



Contribution ID: 75

Type: not specified

## Control of the magnetic behaviour of cyanide-bridged Mn<sup>II</sup>-Nb<sup>IV</sup> coordination polymers by the introduction of supporting ligands.

Tuesday, July 7, 2015 8:30 PM (1h 30m)

In our contribution we describe syntheses, single-crystal X-ray crystallographic structures and magnetic properties of a new family of cyanide-bridged coordination polymers  $\{(\text{NH}_4)(\text{H}_2\text{O})\text{Mn}^{\text{II}}(\mu\text{-L})\text{-Mn}^{\text{II}}(\text{H}_2\text{O})\}[\text{Nb}^{\text{IV}}(\text{CN})_8]_x \cdot \text{H}_2\text{O}$  ( $x = 2$  or  $3$ ).

$\text{MnNb}$  stems from a prototypical three-dimensional cyanide-bridged  $[\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2]_2$  compound [1] which shows ferrimagnetic behaviour with magnetic ordering temperature  $T_c = 50$  K. Each bridging CN in  $\text{MnNb}$  connects the Mn<sup>II</sup> ( $d^5$  configuration,  $S = 5/2$ ) and Nb<sup>IV</sup> ( $d^1$ ,  $S = 1/2$ ) metal centres and enables relatively strong antiferromagnetic exchange interactions  $J_{\text{NbMn}}$  within the Nb<sup>IV</sup>-CN-Mn<sup>II</sup> motif.

We have managed to introduce the extra ligands that connect each two neighbouring Mn<sup>II</sup> centres. The ligands were introduced at the self-assembly stage. This was done by taking advantage of the potential 'cavities' within the  $\text{MnNb}$  framework with the Mn-Mn distance of 6.147 Å. Additional bridging ligands change this distance to 5.631 Å in case of cyanide or 6.253 Å for formate and tune in this way the structural properties of the -Nb-CN-Mn- framework. Moreover, the bridging of the two Mn<sup>II</sup> centres in  $\text{MnNb}$  introduces additional magnetic interaction pathways with significant  $J_{\text{MnMn}} < 0$ . The new compounds show a unique magnetic behavior that might be related to magnetic frustration within a triangle of three antiferromagnetically coupled magnetic centres: two Mn<sup>II</sup> and one Nb<sup>IV</sup> (Figure 1). These new octacyanometallate-based compounds with additional bridging ligands demonstrate how chemists can exert considerable control over the magnetic behaviour of molecular magnets.

Literature:

[1] J. M. Herrera, P. Franz, R. Podgajny, M. Pilkington, M. Biner, S. Decurtins, H. Stoeckli-Evans, A. Neels, R. Garde, Y. Dromzee, M. Julve, B. Sieklucka, K. Hashimoto, S. Ohkoshi, M. Verdaguer, C. R. Chimie 11 (2008), 1192-1199

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**Session Classification:** Posters