

**Название публикации:**

Family of penta- and hexanuclear metallasilsesquioxanes: Synthesis, structure and catalytic properties in oxidations

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**Аннотация:**

The deliberate synthesis of two types of prismatic cage-like metallasilsesquioxanes (hereinafter, referred to as CLMSs), viz., penta- and hexanuclear ones, is reported. It is shown that the size of the prismatic cage can be readily and reliably controlled by synthesis parameters. More specifically, the nuclearity shift from six, which is most common in CLMS chemistry (complexes 1–6, 8), to five, which is observed significantly more rarely, is achieved by applying pyridine as a key solvent/crystallization medium (complexes 7, 9–12). Structures of 1–12 were established by single-crystal X-ray diffraction. In sum, their composition could be described as  $[\text{PhSiO}_{1.5}]_{12}[\text{CuO}]_6$  (for hexanuclear products) or  $[\text{RSiO}_{1.5}]_{10}[\text{MO}]_5$  ( $\text{R} = \text{Ph}$ ,  $\text{Vin}$ ,  $\text{M} = \text{Cu}$ ,  $\text{Ni}$ ,  $\text{Co}$  for pentanuclear products). Compounds 7, 9–10 represent the rare examples of cage silsesquioxanes comprising pentagonal metalla-oxa rings of  $\text{Cu(II)}$  ions. The complex 10 is the very first observation of a co-crystal composed of different CLMS (i.e., two  $\text{Co(II)}_5$  and one  $\text{Cu(II)}_5$  prismatic cages). The compound 12 ( $\text{Co}_5$  cage with vinyl substituents at the silicon atoms) is the very first example of a pentanuclear CLMS-based coordination polymer. Complex 7 efficiently catalyzes oxidation of secondary alcohols to the corresponding ketones and alkanes to the corresponding alkyl hydroperoxides.

**Ключевые слова:**

Alkanes, Catalysis, Complexes of copper, Functionalization of CH bonds, Metallasilsesquioxanes, Nickel and cobalt, Oxidation with hydrogen peroxide, Catalysis, Cobalt, Cobalt compounds, Hydrogen bonds, Ketones, Metals, Nickel, Oxidation, Paraffins, Single crystals, X ray diffraction