates of $2\,K{\cdot}min^{-1}$ (300–130 K), $0.03\,K{\cdot}min^{-1}$ (130–74 K), and $0.5\,K{\cdot}min^{-1}$ (74–2 K) and warming mode at rates of $0.5\,K{\cdot}min^{-1}$ (2–82 K), $0.03\,K{\cdot}min^{-1}$ (82–98 K), and $1\,K{\cdot}min^{-1}$ (98–300 K) on an MPMS-XL Quantum Design SQUID magnetometer. Figure 2 shows the thermal dependence of $\chi_M T$. At room temperature, $\chi_M T$ is 3.87 $cm^3\,K\,mol^{-1}$. This value is slightly higher than usual for paramagnetic Fe^{II} compounds, possibly due to contribution of the orbital angular moment. Upon cooling, $\chi_M T$ remains almost constant down to 150 K; below this temperature, $\chi_M T$ undergoes a sharp decrease. The complex displays a two-step spin transition with a characteristic plateau centred at around 50% conversion and the warming mode reveals the occurrence of a wide hysteresis loop (second step). The spin-crossover phenomenon for this complex causes a reversible change of color from blue to purple. The critical temperature ($T_c{}^1$) is 147.9 K in the first step and the cooling ($T_c{}^{2\ down}$) and warming ($T_c{}^{2\ up}$) modes in the second step are 98.2 and 118.6 K, giving an approximately 20.4 K wide hysteresis loop. The magnetic behavior on warming after rapid cooling ($10\,K{\cdot}min^{-1}$ 300–2 K) is very different owing to the kinetic relaxation from the high-spin to the low-spin state.

We have found a simple synthetic method to create a new hetero-metal $Fe^{II}Au^I$ bilayer 2-dimensional complex, $\{[Fe^{II}(3\text{-}Fpy)_2][Au^I(CN)_2]_2\}_n$, from a mononuclear Au^I complex $K[Au^I(CN)_2]$, Mohl's salt $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ and 3-fluoropyridine and structurally characterized at 223 K. The coordination polymer undergoes thermally induced spin-crossover transitions with magnetic and chromatic bistability. The introduction of the pyridine ligands plays an important role in spin-crossover.

Recently, Real and co-workers synthesized the compounds $\{Fe(3\text{-}Xpyridine)_2[Ag(CN)_2]_2\}$ (X = F, Cl, Br, and I).[9] In comparison with $\{Fe(3\text{-}Fpy)_2[Ag(CN)_2]_2\}$ (**1**) and $\{Fe(3\text{-}Fpy)_2[Au(CN)_2]_2\}$ (**2**), **1** undergoes a gradual two-step transition with no hysteresis, whereas **2** undergoes a rapid two-step transition with wide hysteresis. The reason for two-step transition in the **1** is occurrence of two crystallographically distinct Fe^{II} sites whereas in the **2** is maybe occurrence of local different 3-Fpy ligands sites.

The exploitation of such hetero-metal coordination polymers exhibiting spin-crossover phase transitions, could be important in new functional materials. Thus, this simple synthetic method for the preparation of hetero-metal $Fe^{II}Au^I$ 2-dimensional complexes might be useful for generating a variety of functional complexes, which are presently the subject of intensive studies by chemists and physicists, aiming at the eventual use of their potential switching properties in thermal and pressure sensors as well as optical devices.

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8 Crystal structural data of $\{[Fe^{II}(3\text{-}Fpy)_2][Au^I(CN)_2]_2\}_n$: monoclinic, space group $P2_1/c$ (No. 14); $a = 9.0141(9)$, $b = 13.8546(13)$, $c = 15.4343(15)$ Å, $\beta = 96.343(3)°$, $V = 1915.74(3)$ Å^3, $Z = 4$, $D_{calcd} = 2.594\,g{\cdot}cm^{-1}$. A crystal of dimensions $0.37 \times 0.36 \times 0.35$ mm was selected for indexing and intensity data collected at 223 K. Total number of measured and observed independent reflections ($I_{obs} > \sigma 2(I)$) were 13700 and 2248. Final $R_1 = 0.0487$, $wR_2 = 0.1245$. Data collection was performed on a BRUKER APEX SMART CCD area-detector diffractometer with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The diffraction data were treated using SMART and SAINT, and absorption correction was performed using SADABS. The structure was solved by direct methods using SHELX. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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