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Novel Structural and Magnetic Properties of a 1-D Iron(II)–Manganese(II) LIESST Compound Bridged by Cyanide

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The 1-D compound $[Fe(L)(CN)_2][Mn(hfac)_2]$ (**1**), which adopts the –NC–Fe–CN–Mn– heterometallic structure, has been shown to exhibit light-induced excited spin-state trapping effects. After illumination, anti-ferromagnetic coupling was observed between the iron(II) ($S = 2$) and manganese(II) ($S = {}^5/_2$) ions.

There has recently been a great interest in studying the magnetic properties of molecular compounds.[1] In particular, the design of spin-crossover compounds that exhibit bistable behavior between the high-spin (HS) and low-spin (LS) states has recently attracted great attention.[2] Usually, the spin-transition phenomena can be induced by variations in temperature or in pressure. On the other hand, Decurtins et al. have reported a light-induced excited spin-state trapping (LIESST) effect in a mononuclear iron(II) compound.[3] Spin-transition behavior greatly affects the cooperativity of intermolecular forces,[4] and one way of increasing cooperativity is to introduce dimensionality into spin-transition compounds.[5] Furthermore, spin-transition compounds that feature dimensionality can be expected to exhibit magnetic interactions between the central metal ions when the distance between the metal ions is sufficiently short. van Koningsbruggen et al. have recently reported the first example of 1-D and 3-D polymeric compounds that exhibit LIESST effects.[6] However, although the iron(II) ions are bridged by molecular ligands in these LIESST complexes, no appreciable magnetic interactions are observed in those compounds because of the distance (ca. 8.5 Å) between the iron(II) ions. Furthermore, Hoffman clathrate analogues constructed by an alternate linkage between square-planar Ni(II) and octahedral Fe(II) ions through cyano bridges cannot be expected to undergo any magnetic interactions.[7] However, in 1999, Létard et al. reported magnetically coupled binuclear LIESST complexes. In these compounds, the spin on each iron(II) ion interacts anti-ferromagnetically, leading to the $S = 0$ ground state after illumination.[8] However, up to now, no magnetically coupled polynuclear LIESST compounds have been reported. Here we report on the first example of such a 1-D LIESST compound, which features a magnetic interaction between Fe(II) and Mn(II) ions. The compound is $[Fe(L)(CN)_2][Mn(hfac)_2]$ (**1**), where

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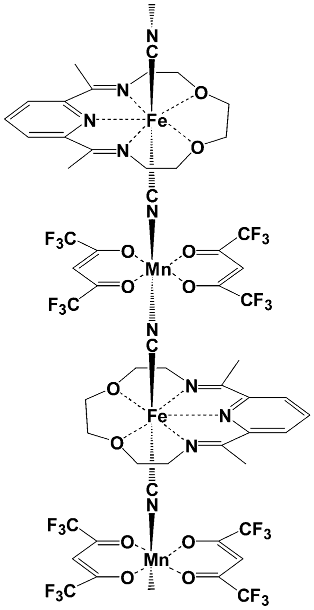

Figure 1. Schematic representation of 1-D $[Fe(L)(CN)_2][Mn(hfac)_2]$ (**1**).

L is a Schiff base macrocyclic ligand derived from the condensation of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine and hfac is hexafluoroacetylacetone. This compound was constructed in a rational way by using an iron(II) LIESST mononuclear compound with bidentate cyanide ligands (Figure 1).[9]

To construct a 1-D bimetallic LIESST compound, we first searched for a mononuclear LIESST compound with bidentate CN ligands. Through our exploration of many molecular compounds, we discovered that $[Fe(L)(CN)_2]\cdot H_2O$ (**2**) exhibits such ideal properties.[10] Second, to form a 1-D −NC−Fe−CN−Mn− structure by making use of the coordination ability of the nitrogen end of the CN group in **2**, compound **2** and $[Mn(hfac)_2(H_2O)_2]$ (**3**) were mixed in a dichloromethane solution. As a result, a fine blue powder with a stoichiometry of **1** was precipitated.[11]

