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# OCTAHEDRAL CLUSTERS WITH MIXED INNER LIGAND ENVIRONMENT: SELF-ASSEMBLY, MODIFICATION AND ISOMERISM

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Octahedral cluster complexes of transition metals are associated with halogen or chalcogen inner ligands to form edge-bridged $\{M_6(\mu_2\text{-}X)_{12}\}$ or face-capped $\{M_6(\mu_3\text{-}X)_8\}$ cluster cores. The partial exchange of X atoms leading to mixed inner ligand environment invokes a distortion of metallic cluster, reduction of symmetry as well as an isomerism of the cluster cores. This review summarizes preparation methods of mixed ligand cluster complexes with the general formulas $[\{M_6(\mu_2\text{-}X)_{12}\}L_6]^n$ or $[\{M_6(\mu_3\text{-}X)_8\}L_6]^n$ and their structural features.

**Keywords:** octahedral cluster, ligand, structure, isomerism, substitution, niobium, molybdenum, rhenium.

## INTRODUCTION

In the chemistry of transition metal clusters the octahedral complexes are one of the most representative compounds [1—4]. There are two main structural types of the octahedral cluster complexes that are defined by composition and structure of the cluster core. Complexes of the first type are typical for halides of niobium and tantalum and represent an octahedral metal cluster $M_6$ with edges coordinated by halide ions resulting in the core $\{M_6(\mu_2\text{-}X)_{12}\}^{m+}$ (M = Nb or Ta; X = F, Cl, Br, or I) (Fig. 1, *a*). Some reviews summarized details on syntheses, structures and properties of various cluster

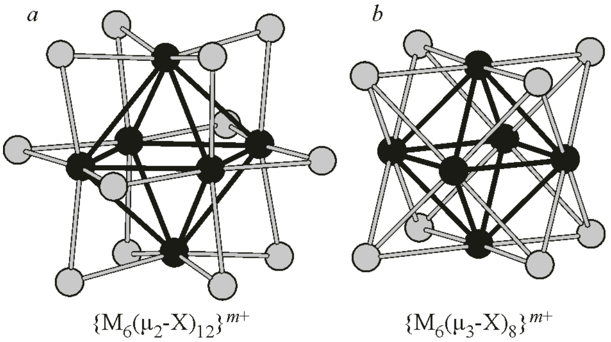


*Fig. 1.* Two types of cluster cores in octahedral cluster complexes

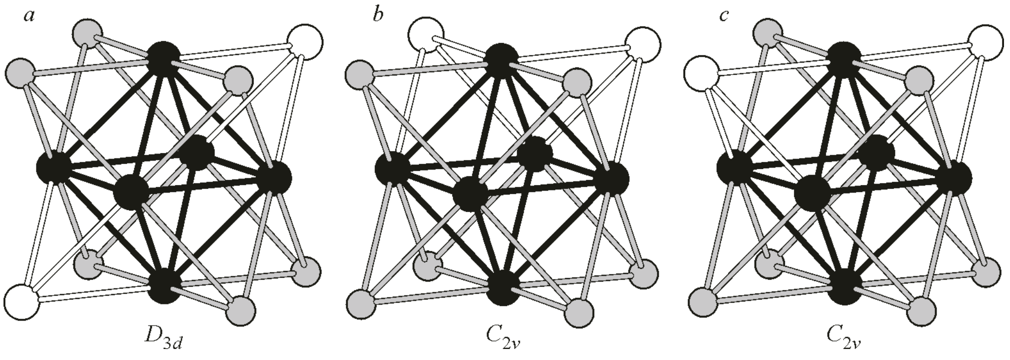


*Fig. 2*. Possible geometric isomers for $\{Mo_6Se_2Br_6\}$ cluster core

complexes including those heteroleptic inner ligand environment [5—9]. In halides and chalcogenides of molybdenum, tungsten and rhenium each face of the octahedron $M_6$ is coordinated by a ligand forming the cluster core $\{M_6(\mu_3\text{-}X)_8\}^{m+}$ (M = Mo, W or Re; X = Cl, Br, I, S, Se, or Te) (Fig. 1, *b*). Metal atoms in the cluster cores of both types are coordinatively unsaturated and consequently tend to be ligated by an additional apical ligand (L) to give complexes with the general formulas $[\{M_6(\mu_2\text{-}X)_{12}\}L_6]^n$ or $[\{M_6(\mu_3\text{-}X)_8\}L_6]^n$, respectively. The ligands L are often labile and can be substituted by various ions or molecules. At the same time, the inner ligands $\mu_2$-X and $\mu_3$-X are quite strongly connected to metal cluster $M_6$ and their exchange is not a trivial task for experimenters. However, the exchange of inner ligands in cluster cores can drastically change the properties of the complexes.

In general, octahedral clusters with homoleptic inner ligand environment $[\{M_6(\mu_2\text{-}X)_{12}\}L_6]$ and $[\{M_6(\mu_3\text{-}X)_8\}L_6]$ possess high local symmetry. Introduction of a second type of ligand into the cluster core decreases the local symmetry of complex that can affect on the photophysical properties of compounds. Another problem is isomery of ligand environment. For example, a heteroleptic complex with $\{Mo_6Se_2Br_6\}$ cluster core have three geometric isomers (Fig. 2) with different symmetry [10], that was confirmed by $^{77}$Se NMR spectroscopy.

In complexes with isovalent substitution $\{Re_6Te_{8-x}Se_x\}$ ($0 \le x \le 8$) 22 possible moieties and their isomers was confirmed by $^{77}$Se and $^{125}$Te NMR spectroscopy [11, 12]. These data should be taken into account when such compounds will be used.

Indeed, isovalent substitution of $\mu_2$-X or $\mu_3$-X ligands in cluster core (e.g., iodine by bromine or chlorine, or tellurium by selenium or sulfur) should not give significant changes in electronic structure, though inner ligand environment is responsible for photophysical properties of clusters. Non-isovalent substitution, for example, replacing of chalcogenides by halides leading to change of charge of cluster core ($\{Re_6Se_8\}^{2+} \rightarrow \{Re_6Se_4Br_4\}^{6+}$) greatly impacts also the electronic structure and redox properties of cluster compounds.

This review summarizes preparation methods of mixed ligand cluster complexes with the general formulas $[\{M_6(\mu_2\text{-}X)_{12}\}L_6]^n$ or $[\{M_6(\mu_3\text{-}X)_8\}L_6]^n$ and their structural features.

## OCTAHEDRAL CLUSTERS OF $\{M_6X_{12}\}$ FAMILY

The binary clusters of $\{M_6X_{12}\}$ family are known for X = F, Cl and Br; they are $Nb_6F_{15}$ [13], $Nb_6Cl_{14}$ [14], $Ta_6X_{14}$ (X = Br, I) [15, 16], and $Ta_6X_{15}$ (X = Cl, Br) [13, 17]. The fluoride species are known only for Nb, whereas the iodides — for Ta. These halides belong to $\{M_6X_{12}\}$ family with $\mu_2$ bridging inner ligands. To date there are also numerous mixed ligand clusters of Nb and Ta. Most of mixed ligand compounds of the $\{M_6X_{12}\}$ family belong to niobium halides and oxyhalides. Table 1 summarizes known examples of halide mixed ligand octahedral cluster complexes of niobium cluster units.

In the Nb—Cl—I system two mixed halide compounds were isolated: $Nb_6Cl_{10.8}I_{3.3}$ and $Nb_6Cl_{12}I_2$. The former contains a mixed ligand cluster core $\{Nb_6Cl_{11}I\}^{2+}$, while the latter is built from the

Table 1

*Examples of mixed ligand halides with ordered ligand distribution*

| Compound | Cluster core | VEC | M—M, Å | M—L$^i$, Å | Ref. |
|---|---|---|---|---|---|
| $Nb_6Cl_{10.8}I_{3.3}$ | $\{Nb_6Cl_{11}I\}^{2+}$ | 16 | 2.907<br>2.933 | 2.449 (Cl)<br>2.630 (I) | [ 18 ] |
| $Cs_4[Nb_6F_{8.5}I_{3.5}I_6]$ | $\{Nb_6F_9I_3\}^{2+}$<br>$\{Nb_6F_8I_4\}^{2+}$<br>$\{Nb_6F_7I_5\}^{2+}$<br>$\{Nb_6F_6I_6\}^{2+}$ | 16 | 2.824—2.943 | 2.812 (I)<br>2.092 (F) | [ 25 ] |
| $Cs_2Nb_6Br_5F_7F_4F_{2/2}$ | $\{Nb_6F_7Br_5\}^{3+}$ | 15 | 2.797—2.854 | 2.06—2.11 (F)<br>2.506—2.640 (Br) | [ 19 ] |
| $Nb_6Br_5F_7Br_{6/2}$ | $\{Nb_6F_7Br_5\}^{3+}$ | 15 | 2.824—2.943 | 2.812 (I)<br>2.092 (F) | [ 21 ] |
| $Na_2NbF_6$—$Nb_6F_{12-y}Cl_yF_{6/2}$ | $\{Nb_6F_4Cl_8\}^{3+}$ | 15 | 2.831 | 2.361<br>(0.64 Cl + 0.36 F) | [ 21 ] |
| $Cs_{1.6}K_{2.4}[Nb_6F_6I_6(NCS)_6]$ | $\{Nb_6F_6I_6\}^{2+}$ | 16 | 2.824—2.943 | 2.812 (I)<br>2.092 (F) | [ 25 ] |
| $(Et_4N)_4[Nb_6F_6Br_6(NCS)_6]\cdot 2Et_4NBr$ | $\{Nb_6F_6Br_6\}^{2+}$ | 16 | 2.821—2.919 | 2.6174 (Br)<br>2.081 (F) | [ 25 ] |
| $(Me_4N)_2[Nb_6F_6Br_6(H_2O)_2Cl_4]\cdot 6H_2O$ | $\{Nb_6F_6Br_6\}^{2+}$ | 16 | 2.8173 (L = F)<br>2.9047 (L = Br) | 2.078 (F)<br>2.611 (Br) | [ 26 ] |
| $(Et_4N)_4[Nb_6F_6Br_{12}]$ | $\{Nb_6F_6Br_6\}^{2+}$ | 16 | 2.824—2.942 | 2.616 (Br)<br>2.073 (F) | Unpublished |
| $(Bu_4N)_3[Nb_6F_6Br_{12}]$ | $\{Nb_6F_6Br_6\}^{3+}$ | 15 | 2.851—2.972 | 2.585 (Br)<br>2.06 (F) | Unpublished |

$\{Nb_6Cl_{12}\}^{2+}$ clusters with iodide bridges: $[\{Nb_6Cl_{12}\}I^{a-a-a}_{6/3}]$. It seems that the $\{Nb_6Cl_{12}\}$ can accommodate no more than one iodine [ 18 ]. In the structure of $Nb_6Cl_{10.8}I_{3.3}$ six $\mu_2$-Cl ligands are located in a plane, bridging between the two opposite $Nb_3$ triangles. The single iodine atom is shared over six other positions with occupancy 0.208 (Fig. 3).

