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On the Way Towards Fine Inorganic Synthesis: Manipulating Bridging Ligands in Chalcogenide Clusters

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Abstract—This review describes approaches to the targeted multistep synthesis of coordination compounds exemplified by Group 5 and 6 metal chalcogenide and oxide clusters and polynuclear compounds. Methods for the introduction of two different chalcogen atoms and methods for the synthesis of mixed oxide chalcogenide complexes are considered.

Keywords: inorganic synthesis, clusters and polynuclear compounds, polyoxometallates, transition metals
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Synthesis of new compounds is the core of chemistry. This is not only an efficient means for understanding of chemical laws, but also a necessary stage on the way to the long-proclaimed goal, namely, creation of compounds and materials with specified properties. The advances in the synthesis are usually demonstrated by vivid examples from organic chemistry in which planning and implementation of multistep (tens of steps!) syntheses of complex compounds, mainly natural ones, became possible back several decades ago. It became possible to speak of fine organic synthesis. Is anything like that possible in coordination chemistry, a field that is traditionally attributed to inorganic chemistry, but resembles organic chemistry in ideology? It is symptomatic that two key persons of coordination chemistry, Werner and Chugaev, first worked as organic chemists. Indeed, both researchers heading their schools made a large body of work in the coordination chemistry of Cr(III), Co(III), Pt(II), and Pt(IV), being guided by the classical strategy of organic chemistry: substitution, addition, elimination, and isomerization [1]. The formulation and ingenious use of the *trans*-effect principle allowed, for example, the targeted synthesis of Pt(IV) complexes with six different ligands [2]. However, soon the applicability limits were revealed for the classical approach, which is suitable only for complexes that are kinetically inert to substitution and have d^3 and low-spin d^6 and d^8 electron configurations. Exactly the inertness of these complexes is responsible for applicability of strategy developed for organic synthesis. The classical strategy is still utilized to develop the chemistry of Ru(II) and Os(II) nitrosyl complexes (the low-spin d^6-configuration ensures the required inertness) [3, 4]. In other cases, the lability of the coordination sphere precludes this approach. An exception is provided by low-spin transition metal carbonyl complexes and π-complexes derived from them, which resemble organic compounds by not only "preparative" inertness, but also the predictable electronic structure (18-electron rule) and invariable coordination number. This analogy is vividly illustrated by the isolobal principle proposed and developed by R. Hoffmann [5]. Therefore, organometallic chemistry of transition metals is now characterized by a high degree of predictability and the possibility to conduct rather multistep sequences of transformations [6, 7]. Recently, a promising trend appeared in the chemistry of polynuclear carboxylates, in particular, rather predictable step-by-step assembly of polynuclear systems from stable homo- and heterometallic fragments of lower nuclearity and binding of such fragments to give coordination polymers. This can be done by using combinations of 3*d* and 4*f* elements and even *d* and *s* elements [8, 9]. The supramolecular coordination chemistry stands somewhat apart; its current state enables the synthesis of topologically complex structures, molecular machines, and devices; however, it is largely based on multistep fine organic synthesis [10–12].

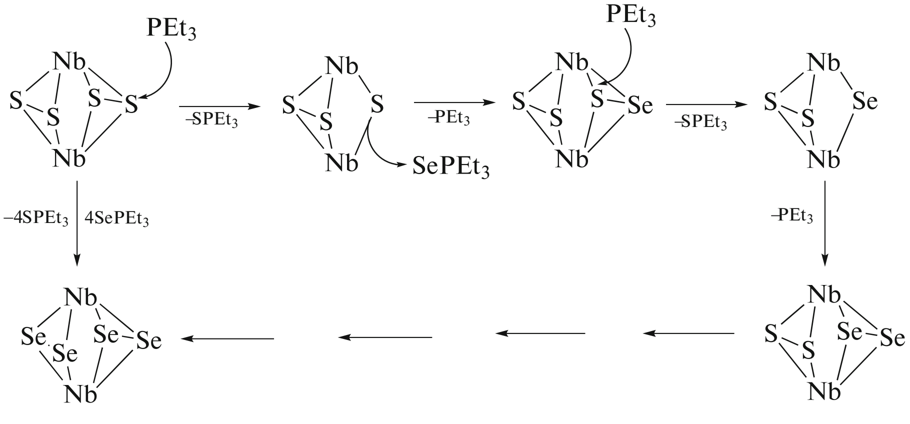
New opportunities for intricate, multistep inorganic synthesis were provided in the 1970–1980s by vigorous development of the chemistry of cluster compounds [13]. The possibility of modification of the number and nature of metal atoms in the metal core was widely used, first of all, in the chemistry of carbonyl and related organometallic clusters, including the synthesis of chiral cluster cores [14–18].

The chemistry of transition metal chalcogenide clusters has been elaborated somewhat later; currently it can serve for rather intricate, multistep transformations to prepare clusters with a specified structure and composition of the metal core, including nitrogenase models based on iron sulfide and iron molybdenum sulfide clusters [19–23].

A specific feature of the chemistry of non-carbonyl, so-called “high-valence” clusters is the presence of bridging (or capping) ligands, most often, halide, oxide, or chalcogenide ones, strongly bound to the metal core. Unlike manipulations with the number and nature of metal atoms, the development of selective methods for the synthesis of transition metal clusters with different types of bridges is a non-trivial task and a sort of challenge for a synthetic chemist. The difficulties of this trend are well illustrated in a recent review [24]. In the case of metal clusters containing bridging chalcogen atoms differing in geometric positions, the selectivity can be attained by either cluster self-assembly in which two different chalcogen atoms enter specific positions or selective exchange associated with different reactivities of structurally nonequivalent chalcogen atoms.

