

MS35-P07**Extended networks based on nickelsiloxane units**Marina Eskova¹, Alexander Korlyukov¹

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New family of bi-, tetra-, penta-, and hexanickel cage-like phenylsilsesquioxanes **1-3** (Fig.1) was obtained by self-assembly and transmetalation procedures. Their crystal structures were established by single crystal X-ray analysis; and features of crystal packing relevant to the networks formation were studied by a topological analysis. The geometry of metallosiloxane units **1** and **2** could be assigned to a distorted prism, with prominent shift of prism' bases (silsesquioxane ligands) from the vertical axis. In turn, molecular architecture of compound **3** is regular prismatic one. Compounds **1-3** form extended networks in crystal via coordination bonds between alkali metals (Na, K, Cs) and oxygen atoms of siloxanolate moieties or coordinated solvent molecules (see, for instance Fig. 2). The investigation of magnetic properties revealed the presence of ferro- or antiferromagnetic interactions between Ni(II) ions giving rise in the most cases the presence of a slow relaxation of the magnetization, which can arise from the spin frustration.

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MS35-P08**Engineering novel porous 3D metallacrown-frameworks, through the ligand periphery design**Vittoria Marzaroli¹, Luciano Marchiò², Giulia Spigolon³, Giulia Licini³, Vincent L. Pecoraro⁴, Matteo Tegoni²

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Metallacrowns are metallamacrocycles characterized by the (M-N-O)_n connectivity and originated by self-assembly of bischelating ligands (e.g. hydroxamic acids) and metal ions. Properties and structure of this class of compounds are tunable through a wise choice of the building blocks set. [1] Moreover a relatively large amount of metal ions are confined in a small molecular volume, resulting in peculiar chemical physical features, such as luminescence or single-molecule magnets behavior. [2]

We present here three new metallacrowns-based materials, that were prepared using salicylhydroxamic acid derivatives as ligands and Mn(II/III) as metal ion.

The salicylhydroxamic acid (H₃Shi) react with Mn, forming a tightly packed, not porous coordination polymer. The nodes are endeca-manganese clusters, resembling a 3-blade propeller, where each blade is a half of a 16-metallacrown-6. Both the amino (H₃p-aShi) and the pyridyl (H₃p-pyShi) derivatives result in a novel porous arrays having the same Mn₁₁ cluster node. The amino function of H₃p-aShi drives the propellers to interact through sodium ions and supramolecular interactions (i.e. hydrogen bonds). The resulting architecture shows hexagonal channels, which correspond to 39 % of the unit cell volume. The pyridyl function of H₃p-pyShi coordinates one Mn of the neighboring propeller. As a result H₃p-pyShi originates a metallacrown-based network, which shows channels in all the three dimensions and has cavities corresponding to 55% of the unit cell volume. The array, shown in the Figure, can be considered a novel metal-organic-framework with an endeca-Mn node.