The $\{Nb_6F_{12}\}$ core is more favourable for the substitution of fluorine by other halogen atoms. Indeed, combined use of niobium fluoride with another halide in high temperature solid state reactions resulted in the formation of a series of compounds with mixed $\{Nb_6F_{12-y}X_y\}$ cluster cores — double salts $Na_2NbF_6$—$\{Nb_6F^i_{12-y}X^i_y\}F^{a-a}_{6/2}$ (X = Cl ($y = 8$), Br ($y = 4$)) series, $Cs_2[\{Nb_6Br_5F_7\}F^a_4F^{a-a}_{2/2}]$ or $[\{Nb_6Br_5F_7\}Ba^{a-a}_{2/2}]$ [ 19—22 ], and $Cs_4[\{Nb_6I_{8.5}F_{3.5}\}F_6]$ [ 23 ]. In the structure of $Cs_4[\{Nb_6F_{8.5}I_{3.5}\}I_6]$ three iodine and six fluorine ligands are ordered over nine inner positions, whilst the remaining three are randomly occupied by fluorine and iodine with a I/F ratio close to 0.5/2.5 (Fig. 4, *a*). This disorder is related to the coexistence of cluster units with different I/F stoichiometries in the parent solid, and disordered over the same positions (Fig. 4, *b*).

The experimental I/F ratio (9.5/8.5) in $Cs_4[\{Nb_6F_{8.5}I_{3.5}\}I_6]$ can result from an equimolar mixture of $\{Nb_6F_8I_4\}$ and $\{Nb_6F_9I_3\}$ cluster cores, or a mixture of $\{Nb_6F_9I_3\}$ and $\{Nb_6F_6I_6\}$ with ratio 5:1. The isolation of $(Et_4N)_4[\{Nb_6F_6Br_6\}(NCS)_6]\cdot 2Et_4NBr$ in a low yield favors the latter possibility, although the presence of

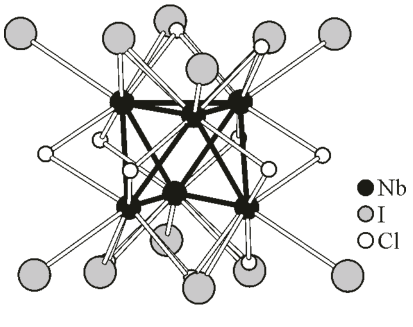
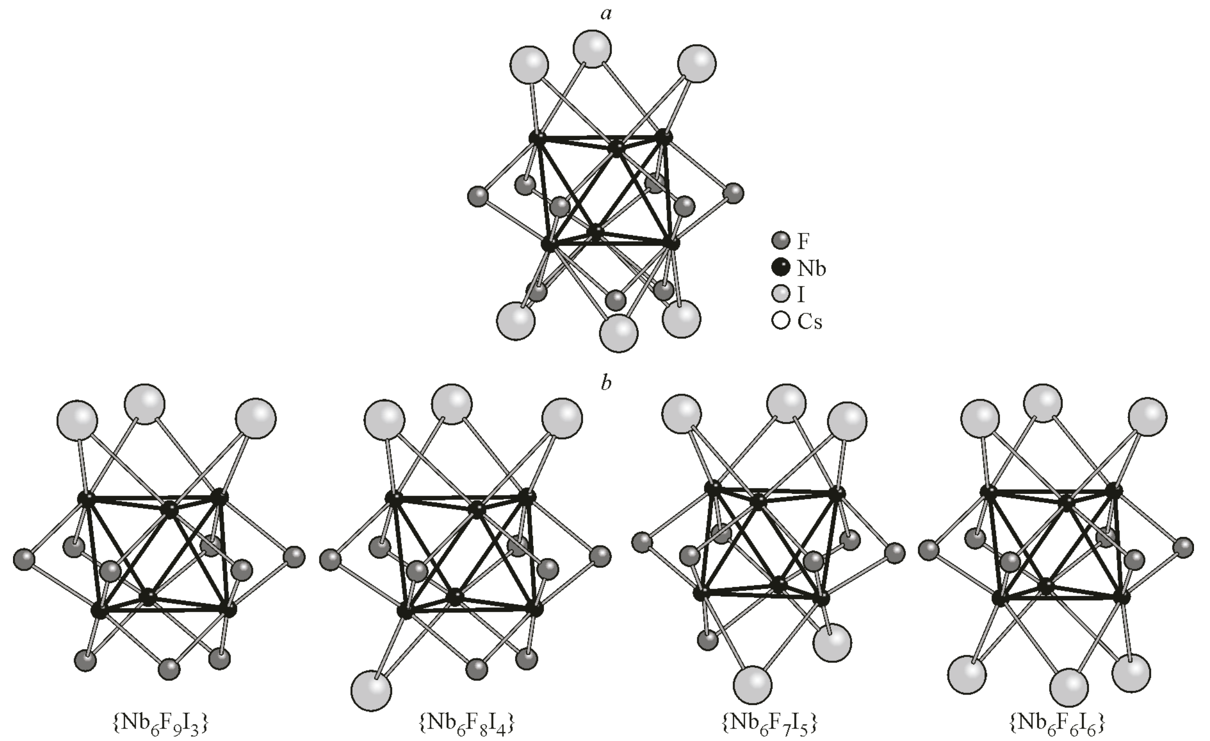


*Fig. 3*. Orientational disorder of $[\{Nb_6Cl_{11}I\}Cl_6]$ cluster unit in $Nb_6Cl_{10.8}I_{3.3}$.
Iodide atoms are randomly distributed over six positions



$\{Nb_6F_9I_3\}$ $\{Nb_6F_8I_4\}$ $\{Nb_6F_7I_5\}$ $\{Nb_6F_6I_6\}$

*Fig. 4.* Details of structure of $Cs_4Nb_6F_{8.5}I_{9.5}$: *a*) environment of $Nb_6$ cluster in $Cs_4Nb_6F_{8.5}I_{9.5}$ (occupancies of disordered $I^i$ and $F^i$ in $Cs_4[\{Nb_6F_{8.5}I_{3.5}\}I_6]$ are 0.5 and 2.5, respectively); *b*) possible isomers of $\{Nb_6L_{12}\}$ cluster core in $Cs_4Nb_6F_{8.5}I_{9.5}$

traces of other isomers from the units ($\{Nb_6F_9I_3\}$, $\{Nb_6F_8I_4\}$, $\{Nb_6F_7I_5\}$ and $\{Nb_6F_6I_6\}$) can not be excluded.

Dissolution of $Cs_3[\{Nb_6F_6Br_6\}Br_6]$ and $Cs_4[\{Nb_6F_{8.5}I_{3.5}\}I_6]$ in aqueous solution of KSCN afforded isolation of isomerically pure $[\{Nb_6F_6X_6\}(NCS)_6]^{4-}$ (X = Br, I), that were isolated as $(Et_4N)_4[\{Nb_6F_6Br_6\}(NCS)_6]\cdot 2Et_4NBr$ and $Cs_{1.6}K_{2.4}[\{Nb_6F_6I_6\}(NCS)_6]$ [ 8 ]. Discrete anionic units $[\{Nb_6F_6X_6\}(NCS)_6]^{4-}$ have six $\mu_2$-F ligands located in the plane between two opposite $Nb_3$ triangles, which are edge-bridged by the six $\mu_2$-X ligands. Yield of $[\{Nb_6F_6X_6\}(NCS)_6]^{4-}$ was low according to the proposed mixture of isomers, of which the $\{Nb_6F_6X_6\}$ species formed only a fraction. Large discrepancy between atomic radii of the halide ligands caused a strong distortion of the metal cluster. The apical NCS groups can be substituted by treatment with strong acids [ 24 ].

The discovery of the first mixed oxyhalide cluster $ScNb_6Cl_{13}O_3$ [ 27 ] has opened the field of a new class of niobium octahedral clusters in which ordered oxygen/halogen distribution within the $\{Nb_6X_{18}\}$ unit (L = O, Cl or Br) leads to clusters with greater distortions of the $Nb_6$ octahedra, possessing valency electron concentration (VEC) from 13 to 16. Numerous cluster oxychlorides were isolated and structurally investigated [ 27—35 ]. All these compounds contain the $\{Nb_6Cl_{12-x}O_x\}^{n+}$ cluster cores with $x$ = 1—6. The $\{Nb_6X_{18}\}$ units exhibit from one to six oxygen ligands in the inner positions, while the apical ones are always occupied by halogens, with the exception of $CsNb_6Cl_{12}O_2$ ($Cs[\{Nb_6Cl^i_{10}O^i_2\}O^a_2Cl^a_4]$) that exhibits two inner and two apical oxygen atoms shared between the adjacent units.

A general approach for preparation of similar oxyhalide clusters is high temperature reduction of $NbCl_5$ with Nb metal in the presence of suitable binary inorganic compounds containing alkali metals, Ln, Ti, or Pb. $Nb_2O_5$ or $Ln_2O_3$ serve as oxygen source. The stoichiometry and nature of the reagents predetermine composition and symmetry of the cluster core. Table 2 summarizes known examples of mixed ligand octahedral cluster complexes of niobium and tantalum with $[\{Nb_6Cl_{12-x}O_x\}L_6]$ ($x$ = 1—8), and $[\{Ta_6Br_9O_3\}Br_6]$ cluster units.

Table 2

*Examples of mixed ligand octahedral cluster complexes of niobium and tantalum with anionic units* $[\{Nb_6Cl_{12-x}O_x\}L_6]$ ($x$ = 1—8) *and* $[\{Ta_6Br_9O_3\}Br_6]$

