

## Pressure-induced conversion of a family of cyanide-bridged Fe/Co square complexes from paramagnetic to bistable state

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Molecular magnetic switches are molecules, which undergo reversible conversions between two distinct electronic states under external stimuli: temperature, light, pressure... The change of electronic state can be associated to the drastic modification in the magnetic properties but also in the optical, dielectric and mechanic properties. Up to now, the most investigated molecular magnetic switches are spin-crossover complexes (SCO) and more specifically Fe<sup>II</sup> octahedral complexes. Another class of bistable magnetic compounds have later emerged involving the cyanide-bridged bimetallic clusters, where the electronic reorganization often implies a metal-to-metal electron transfer coupled to a spin transition on one metal ion (ETCST). The effect was first evidenced in inorganic polymers (Fe/Co Prussian Blue Analogs), but strong research efforts have recently been devoted to the design of their discrete molecular analogs. To date, the effect of pressure as stimulus has remained scarcely investigated. Aware of the potential application as sensors and aiming at getting a better understanding of the pressure-induced ETCST process, our group has recently focused its interest on the paramagnetic Fe/Co square compounds:  $\{[\text{Fe}^{\text{III}}(\text{L}_1)(\text{CN})_3]_2[\text{Co}^{\text{II}}(\text{L}_2)_2]_2\}(\text{A})_2 \cdot n\text{S}$ , where  $\text{L}_1$  is Tp, hydrotris(pyrazol-1-yl)borate or Tp\*, hydrotris(3,5-dimethylpyrazol-1-yl)borate;  $\text{L}_2$  is bik, bis(1-methylimidazol-2-yl)ketone, or vbik, bis(1-vinylimidazol-2-yl)ketone; A stands for counter-anions and S, for the co-crystallized solvent. We have shown that these paramagnetic compounds can be converted into molecular switches upon pressure application<sup>[1]</sup>. The high pressure XRD results showed slight differences in both square core structure and the intermolecular interaction of three compounds, which surprisingly have led to very different thermal ETCST properties. We have tried to rationalize the structure-property relationship of those compounds and the main results will be presented here.

1. Li, Y., Benchohra, A., Xu, B., Baptiste, B., Béneut, K., Parisiades, P., Delbes, L., Soyer, A., Boukheddaden, K., et Lescouëzec, R., *Angewandte Chemie International Edition*. **2020**, vol. 59(39), p. 17272-17276.

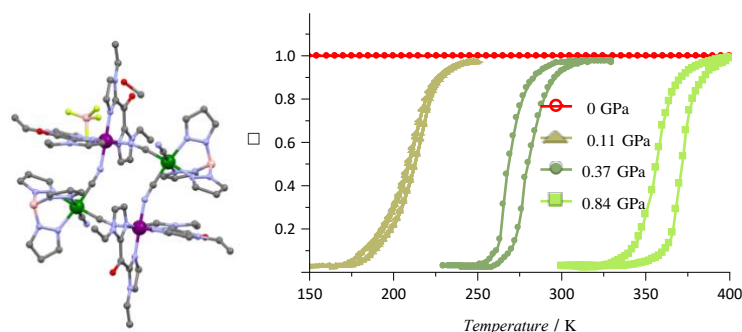


Fig. 1: The structure of  $\{[\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]_2[\text{Co}^{\text{II}}(\text{vbik})_2]_2\}(\text{BF}_4)_2 \cdot 2\text{MeOH}$  at 0.85 GPa (left), thermal variation of paramagnetic  $\{\text{Fe}^{\text{III}}_2\text{Co}^{\text{II}}_2\}$  molar fraction  $\gamma_{HS}$  for 1 under different hydrostatic pressures (right).