

From Polymeric Cluster Compounds to Molecular Complexes and Back to Polymer Cluster Materials

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Abstract

The reactions that convert polymer cluster compounds to molecular form and provide their chemical modifying are considered using as an example cluster compounds of some metals occupying the positions at the beginning of the transition metal rows of the Periodic Table (Nb, Mo, Re).

INTRODUCTION

Cluster compounds of metals occupying the positions at the beginning of transition rows (Nb, Ta, Mo, W, Re) with typical acido ligands – halide and chalcogenide ions – are usually synthesized by means of high-temperature chemistry [1]. As a rule, thus obtained cluster compounds possess polymer structure in which cluster nuclei are connected to each other through bridge ligands of different types and sometimes by direct metal-to-metal bonds.

Polymer structure of the compounds hinders the investigation of their chemical properties since these compounds are insoluble in water and organic solvents; besides, they are extremely inert in chemical reactions. The most original approach to the investigation of chemical reactions of these systems is to cut a cluster nucleus of the polymer system and then to transform it into molecular complexes characterized by the presence of discrete clusters in their structure [2]. As a rule, molecular complexes are soluble which allows to study their chemical properties by means of traditional solution chemistry.

Reactions in solutions can be used to modify the composition and properties of cluster complexes within a wide range. Modified cluster

complexes can be used as structural blocks to construct new polymer structures. The present study is dedicated to the above-mentioned ideas of the investigation of cluster compounds, namely, the search for ways how to cut clusters off the polymer compounds, and the development of principles for the design of cluster materials using molecular cluster complexes as structural blocks to synthesize new polymer structures.

STRUCTURES OF POLYMER CLUSTER COMPOUNDS

The series of polymer compounds under consideration includes several cluster chalcogenides and chalcogenides of the metals occupying the positions at the beginning of transition rows that were found to be very appropriate for these studies: binuclear niobium chalcogenides $Nb_2X_4Y_4$ ($X = S, Se; Y = Cl, Br$), trinuclear molybdenum chalcogenides $Mo_3X_7Y_4$ ($X = S, Se; Y = Cl, Br$) and several molybdenum and rhenium chalcogenides and chalcogenides with octahedral metal clusters – Mo_6Se_8 , Re_6Te_{15} , $Re_6Se_8Br_2$, $Re_6Se_5Br_8$, and $Re_6Se_6Br_6$. In these compounds, cluster nuclei are bound in different manners to form a polymer structure.

The simplest binding type is observed in rhenium selenobromide $\text{Re}_6\text{Se}_5\text{Br}_8$ [3] (Fig. 1, *a*) in which octahedral cluster nuclei $[\text{Re}_6\text{Se}_5\text{Br}_3]$ are bound *via* two μ_2 -bridging bromide atoms occupying *trans*-positions, according to the crystal chemical formula $\{[\text{Re}_6\text{Se}_5\text{Br}_3]\text{Br}_4\text{Br}_{2/2}\}_\infty^1$. As a

result, chain-like structure of bound metal clusters of the type $-\text{Re}_6-(\mu_2\text{-Y})-\text{Re}_6-$ is formed. In selenobromide $\text{Re}_6\text{Se}_6\text{Br}_6$ (see Fig. 1, *b*), four apical ligands occupying equatorial positions are involved in bonding which leads to layered structure $\{[\text{Re}_6\text{Se}_6\text{Br}_2]\text{Br}_2\text{Br}_{4/2}\}_\infty^2$ [3]. In