| Compound | Cluster unit | VEC | Mean M—M ($\mu_2$-O), Å | Mean M—M ($\mu_2$-X), Å | Mean M—M, Å | Ref. |
|---|---|---|---|---|---|---|
| $Cs_2LuNb_6Cl_{17}O$ | $[\{Nb_6Cl_{11}O\}Cl_6]^{5-}$ | 16 | | | 2.916 | [ 29 ] |
| $CsNb_6Cl_{12}O_2$ | $[\{Nb_6Cl_{10}O_2\}Cl_6]^{5-}$ | 15 | 2.805 | 2.958 | 2.933 | [ 39 ] |
| $Cs_2UNb_6Cl_{15}O_3$ | $[\{Nb_6Cl_9O_3\}Cl_6]^{5-}$ | 14 | 2.778 | 3.005 | 2.948 | [ 40 ] |
| $Cs_2BaTa_6Br_{15}O_3$ | $[\{Ta_6Br_9O_3\}Br_6]^{5-}$ | 13 | 2.798 | 3.042 | 2.981 | [ 38 ] |
| $Cs_2LaTa_6Br_{15}O_3$ | $[\{Ta_6Br_9O_3\}Br_6]^{5-}$ | 14 | 2.754 | 3.010 | 2.954 | [ 38 ] |
| $LuTa_6Br_{15}O_3$ | $[\{Ta_6Br_9O_3\}Br_6]^{5-}$ | 14 | 2.797 | 2.978 | 2.933 | [ 36 ] |
| $ScNb_6Cl_{13}O_3$ | $[\{Nb_6Cl_9O_3\}Cl_6]^{5-}$ | 14 | 2.824 | 2.984 | 2.944 | [ 27 ] |
| $Cs_5[Nb_6Cl_9O_3(CN)_6]\cdot 4H_2O$ | $[\{Nb_6Cl_9O_3\}(CN)_6]^{5-}$ | 14 | 2.793 | 2.987 | 2.939 | [ 41 ] |
| $Cs_3Mn[Nb_6Cl_9O_3(CN)_6]\cdot 4H_2O$ | $[\{Nb_6Cl_9O_3\}(CN)_6]^{5-}$ | 14 | | | 2.951 | [ 42 ] |
| $(Me_4N)_5[Nb_6Cl_9O_3(CN)_6]\cdot 5H_2O$ | $[\{Nb_6Cl_9O_3\}(CN)_6]^{5-}$ | 14 | 2.792 | 3.004 | 2.951 | [ 41 ] |
| $Cs_{4.75}K_{0.25}[Nb_6Cl_9O_3(NCS)_6]\cdot 5.5H_2O$ | $[\{Nb_6Cl_9O_3\}(NCS)_6]^{5-}$ | 14 | 2.784 | 2.987 | 2.936 | [ 24 ] |
| $Cs_{2.5}K_{2.5}[Nb_6Cl_9O_3(NCS)_6]\cdot 2H_2O$ | $[\{Nb_6Cl_9O_3\}(NCS)_6]^{5-}$ | 14 | 2.823 | 2.973 | 2.965 | [ 24 ] |
| $Cs_5[Nb_6Cl_{15}O_3]\cdot CsCl\cdot 6H_2O$ | $[\{Nb_6Cl_9O_3\}Cl_6]^{5-}$ | 14 | 2.777 | 3.002 | 2.946 | [ 24 ] |
| $Ti_2Nb_6Cl_{14}O_4$ | $[\{Nb_6Cl_8O_4\}Cl_6]^{6-}$ | 14 | 2.826 | 2.978 | 2.927 | [ 33 ] |
| $Cs_2Ti_3Nb_6Cl_{12.5}O_4Cl_2$ | $[\{Nb_6Cl_8O_4\}Cl_6]^{6-}$ | 14 | 2.787 | 2.976 | 2.929 | [ 43 ] |
| $M_2Ti_2Nb_6Cl_{14}O_5$ | $[\{Nb_6Cl_7O_5\}Cl_6]^{7-}$ | 14 | 2.815 | 2.933 | 2.893 | [ 44 ] |
| $Cs_2Ti_4Nb_6Cl_{18}O_6$ | $[\{Nb_6Cl_6O_6\}Cl_6]^{8-}$ | 14 | 2.811 | 2.979 | 2.895 | [ 35 ] |
| $PbLu_3Nb_6Cl_{15}O_6$ | $[\{Nb_6Cl_6O_6\}Cl_6]^{8-}$ | 14 | 2.799 | 3.002 | 2.900 | [ 45 ] |
| $K_{2.6}Cs_{3.4}[Nb_6Cl_4O_4(OH)_4(CN)_6]\cdot 3H_2O$ | $[\{Nb_6Cl_4O_4(OH)_4\}(CN)_6]^{6-}$ | 14 | 2.817 ($\mu_2$-O)<br>2.897 ($\mu_2$-OH) | 2.912 | 2.875 | [ 46 ] |

The presence of two types of ligands again enables the cluster core isomerism. To date, three examples of such isomerism have been found featuring cluster cores $\{Nb_6Cl_9O_3\}$, $\{Nb_6Cl_8O_4\}$, and $\{Nb_6Cl_6O_6\}$ (Fig. 5). For example, two distinct isomers of $\{Nb_6Cl_9O_3\}$ cluster core were found in oxyhalides $A_2LnNb_6Cl_{15}O_3$ (A = Cs, Rb or K; Ln = rare earth (RE) from La to Gd or U) and $ScNbCl_{13}O_3$. As an illustration, $Cs_2UNb_6C1_{15}O_3$ and $ScNbCl_{13}O_3$ are both based on a $\{Nb_6Cl_9O_3\}$ cluster core with similar average Nb—Nb bond lengths of 2.947(1) Å and 2.943(1) Å, respectively. However, the oxygen atoms in *cis*-arrangement (Fig. 5, type *C*) leading to a much more distorted unit with a $C_2$ symmetry in $ScNbCl_{13}O_3$, than in $Cs_2UNb_6C1_{15}O_3$. In the latter, oxygens of $\{Nb_6Cl_9O_3\}$ cluster core are in *trans*-arrangement leading to a $D_3$ symmetry (Fig. 5, type *B*). The cluster core is stabilized by apical chlorine with close Nb—Cl distances of 2.581(1) Å and 2.590(3) Å for $Cs_2UNb_6C1_{15}O_3$ and $ScNbCl_{13}O_3$, respectively. Owing to its small size, $Sc^{3+}$ has a low coordination number equal to 5. Its environment is built up from two chlorine atoms and three oxygen atoms belonging to three cluster units. The $[\{Nb_6Cl_9O_3\}Cl_6]$ units are connected one to each other to form a tridimensional $\{Nb_6Cl_9O_3\}Cl_{4/2}Cl_2$ framework. On the other hand, the structure of $CsUNb_6Cl_9O_3Cl_6$ is based on discrete $[\{Nb_6Cl_9O_3\}Cl_6]^{5-}$ units. $U^{3+}$ has a coordination number of 9 with an environment made by three oxygen and six chlorine atoms belonging to three adjacent units. Moreover, if no other $Nb_6$-cluster based oxyhalide has been found with the $ScNbCl_{13}O_3$ structure type, several other $Nb_6$-cluster based oxyhalides adopt the $CsUNb_6Cl_9O_3Cl_6$ structure type. It has been observed for large RE cations (La to Gd) and large alkali metal cations (Cs, Rb or K). These findings furnish evidence that the charge, geometry and connectivity of the cluster units are directly governed by the nature of counter cations.

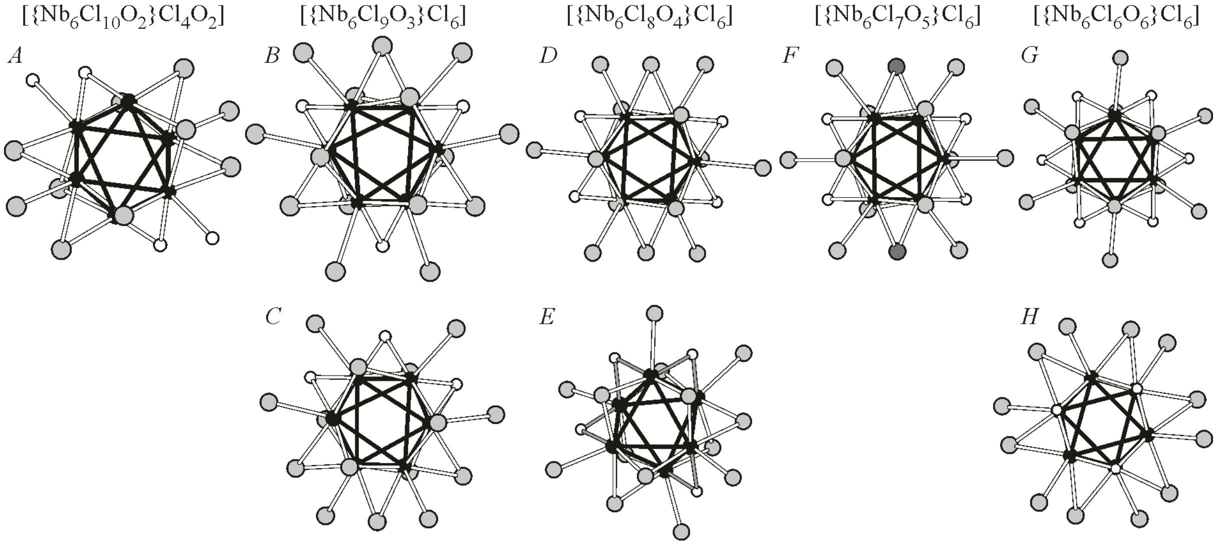


*Fig. 5*. Examples of cluster units $[\{Nb_6Cl_{12-x}O_x\}L_6]$ ($x$ = 2—6) viewed along pseudo-three-fold axis of the cluster

Tantalum oxybromides are quite rare and are limited to two families: $A_2BTa_6Br_9O_3Br_6$ (A = Cs; B = Ba, La and Ce) and $LnTa_6Br_9O_3Br_{4/2}Br_2$ (Ln = Sm to Lu except Eu and Yb), respectively [36]. It is worth noting that in $Cs_2LaTa_6Br_9O_3Br_6$ and $Cs_2BaTa_6Br_9O_3Br_6$ the charges of the $[\{Ta_6Br_9O_3\}Br_6]^{n-}$ units are 4– and 3–, meaning an unusually low VEC value of 13 electrons per cluster [37, 38].

In oxyhalides considered steric effects of oxide and halide determine the M—M intracluster distances. The oxide bridged Nb—Nb intracluster bonds are shorter than the chloride bridged ones in agreement with the ionic radii of the bridging ligands (See Table 2 and Fig. 6) that results in a greater distortion of the $Nb_6$ cluster. For example, the cluster units with three-fold symmetry, namely $\{Nb_6Cl_9O_3\}$ (in $Cs_2UNb_6Cl_{15}O_3$) and $\{Nb_6Cl_6O_6\}$ (in $PbLu_3Nb_6Cl_{15}O_6$), are compressed along three-fold axis, while $\{Nb_6Cl_6O_6\}$ (in $Cs_2Ti_4Nb_6Cl_{18}O_6$) are elongated.

When the number of inner oxygen atoms in the $\{Nb_6Cl_{12-x}O_x\}$ cluster core increases, the Nb—O$^i$ antibonding contribution also increases and it becomes preponderant for three oxygens per unit leading to an overall nonbonding character for $a_{2u}$ level. Indeed, the usual VEC for the $\{Nb_6Cl_{12-x}O_x\}$ cluster core in the oxychlorides with $x < 3$ was found to be 16 or 15 whereas this value drops to 14 for $x \geq 3$ and even below 14 in some cases. Let us recall that for molecular compounds, a fractional value of VEC per cluster corresponds, obviously, to an average of local integer VEC values.

The mean M—M distances are related to the number of valence electrons, involved in the M—M bonding orbitals. Calculations [30, 47] performed on $\{M_6L_{18}\}$ units have shown that the highest molecular orbital levels occupied by the electrons have a M—M bonding character. Consequently, the more electrons occupy these levels, the stronger M—M intracluster bonds are, and the shorter M—M distances became. In addition to a M—M bonding character, the $a_{2u}$ HOMO level (fully occupied when VEC is 16) exhibits an antibonding M—L$^i$ character. Two isostructural phases, namely $Cs_2LaTa_6Br_{15}O_3$ and $Cs_2BaTa_6Br_{15}O_3$ have 14 and 13 cluster valence electrons, respectively. Removal one bonding cluster valence electron on going from VEC = 14 to VEC = 13 resulted in increase of mean Ta—Ta distance from 2.954 Å to 2.981 Å.

