

Isotope Effect on Spin-crossover Transition in a New Two-dimensional Coordination Polymer $[\text{Fe}^{\text{II}}(\text{C}_5\text{H}_5\text{N})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2$, $[\text{Fe}^{\text{II}}(\text{C}_5\text{D}_5\text{N})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2$, and $[\text{Fe}^{\text{II}}(\text{C}_5\text{H}_5^{15}\text{N})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2$

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A new Hofmann-like heterometal $\text{Fe}^{\text{II}}\text{Au}^{\text{I}}$ two-dimensional (2D) spin-crossover compound, $\{[\text{Fe}^{\text{II}}(\text{pyridine})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2\}_n$ (**1**) and its isotope-substituted analogues $\{[\text{Fe}^{\text{II}}(\text{pyridine-}D_5)_2][\text{Au}^{\text{I}}(\text{CN})_2]_2\}_n$ (**2**) and $\{[\text{Fe}^{\text{II}}(\text{pyridine-}^{15}\text{N})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2\}_n$ (**3**) have been synthesized in a simple synthetic method and characterized crystallographically and magnetically. Complex **1** consists of an octahedral Fe^{II} ion coordinated with the pyridine ligands and a mononuclear $[\text{Au}^{\text{I}}(\text{CN})_2]^-$ unit with a linear coordination geometry, which combine to form an infinite 2D structure. The spin transitions observed for **1** and **3** are accompanied by drastic and reversible change of color from colorless to purple. In complexes **1** and **3**, about 10 and 3.5% high-spin states are changed to low-spin states at 75 K. However, HS states in **2** are slightly more stable than those in **3**.

Spin-crossover complexes of transition-metal ions have attracted much attention from a fundamental point of view and constitute a unique kind of switchable material in the field of molecular magnetism.¹ On external stimulation, such as heat or light, spin-crossover complexes change between the low-spin (LS) and high-spin (HS) ground states because the strength of the ligand field in the complexes is at the borderline between the low- and high-spin states.² In the solid state, the purely molecular spin-crossover phenomenon is substantially influenced by short- and long-range intermolecular interactions,³ giving rise in certain cases to a cooperative, discontinuous spin transition. The actual mechanism of these cooperative interactions is one of the most intriguing questions in spin-crossover research. For complexes containing the Fe^{II} ion, detailed investigations using ⁵⁷Fe Mössbauer spectroscopy have also been carried out.⁴

Recently, many researchers found a number of 2D⁵ and 3D⁶ Hofmann-like clathrates containing Fe^{II} ions which have occurrence of spin transition. We have afforded a synthetic route to prepare several 2D coordination polymers with a mononuclear $[\text{Au}^{\text{I}}(\text{CN})_2]^-$ unit.

In our efforts to better understand the mechanism of spin crossover in these interesting polymer materials we decided to study the isotope effect on the spin-crossover behavior.

In this paper, we report the synthesis and magnetic properties of a new heterometal $\text{Fe}^{\text{II}}\text{Au}^{\text{I}}$ 2D complex, $\{[\text{Fe}^{\text{II}}(\text{pyridine})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2\}_n$ (**1**) and its isotope-substituted analogues $\{[\text{Fe}^{\text{II}}(\text{pyridine-}D_5)_2][\text{Au}^{\text{I}}(\text{CN})_2]_2\}_n$ (**2**) and $\{[\text{Fe}^{\text{II}}(\text{pyridine-}^{15}\text{N})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2\}_n$ (**3**). Furthermore, X-ray crystal structures of **1** are also reported (shown in Figure 1).

The complex **1** was synthesized by reaction of an aqueous mixture, one containing a mixture of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (0.25 mmol, 98 mg) and pyridine (0.5 mmol, 39.5 mg) in 10 mL of water, the other contained $\text{K}[\text{Au}^{\text{I}}(\text{CN})_2]$ (0.25 mmol, 72 mg)