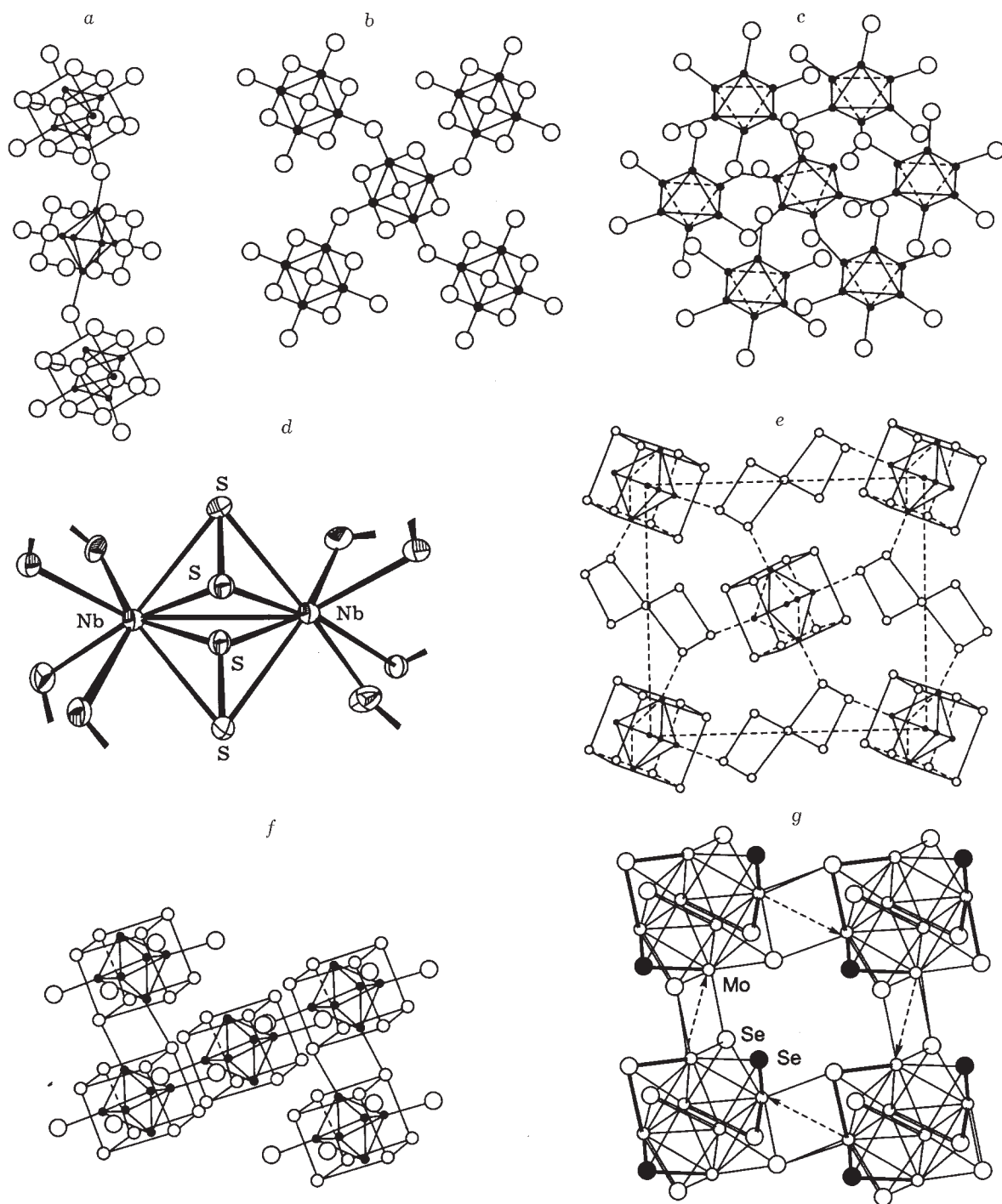


Fig. 1. Different types of cluster nuclei bonding into polymer structures: *a* - $\text{Re}_6\text{Se}_5\text{Br}_8 = \{[\text{Re}_6\text{Se}_5\text{Br}_3]\text{Br}_4\text{Br}_{2/2}\}_\infty^1$; *b* - $\text{Re}_6\text{Se}_6\text{Br}_6 = \{[\text{Re}_6\text{Se}_6\text{Br}_2]\text{Br}_2\text{Br}_{4/2}\}_\infty^2$; *c* - $\text{Re}_6\text{Se}_7\text{Br}_4 = \{[\text{Re}_6\text{Se}_7\text{Br}]\text{Br}_{6/2}\}_\infty^3$; *d* - $\text{Nb}_2\text{S}_4\text{Br}_4 = \{[\text{Nb}_2(\text{S}_2)_2]\text{Br}_{8/2}\}_\infty^2$; *e* - $\text{Re}_6\text{Te}_{15} = [\text{Re}_6\text{Te}_8]\text{Te}_7$; *f* - $\text{Re}_6\text{Se}_6\text{Br}_2 = \{[\text{Re}_6\text{X}_6\text{X}_{2/2}]\text{Br}_{4/2}\text{X}_{2/2}\}_\infty^3$; *g* - $\text{Mo}_6\text{Se}_8 = \{[\text{Mo}_6\text{Se}_2\text{Se}_{6/2}]\text{Se}_{6/2}\}_\infty$.

the layered structure of niobium thiobromide $\text{Nb}_2\text{S}_4\text{Br}_4$ (see Fig. 1, d) that can be described by crystal chemical formula $\{[\text{Nb}_2(\text{S}_2)_2]\text{Br}_{8/2}\}_\infty^2$ the cluster nuclei $[\text{Nb}_2\text{S}_4]$ are bound by all the eight μ_2 -bridging halogen atoms [4]. In $\text{Re}_6\text{Se}_7\text{Br}_4$ [3] (see Fig. 1, c) cluster nuclei $[\text{Re}_6\text{Se}_7\text{Br}]$ are bound to form a three-dimensional structure by using all the six apical ligands $\{[\text{Re}_6\text{Se}_7\text{Br}]\text{Br}_{6/2}\}_\infty^3$. In three-dimensional structure of rhenium telluride $\text{Re}_6\text{Te}_{15}$ [5] (see Fig. 1, e), cluster nuclei $[\text{Re}_6\text{Te}_8]$ are bound to each other through complicated groups composed of Te_7 that can be considered also as bridging fragments. It can be stated *a priori* that with increasing the number of bridging μ_2 -ligands in the structure of similar compounds their ability to depolymerize in a reaction system will decrease, as it is, for example, in the row: $\{[\text{Re}_6\text{Se}_5\text{Br}_3]\text{Br}_4\text{Br}_{2/2}\}_\infty^1 \rightarrow \{[\text{Re}_6\text{Se}_6\text{Br}_2]\text{Br}_2\text{Br}_{4/2}\}_\infty^2 \rightarrow \{[\text{Re}_6\text{Se}_7\text{Br}]\text{Br}_{6/2}\}_\infty^3$. Of course, the nature of bridging ligands would also have an effect on the reactivity of polymer compounds.