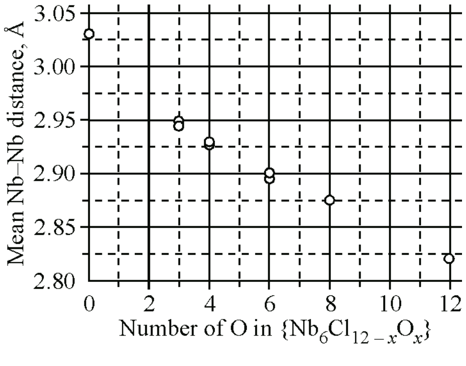


*Fig. 6*. Influence of number of oxygen atoms in the cluster core on mean interatomic distances

### *Solution chemistry of niobium oxychloride clusters*

The oxyhalide cluster phases are not directly soluble in aqueous solutions or common organic solvents, but they can be extracted into a solution by apical ligand exchange. Thus, the reactions of $Cs_2LaNb_6Cl_{15}O_3$ and $ScNb_6Cl_{13}O_3$ with aqueous solutions of KCN and KNCS resulted in excision of the intact cluster cores and formation of complexes $[\{Nb_6Cl_9O_3\}L_6]^{5-}$ (L = CN, NCS). The structures of $Cs_2LaNb_6Cl_{15}O_3$ and $ScNb_6Cl_{13}O_3$ are based on *trans*- and *cis*-isomers of the $\{Nb_6Cl_9O_3\}^+$ cluster core, respectively. Interaction with cyanides results in apical ligand exchange and in the formation of expected isomeric complexes, isolated and structurally characterized as $Cs_5[\{Nb_6Cl_9O_3\}(CN)_6]\cdot 4H_2O$ ($D_3$ isomer) and $(Me_4N)_5[\{Nb_6Cl_9O_3\}(CN)_6]\cdot 5H_2O$ ($C_2$ isomer). The same pair of isomers was obtained in the reactions with KNCS. The apical ligands in these anions are rather labile and can be substituted with chloride ligands [24, 41]. It turned out that no inner ligand exchange and no redox process occurred in these reactions and consequently the $\{Nb_6Cl_9O_3\}$ cluster core remains identical in the starting and final compounds.

Both $Cs_2La[\{Nb_6Cl_9O_3\}Cl_6]$ solid state precursor, as well as the resulting $Cs_5[\{Nb_6Cl_9O_3\}(CN)_6]\cdot 4H_2O$ contain ordered $[\{Nb_6Cl_9O_3\}L_6]^{5-}$ units with a local idealized $D_3$ symmetry. However, in $Cs_2La[\{Nb_6Cl_9O_3\}Cl_6]$ (space group $P\bar{3}1c$) the unit is centered on a 3*a* Wyckoff position with a 32 site symmetry ($D_3$), while in $Cs_5[\{Nb_6Cl_9O_3\}(CN)_6]\cdot 4H_2O$ the unit is centered on a 4*b* Wyckoff position with 2 site symmetry ($C_2$). In both cases the units exhibit lower symmetry than the idealized $D_3$ one. On the other hand, crystallization of the $[\{Nb_6Cl_9O_3\}L_6]^{5-}$ anion with manganese cation leads to the formation of the salt $Cs_3Mn[\{Nb_6Cl_9O_3\}(CN)_6]\cdot 0.6H_2O$, in which the unit is centered on a $m3m$ position, and exhibits high $O_h$ symmetry. The framework in $(Mn[\{Nb_6Cl_9O_3\}(CN)_6])^{3-}$ is strongly related to that found in $(Me_4N)_2Mn[\{Nb_6Cl_{12}\}(CN)_6]$ compound [48]. The positions of oxygen and chlorine atoms have been well discriminated, but niobium atoms fully occupy only one crystallographic position. The steric effect of bridging Cl and O that influences locally the Nb—Nb bond length is too small to affect significantly the niobium positions, and is absorbed in the atomic displacement parameters. Consequently, the mean square displacement parameters reveal a higher anisotropy for niobium atoms in the case of $Cs_3Mn[\{Nb_6Cl_9O_3\}(CN)_6]\cdot 0.6H_2O$ (0.0428, 0.0428, 0.0307), than in the case of $Cs_5[\{Nb_6Cl_9O_3\}(CN)_6]\cdot 4H_2O$ (*average*: 0.0366, 0.0341, 0.0292) related to a local distortion of the $Nb_6$ cluster.

Cluster oxychloride with the highest content of oxygen in the $\{M_6X_{12}\}$ cluster core was obtained *via* soft chemistry route by the interaction of $Cs_2Ti_3Nb_{12}Cl_{27}O_8$, a $[\{Nb_6Cl_8O_4\}Cl_6]$ unit based oxyhalide [34], with an aqueous solution of KCN. Beyond the substitution of apical ligands by the cyanide group, such a reaction leads to inner ligand exchanges and to the formation of a new $\{Nb_6O_4(OH)_4Cl_4\}$ cluster core with 4 inner oxygen atoms and 4 hydroxyl groups, that was crystallized as salt $K_{2.6}Cs_{3.4}[\{Nb_6Cl_4O_4(OH)_4\}(CN)_6]\cdot 3H_2O$. Comparison of inner ligand environments in starting $Cs_2Ti_3Nb_{12}Cl_{27}O_8$ and resulting $K_{2.6}Cs_{3.4}[\{Nb_6Cl_4O_4(OH)_4\}(CN)_6]\cdot 3H_2O$ reveals that during dissolution not only chlorine atoms were substituted by oxygen atoms, but *vice versa* oxygen atoms by chlorine atoms.

## OCTAHEDRAL CLUSTERS OF $\{M_6Q_8\}$ FAMILY

Mixed ligand octahedral clusters of the $\{M_6Q_8\}$ family are well known for molybdenum and rhenium. A general approach for the preparation of compounds based on hexamolybdenum or hexarhenium clusters with mixed inner ligand environment is the high temperature synthesis from the elements and, if necessary, binary metal halides or chalcogenides in the systems M—Q—X (M = Mo, Re; Q = S, Se, Te; X = Cl, Br, I). As a rule, such reactions lead to polymeric thermodynamically stable phases with specified Q/X ratio in the cluster core. Similar reactions run with an excess of halides of alkali metals allow to obtain corresponding salts of anionic cluster complexes that are soluble in water and organic solvents.

### *High temperature synthesis*

C. Perrin et al. reported that the series of the compounds with the general formula $Mo_6Cl_{10}Q$ (Q = S, Se, Te) can be obtained by reactions ″$5MoCl_2 + Mo + Q$″ or ″$10/3MoCl_3 + 8/3Mo + Q$″ in sealed silica tubes heated at 1000 °C for 24 h [ 49 ]. The compounds have found to be isostructural with $Nb_6I_{11}$ and can be described by a formula $\{Mo_6Cl^i_7Q^i\}Cl^{a-a}_{6/2}$. The Q atom is statistically distributed over the $\{Mo_6X_8\}$ cluster core with $X \approx 7/8Cl + 1/8Se$. Similar reactions according to the reagent stoichiometries ″$MoBr_2 + 5Mo + 6S$″ (1100 °C, 24 h) or ″$3MoBr_2 + 3Mo + 3S$″ (1200 °C, 24 h) resulted in $Mo_6S_6Br_2$ ($\{Mo_6Br^i_2S^{i-a}_{6/2}\}S^{a-i}_{6/2}$) or $Mo_6Br_6S_3$ ($\{Mo_6Br^i_4S^{i-i}_{2/2}S^{i-a}_{2/2}\}Br^{a-a}_{4/2}S^{a-i}_{2/2}$), respectively [ 50, 51 ].

The complete systems of the mixed halide ligand clusters $\{Mo_6Br_xCl_{8-x}\}^{4+}$ and $\{Mo_6I_xCl_{8-x}\}^{4+}$ were obtained by exchange innersphere bound $Cl^i$ by outersphere bound $Br^a$ or $I^a$ on tempering the solids $\{Mo_6Cl_8\}Br_4$ (at 500 °C) and $\{Mo_6Cl_8\}I_4$ (at 400 °C), respectively [ 52, 53 ]. By $^{19}F$ NMR the complexes $[\{Mo_6Br_xCl_{8-x}\}F_6]^{2-}$ and $[\{Mo_6I_xCl_{8-x}\}F_6]^{2-}$ were found to be composed as mixtures of 22 and 21 different species, respectively, with various $x$ values and arrangements of inner ligands around the $Mo_6$ octahedron.

The compounds $Cs_4Mo_6Br_{12}S_2$ and $Cs_4Mo_6Br_{12}Se_2$ were prepared by solid state routes from a stoichiometric amount of $Mo_6Br_{12}$, Mo powder, CsBr, and S or Se (1100 °C for sulfide or 900 °C for selenide, 1 week). The structures are based on the $[\{Mo_6Br_6Q_2\}Br_6]^{4-}$ (Q = S or Se) discrete units in which two chalcogen and six bromine ligands randomly occupy the inner positions, while the six apical ones are fully occupied by bromine atoms [ 10 ]. The interaction of these two compounds with aqueous KCN solution at room temperature results in apical ligand exchange giving the anionic cyanochalcohalide complexes.

The series of cluster compounds $Rb_{2+x}[\{Mo_6Br_{8-x}Q_x\}Br_6]$ (Q = Se or Te) was synthesized by high temperature reactions (900 °C, 3 days) between RbBr, Mo, $MoBr_2$ and corresponding Q in a sealed silica tubes [ 54 ]. Combined single-crystal and powder X-ray diffraction investigations of the resulting products revealed a phase breadth for the $Rb_{2+x}[\{Mo_6Br_{8-x}Se_x\}Br_6]$ series (with $0.25 \le x \le 0.7$) and a defined composition for $Rb_{2.5}[\{Mo_6Br_{7.5}Te_{0.5}\}Br_6]$. The double salts $Rb_{12}[MoBr_6]_3[\{Mo_6Br_7Q\}Br_6]$ (Q = Se, Te) resulted from the partial disproportionation of the $Mo_6Br_{12}$ in the presence of corresponding chalcogenides and RbBr salt (″$12RbBr + 19/12Mo_6Br_{12} + Q$″ in a sealed silica tube, 900 °C, 3 days) [ 55 ]. The $[\{Mo_6Br_7Q\}Br_6]^{3-}$ cluster units characterised by a random distribution of seven bromine and one chalcogen ligands on all the eight inner positions. Such a distribution implies a static orientational disorder of the cluster units around the origin of the unit cell.

The compound $Cs_3[\{Mo_6I_6I_{2-x}Se_x\}I_6]$ has been obtained by the reaction between CsI, Se, Mo and $Mo_6I_{12}$ (950 °C, 3days) [ 56 ]. For a particular $x$ value, the structure of $Cs_3[\{Mo_6I_6I_{2-x}Se_x\}I_6]$ is based on a mixture of paramagnetic $[\{Mo_6I_6Se_2\}I_6]^{3-}$ and diamagnetic $[\{Mo_6I_7Se\}I_6]^{3-}$ units with 23 and 24 valence electrons per $Mo_6$ cluster, respectively. The two inner positions of the average face-capped $[\{Mo_6I_6I_{2-x}Se_x\}I_6]^{3-}$ ionic units (located on the threefold axis of the unit) are randomly occupied by iodine and selenium, whereas the other ligand positions are fully occupied by iodine.

The first molybdenum octahedral cluster oxyhalide complex $[\{Mo_6Br_6L_2\}Br_6]^{3-}$ ($L = 0.5Br + 0.5O$) in which two inner positions, located on the threefold axis of the unit, are randomly occupied by one bromine and one oxygen whereas the other ligand positions are fully occupied by bromine, was obtained as a byproduct (a few red colored single crystals of $Cs_3[\{Mo_6Br_7O\}Br_6]$) in a reaction designed to synthesize $Cs_2[\{Mo_6Br_8\}Br_6]$: a stoichiometric mixture of CsBr and $MoBr_2$ was heated at 950 °C for 3 days [ 57 ]. Several attempts to obtain the bulk compound, in particular with $MoO_3$ as starting material, failed. The presence of oxygen in the single crystals of the title compound was explained by some oxygen contamination during the preparation of $MoBr_2$. The increase of the anionic charge on the cluster unit going from $[\{Mo_6Br_8\}Br_6]^{2-}$ to a $[\{Mo_6Br_7O\}Br_6]^{3-}$ is accompanied by a decrease of the average Mo—Mo bond length from 2.6348(7) Å to 2.6133(7) Å. It seems that the increase of the O/Br ratio in the inner positions of the $[\{Mo_6L^i_8\}L^a_8]$ unit affects significantly their structural and electronic properties, and could also lead to $[\{Mo_6L_{12}\}L_6]$ unit-based compounds [ 57 ].

