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Cyano-bridged bimetallic chains based on cyclam complexes of Ni(III) or Mn(III) and hexacyanometallates(III)

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Four new compounds of the general formula: $\{[M_A(\text{cyclam})][M_B(\text{CN})_6] \cdot 6\text{H}_2\text{O}\}_\infty$, where $M_A = \text{Ni}^{\text{III}}, \text{Mn}^{\text{III}}$; $M_B = \text{Fe}^{\text{III}}, \text{Cr}^{\text{III}}$; were obtained in the reaction between the respective cationic building blocks: $[\text{Ni}(\text{cyclam})]^{3+}$ and $[\text{Mn}(\text{cyclam})]^{3+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), and anionic building blocks: $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{CN})_6]^{3-}$ [1,2]. All compounds are isostructural and crystallise in space group $C 2/m$. They are characterised by one-dimensional chain topology, in which the metal centres are connected by CN-bridges. At the temperature of 40 °C partial dehydration takes place which leads to the relatively stable forms containing 2-3 water molecules. Powder X-ray diffraction studies show that the process causes significant structural changes. Moreover, it is reversible for compounds based on the Ni^{3+} ions and irreversible for those based on Mn^{3+} ions. Ferromagnetic interactions are observed within the NiFe, NiCr and MnFe chains mediated by the CN-bridges, while in MnCr compound the intra-chain interactions show antiferromagnetic character. In all four compounds antiferromagnetic interactions between the chains are present. In the case of the MnCr chain it leads to long range ferrimagnetic ordering and appearance of magnetic hysteresis. The partial dehydration process causes marked changes in the magnetic properties of all compounds.

References

- [1] B. Nowicka, M. Heczko, M. Reczyński, M. Rams, B. Gaweł, W. Nitek, B. Sieklucka; *CrystEngComm*; 2016, **18**, 7011-7020.
- [2] B. Nowicka, M. Heczko, M. Rams, M. Reczyński, B. Gaweł, W. Nitek, B. Sieklucka; *Eur. J. Inorg. Chem.*; 2017, 99-106.

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