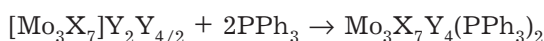
A more complicated character of binding is observed in the structure of compounds $\text{Re}_6\text{X}_8\text{Br}_2$ ($\text{X} = \text{S}, \text{Se}$) [6] (see Fig. 1, f). Here, the role of bridging atoms is played both by bromine atoms and by the inner (μ_3 -X) ligands of cluster nuclei, *i. e.* chalcogen atoms; in this type of bonding, the carcass structure of these compounds can be described by the formula $\{[\text{Re}_6\text{X}_6\text{X}_{2/2}]\text{Br}_{4/2}\text{X}_{2/2}\}_\infty^3$ which indicates that the polymer structure is formed due to the bonds of the $-\text{Re}_6-(\mu_4\text{-X})-\text{Re}_6-$ type. It is believed that these bonds are more strong, compared to the $\text{Re}_6-(\mu_2\text{-Y})-\text{Re}_6$ type bonds. Because of this, even stronger is molybdenum selenide Mo_6Se_8 [7] (see Fig. 1, g) in which six inner ligands are involved in three-dimensional binding of the same type $\{[\text{Mo}_6\text{Se}_2\text{Se}_{6/2}]\text{Se}_{6/2}\}_\infty^3$.

REACTIONS CUTTING OFF CLUSTER NUCLEI

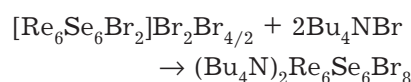
To perform depolymerization reactions, it is important to select a proper reagent that would be able to tear bridging bonds of the polymer structure and to form a corresponding molecular complex. To select reaction conditions, it is important to take account of both the strength

of bridging bonds and thermal stability of the initial compounds and products, as well as reaction kinetics.

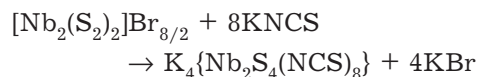
Our experimental studies into cutting cluster nuclei off polymer structures are mainly in a good agreement with the above considerations. For example, polymer molybdenum chalcogenides $\text{Mo}_3\text{X}_7\text{Y}_4$ with simple halide μ_2 -bridges are easily transformed into molecular complexes when boiling the solid phase with acetonitrile solutions of PPh_3 [8]:



Similarly, selenobromide $\text{Re}_6\text{Se}_6\text{Br}_6$ reacts with Bu_4NBr in dimethylformamide at 140°C transforming into the anion molecular complex:



In the case of niobium thiobromide $\text{Nb}_2\text{S}_4\text{Br}_4$, successful depolymerization takes place in potassium thiocyanate melt at 180°C [9]:



These soft conditions were found out to be ineffective for more strong polymer compounds. We found that the strongest depolymerizing reagents for cluster systems are the melts of alkaline metal cyanides (NaCN , $T_{\text{melt}} = 563^\circ\text{C}$, and KCN , $T_{\text{melt}} = 635^\circ\text{C}$). Using sodium and potassium cyanides we succeeded in cutting clusters off very strong compounds including those with three-dimensional bonding: $\text{Re}_6\text{X}_8\text{Br}_2$ ($\text{X} = \text{S}, \text{Se}$), $\text{Re}_6\text{Te}_{15}$ and Mo_6Se_8 . As a result of these reactions, new molecular chalcocyanide cluster anion complexes of rhenium and molybdenum were synthesized: $\{[\text{Re}_6\text{X}_8](\text{CN})_6\}^{4-}$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$) [9–13] and $\{[\text{Mo}_6\text{Se}_8](\text{CN})_6\}^{7-/6-}$ [14] (Fig. 2).