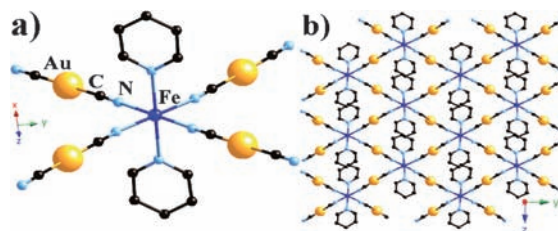


Figure 1. Drawing showing a $[\text{Fe}^{\text{II}}(\text{pyridine})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2$ fragment. The hetero-metals $\text{Fe}^{\text{II}}\text{Au}^{\text{I}}$ are linked in an infinite 2D lattice frame-work (a). The cylinder drawing, 2D structure of $\{[\text{Fe}^{\text{II}}(\text{pyridine})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2\}_n$ (b). In this picture, hydrogen atoms are omitted for clarity.

in 10 mL of water at room temperature. Colorless 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. Compounds **2** and **3** were synthesized by the same method as **1**, but using pyridine- D_5 and pyridine- ^{15}N which are not suitable for single-crystal X-ray diffraction. The samples were identified by elemental analysis confirming the organic content (Found, **1**: C, 23.58; H, 1.45; N, 11.81%. Calcd for $\text{C}_{14}\text{H}_{10}\text{N}_6\text{FeAu}_2$: C, 23.61; H, 1.42; N, 11.80%. Found, **2**: C, 23.21; D, 2.95; N, 11.69%. Calcd for $\text{C}_{14}\text{D}_{10}\text{N}_6\text{FeAu}_2$: C, 23.29; D, 2.79; N, 11.64%. Found, **3**: C, 23.39; H, 1.46; N, 12.11%. Calcd for $\text{C}_{14}\text{H}_{10}^{15}\text{N}_6\text{FeAu}_2$: C, 23.54; H, 1.41; N, 12.05%), IR spectroscopy, and powder X-ray diffraction pattern.

The crystal structure for **1** was analyzed by single-crystal X-ray diffraction at 300 K.⁷ The asymmetric unit of the complex consists of the mixed-metal $\text{Fe}^{\text{II}}\text{Au}^{\text{I}}$ unit of $[\text{Fe}^{\text{II}}(\text{pyridine})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2$ (shown in Figure 1). The Fe^{II} ion in $[\text{Fe}^{\text{II}}(\text{pyridine})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2$ 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. The structure comprises flat 2D cyano-bridged array (shown in Figure 2). The 2D array is similar to that of $\{[\text{Fe}^{\text{II}}(\text{pyridine})_2][\text{Ag}^{\text{I}}(\text{CN})_2]_2\}_n$ (**4**) (ref 5d). Recently, similar compounds $\{[\text{Fe}^{\text{II}}(3\text{-Xpyridine})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2\}_n$ (X = CN, F, Cl, Br, and I) have been prepared.⁸ The structure of $\{[\text{Fe}^{\text{II}}(3\text{-Xpyridine})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2\}_n$ comprises a corrugated 2D cyano-bridged array with strong auriphilic interactions ($\text{Au}\cdots\text{Au}$ distance 3.15 Å). The layers interact by pairs defining bilayers, while **1** is not auriphilic interactions ($\text{Au}\cdots\text{Au}$ distance 4.24 Å).

Magnetic measurements for **1**, **2**, and **3** were performed on powder samples, in the cooling mode at rates of $2\text{ K}\cdot\text{min}^{-1}$ (300–2 K) and warming mode at rates of $2\text{ K}\cdot\text{min}^{-1}$ (2–300 K) on a MPMS-XL Quantum Design SQUID magnetometer. Figure 3 shows the thermal dependence of $\chi_{\text{M}}T$ for **1**, **2**, and **3**. At room temperature $\chi_{\text{M}}T$ for **1**, **2**, and **3** are 4.27, 4.26,

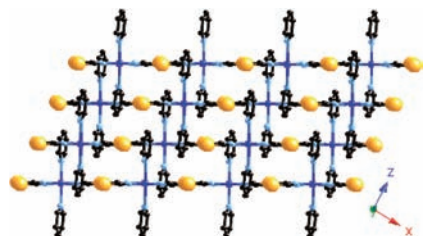


Figure 2. Stacking of four consecutive layers of $\{[\text{Fe}^{\text{II}}(\text{pyridine})_2][\text{Au}^{\text{I}}(\text{CN})_2]_2\}_n$. In this picture, hydrogen atoms are omitted for clarity.

