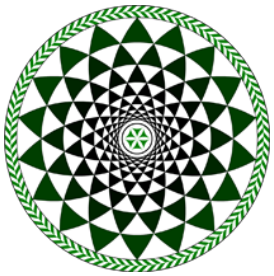

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Magnetocaloric effect in a matrix of high-spin clusters

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One of the strategies to obtain new magnetic materials displaying substantial magnetocaloric effect is to tailor molecular magnetic materials with high spin ground state. Following this course of research a new family of coordination compounds based on Ni(II) and W(V) ions with a general formula Ni[Ni(L)(solv)]₈[W(CN)₈]₆ where L=2,2'-bipyridine (1), 4,4'-dimethyl-2,2'-bipyridine (2), 5,5'-dimethyl-2,2'-bipyridine (3) or 4,4'-ditertbutyl-2,2'-bipyridine (4) and solv = H₂O or ethanol has been synthesized [1]. Detailed crystallographic analysis indicated that the compounds appear in several isomeric forms. The skeleton of the compounds comprises a central Ni(II) ion surrounded by six octacynotungstate complexes forming an octahedron and each of these complexes forms additional four bridges to the remaining Ni(II) ions placed at the corners of a cube. The nickel ions on the surface of the cluster have three facial coordination sites which are not engaged in bridging. Two of them are occupied by the bidentate bpy derivative and the remaining one by the solvent molecule. Preliminary magnetic studies showed that the exchange interaction mediated by the cyanide bridges is of ferromagnetic character, which implies that the ground state of the cluster has total spin S=12. In the poster we focus on compound (4) with the most spacially extended ligand L. The isthermal magnetization was detected in the applied fields ranging from 0 to 7 T for an array of temperatures below 20 K. The analysis based on the Maxwell thermodynamic relation enabled to estimate the isothermal entropy change associated with switching on the external field. It turned out that at low temperature the compound exhibits the inverse magnetocaloric effect, i.e. cooling down on application of magnetic field in an adiabatic process. The reason for this may be twofold. On the one hand, a positive axial anisotropy, which was corroborated in the compound by theoretical calculations, can lead to the downshift of the magnetocaloric signal at low temperatures. On the other hand, the damping of the χT signal at low temperatures points to the presence of a negative inter-cluster coupling (probably of dipolar origin), which in turn can account for the inverse magnetocaloric effect below the temperature where the long-range antiferromagnetic order sets in [2].

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