

s9.m3.p3 **Structural diversity in octahedral rhenium cyanocluster complexes with M^+ ($M = Mn, Co, Ni$) cations.** S.B. Artemkina, A.V. Virovets, N.G. Naumov, V.E. Fedorov. *Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, Lavrentiev Avenue, 3, Novosibirsk, 630090, Russia.*

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The rhenium octahedral cyanocluster anion $[Re_6X_8(CN)_6]^{4+}$ ($X = S, Se$) is the basic synthetic block used in this work. It consists of Re octahedron capped by eight μ_3 -chalcogen atoms. Six terminal CN-groups bound to Re atoms are capable for coordination. Compounds containing cluster anion and cation M^{2+} ($M = Mn, Co, Ni$) are obtained and structurally characterized. From the point of view that ReCN—M bonds are formed, there are several structural types with various dimensionality. Transition metal cations, in each case, possess 6 as a coordination number and octahedral environment. Linkage in these compounds also depends on the size of additional tetraalkylammonium cation.

3D-type (space group $Im\bar{3}m$) includes polymeric framework built from cluster anions and cations M^{2+} , metal cation has $(4N+2O)$ environment. In the cavities of the framework additional cations Alk_4N^+ ($Alk = CH_3, C_2H_5$) are inclined.

For the case $Alk = n-(C_3H_7)$, compounds of two structure types¹ are formed. First, 1D-type (space group $I4/m$), demonstrates polymeric chains « M^{2+} - cluster - M^{2+} - cluster» with environment of metal cation $(2N+4O)$. Second, molecular type (space group $P2_12_12_1$), includes ionic pairs $\{Mn(H_2O)_5[Re_6X_8(CN)_6]\}^{2-}$, which are packed with tetraalkylammonium cations.

s9.m3.p4 **Development of New Layered Metal Phosphonates as Protective Thin Films: Design, Synthesis, Structure and Properties.** A.H. Mahmoudkhani^a and V. Langer^b, *a) Department of Inorganic Chemistry, Göteborg University, SE-41296 Göteborg, Sweden and b) Department of Environmental Inorganic Chemistry, Chalmers University of Technology, SE-41296 Göteborg, Sweden.*

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Chemists have become so qualified at designing and constructing molecules with a defined set of properties. Many of them are now turning their skills to building much larger systems, where natural chemical affinities are used to direct the growth of multi-molecular arrays, well-defined layered structures, clusters and self-assembled macromolecules for use in different areas of fundamental research and industrial applications. Phosphate and phosphite groups have a strong affinity toward many metal ions. Metal phosphonates are a rich class of inorganic-organic hybrid materials and are related to metal phosphites and phosphates, where a P-H or P-OH is replaced by an organic radical. The combination of nature of the bonding between oxygen and the metal ions and the tetrahedral geometry of the phosphorus atoms controls the orientation of the organic substituents. The general interest in the chemistry of metal phosphonates is mainly due to the unusual compositional and structural diversity, which results in a wide range of applications such as ion exchange, catalysis, sensors, proton conductors, etc.

So far several di-, tri- and tetravalent metal phosphonates with a wide variety of chemical and physical properties have been synthesized and structurally characterized, but little attention has been paid to alkaline-earth metals. Recently, there has been a great interest in the chemistry calcium phosphonates due to the use of phosphonate-based drugs for diagnostic and therapeutic of various diseases of bone and calcium metabolism. We are going to use the chemical characteristics of the phosphites and phosphonates of alkaline-earth metal ions to make chemically modified surfaces and thin films for the protection of different objects such as stones and metals against atmospheric influences, corrosion and decay. We have prepared a number of calcium and strontium phosphites and phosphonates in order to investigate their chemical properties and its correlation with structure and bonding. Possible design of a new class of metal phosphonates for use as protective thin films will be presented.

[1] Naumov, N.G.; Virovets, A.V.; Artemkina, S.B.; Fedorov, V.E. *Solid State Sciences*, **1999**, vol. 1, p. 463