As the above examples show, cutting the cluster nucleus off is often accompanied by the change in ligand composition, *i. e.* chemical modification of the cluster complex occurs. This opens the way to the synthesis of new compounds with various composition and structures. One of the most interesting approaches to the synthesis involves the use of the obtained cluster complexes as construction blocks to build up polymer cluster materials. For this ap-

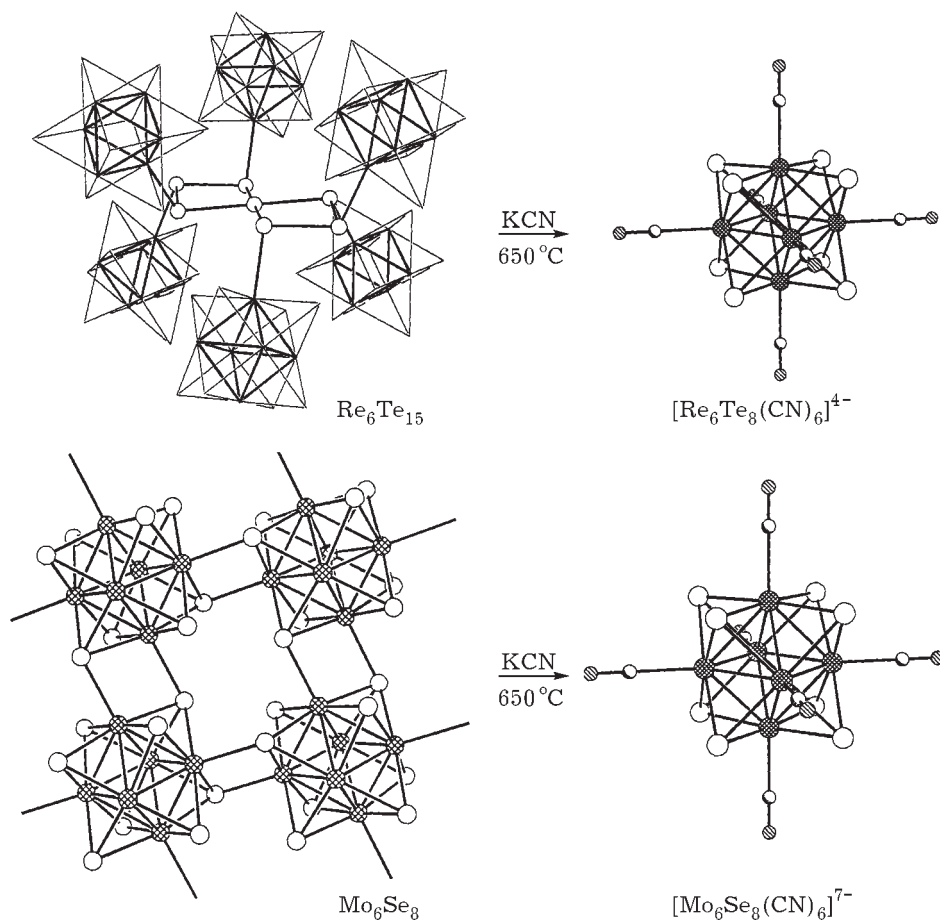


Fig. 2. Examples of the reactions to transform polymer cluster compounds to molecular form.

proach, the most convenient reagents were chalcocyanide complexes since ambidentate nature of CN ligands allows to perform their polymerization by binding through transition metals according to the formula $-\text{Re}_6-\text{C}\equiv\text{N}-\text{M}-\text{N}\equiv\text{C}-\text{Re}_6-$. We performed systematic investigations of the reactions of cluster chalcocyanide anions with the cations of 3d-transition metals Mn, Fe, Co, Ni, Cu, Zn. It was stated that this interaction leads to the formation of polymer structures of different nuclearity including unidimensional (chain), two-dimensional (layered) and three-dimensional (carcass) ones.

**THE DESIGN OF A SOLID:
CONSTRUCTION OF POLYMERIC MATERIALS
FROM CLUSTER CHALCOCYANIDE ANIONS
[Re₆X₈(CN)₆]⁴⁻ AND THE CATIONS
OF TRANSITION METALS**

As structural studies showed, in the compounds based on chalcocyanide ions

$[\text{Re}_6\text{X}_8(\text{CN})_6]^{4-}$ with transition metals, CN ligands act as bridges between the cluster nuclei $\{\text{Re}_6\text{X}_8\}$ and the cations of 3d-transition metals M^{2+} forming polymer systems of the type $-\text{[Re}_6\text{X}_8]-\text{C}\equiv\text{N}-\text{M}-\text{N}\equiv\text{C}-\text{[Re}_6\text{X}_8]-$. The structures of these compounds can be classified according to the dimension type of the polymer, *i. e.* isle, chain (unidimensional), layered (two-dimensional) and carcass (three-dimensional) [15].

Isle structures

The structure of $(p\text{-Pr}_4\text{N})_2\text{M}[\text{Re}_6\text{X}_8(\text{CN})_6]\cdot 6\text{H}_2\text{O}$, $\text{M} = \text{Mn, Co}$; $\text{X} = \text{S, Se}$. The structure of these compounds can be described as the packing of ion pairs $\{[\text{Re}_6\text{X}_8(\text{CN})_6]-\text{M}(\text{H}_2\text{O})_5\}^{2-}$ and tetrapropyl ammonium cations (Fig. 3, a) [16]. Water molecule coordinated to M^{2+} in *trans*-position towards the nitrogen atom of the CN ligand forms hydrogen bond with the nitrogen atom of the neighbouring anion.