The structure of **1** was investigated by EXAFS spectroscopy based on the structure of **2** and **3** because we could not grow crystals of **1** that were suitable for X-ray diffraction studies. The Fe *K*-edge XANES spectra of **1** at 300 K are almost consistent with those of **2**. This means that the local structure of Fe in complexes **1** and **2** is $[Fe(L)(CN)_2]$. On the other hand, the Mn *K*-edge XANES spectra of **1** at 300 K are slightly different from those of **3**. The shoulder at 6545 eV is only observed in the spectrum of **1**. Furthermore, the second maximum for **1** is observed at 6560 eV, while the equivalent feature for **3** is observed at 6565 eV. This indicates that the local structures of Mn in **1** and **3** are slightly different from each other. The EXAFS oscillation functions $k^3\chi(k)$ were obtained by means of standard analysis procedures: preedge baseline subtraction and postedge background estimation using the cubic-spline function. The Fe and Mn *K*-edge EXAFS measurements were interrupted around $k = 12.3$ Å^{-1} because of the presence of ca. 0.1% Co impurities. The corresponding Fourier transforms of the spectra for **1**−**3** at 300 K are shown in Figure 2. The Fe EXAFS spectra of **1** at 300 K are almost identical with those of **2**, which is consistent with the XANES spectrum. On the other hand, a distinct difference is observed between the spectra of **1** and **3**, in that a characteristic contribution is observed at 2.7 Å in the spectra of **1**, while it is not observed in the spectra of **3**. The newly visible peak at 2.7 Å can be attributed to the Mn−C shell. This means that compound **1** contains Mn−N−C units, which are arranged in a straight line. Curve-fitting analysis was performed for the second-nearest-neighbor shell. It shows the presence of the local structures of $[Mn(hfac)_2]$ and $[Fe(L)(CN)_2]$ in **1**. These results confirm that a 1-D −NC−Fe−CN−Mn− structure is formed in **1**. The IR spectra of **1** and **2** support this conclusion. The CN stretching mode, $\nu(C\equiv N)$, was observed at 2133 cm^{-1} for **1** at 300 K. On the other hand, it was observed at 2106 and 2102 cm^{-1} for **2**. This means that the N of the CN group in $[Fe(L)(CN)_2]$ is coordinated to the Mn ion in $[Mn(hfac)_2]$, forming the 1-D −NC−Fe−CN−Mn− structure.

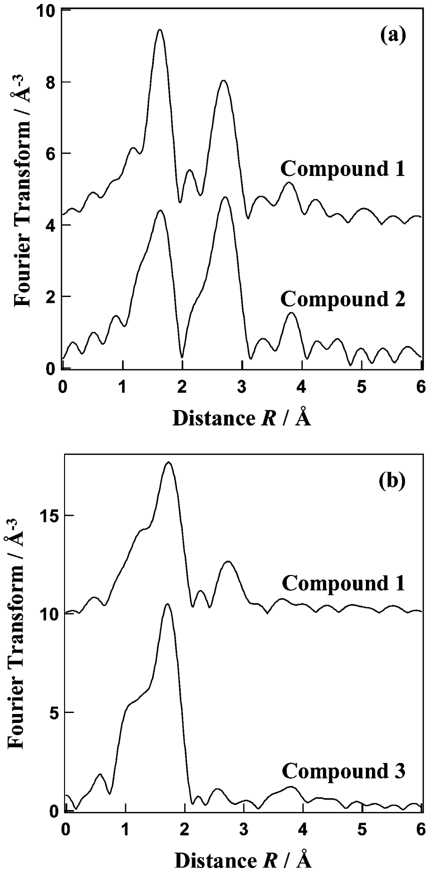

Figure 2. Fourier transforms of the EXAFS spectra at 300 K for (a) the Fe *K* edge of compounds **1** and **2** and (b) the Mn *K* edge of compounds **1** and **3**.

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(11) The compound **1** was obtained by dissolving 0.51 g (1 mmol) of $[Mn(hfac)_2]\cdot 2H_2O$ in a mixture of 5 mL of *n*-hexane and 10 mL of dichloromethane, followed by the addition of 0.40 g (1 mmol) of **2** in 10 mL of dichloromethane. Blue powder formed from the solution. Elemental analytical data show that the composition is 1:1 for $[Fe(L)(CN)_2]$ and $[Mn(hfac)_2]$. Anal. Calcd for $C_{27}H_{23}O_6N_5Fe_1Mn_1$ (**1**): C, 38.05; H, 2.72; N, 8.22. Found: C, 38.16; H, 2.56; N, 8.27.

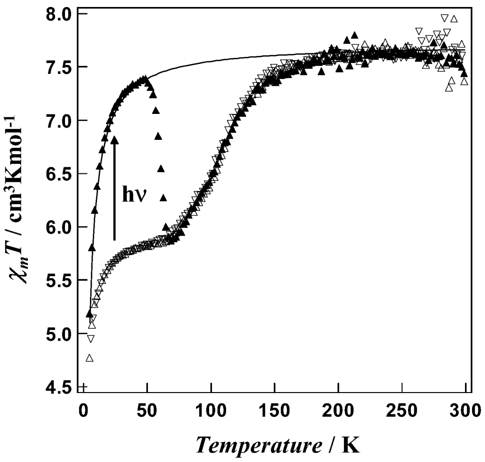

Figure 3. Temperature dependence of a $\chi_m T$ plot for compound **1**: (□) data recorded in the cooling mode and (□) in the warming mode before illumination; (▲) data recorded in the warming mode after illumination.

