

Two-Step Electron Transfer Coupled Spin Transition in a Cyanide Bridged Molecular Square

A cyanide bridged Fe-Co molecular square, $[\text{Co}_2\text{Fe}_2(\text{CN})_6(\text{tp}^*)_2(\text{bpy}^*)_4](\text{PF}_6)_2 \cdot 2\text{MeOH}$ (**1**) (tp^* = hydrotris(3,5-dimethylpyrazol-1-yl)borate, bpy^* = 4,4'-di-*tert*-butyl-2,2'-bipyridine) was prepared. Fe and Co ions in **1** are alternately bridged by cyanide ions, forming a macrocyclic tetranuclear core. Variable temperature X-ray structural analyses and magnetic susceptibility measurements confirmed that **1** exhibits two-step electron-transfer coupled spin transitions (ETCST) of which transition temperatures were $T_{1/2} = 275$ and 310 K in the solid state. **1** showed a paramagnetic high-temperature (HT) phase at 330 K, while a diamagnetic low-temperature (LT) phase was dominant below 260 K. X-ray diffraction study using synchrotron radiation revealed that in the intermediate (IM) phase at 298 K the molecular square exhibits long-range ordering of paramagnetic and diamagnetic molecules with a 2:2 ratio.

Prussian blue analogues (PBAs) are 3-D bulk materials in which cyanide ions bridge metal ions with electronic and magnetic interactions. Fe-Co PBA, $\text{K}_{0.2}\text{Co}_{1.4}[\text{Fe}(\text{CN})_6] \cdot 6.9\text{H}_2\text{O}$, has been reported to show photo-induced magnetization due to an electron transfer coupled spin transition (ETCST), in which electron transfers between Co(II) and Fe(III) ions are coupled with spin transition in the Co ions [1]. On the other hand, discrete cyanide-bridged multi-nuclear complexes have flexible molecular and electronic structures. Since the first observation of temperature-driven ETCST at the molecular level was reported in 2002, several mixed-valence Fe-Co clusters exhibiting ETCST have been reported [2–4]. However, all previously reported ETCST in molecular and bulk systems showed one-step transitions. We report here the first two-step ETCST in a cyanide bridged Fe-Co molecular square, $[\text{Co}_2\text{Fe}_2(\text{CN})_6(\text{tp}^*)_2(\text{bpy}^*)_4](\text{PF}_6)_2 \cdot 2\text{MeOH}$ (**1**) [5, 6].

The reactions of $[\text{Fe}(\text{CN})_6(\text{tp}^*)]^-$ with Co^{2+} , bpy^* , and NH_4PF_6 in MeOH yielded the tetranuclear Fe-Co complex, **1** (Fig. 1(a)). **1** has a square-shaped macrocyclic core, in which Fe and Co ions are alternately bridged by cyanide ions, and the complex cation resides on a

center of inversion. The Fe ions are coordinated by tridentate tp^* and three cyanide carbon atoms. The two bidentate bpy^* ligands coordinate to the Co ion, and the bridging cyanide ions in the *cis* positions are linked to the neighboring $[(\text{tp}^*)\text{Fe}]$ units.

Magnetic susceptibility measurements were performed on **1** in the temperature range of 5–330 K (Fig. 1(b)). The $\chi_m T$ values below 250 K are nearly constant with a value of $0.18 \text{ emu mol}^{-1} \text{ K}$ at 250 K, suggesting that **1** is in the diamagnetic LT phase ($[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{LS}}]$, LS = low-spin). As the temperature was raised from 250 to 330 K, the $\chi_m T$ values increased in a two-step fashion centered at $T_{1/2} = 275$ and 310 K. The $\chi_m T$ value ($6.57 \text{ emu mol}^{-1} \text{ K}$) at 330 K is close to the Curie constant expected for the uncorrelated two LS Fe^{III} ($S = 1/2$) and two HS ($S = \text{high-spin}$) Co^{II} ions ($S = 3/2$), indicating the occurrence of ETCST from the LT to the HT ($[\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}]$) phases via the IM phase. The $\chi_m T$ value ($3.33 \text{ emu mol}^{-1} \text{ K}$) in the IM phase corresponds to the value expected for either 1:1 mixture of the $[\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}]$ and $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{LS}}]$ or a one electron transfer $[\text{Fe}^{\text{III}}_{\text{LS}}\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}\text{Co}^{\text{II}}_{\text{LS}}]$ states.