Chain structures

The structure of $(p\text{-Pr}_4\text{N})_2\text{M}[\text{Re}_6\text{S}_8(\text{CN})_6] \cdot 4\text{H}_2\text{O}$, $\text{M} = \text{Mn}, \text{Ni}$. In this structural type, cluster anions are bound by the cations of transition metals only through two CN ligands occupying *trans*-positions; as a result, negatively charged infinite chains are formed: $\text{—NC—}[\text{Re}_6\text{X}_8(\text{CN})_4]\text{—CN—M(H}_2\text{O)}_4\text{—NC—}[\text{Re}_6\text{X}_8(\text{CN})_4]\text{—CN—}$ [17]. The charge of chains is compensated by tetra-*p*-propyl ammonium cations located in the hollows between them (see Fig. 3, b).

Layered structures

The structure of $\text{Cs}_2\text{M}[\text{Re}_6\text{S}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$, $\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Cd}^{2+}$. In the compounds of this type [18] (Fig. 4, a), four of six apical CN ligands of the cluster anions $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ participate in binding with each other through M^{2+} cations. As a result, a polymer negatively charged layered grid is formed; two remaining

end CN ligands are not coordinated. The ions M^{2+} are coordinated octahedrally (four nitrogen atoms of CN groups and two water molecules in a *trans*-position). The adjacent layers $\{\text{M(H}_2\text{O)}_2[\text{Re}_6\text{S}_8(\text{CN})_6]\}^{2-}$ are shifted with respect to each other so that the channels are formed in the structure. These channels are filled with caesium cations $\text{Cs}^+(2)$ disordered with the population of 50% over two symmetrically equivalent positions. The cations $\text{Cs}^+(1)$ are localized inside the layer. Rather strong hy-

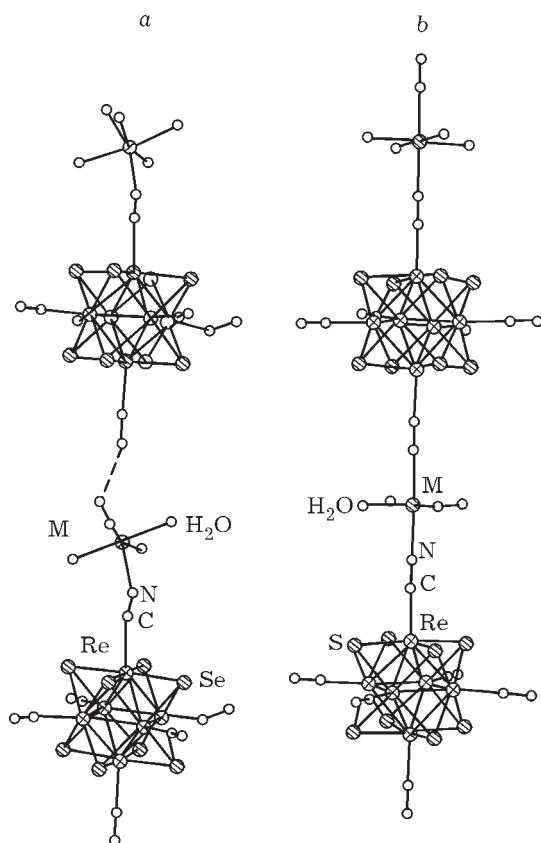


Fig. 3. Bonding of cluster anions $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ to isle or chain structures:
 a - structure of $(\text{Pr}_4\text{N})_2\text{Mn}[\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot 6\text{H}_2\text{O}$;
 b - structure of $(\text{Pr}_4\text{N})_2\text{Mn}[\text{Re}_6\text{S}_8(\text{CN})_6] \cdot 4\text{H}_2\text{O}$.