The temperature dependence of the magnetic moment for **1** before and after illumination was investigated using a Quantum Design MPMS-5S SQUID magnetometer (Figure 3). The value of $\chi_m T$ at 300 K is equal to 7.40 cm^3 K mol^{-1}, which corresponds to the HS state for iron(II) ions and the HS state for manganese(II) ions. On cooling, the value of $\chi_m T$ decreases abruptly from 130 to 100 K ($T_{1/2} = 110$ K). At 65 K, the value of $\chi_m T$ is close to 5.86 cm^3 K mol^{-1}, which corresponds to 50% of the HS iron(II) ions and 50% of the LS iron(II) and the HS manganese(II) ions. Light illumination was performed using a Hg−Xe lamp. Light ($\lambda \approx 550$ nm, 2 mW cm^{-2}) was passed through IR and green filters and was guided into the SQUID via an optical fiber. When the sample was illuminated at 5 K, an increase in susceptibility was observed. The $\chi_m T$ value increased from 4.77 to 5.18 cm^3 K mol^{-1} after illumination (Figure 3). This change in magnetization persisted for many hours, even after the illumination was stopped. This suggests that a transition from the LS state to the metastable HS state was induced by illumination of the iron(II) ions.

The IR spectra measured before and after illumination are consistent with the induction of the LIESST effect. The IR spectra at 20 K show that a CN stretching peak with the −NC−Fe^{II}(LS)−CN−Mn− structure appears at 2130 cm^{-1}. When the sample was illuminated at 20 K, the peak disappeared and the peak at 2139 cm^{-1}, which is ascribable to CN stretching in the −NC−Fe^{II}(HS)−CN−Mn− structure, increased.

When the sample was heated from 5 to 300 K after illumination, the value of $\chi_m T$ increased in the temperature region between 5 and 49 K and decreased between 49 and 69 K. The second decrease corresponds to thermally induced relaxation from the metastable HS state to the LS state. On further heating, compound **1** exhibited spin-crossover behavior of the LS iron(II) ions (Figure 3).

The first increase (where it reached a value of 7.39 cm^3 K mol^{-1}) corresponds to the occurrence of zero-field splitting of the HS iron(II) ions. Furthermore, an anti-ferromagnetic interaction between iron(II) and manganese(II) ions also contributes to the increase after illumination because the increase in the magnetic response at low temperature after illumination is more abrupt than that before illumination. The simplest model that fits the magnetic behavior of this compound, both before and after illumination, is the Curie−Weiss law. Because of the conversion between the two spin states, the model was only applied in the low-temperature ranges (5−45 and 60 K) before and after illumination, respectively. This yielded Curie constants (C) of 12.2 and 16.3 cm^3 K mol^{-1} before and after illumination, respectively. These values are a little higher than the theoretical values with $g_{Fe} = g_{Mn} = 2$ (11.75 and 14.75 cm^3 K mol^{-1}). The Weiss constants (θ) are −1.2 and −2.6 K, respectively; the negative signs prove the anti-ferromagnetic nature of the coupling between the paramagnetic centers. To estimate the exchange interaction, the magnetic susceptibility data were fitted by eq 1 where $F(\beta J) = \coth(\beta J) - 1/\beta J$, $g = (1/2)(g_{Fe}$

$$\chi = \frac{N\beta^2}{3kT}\left[g^2\frac{1 + F(\beta J)}{1 - F(\beta J)} + \delta g^2\frac{1 - F(\beta J)}{1 + F(\beta J)}\right] \qquad (1)$$

$+ g_{Mn})$, and $\delta g = (1/2)(g_{Fe} - g_{Mn})$.[12] The best-fit parameters are $J = -0.10$ cm^{-1} with Lande factors $g_{Fe} = 1.976$ and $g_{Mn} = 2.42$. The presence of anti-ferromagnetic coupling between iron and manganese ions is consistent with the localized orbital model developed by Kahn and the experimental results observed for Prussian blue analogues.[13] Consequently, the photoinduced effect can be explained as follows. Before illumination, compound **1** consists of 50% of LS iron(II) ($S = 0$) moieties and 50% of HS iron(II) ($S = 2$) moieties and HS manganese(II) ($S = {}^5/_2$). Because of the diamagnetic nature of the LS iron(II), the intrachain magnetic interaction is small. On the other hand, LS iron(II) ions can be transformed to the metastable HS state by illumination, forming a 1-D −Fe ($S = 2$)−Mn ($S = {}^5/_2$)−Fe ($S = 2$)−Mn ($S = {}^5/_2$)− structure. Because the bridging ligand CN can act as a mediator for magnetic interactions, the spins on the iron and manganese ions are not isolated but interact with each other anti-ferromagnetically.

In summary, we have reported that compound **1** has the 1-D −NC−Fe−CN−Mn− heterometallic structure. Compound **1** exhibited LIESST effects. After illumination, anti-ferromagnetic coupling is observed between iron(II) and manganese(II) ions.

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Supporting Information Available: Figure S1 contains the normalized XANES spectra at the Mn and Fe *K* edges. The energy and relative intensity of the EXAFS are given in Table S1, and parameters resulting from the analysis of the EXAFS data for the Fe and Mn *K* edges are given in Tables S2 and S3, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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