The reaction of $Mo_6Se_8$ with a KCN—KSCN mixture (650 °C, 12 h) afforded a mixed-ligand cluster anion $[\{Mo_6(Se,S)_8\}(CN)_6]^{7-}$, which was isolated in the form of $K_{1.5}Cs_{5.5}[\{Mo_6Se_{6.8}S_{1.2}\}(CN)_6]\cdot$ $\cdot 8H_2O$ [ 58 ].

Molecular rhenium chalcohalides of composition $Re_6Q_4X_{10}$ have a minimal amount of chalcogen atom possible for this type of compounds. The first synthesis of a series of hexanuclear rhenium chalcohalide cluster compounds, formulated as $Re_3Q_2X_5$ (Q = Se, X = Cl, Br; Q = Te, X = Br), was reported in 1971 [ 59, 60 ]. The composition of these compounds was estimated from chemical analysis of the products of reactions between $ReSe_2$ and $Cl_2$ at 480°C, and $Br_2$ at 580°C. In contrast, $Re_2Te_5$ begins to react with $Br_2$ at room temperature and fully transformation in $Re_3Te_2Br_5$ at 70°C. The compounds $Re_3Q_2X_5$ (X = Cl, Br) were also obtained by reaction of $ReSe_2$ with $ReCl_3$ or $ReBr_3$ at 700—720 °C in an evacuated silica tube.

The first single-crystal X-ray structure determination was reported for $Re_6Se_4Cl_{10}$ independently by two groups of authors [ 61, 62 ]. Other members of these series, namely $Re_6S_4Cl_{10}$, $Re_6Te_4Cl_{10}$, $Re_6Se_4Br_{10}$ and $Re_6Te_4Br_{10}$ have been structurally characterized later [ 63—65 ]. Note that the temperature required for the preparation of $Re_6Te_4Cl_{10}$ (~450 °C) is lower than that usually required for the syntheses of the S and Se analogs. All these compounds are isostructural and crystallize in a triclinic space group with two geometrically similar but independent molecules per unit cell. Evidently, other loading stoichiometries lead to compounds with larger chalcogen content in cluster core.

Step by step substitution of the halide $X^-$ in $Re_6Q_4X_{10}$ by chalcogenide $Q^{2-}$ leads to polymerization through the formation of halide bridges between the clusters, that allows to obtain three groups of mixed-ligand (X/Q) compounds, namely $Re_6Q_5X_8$, $Re_6Q_6X_6$ and $Re_6Q_7X_4$. In the compound $Re_6Se_5Cl_8$ the cluster core $\{Re_6Se_5Cl_3\}^{5+}$ is surrounded by six apical chlorine atoms. Four of them are terminal, while the two remaining ones are bridging between two adjacent units resulting in neutral zig-zag chains [ 66 ]. $Re_6S_5Cl_8$ is isostructural with its selenium analogue [ 63 ]. Both compounds can be represented by the formula $\{Re_6Q^i_5Cl^i_3\}Cl^a_4Cl^{a-a}_{2/2}$. Between the chains there are only Van der Waals interactions. $Re_6Se_6Cl_6$ is the prototypical two-dimensional polymer, which is described as $\{Re_6Se_6Cl_2\}Cl^a_2Cl^{a-a}_{4/2}$, and is isostuctural with the well-known molybdenum dichloride $Mo_6Cl_{12}$ [ 66 ].

The structure of $Re_6Q_7Br_4$ (Q = S, Se) [ 66, 67 ] represents a three-dimensional halogen-bridged octahedral rhenium cluster architecture of general formula $\{Re_6Q^i_7Br^i\}Br^{a-a}_{6/2}$. Within the rhombohedral structure, each $\{Re_6Se_7Br\}^{3+}$ core is linked via halogen-bridged atoms to six neighboring cluster cores.

Unique molecular chalcohalide compound $[\{Re_6Te_6Cl_2\}Cl_4(TeCl_2)_2]$ (Fig. 7) has been obtained by reaction of $ReCl_5$ with Te at 450 °C, the same yields $Re_6Te_4Cl_{10}$ mentioned above [ 68 ]. This compound contains a $Re_6$ octahedron residing inside a $Te_6Cl_2$ pseudocube, where six of the corners are occupied exclusively by Te atoms, and the two other corners of the cube are occupied exclusively by Cl atoms. The four Re atoms that are bonded to $\mu_3$-Cl ligands have terminal Cl ligands, while the two Re atoms that are bonded to $\mu_3$-Te anions are ligated by neutral $TeCl_2$ groups.

The whole families of $M[\{Re_6Q_5X_3\}X_6]$ (M = an alkaline cation, Cu or Ag; Q = S, Se; X = Cl, Br) have been synthesized by high-temperature reactions [ 69—71 ]. Cation exchange with tetrabutylammonium chloride yields $(Bu_4N)[\{Re_6S_5Cl_3\}Cl_6]$, which is soluble in polar organic solvents [ 63 ]. $K[\{Re_6Se_5Cl_3\}Cl_6]\cdot 2H_2O$ was obtained by crystallization of $K[\{Re_6Se_5Cl_3\}Cl_6]$ from wet ethanol, while $Bu_4N[\{Re_6Se_5Cl_3\}Cl_6]$ was obtained by recrystallization of $K[\{Re_6Se_5Cl_3\}Cl_6]$ in the presence of $Bu_4NX$ ($X = Cl^-$, $SCN^-$, etc.).

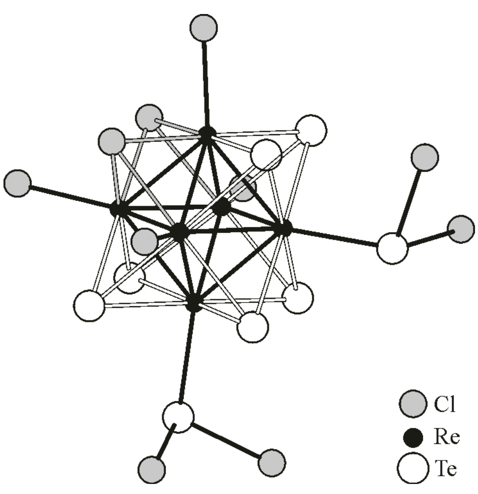


*Fig. 7.* The neutral cluster complex $[\{Re_6Te_6Cl_2\}Cl_4(TeCl_2)_2]$

An increase by 1 molar equivalent of the chalcogen content together with the use of a divalent cation ($M^{2+}$), led to a series of compounds formulated $M[\{Re_6Q_6Cl_2\}Cl_6]$. With divalent cations, the high temperature synthesis was reported for alkalin-earth salts (M = Mg, Ca; Q = S, Se) that were structurally characterized, after extraction in $H_2O$, in the form of $[Ca(H_2O)_x][\{Re_6Q_6Cl_2\}Cl_6]\cdot yH_2O$ (Q = S or Se) and $[Mg(H_2O)_6][\{Re_6Q_6Cl_2\}Cl_6]\cdot 2H_2O$ [ 72 ]. In addition, the compound with composition $K_2[\{Re_6Se_6Br_2\}Br_6]$ was obtained as a soluble salt by reacting a mixture of $Re_3Br_9$, PbS and KBr at 550 °C [ 73 ].

$Ca[\{Re_6Se_6Cl_2\}Cl_6]$, prepared by high-temperature reaction from $ReCl_5$, Re, Se and anhydrous $CaCl_2$, was used for preparation of single crystals of $(Bu_4N)_2[\{Re_6Se_6Cl_2\}Cl_6]$ by crystallization from ethanol in presence of $Bu_4NCl$ [ 70 ].

The cluster compound $(Pr_4N)_2[\{Re_6Te_6Br_2\}Br_6]$ was prepared by reaction of $Re_3Br_9$ with $Li_2Te$ and following crystallization from water in presence of $Pr_4NBr$, and structurally characterized [ 71 ]. The dianionic and trianionic molecular forms $[\{Re_6S_6Cl_2\}Cl_6]^{2-}$ and $[\{Re_6S_7Cl\}Cl_6]^{3-}$, respectively, were found to coexist in 1:1 ratio in the cluster compound $Rb_5[\{Re_6S_6Cl_2\}Cl_6][\{Re_6S_7Cl\}Cl_6]$ [ 63 ].

In the $K_2[\{Re_6S_6Br_2\}Br_6]$—$Ph_3PO$—HBr system a complex with the composition $[H(Ph_3PO)_2]_2[\{Re_6S_6Br_2\}Br_6]$ was obtained in a high yield. In this compound there are two types of cluster anions, $[\{Re_6S_2(S_{2/3}Br_{1/3})_6\}Br_6]^{2-}$ and $[\{Re_6S_4(S_{1/2}Br_{1/2})_4\}Br_6]^{2-}$, with different distributions of the $\mu_3$-ligands within the cluster core $\{Re_6S_6Br_2\}^{4+}$. In $[\{Re_6S_2(S_{2/3}Br_{1/3})_6\}Br_6]^{2-}$, four sulfur and two bromine atoms alternatively occupy six corners of a $S_6Br_2$ cube, whereas in $[\{Re_6S_4(S_{1/2}Br_{1/2})_4\}Br_6]^{2-}$, two sulfur and two bromine atoms are distributed over four positions [ 74 ].

$K_3[\{Re_6S_7Br\}Br_6]$ results from substitution of $Br^-$ by $S^{2-}$ in $[\{Re_6S_4Br_4\}Br_6]$ in its reaction with KCSN [ 73 ]. The most striking feature of its structure is the considerable disorder of $K^+$ cations, that arrange as partially occupied $(K_4)^{4+}$ tetrahedral groups and $(K_3)^{3+}$ angular groups. In similar ABr—Re—Q—Br systems (A = Rb, Q = S; A = Cs, Q = Se) two others salts, $Rb_3[\{Re_6S_7Br\}Br_6]$ [ 75 ] and $Cs_3[\{Re_6Se_7Br\}Br_6]$ [ 76 ], have been obtained and characterized. The main difference between the two salts is the alkaline environment: $Rb^+$ fully occupies a single site, while $Cs^+$ is distributed over three different sites. The salts of cluster anions $[\{Re_6Q_7Br\}Br_6]^{3-}$ (Q = S, Se) with lanthanide cations were prepared by classical methods of solution chemistry, namely, by crystallization from a DMF solution [ 77 ].

### ***Low temperature syntheses***

Already the first studies by J.C. Sheldon revealed that inner halide ligands in the hexamolybdenum cluster complexes can be partially substituted even in mild conditions. He demonstrated that an alkalinization of an aqueous solution of $[\{Mo_6X_8\}X_6]^{2-}$ (Cl or I) results in substitution of all apical and some inner chalcogenides by OH groups producing a dark brown precipitate that was described by the formula $\{Mo_6X_{8-x}(OH)_x\}(OH)_4\cdot yH_2O$ [ 78—80 ]. $\{Mo_6Cl_{8-x}(OH)_x\}(OH)_4\cdot yH_2O$ can be dissolved in hydrohalic acids, and the salts $[Et_4N]_2[\{Mo_6Cl_7OH\}Cl_6]$ and $[Et_4N]_2[\{Mo_6Cl_4Br_3OH\}Br_6]$ were precipitated from the solution in hydrochloric or hydrobromic acid, respectively, by addition of tetrabutylammonium [ 78 ].