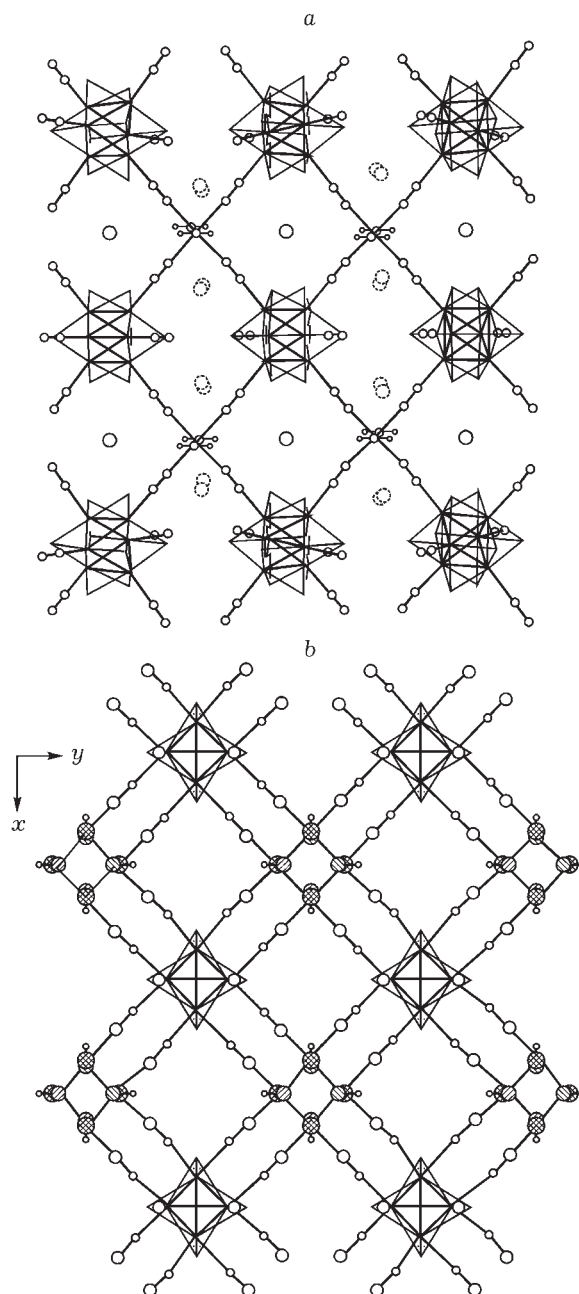


Fig. 4. Bonding of cluster anions to layered structure:
 a - structure of $\text{Cs}_2\text{Co}[\text{Re}_6\text{S}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$;
 b - structure of $[\text{Cu}_4(\text{OH})_4]\{\text{Re}_4\text{Te}_4(\text{CN})_{12}\}$.

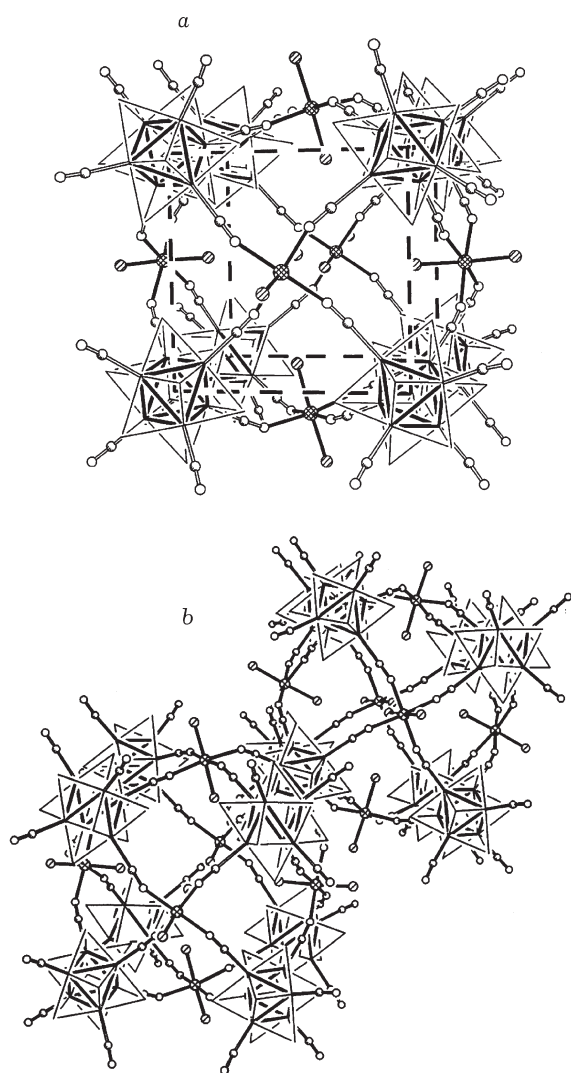


Fig. 5. Bonding of cluster anions $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ to carcass structure $\text{Cs}_2\text{Mn}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 15\text{H}_2\text{O}$: *a* – a selected structural fragment; *b* – the formation of a three-dimensional carcass.

drogen bonds between the hydrogen ions of water molecules and nitrogen atoms of the end CN groups, as well as sulphur atoms of the cluster nucleus $[\text{Re}_6\text{S}_8]$ are observed in the structure leading to the binding of the adjacent layers $\{\text{M}(\text{H}_2\text{O})_2[\text{Re}_6\text{S}_8(\text{CN})_6]\}^{2-}$.

The layered structure was observed also in the similar compound of rhenium $[\text{Cu}_4(\text{OH})_4]\{[\text{Re}_4\text{Te}_4](\text{CN})_{12}\}$ formed in the interaction of tetrahedral tellurium cyanide anions $\{[\text{Re}_4\text{Te}_4](\text{CN})_{12}\}^{4-}$ with aqueous solution of Cu^{2+} [19]. The structure is represented by ideally flat layers bound to each other only by hydrogen bonds (see Fig. 4, *b*).