1 crystallized in the monoclinic space group $C2/c$ at 100, 298 and 300 K, where the data were collected using a conventional X-ray source. The coordination bond lengths and Mössbauer measurements confirmed that the oxidation and spin states of **1** can be represented by $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{LS}}]$ in the LT phase. In the HT phase at 330 K, the average coordination bond lengths about the Co and Fe ions are 2.113(4) and 1.964(5) Å, respectively, suggesting the occurrence of complete ETCST from the LT phase to the HT phase ($[\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}]$). In the IM phase at 298 K, the average coordination bond length about Co ions is 2.020(5) Å, which is in the middle of the typical bond lengths for LS Co(II) and HS Co(II) ions. Such intermediate bond length observed at 298 K might be due to either the positional disorder of LS Co(II) and HS Co(II) ions in $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}\text{Co}^{\text{II}}_{\text{LS}}]$, or a 1:1 mixture of $[\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}]$ and $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{LS}}]$. The latter should result in crystallographic super lattice reflections originating from a long-range order which may have been missed due to their low intensity. We therefore collected single-crystal X-ray diffraction data of the IM phase at 298 K using synchrotron radiation. The super lattice reflections were clearly observed in the synchrotron data and structural analysis was carried out on the data including the super lattice reflections (Fig. 2(a)). **1** in the IM phase has the same space group of $C2/c$ as in the LT and HT phases, while the unit cell has a quadrupled cell volume with the *a* and *b* axes doubled in length. The superstruc-

ture contains four unique complex cations. The average coordination bond lengths suggested that two cations are in the $[\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}]$ state, and the other two are in the $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{LS}}]$ state. The complex cations on the *ab* plane form a checkerboard arrangement composed of $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{LS}}]$ and $[\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}]$ cations, leading to the long-range ordering with the quadrupled unit cell (Fig. 2(b)).

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M. Nihei¹, Y. Sekine¹, N. Suganami¹, K. Nakazawa¹, A. Nakao², H. Nakao², Y. Murakami² and H. Oshio¹ (¹Univ. of Tsukuba, ²KEK-PF)

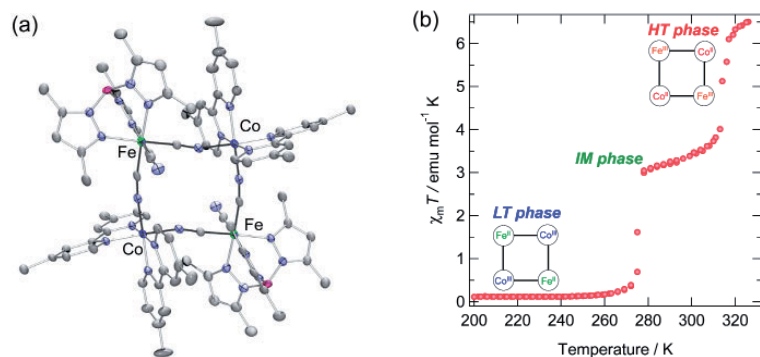


Figure 1
(a) ORTEP diagram of the cation, and (b) two-step ETCST in **1**.

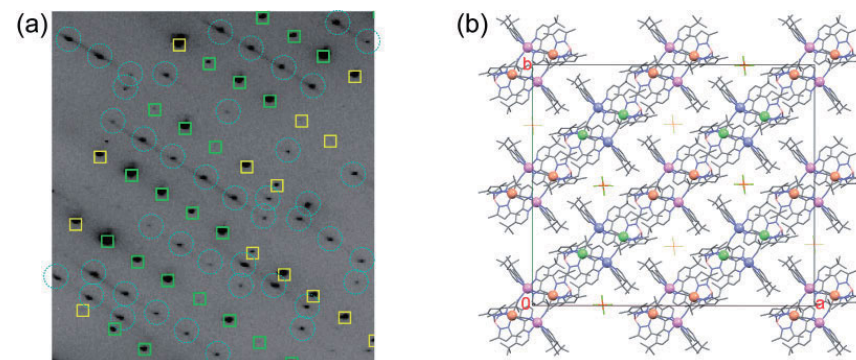


Figure 2

(a) Reflection image of **1** at 298 K. Yellow and green boxes indicate reflections corresponding to the original cell, and super lattice reflections due to long-range order are marked with blue circles. (b) Projection view on an *ab* plane of **1** in the IM phase at 298 K. Pink: Co(II), orange: Fe(III), pale blue: Co(II), pale green: Fe(II).