

## Characterization of an Intermediate Phase in a Two-stepped Electron Transfer-coupled Spin Transition

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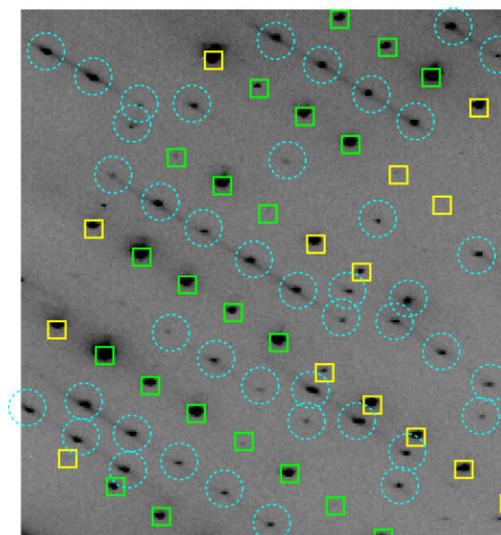
### Introduction

Cyanide-bridged multi-nuclear complexes have potential to show specific molecular functions due to electronic and magnetic interactions between metal ions. We have previously reported a novel cyanide-bridged molecular square of  $[\text{Co}_2\text{Fe}_2(\text{CN})_6(\text{tp}^*)_2(\text{dtbbpy})_4](\text{PF}_6)_2 \cdot 2\text{MeOH}$  (**1**) ( $\text{tp}^*$  = hydrotris(3,5-dimethylpyrazol-1-yl)borate,  $\text{dtbbpy}$  = 4,4'-di-*tert*-butyl-2,2'-bipyridine).<sup>[1]</sup> In **1**, Fe and Co ions are alternately bridged by cyanide ions, forming macrocyclic tetranuclear cores. Magnetic susceptibility measurements confirmed that **1** exhibits two-step electron transfer-coupled spin transitions (ETCST) centred at  $T_{1/2} = 275$  and 310 K in the solid state. In the X-ray diffraction study using the conventional X-ray source (Mo-K $\alpha$ ), the Fe and Co ions are the low-spin (LS) Fe(III) and high-spin (HS) Co(II) ions in the high-temperature (HT) phase ( $[\text{Fe}^{\text{III}}_{\text{LS}2}\text{Co}^{\text{II}}_{\text{HS}2}]$ ) at 330 K, while a low-temperature (LT) phase ( $[\text{Fe}^{\text{II}}_{\text{LS}2}\text{Co}^{\text{III}}_{\text{LS}2}]$ ) with LS Fe(II) and Co(III) ions was dominant below 260 K. At 298 K one dinuclear unit of  $[(\text{tp}^*)\text{Fe}(\text{CN})_2-(\mu\text{-CN})\text{-Co}(\text{dtbbpy})_2]$  was observed as the asymmetric unit, and the average coordination bond length about the Co ions were in the middle of the typical bond lengths for LS Co(III) and HS Co(II) ions in the IM phase at 298 K. It remained unclear whether  $[\text{Fe}^{\text{II}}_{\text{LS}2}\text{Co}^{\text{III}}_{\text{LS}2}]$  and  $[\text{Fe}^{\text{III}}_{\text{LS}2}\text{Co}^{\text{II}}_{\text{HS}2}]$  are positionally disordered or not, and weak super lattice reflections originating from long-range order could be missed in the X-ray diffraction data using conventional X-ray source. We, therefore, collected a single crystal X-ray diffraction data of the IM phase at 298 K using synchrotron radiation.<sup>[2]</sup>

### Results and discussion

The super lattice reflections were clearly observed in the synchrotron data (Figure 1) and structural analysis was carried out on the data including the super lattice reflections. **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 superstructure contains four unique complex cations, named  $[\text{FeA}_2\text{CoA}_2]$ ,  $[\text{FeB}_2\text{CoB}_2]$ ,  $[\text{FeC}_2\text{CoC}_2]$ , and  $[\text{FeD}_2\text{CoD}_2]$ . The cations interact through hydrophobic interactions between ligands, forming layers on the *ab* plane. The layers are stacked along the *c* axis through hydrogen bonds with the counter anions, and

methanol molecules are located between the layers. The average coordination bond lengths about the CoA-D ions are 2.092(8), 2.008(8), 2.071(8) and 1.990(8) Å, respectively, suggesting that the CoA and CoC ions are HS Co(II), while the CoB and CoD ions are LS Co(III). Magnetic data revealed that the ratio of  $[\text{Fe}^{\text{II}}_{\text{LS}2}\text{Co}^{\text{III}}_{\text{LS}2}]/[\text{Fe}^{\text{III}}_{\text{LS}2}\text{Co}^{\text{II}}_{\text{HS}2}]$  in the IM phase is 2:2, and the electronic states of  $[\text{FeA}_2\text{CoA}_2]$  and  $[\text{FeC}_2\text{CoC}_2]$  can be, therefore, assigned as  $[\text{Fe}^{\text{II}}_{\text{LS}2}\text{Co}^{\text{II}}_{\text{HS}2}]$ , and  $[\text{FeB}_2\text{CoB}_2]$  and  $[\text{FeD}_2\text{CoD}_2]$  are in the  $[\text{Fe}^{\text{II}}_{\text{LS}2}\text{Co}^{\text{III}}_{\text{LS}2}]$  state. The complex cations on the *ab* plane form a checkerboard arrangement composed of  $[\text{Fe}^{\text{II}}_{\text{LS}2}\text{Co}^{\text{III}}_{\text{LS}2}]$  and  $[\text{Fe}^{\text{III}}_{\text{LS}2}\text{Co}^{\text{II}}_{\text{HS}2}]$  cations, leading to the long range ordering with the quadrupled unit cell.



**Figure 1** 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.

### References

- [1] M. Nihei, Y. Sekine, N. Suganami, H. Oshio, Chem. Lett. 39, 978 (2010).  
[2] M. Nihei, Y. Sekine, N. Suganami, K. Nakazawa, A. Nakao, H. Nakao, Y. Murakami, H. Oshio, J. Am. Chem. Soc. 133, 3592 (2011).

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