Carcass structures

Cations with tetrahedral surroundings.

The compounds of this type have similar composition: $\text{Kat}_2\text{M}_3[\text{Re}_6\text{X}_8(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ ($\text{Kat} = \text{H}_3\text{O}^+, \text{Cs}^+, \text{Me}_4\text{N}^+, \text{Et}_4\text{N}^+$; $\text{M} = \text{Mn}, \text{Co}, \text{Cu}$; $\text{X} = \text{S}, \text{Se}$) and the common structural motif which is a three-dimensional covalent-bonded carcass [20, 21]. The details of the structure can be viewed with $\text{Cs}_2\text{Mn}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 15\text{H}_2\text{O}$ as an example [20]. Manganese atoms in this structure are surrounded octahedrally. Four coordination positions are occupied by the nitrogen atoms of CN ligands, of four different anions; oxygen atoms of two water molecules (O1 and O2) occupy two other positions. Each anion is bound with six transition metal cations. Figure 5, *a* shows a structural fragment which is a cube composed of the $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ anions. Each face of the cube is coordinated by manganese cation. These selected cubes are connected with each other to form a three-dimensional carcass as shown in Fig. 5, *b*. This character of bonding leads to the formation of negatively charged infinite three-dimensional carcass with the stoichiometry $\{\text{Mn}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]\}^{2-}$. Strongly disordered caesium cations compensating the charge of the carcass are present in

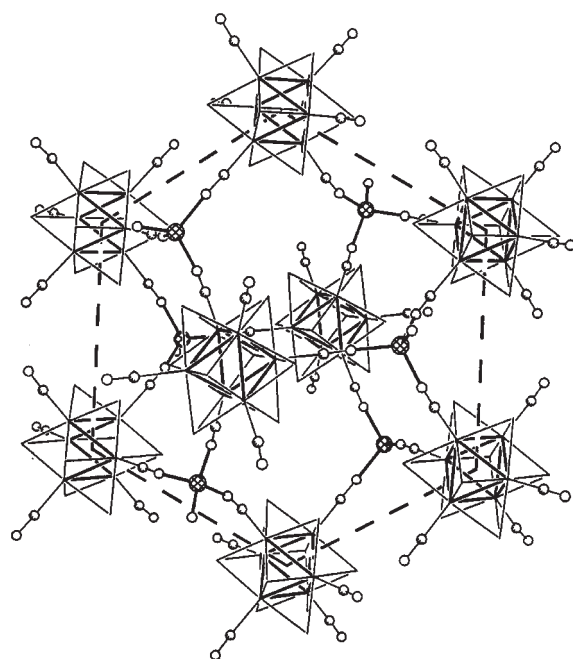


Fig. 6. Three-dimensional carcass in the compound $(\text{H}_3\text{O})_2\text{Zn}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 20\text{H}_2\text{O}$.

the structure, as well as water molecules that occupy the hollows.

The molecules of solvation water and cations compensating the charge of the carcass are located between the selected cubes. It is most likely that the cation Et_4N^+ is the largest one among those able to be located in the hollows of the carcass. The attempts to increase cation size to Pr_4N^+ lead to the breakage of some M—N bonds and to the formation of the chain structure $(\text{Pr}_4\text{N})_2\text{M}[\text{Re}_6\text{S}_8(\text{CN})_6] \cdot 4\text{H}_2\text{O}$ or an isle-like one $(\text{Pr}_4\text{N})_2\text{M}[\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot 6\text{H}_2\text{O}$ described above.

Cations with tetrahedral surroundings. Octahedral surroundings of the transition metal

cation are characteristic for the above-described structures. The variety of the structures obtained depends mainly on the number of cyanide ligands involved in bonding with the transition metal cation: 1 in $(\text{Pr}_4\text{N})_2\text{M}[\text{Re}_6\text{X}_8(\text{CN})_6] \cdot 6\text{H}_2\text{O}$, 2 in $(\text{Pr}_4\text{N})_2\text{M}[\text{Re}_6\text{S}_8(\text{CN})_6] \cdot 4\text{H}_2\text{O}$, 4 in other structures. However, in the interaction of Zn^{2+} with $\text{K}_4\text{Re}_6\text{Se}_8(\text{CN})_6$ in acidic medium the salt $(\text{H}_3\text{O})_2\text{Zn}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 20\text{H}_2\text{O}$ was obtained [22]. The structure of this salt is shown in Fig. 6. All the six cyanide ligands of each anion are bound with different zinc atoms. Zinc atom is surrounded by the tetrahedron of nitrogen atoms of the CN ligands. This character of bonding leads to the formation of an unusual