A synthetic procedure has been devised for displacement of one chloride by sulfide, selenide or telluride ions in the $\{Mo_6Cl_8\}^{4+}$ cluster via reaction of $Mo_6Cl_{12}$ with NaHS, NaHSe or NaHTe, respectively, in refluxing pyridine for 24 h, followed by extraction of the reaction product into a mixture of concentrated HCl and alcohol [ 81—83 ]. The $\{Mo_6Cl_7Q\}^{3+}$ (Q = S, Se or Te) clusters have been isolated in the form of different salts containing the anions $[\{Mo_6Cl_7Q\}Cl_6]^{3-}$. The same approach can also be applied for preparation of $[\{Mo_6Br_7S\}Cl_6]^{3-}$ [ 82 ] or $[\{Mo_6Cl_7Q\}Br_6]^{3-}$ [ 84 ]. The substitution of a single halide-ion by chalcogenide-ion dramatically alters the electronic structure of the cluster and changes the color from yellow $\{Mo_6X_8\}^{2+}$ (X = Cl or Br) to red $\{Mo_6X_7Q\}^{3+}$. Similar reaction with higher molar $NaHSe/Mo_6Cl_{12}$ ratio allowed to make two substituted complex $[\{Mo_6Cl_6Se_2\}Br_6]^{4-}$ [ 85 ]. Tetrabutylammonium salts of oxidized cluster complexes $[\{Mo_6X_7Q\}Cl_6]^{2-}$ (X = Cl, Q = S or Se; X = Br, Q = S) were also synthesized [ 84 ].

Reaction of $[\{Mo_6Cl_8\}Cl_6]^{2-}$ with $H_2Se$, generated in situ from ZnSe and HCl under hydrothermal conditions lead to the substitution of one or two bridging chlorides, depending on the reagents ratio [ 86 ]. With the $Mo_6$/ZnSe 1:3 molar ratio $[\{Mo_6Cl_7Se\}Cl_6]^{3-}$ forms selectively in high yield. Further substitution is more hindered, and even at 1:20 cluster-to-selenide molar ratio a mixture of $[\{Mo_6Cl_7Se\}Cl_6]^{3-}$ and $[\{Mo_6Cl_6Se_2\}Cl_6]^{4-}$ is formed.

Deeper and more facile sulfide substitution of inner chloride ligands in $Mo_6Cl_{12}$ up to sulfide cluster core $\{Mo_6S_8\}$ can be realized by the addition of a proton acceptor like $OBu^-$ in 1-butanol to the reaction mixture "$Mo_6Cl_{12}$ + NaHS in pyridine" [ 87 ].

Isostructural compounds based on octahedral molybdenum cluster cyanide complexes with mixed selenide/halide ligands in the cluster core, $Cs_5[\{Mo_6Se_{3.6}Cl_{4.4}\}(CN)_6]$ and $Cs_5[\{Mo_6Se_{3.4}Br_{4.6}\}(CN)_6]$, have been synthesized by the reaction of $Mo_6Cl_{12}$ or $Mo_6Br_{12}$ with an aqueous solution of $Cs_2Se_3$, followed by treatment with an aqueous solution of KCN [ 88 ]. Based on the magnetic measurements in was proposed, that the crystalline products contain solid solutions of $Cs_5[\{Mo_6Se_3X_5\}(CN)_6]$ and $Cs_5[\{Mo_6Se_4X_4\}(CN)_6]$ (X = Cl or Br) approximately in 1:1 ratio.

Reactions between $W_6Cl_{12}$ and $Na_2Se$ or $K_2Se$ in toluene in the presence of triethylphosphine (under reflux for 3 days) result in the formation of mixed chloride - selenide cluster cationic complexes [ 89 ]. The structures of two crystals from different preparations, using $Na_2Se$ and $K_2Se$ as reagents, were determined and found to have different compositions, $[\{W_6Se_7Cl\}(PEt_3)_6][Cl(CHCl_3)_6]$ and $[\{W_6Se_{6.4}Cl_{1.6}\}(PEt_3)_6][Cl(CHCl_3)_6]$, respectively. The chlorine and selenium atoms are disordered over all $\mu_3$-ligand sites in both structures. In the latter case the crystal contains both the 20-electron cluster $[\{W_6Se_7Cl\}(PEt_3)_6]^+$ and the 21-electron cluster $[\{W_6Se_6Cl_2\}(PEt_3)_6]^+$ in the mole fractions 0.40 and 0.60, respectively.

The oxo-compound $(Bz_3NH)_3[Mo_6OCl_{13}]$ ($Bz_3NH$ = tribenzylammonium) containing a cluster anionic complex $[\{Mo_6OCl_7\}Cl_6]^{3-}$ with the $\mu_3$-O atom in the ordered cluster core was obtained by the reaction of $Mo_6Cl_{12}$ with molten wet tribenzylamine (170 °C, 10 h) [ 90 ]. The Mo—Cl distances in the cluster unit vary within a broad range — from 2.464(5) to 2.529(5) Å, and the longest bonds Mo—Cl (2.517—2.529 Å) are those in the *trans*-position to the O atom in the cluster core. Such elongation can result in a higher lability of the corresponding Cl atoms in $[\{Mo_6OCl_7\}Cl_6]^{3-}$ as compared with other $\mu_3$-Cl ligands characterized by usual Mo—Cl bond lengths (2.464—2.496 Å).

Oxidative treatment of $Mo_6Te_5I_3$ in dry acetonitrile with dry chlorine and further extraction of into HCl gave mixed ligand $\{Mo_6Cl_{8-x}I_x\}$ compounds. Their compositions and structures were determined by the X-ray analysis as $(H_7O_3)_2[\{Mo_6Cl_{7.22}I_{0.78}\}Cl_6]\cdot 3H_2O$, $(H_9O_4)_2[\{Mo_6Cl_{6.66}I_{1.34}\}Cl_6]$ and $(H_5O_2)_2[\{Mo_6Cl_{6.36}I_{1.64}\}Cl_6]\cdot 2H_2O$ [ 91 ]. The crystallographic and mass-spectroscopic data show that the compounds are in fact solid solutions that contain the $[\{Mo_6Cl_8\}Cl_6]^{2-}$, $[\{Mo_6Cl_7I)Cl_6]^{2-}$ and $[\{Mo_6Cl_6I_2\}Cl_6]^{2-}$ anions in different ratios for each phase. Relative Cl/I occupancies of the $\mu_3$-positions vary for different sites.

$(Pr_4N)_2[\{Re_6Se_6Cl_2\}Cl_6]$ and $(Bu_4N)_2[\{Re_6Se_6Cl_2\}Cl_6]$ were obtained by reaction of $Pr_4N[\{Re_6Se_5Cl_3\}Cl_6]$ and $Bu_4N[\{Re_6Se_5Cl_3\}Cl_6]$, respectively, with $Li_2Se$ in THF [ 92 ]. The reactions take place at room temperature with relatively high yield. Another way of introducing $Q^{2-}$ is demonstrated by modification of cluster anion $[\{Re_6Q_5Cl_3\}Cl_6]^-$ (Q = S, Se) in reaction with $((CH_3)_3Si)_2E$ (E = O, S, Se or Te) [ 93 ]:

$$[\{Re_6Q_5Cl_3\}Cl_6]^- + ((CH_3)_3Si)_2E \rightarrow [\{Re_6Q_5ECl_2\}Cl_6]^{2-} + (CH_3)_3SiCl.$$

(Q = S, E = O, S, Se; Q = Se, E = S, Se, Te)

The reactions allow preparation a large range of mixed ligand anionic rhenium cluster complexes. This chemistry was extended to the synthesis of the tetrabutylammonium salts of $\mu_3$-imido-functionalized molecular hexanuclear chalcohalide rhenium cluster dianions, namely $[\{Re_6Q_5(NR)Cl_2\}Cl_6]^{2-}$ (Q = S, Se; R = H, $SiMe_3$, methyl, benzyl) [ 94 ]. When E = NH, $NSiMe_3$ group in the compound $[\{Re_6Q_5(NSiMe_3)Cl_2\}Cl_6]^{2-}$ (Q = S, Se) formed at the first step was converted into NH by reaction with $Bu_4NF$. Reactions of THF/MeCN solutions of $Ca[\{Re_6S_6Cl_2\}Cl_6]$ with $E(SiMe_3)_2$ (E = PhAs,

$PSiMe_3$, HN, O, S) afforded after addition of $PPr_3$ either the neutral cluster $[\{Re_6S_6X_2\}(PPr_3)_6]$ (X = As, P) or the ionic compounds $[\{Re_6S_6X_2\}(PPr_3)_6]^{2+}[\{Re_6S_6Cl_2\}Cl_6]^{2-}$ (X = NH, O, S) in high yields (> 60 %) [ 95 ]. A slightly different approach is the use of molten ligands or salts, for instance, reaction of $[\{Re_6S_4Br_4\}Br_6]$ with KNCS in a silica tube at 550 °C gives an access to the $[\{Re_6S_7Br\}Br_6]^{3-}$ ion which was crystallized as the salt $(PPh_4)_3[\{Re_6S_7Br\}Br_6]$ [ 73 ].

Oxygen atoms also may be incorporated into the cluster core. Heating a suspension of $[\{Re_6Se_4Cl_4\}Cl_6]$ in wet DMF afforded $[\{Re_6Se_4O_2Cl_2\}Cl_6]^{2-}$, whose two isomers were isolated [ 92 ]. In α-isomer the oxygen atoms are at opposite ends of a body diagonal of the cube $Se_4O_2Cl_2$, whereas in β-isomer they are *trans* on the same face. Note that similar ligand exchange was also observed in a high temperature solid state synthesis, namely oxy-bridged dicluster with oxychalcohalide core $[(\{Re_6S_5OCl_2\}Cl_5)_2O]^{4-}$ formed at 850 °C in a sealed silica tube [ 96 ].

Two octahedral rhenium cluster complexes with mixed ligand cluster core $\{Re_6Q_7O\}^{2+}$, namely $[\{Re_6Q_7O\}(3,5\text{-}Me_2PzH)_6]Br_2\cdot 3,5\text{-}Me_2PzH$ (Q = S or Se) have been obtained from reaction of $Cs_3[\{Re_6Q_7Br\}Br_6]$ (Q = S, Se) with wet molten 3,5-dimethylpyrazole (3,5-$Me_2PzH$) [ 97 ]. During the reaction, all six apical bromine ligands of the cluster complexes are substituted by the organic ligand. Additionally, the inner ligand $\mu_3$-Br in the cluster core $\{Re_6Q_7Br\}^{3+}$ is substituted by oxygen, giving cluster cores with mixed chalcogen/oxygen ligands. Note that there is no disorder: seven corner positions of the $Q_7O$ cube are occupied exclusively by S or Se atoms and one by an O atom. Reactions of $Cs_3[\{Re_6Q_7Br\}Br_6]\cdot H_2O$ (Q = S or Se) with molten $EPh_3$ (E = P, As or Sb) lead to *fac*-$[\{Re_6Q_7Br\}\cdot(EPh_3)_3Br_3]$ in a high yield without core modification [ 98, 99 ].