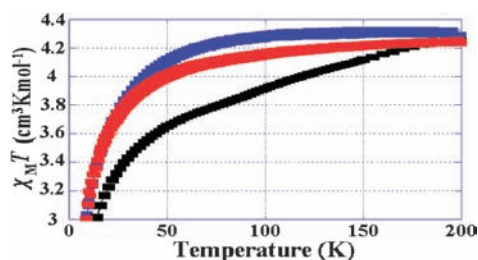


Figure 3. Thermal dependence of $\chi_{\text{M}}T$ for **1** (black), **2** (blue), and **3** (red). The samples were cooled from 300 to 2 K then warmed from 2 to 300 K.

and $4.25 \text{ cm}^3 \text{ K mol}^{-1}$. These values are higher than usual for paramagnetic Fe^{II} compounds, possibly due to contribution of the orbital angular moment. Upon cooling, $\chi_{\text{M}}T$ for **1** remains almost constant down to 180 K; below this temperature, $\chi_{\text{M}}T$ undergoes a widely and gradual decrease between 180 and 75 K. At 75 K, $\chi_{\text{M}}T$ for **1** and **3** are 3.75 and $4.10 \text{ cm}^3 \text{ K mol}^{-1}$. About 10 (complex **1**) and 3.5% (complex **3**) high-spin states are transformed into low-spin states. The complexes **1** and **3** cause a reversible change of color from colorless to purple. The spin-crossover behavior of **1** is different from **4**. $\chi_{\text{M}}T$ for **2** stands almost constant down to 75 K, which is ca. 100 K lower than **1**. Complex **2** does not change color on cooling from room temperature to 77 K. The field dependence of the magnetization of **1**, **2**, and **3** at 2 K reveals these curves are not due to antiferromagnetic interactions, and the data also show the rate of HS states of **1**, **2**, and **3**.¹¹ The decreases of the $\chi_{\text{M}}T$ at lower temperatures around 2 K are most likely due to the zero-field splitting of the HS species, as often happens in spin-crossover complexes.

Many spin-crossover complexes that include Fe^{II} atoms at their center have been reported, but their isotope effects have been little investigated.² One of the most interesting observations of the present study is the significant shift of the spin transition towards lower temperatures upon isotope substitution. Usually, LS state appeared to be stabilized by deuteration. It is thought in those cases that the temperature shifted higher because the energy gap between the LS and HS states was widening in order to increase the reduced mass. However, in this study, the HS states appear to be stabilized by deuteration as demonstrated in **2**. This new result for **1**, **2**, and **3** is different from the former explanation.

The magnetic measurements indicate that the order of high spin stability is **2**, **3**, and **1**. This new isotope effect in **1**, **2**, and **3** in this system agrees with the trend in the isotope effect in $\text{Fe}^{\text{II}}(\text{pyridine})_2\text{Ni}^{\text{II}}(\text{CN})_4$ system.⁹ The reason for this result in the **1**, **2**, and **3** is probably due to the coordination polymeric

network as well as $\text{Fe}^{\text{II}}(\text{pyridine})_2\text{Ni}^{\text{II}}(\text{CN})_4$ system, being associated with the energy gap between the LS and HS states.

The space group and spin-crossover behavior of **1** is different from **4**. The differences between **1** and **4** are probably associated with ionic radii between Au^{I} and Ag^{I} ions.

The isotope effect of **1**, **2**, and **3** may be associated with the pressure effect on SCO behavior. Pressure experiments on Hofmann-type $\text{Fe}^{\text{II}}(3\text{-methylpyridine})_2\text{Ni}^{\text{II}}(\text{CN})_4$ were reported.¹⁰ Pressure experiments for **1**, **2**, and **3** will be helpful for better understanding the isotope effect in these compounds.

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- Crystal structural data of **1**: monoclinic, space group $P2_1/c$ (No. 14); $a = 7.2157(19)$, $b = 14.067(4)$, $c = 8.462(2) \text{ \AA}$, $\beta = 96.441(6)^\circ$, $V = 853.5(4) \text{ \AA}^3$, $Z = 2$, $D_{\text{calcd}} = 2.771 \text{ g}\cdot\text{cm}^{-3}$. A crystal of dimensional $0.09 \times 0.11 \times 0.10 \text{ mm}^3$ was selected for indexing and intensity data collected at 300 K. Final $R_1 = 0.0352$, $wR_2 = 0.0751$. CCDC Reference No. 681757.
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