High pressure effects in molecular magnetic materials with cyanide bridges

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External stimuli such as temperature, electric and magnetic field, light or guest molecules can be used to control the magnetic properties of molecule-based solids. This in turn can lead to interesting magnetic switching behavior.[1, 2] Molecular magnets are also very susceptible to mechanical stress and yet external pressure is rarely used in this field to study magneto-structural correlations. This is most probably caused by a common belief that molecular crystals are mechanically fragile. In fact, they show very good stability under high *quasi*-hydrostatic conditions even up to 3 GPa, which is sometimes accompanied by astonishing changes/transformations.

Herein a combined structural, magnetic and spectroscopic study of a family of octacyanoniobate(IV)-based molecular magnets $\{[M^{II}(pyrazole)_4]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$ [3] **MNb** (M = Mn, Fe, Co or Ni) will be presented and discussed. The four compounds are isostructural and exhibit a three-dimensional (3-D) cyanide-bridged framework with a diamond-like topology (Fig. 1). The 3*d* transition metal ions M define their optical and magnetic properties under ambient pressure: **MnNb** (yellow) and **FeNb** (dark violet) are ferrimagnetic with the critical temperatures of 25 and 9 K, while **CoNb** (dark yellow) and **NiNb** (greenish) are both ferromagnetic with Curie temperatures of 6 and 13 K, respectively. The **MNb** family shows also stunning differences in their pressure responses depending on the metal ion M. The **MnNb** exhibits one of the highest shifts of the magnetic ordering temperature from 24 K to 37 K in response to pressure,[4] **FeNb** is a pressure-induced spin-crossover photomagnet based on the LIESST effect (LIESST = light induced excited spin state trapping),[4] while the long range magnetic ordering in **CoNb** switches from ferromagnetic to ferrimagnetic character under pressure. Finally, **NiNb** shows significant lowering of the Curie temperature under pressure – completely opposite to **MnNb**.[5] The thorough high pressure magnetic studies of **MNb** are correlated with the high pressure single-crystal X-ray diffraction structural analysis, enabling a full understanding of the observed pressure-induced changes [4, 5].

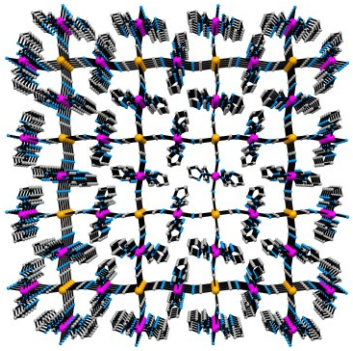

Figure 1. The topology of the CN-bridged framework of **MNb** 'decorated' with pyrazole ligands (Nb – orange, M – magenta, C – gray, N – blue) as viewed along the *c* direction (H_2O, terminal cyanide ligands and H-atoms omitted for the sake of clarity).

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