

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, $\text{bpy}^* = 4,4'\text{-di-tert-butyl-2,2'-bipyridine}$) 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, $\text{K}_{0.2}\text{Co}_{0.4}[\text{Fe}(\text{CN})_6] \cdot 6.9\text{H}_2\text{O}$, 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 ($[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{LS}}]$, 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^{II} ($S = 1/2$) and two HS (= high-spin) Co^{II} ions ($S = 3/2$), indicating the occurrence of ETCST from the LT to the HT ($[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{HS}}]$) 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 $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{HS}}]$ and $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{LS}}]$ or a one electron transfer $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Fe}^{\text{II}}_{\text{LS}}\text{Cd}^{\text{II}}_{\text{HS}}\text{Co}^{\text{III}}_{\text{LS}}]$ states.

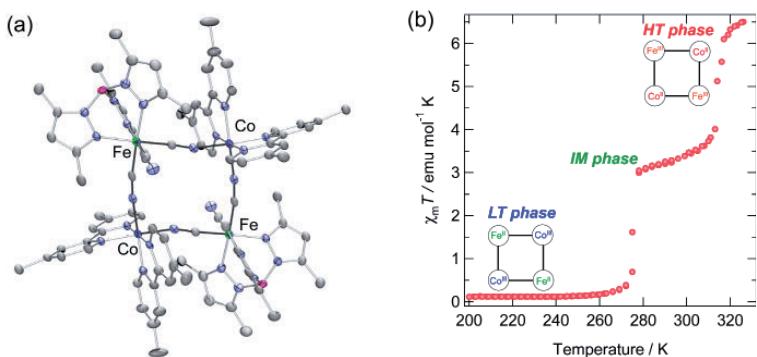


Figure 1
(a)ORTEP diagram of the cation, and (b) two-step ETCST in 1.

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 $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{LS}}]$ 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 ($[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{HS}}]$). 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(III) and HS Co(II) ions. Such intermediate bond length observed at 298 K might be due to either the positional disorder of LS Co(III) and HS Co(II) ions in $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{HS}}\text{Co}^{\text{III}}_{\text{LS}}]$, or a 1:1 mixture of $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{HS}}]$ and $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{LS}}]$. 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 $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{HS}}]$ state, and the other two are in the $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{LS}}]$ state. The complex cations on the *ab* plane form a checkerboard arrangement composed of $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{LS}}]$ and $[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{HS}}]$ cations, leading to the long-range ordering with the quadrupled unit cell (Fig. 2(b)) .

REFERENCES

- O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science* **272** (1996) 704.
- C.P. Berlinguet, A. Dragulescu-Andrasi, A. Sieber, J.R. Galán-Mascarós, H.-U. Güdel, C. Achim and K.R. Dunbar, *J. Am. Chem. Soc.* **126** (2004) 6222.
- D. Li, R. Clérac, O. Roubeau, E. Harté, C. Mathonière, R.L. Bris and S.M. Holmes, *J. Am. Chem. Soc.* **130** (2008) 252.
- Y. Zhang, D. Li, R. Clérac, M. Kalisz, C. Mathonière and S.M. Holmes, *Angew. Chem. Int. Ed.* **49** (2010) 3752.
- M. Nihei, Y. Sekine, N. Suganami and H. Oshio, *Chem. Lett.* **39** (2010) 978.
- M. Nihei, Y. Sekine, N. Suganami, K. Nakazawa, A. Nakao, H. Nakao, Y. Murakami and H. Oshio, *J. Am. Chem. Soc.* **133** (2011) 3592.

BEAMLINE

8A

M. Nihei¹, Y. Sekine¹, N. Suganami¹, K. Nakazawa², A. Nakao², H. Nakao², Y. Murakami² and H. Oshio¹
(¹Univ. of Tsukuba, ²KEK-PF)

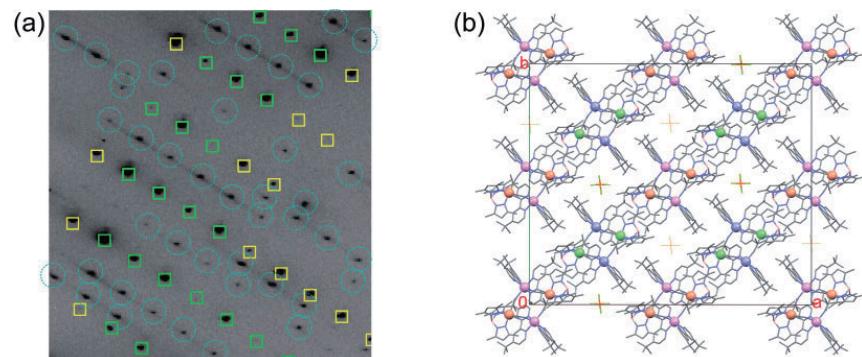


Figure 2
(a) Reflection image of 1 at 298 K. Yellow and green boxes indicate reflections corresponding to the original cell, and super lattice reflections due to long-range order are marked with blue circles. (b) Projection view on an *ab* plane of 1 in the IM phase at 298 K. Pink: Co(III), orange: Fe(III), pale blue: Co(II), pale green: Fe(II).