### *Details of the structures*

Thus, to date a significant number of various cluster complexes with $M_6Q_8$ cluster core with mixed inner ligand environment has been synthesized and described. The Table 3 summarizes known examples of such compounds. Structural and spectroscopic studies showed that often mixed ligand compounds are solid solutions of several isomers and moieties with various inner ligand distribution in the cluster core.

Two types of disorder can be regarded.

1) Orientational disorder of a single cluster moiety in crystal structure. This type of disorder results in averaged arrangement of inner ligands and averaged interatomic distances in cluster core, which prevent detailed structural analysis of interatomic distances as well as of distortion in metal

Table 3

*Interatomic distances in some hexamolybdenum and hexarhenium cluster complexes with mixed ligand ordered cluster cores*

| Compound | Cluster core | VEC | M—M, Å | M—$L^i$, Å | Ref. |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| Hexamolybdenum cluster complexes | | | | | |
| $(Bz_3NH)_3[Mo_6OCl_{13}]$<br>for $Mo_3$ face ligated by $\mu_3$-O | $\{Mo_6OCl_7\}^{3+}$ | 24 | 2.514—2.613<br>2.516—2.518 | 2.464—2.529 (Mo—Cl);<br>2.082—2.109 (Mo—O) | [ 90 ] |
| $Cs_3[Mo_6Br_{13}OBr_6]$ | $\{Mo_6Br_7O\}^{3+}$ | 24 | 2.5778—2.6488 | 2.603—2.6282 (Mo—Br);<br>2.125 (Mo—O) | [ 57 ] |
| $Mo_6Br_6S_3$ | $\{Mo_6Br_4S_4\}$ | 24 | 2.630—2.682 | 2.604—2.616 (Mo—Br);<br>2.396—2.496 (Mo—S) | [ 51 ] |
| $Mo_6S_6Br_2$ | $\{Mo_6S_6Br_2\}$ | 22 | 2.719—2.732 | 2.401—2.625 (Mo—Br);<br>2.475 (Mo—S) | [ 50 ] |
| $Rb_{12}[MoBr_6]_3[Mo_6Br_{13}Te]$ | $\{Mo_6Br_7Te\}^{3+}$ | 24 | 2.6341 | 2.589—2.608 (Mo—Br);<br>2.73 (Mo—Te) | [ 55 ] |
| $Cs_3[Mo_6I_{12.8}Se_{1.2}]$ | $\{Mo_6I_7Se\}^{3+}$ | 24 | 2.6560—2.7023 | 2.761—2.8013 (Mo—I); | [ 56 ] |

Continued Table 3

| 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|
| | and<br>$\{Mo_6I_6Se_2\}^{3+}$ | and<br>23 | | 2.535 (Mo—Se) | |
| $Cs_3[Mo_6I_{12.5}Se_{1.5}]$ | $\{Mo_6I_7Se\}^{3+}$<br>and<br>$\{Mo_6I_6Se_2\}^{3+}$ | 24<br>and<br>23 | 2.6582—2.7136 | 2.776—2.8017 (Mo—I);<br>2.523 (Mo—Se) | [ 56 ] |
| $Cs_3[Mo_6I_{12.4}Se_{1.6}]$ | $\{Mo_6I_7Se\}^{3+}$<br>and<br>$\{Mo_6I_6Se_2\}^{3+}$ | 24<br>and<br>23 | 2.6582—2.7200 | 2.774—2.8003 (Mo—I);<br>2.522 (Mo—Se) | [ 56 ] |
| Hexarhenium cluster complexes | | | | | |
| *fac*-$[Re_6S_7Br(PPh_3)_3Br_3]$<br>for $Re_3$ face ligated by $\mu_3$-Br | $\{Re_6S_7Br\}^{3+}$ | 24 | 2.582—2.627;<br>2.617—2.627 | 2.383—2.469 (Re—S);<br>2.587—2.595 (Re—Br) | [ 98 ] |
| *fac*-$[Re_6S_7Br(AsPh_3)_3Br_3]$<br>for $Re_3$ face ligated by $\mu_3$-Br | $\{Re_6S_7Br\}^{3+}$ | 24 | 2.581—2.630;<br>2.621—2.630 | 2.376—2.433 (Re—S);<br>2.610—2.619 (Re—Br) | [ 99 ] |
| *fac*-$[Re_6S_7Br(pyz)_3Br_3]$<br>for $Re_3$ face ligated by $\mu_3$-Br | $\{Re_6S_7Br\}^{3+}$ | 24 | 2.584—2.596;<br>2.596 | 2.396—2.455 (Re—S);<br>2.533 (Re—Br) | [ 105 ] |
| $[Re_6S_7O(3,5\text{-}Me_2PzH)_6]Br_2$<br>for $Re_3$ face ligated by $\mu_3$-O | $\{Re_6S_7O\}^{2+}$ | 24 | 2.521—2.600;<br>2.521—2.530 | 2.392—2.417 (Re—S);<br>2.114—2.129 (Re—O) | [ 97 ] |
| *cis*-$[Re_6S_6Br_2(PPh_3)_2Br_4]$<br>for $Re_3$ face ligated by $\mu_3$-Br | $\{Re_6S_6Br_2\}^{4+}$ | 24 | 2.595—2.658;<br>2.658* | 2.410—2.487 (Re—S);<br>2.615—2.637 (Re—Br) | [ 98 ] |
| *trans*-$[Re_6S_6Br_2(PPh_3)_2Br_4]$<br>for $Re_3$ face ligated by $\mu_3$-Br | $\{Re_6S_6Br_2\}^{4+}$ | 24 | 2.584—2.630;<br>2.622—2.630 | 2.430—2.459 (Re—S);<br>2.578—2.594 (Re—Br) | [ 98 ] |
| $(Bu_4N)_2[Re_6S_5OCl_8]$<br>for $Re_3$ face ligated by $\mu_3$-O | $\{Re_6S_5OCl_2\}^{4+}$ | 24 | 2.573—2.601;<br>2.516—2.531 | 2.435—2.438 (Re—S);<br>2.08—2.09 (Re—O) | [ 93 ] |
| *fac*-$[Re_6Se_7Br(PPh_3)_3Br_3]$<br>for $Re_3$ face ligated by $\mu_3$-Br | $\{Re_6Se_7Br\}^{3+}$ | 24 | 2.612—2.658;<br>2.632—2.649 | 2.489—2.528 (Re—Se);<br>2.611—2.619 (Re—Br) | [ 98 ] |
| *fac*-$[Re_6Se_7Br(AsPh_3)_3Br_3]$<br>for $Re_3$ face ligated by $\mu_3$-Br | $\{Re_6Se_7Br\}^{3+}$ | 24 | 2.612—2.649;<br>2.638—2.649 | 2.490—2.532 (Re—Se);<br>2.613—2.620 (Re—Br) | [ 99 ] |
| *fac*-$[Re_6Se_7Br(pyz)_3Br_3]$<br>for $Re_3$ face ligated by $\mu_3$-Br | $\{Re_6Se_7Br\}^{3+}$ | 24 | 2.615—2.628;<br>2.628 | 2.498—2.531 (Re—Se);<br>2.580 (Re—Br) | [ 105 ] |
| $[Re_6Se_7O(3,5\text{-}Me_2PzH)_6]Br_2$<br>for $Re_3$ face ligated by $\mu_3$-O | $\{Re_6Se_7O\}^{2+}$ | 24 | 2.547—2.639;<br>2.547—2.551 | 2.509—2.544 (Re—Se);<br>2.022—2.036 (Re—O) | [ 97 ] |
| $(Pr_4N)_2[\alpha\text{-}Re_6Se_4O_2Cl_8]$<br>for $Re_3$ face ligated by $\mu_3$-O | $\{Re_6Se_4O_2Cl_2\}^{4+}$ | 24 | 2.532—2.601<br>2.532—2.538 | 2.488—2.527 (Re—Se);<br>2.07—2.10 (Re—O) | [ 92 ] |
| $(Pr_4N)_2[\beta\text{-}Re_6Se_4O_2Cl_8]$<br>for $Re_3$ face ligated by $\mu_3$-O | $\{Re_6Se_4O_2Cl_2\}^{4+}$ | 24 | 2.516—2.614<br>2.516—2.535 | 2.475—2.527 (Re—Se);<br>2.06—2.09 (Re—O) | [ 92 ] |
| $Cs_{11}(H_3O)[Re_6Se_4O_4Cl_6]_3$ | $\{Re_6Se_4O_4\}^{2+}$ | 24 | 2.610—2.618**;<br>2.461—2.463***<br>2.539—2.548**** | 2.511—2.557 (Re—Se);<br>2.08—2.18 (Re—O) | [ 106 ] |
| $[Re_6Te_6Cl_6(TeCl_2)_2]$<br>for $Re_3$ face ligated by $\mu_3$-Cl | $\{Re_6Te_6Cl_2\}^{4+}$ | 24 | 2.614—2.680<br>2.614—2.648 | 2.634—2.711 (Re—Te);<br>2.476—2.502 (Re—Cl) | [ 68 ] |

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* For the Re atom coordinated by two $\mu_3$-Br atoms.

** For the Re atom coordinated by four $\mu_3$-Se atoms.

*** For the Re atom coordinated by four $\mu_3$-O atoms.

**** For the Re atoms coordinated by both $\mu_3$-Se atoms and $\mu_3$-O atoms.

cluster. Compounds with the $M_6Q_7X$ cluster core are the good examples of such disorder. In the case of large difference in atomic radii of ligands partial ($Cs_3[Mo_6Br_{13}OBr_6]$, $[Re_6Se_7O(3,5\text{-}Me_2PzH)_6]Br_2$) or full ordering ($(Bz_3NH)_3[Mo_6OCl_{13}]$) can take place.

2) Orientational disorder coupled with the presence of several cluster moieties and their isomers. This is a general case for the compounds with cluster core $\{M_6Q_{8-y}X_y\}$.

$^{77}$Se NMR study of solutions $Cs_{0.4}K_{0.6}(Et_4N)_{11}[\{Mo_6Br_6Se_2\}(CN)_6]_3 \cdot 16H_2O$ [ 10 ] showed that despite random Br/Se distribution over the inner positions in the crystal, the $[\{Mo_6Br_6Se_2\}(CN)_6]^{4-}$ anion exists as three geometric isomers with different arrangements of inner ligands: A, B, and C with $D_{3d}$, $C_{2v}$, and $C_{2v}$ symmetry, respectively (Fig. 2).

Each isomer contains one type of selenium atom, which corresponds to one resonance in the $^{77}$Se NMR spectrum. Theoretically in the case of statistic distribution of the isomers the spectrum should have three resonances with intensities 1:3:3. In fact the $^{77}$Se NMR spectrum of a solution of $[\{Mo_6Br_6Se_2\}(CN)_6]^{4-}$ exhibited three sharp signals with relative intensities 1:1.8:6.5 that was explained by an ″extra stability″ of the C isomer.

Similarly, $^{77}$Se NMR spectra of $(PPh_4)_2[\{Re_6Se_6Br_2\}Br_6]$ and $(Bu_4N)_2[\{Re_6Se_6Br_2\}Br_6]$ revealed the presence of three possible isomers, their distribution was nonequivalent. Note that $(PPh_4)_2[\{Re_6Se_6Br_2\}Br_6]$ was obtained by cation exchange from $K_2[\{Re_6Se_6Br_2\}Br_6]$, while $(Bu_4N)_2 \cdot [\{Re_6Se_6Br_2\}Br_6]$ was obtained by refluxing polymeric rhenium selenobromide $Re_6Se_6Br_6$ in DMF in the presence of an excess of $Bu_4NBr$. It shows that this isomery exists both in polymeric and in molecular complexes.