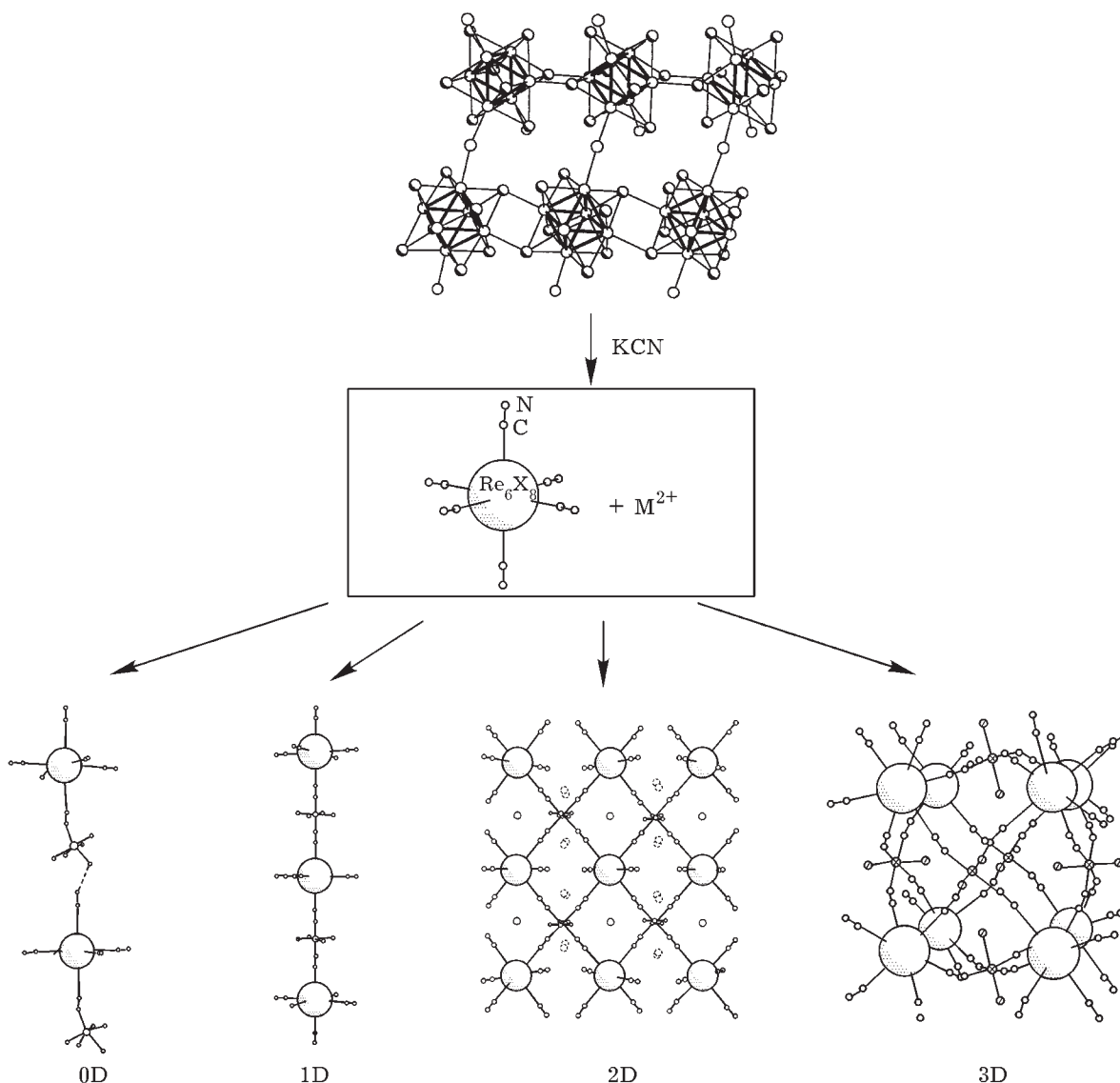


Fig. 7. Types of structures formed by cluster anions $[\text{Re}_6\text{X}_8(\text{CN})_6]^{4-}$ ($\text{X} = \text{S}, \text{Se}$) and the cations of 3d-transition metals. The anion $[\text{Re}_6\text{X}_8(\text{CN})_6]^{4-}$ is represented in a simplified form.

three-dimensional carcass of the composition $\{\text{Zn}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2\}^{2-}$. The centres of cluster anions form a motif of hexagonal graphite packing (grids formed of hexagons shifted with respect to each other with the formation of a two-layer packing *ABAB*). Zinc atoms bond the layers to each other. Hexagonal hollows are thus formed. They are filled with disordered H_5O_2^+ cations and solvate water molecules.

So, important data are obtained concerning the design of polymer cluster materials which opens the way to the synthesis of compounds with the structures of different dimension type, both due to the changes in the nature of metals and ligands, and taking account of dimensional factors of the structural blocks – cluster complexes and counter-ions. As a result, criteria were determined that allow to perform a directed synthesis of new polymer cluster materials with the isle (0D), chain (1D), layered (2D) or carcass (3D) structure (Fig. 7) [15].

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