Full range of mixed chalcogen systems have been synthesized from the polymeric telluride $Re_6Te_{15}$ ($\{Re_6Te^{i}_8\}(Te_7)^{a-a}_{6/6}$). It was found that all 8 Te atoms in the cluster core $\{Re_6Te_8\}$ may be substituted by S or Se in reaction of $Re_6Te_{15}$ with elemental S or Se at 600°C. Thermal stability for these two systems also was studied and it has been shown that the Se/Te system is stable up to 900 °C whereas the S/Te system decomposes at the temperatures higher than 700 °C with the formation of tetrahedral cluster compound $Re_4S_4Te_4$ [ 12, 100 ]. Other series of mixed S/Te and Se/Te $Re_6$ cluster complexes have been synthesized by reaction of $Re_6Te_{15}$ with KSCN or with a mixture of Se and KCN or NaCN [ 11, 101—103 ]. It was shown that in such mixed chalcogen systems there is the possibility of cocrystallization of complexes with different S/Te or Se/Te ratios. Thus, $Re_6Te_{15}$ reacts with a mixture of Se and NaCN to give the salts $Na_4[\{Re_6Te_{8-x}Se_x\}(CN)_6]$. The substitution of Se for Te in the $[\{Re_6Te_{8-x}Se_x\}(CN)_6]^{4-}$ anions is dependent upon both Se/Te and Se/NaCN stoichiometry similar to that previously observed in $[\{Re_6Te_{8-x}S_x\}(CN)_6]^{4-}$. The family of $[\{Re_6Te_{8-x}Se_x\}(CN)_6]^{4-}$ anionic complexes was studied using $^{125}$Te and $^{77}$Se NMR [ 11, 103 ]. Very complex NMR spectra were observed, indicating that any solid phase with mixed ligands contains different chemical forms and includes almost all possible compositions from $[\{Re_6Te_8\}(CN)_6]^{4-}$ to $[\{Re_6Se_8\}(CN)_6]^{4-}$, and their geometric isomers (Fig. 8).

Presence of several moieties and their isomers makes these compounds chemically ingomogenius, since these moieties and their isomers have different chemical and physical properties. Thus, the measurement of photophysical properties of $[\{Re_6Q_7Br\}Br_6]^{3-}$ and isomerically pure $[\{Re_6Q_6Br_2\}Br_6]^{2-}$ (Q = S or Se) and $[\{Re_6Se_5Br_3\}Br_6]^{-}$ has shown that the replacement of one-three $\mu_3$ chalcogenide ligands in the $\{Re_6Q_8\}^{2+}$ core by Br atoms gives rise to extension of the emission band to near-infrared — infrared region. The luminescence intensity of the complex becomes weaker with the increase in the number of the Br atoms in the $\{Re_6Q_{8-x}Br_x\}^{x+2}$ core and lowering the symmetry of the core [ 104 ].

For some of compounds with $\{M_6(\mu_3\text{-}X)_8\}$ cluster core ordered ligand arrangement in crystal structure can occur. Such ordered complexes can be divided into two groups, namely: 1) compounds with oxygen as $\mu_3$-ligand; 2) molecular complexes with two types of terminal ligands, if one of them is a bulky neutral ligand like $TeCl_2$, or an organic molecule. Some interatomic distances for the ordered $Re_6$ complexes are summarized in Table 3.

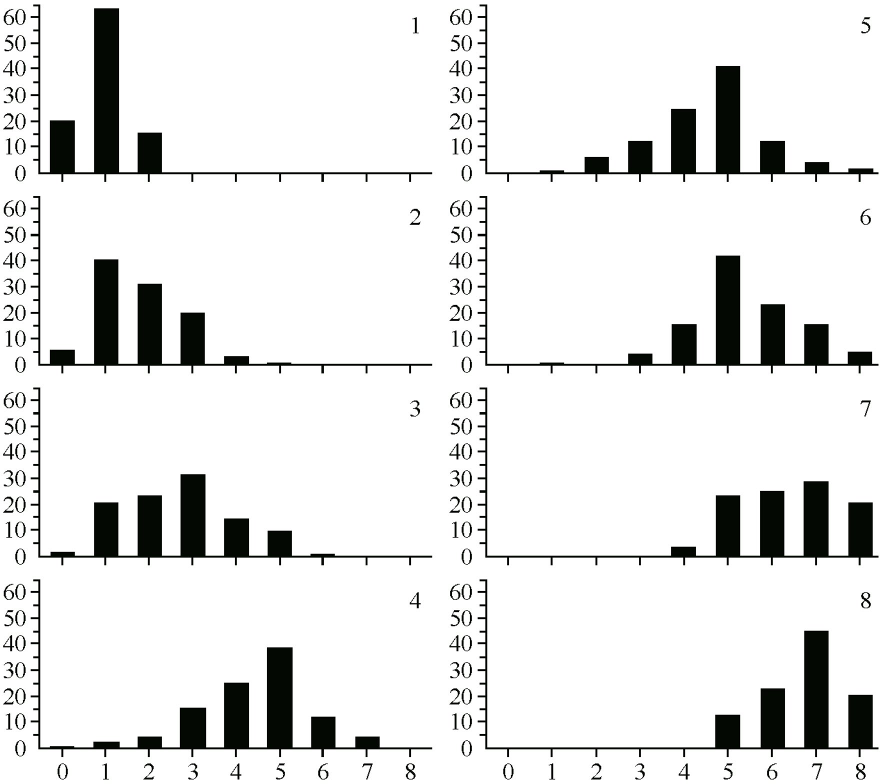

*Fig. 8*. Distribution of the $[\{Re_6Te_{8-x}Se_x\}(CN)_6]^{4-}$ ($x$ = 0—8) cluster anions depending on the composition of the initial cluster [ 11 ]

The reasons of ordering in the structure are:

1) *Large discrepancy of the atomic radii of the ligands*. Indeed, most of ordered structures found when oxygen or fluoride introduced in cluster core. The common distortions of metal cluster in cluster core $\{M_6(\mu_3\text{-}X)_8\}$ are presented in Fig. 9.

The compound $Cs_{11}(H_3O)[\{Re_6Se_4O_4\}Cl_6]_3 \cdot 4H_2O$ contains an unusual cluster core $\{Re_6Se_4O_4\}^{2+}$ with ordered inner ligands, where the 4 positions of one face of the $Se_4O_4$ cube, are occupied exclu-

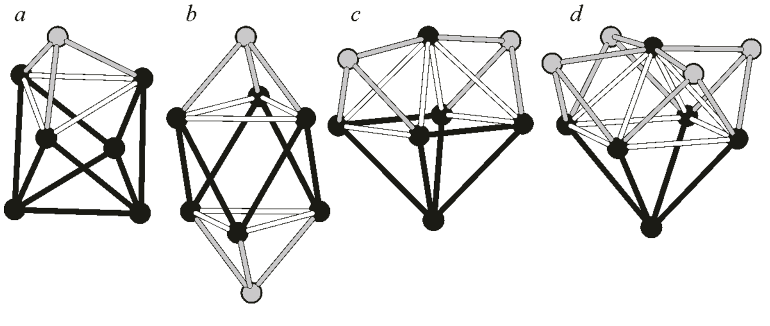

*Fig. 9*. Examples of metal cluster distortions as a consequence of mixed ligand inner environment (shortened Re—Re bonds are colored white; corresponding Re—Re distances can be seen in Table 3): *a*) $\{M_6L_7L'\}$ core exemplified by $\{Re_6Se_7O\}^{2+}$ in $[Re_6Se_7O(3,5\text{-}Me_2PzH)_6]Br_2$; *b*) and *c*) isomeric cores $\{M_6L_6L'_2\}$ exemplified by $\{Re_6Se_4O_2Cl_2\}^{4+}$ in $(Pr_4N)_2[\alpha\text{-}Re_6Se_4O_2Cl_8]$ and $(Pr_4N)_2[\beta\text{-}Re_6Se_4O_2Cl_8]$, respectively; *d*) $\{M_6L_4L'_4\}$ core exemplified by $\{Re_6Se_4O_4\}^{2+}$ in $Cs_{11}(H_3O)[Re_6Se_4O_4Cl_6]_3$. All ligands except oxygen atoms are omitted for clarity

sively by 4 Se atoms, and 4 O atoms lie in the opposite face. The compound was synthesized via interaction of cluster polymer $Re_6Se_8Br_2$ with molten KOH at 280 °C [ 106 ]. The non-equivalence of the $\mu_3$-ligands results in a considerable variation of the Re—Re distances, where the shortest bonds (2.4612(9)—2.4625(9) Å) include Re atom surrounded by O atoms, and the longest ones (2.6105(9)—2.6178(9) Å) are observed for Re surrounded by Se atoms.

2) *Low symmetry of apical ligand environment and packing in crystal structure*. The compound $[\{Re_6Te_6Cl_2\}Cl_4(TeCl_2)_2]$ (Fig. 7) contains a $Re_6$ octahedron residing inside a $Te_6Cl_2$ pseudocube. For the known $Re_6Q_{4+q}X_{10-2q}$ compounds, it is usual that each corner of a $Q_{4+q}X_{4-q}$ cube is occupied statistically by Q and X atoms. However, in this structure there is no disorder, and six corners of the $Te_6Cl_2$ cube are occupied exclusively by Te atoms. The two other corners of the cube are occupied exclusively by Cl atoms. The four Re atoms that are bonded to $\mu_3$-Cl ligands have terminal $Cl^-$ ligands. The two Re atoms that are bonded to $\mu_3$-Te anions are ligated by neutral $TeCl_2$ groups. The set of six outer ligands includes 4 chlorine atoms and 2 $TeCl_2$ groups, the latter being linked to the rhenium atoms through the Te atom.

From reaction of $Cs_2[\{Re_6S_6Br_2\}Br_6]$ with molten $PPh_3$ two type of crystals were separated: *cis*-$[\{Re_6S_6Br_2\}(PPh_3)_2Br_4]$ and *trans*-$[\{Re_6S_6Br_2\}(PPh_3)_2Br_4]$ [ 98 ]. Positions of the inner ligands in mixed chalcobromide cluster cores $\{Re_6S_7Br\}^{3+}$ and $\{Re_6S_6Br_2\}^{4+}$ are ordered. It is interesting to note that these compounds are neutral molecular complexes, the composition strongly depending on the charge of the cluster core $\{Re_6Q_{8-x}Br_x\}^{x+2}$ in the starting complexes. These results differ from the previously described reactions of chalcobromide octahedral rhenium cluster complexes with 3,5-dimethylpyrazol, where all six terminal Br ligands were substituted by organic molecules. Note that the neutral complexes with mixed-ligand apical ligand environment were obtained in reactions with a large excess of $EPh_3$. Reactions of $Cs_3[\{Re_6Q_7Br\}Br_6]\cdot H_2O$ with molten pyrazine (pyz) were investigated [ 105 ]: it turned out that this reaction at 140 °C for 2 days in a sealed glass tube afforded very interesting supramolecular compounds, built up from *fac*-$[\{Re_6Q_7Br\}(pyz)_3Br_3]$ (Q = S, Se).

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