The selective preparation of mixed-chalcogenide clusters can be accomplished by two fundamentally different approaches. If the bridging chalcogen atoms in the cluster are nonequivalent, the selectivity can be attained by either cluster self-assembly in which two different chalcogen atoms enter their specific positions corresponding to the minimum energy (thermodynamic approach) or selective exchange of chalcogen atoms associated with different reactivities of structurally nonequivalent atoms (kinetic approach). The cases where the cluster contains bridging polychalcogenide (most often, dichalcogenide) ligands should be specially distinguished; in this case, bonds can arise between two different chalcogen atoms (SeS^{2-}, TeS^{2-}, and $TeSe^{2-}$ ligands). This situation occurs in a number of binuclear complexes of iron, vanadium, chromium, and niobium. For example, the reaction of a mixture of Na_2TeO_3 and Na_2SeO_3 with $[Fe(CO)_5]$ in the presence of KOH in methanol affords a mixture of trinuclear complexes, $[Fe_3(CO)_9(\mu_3\text{-Se})(\mu_3\text{-Te})]$, $[Fe_3(CO)_9(\mu_3\text{-Se})_2]$, and $[Fe_3(CO)_9(\mu_3\text{-Te})_2]$, which cannot be separated by chromatography. If this mixture is successively treated with sodium methoxide and an acid, the reaction gives a set of binuclear complexes, $[Fe_2(CO)_6(\mu\text{-SeTe})]$, $[Fe_2(CO)_6(\mu\text{-Se}_2)]$, and $[Fe_2(CO)_6(\mu\text{-Te}_2)]$, which can be separated to obtain pure $[Fe_2(CO)_6(\mu\text{-SeTe})]$, the first complex with the $SeTe^{2-}$ ligand [25]. Irradiation of a solution of $[Fe_2(CO)_6(\mu\text{-SeTe})]$ in the presence of $[Fe(CO)_5]$ results in a quantitative formation of $[Fe_3(CO)_9(\mu_3\text{-Se})(\mu_3\text{-Te})]$. The complexes $[Fe_2(CO)_6(\mu\text{-SSe})]$ [26] and $[Fe_2(CO)_6(\mu\text{-STe})]$ [27] were prepared in a similar way. All complexes of the $[Fe_2(CO)_6(\mu\text{-QQ'})]$ type ($Q = Q'$, $Q \neq Q'$) are highly reactive towards insertion of other transition metal atoms into the Q–Q bond, which was used to prepare heterometallic clusters [25, 26, 28].

In the reaction of niobium selenochloride $NbSe_2Cl_2$, which is described by the crystal chemical formula $_\infty[Nb_2(Se_2)_2Cl_{8/2}]$, with a potassium thiocyanate melt, selenium is replaced by sulfur and complexes containing SeS^{2-} ligands are formed as intermediates [29]. However, the reaction is not selective and cannot serve for the preparation of single representatives of the $\{Nb_2S_xSe_{4-x}\}^{4+}$ family. The reverse replacement of sulfur by selenium is also possible: the dithiocarbamate complex $[Nb_2(S_2)_2(Et_4NCS_2)_4]$ reacts with $SePEt_3$ in the presence of PEt_3 to give $[Nb_2(Se_2)_2(Et_4NCS_2)_4]$ [30]. The reaction requires the presence of some free phosphine. The putative sequence of steps is shown in Scheme 1 and includes the formation of intermediates with the SeS^{2-} ligands.



Scheme 1.

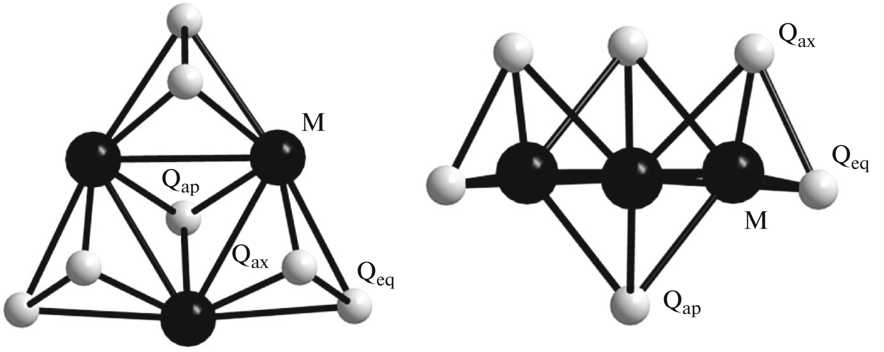
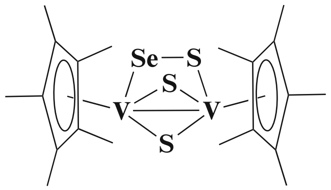


Fig. 1. Structure of $\{M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q_2)_3\}^{4+}$ (M = Mo, W; Q = S, Se, Te): (a) top view and (b) side view.

The intermediate complexes with the SeS^{2-} ligand cannot be isolated in a pure state. However, upon a similar reaction between $[Nb_2(S_2)_2(Et_4NCS_2)_4]$ and $TePEt_3$, the isolation of the complex $[Nb_2(S)(Te_2)(Et_4NCS_2)_4]$ containing simultaneously μ-S and μ-Te_2 ligands was successful [30].

The intermediate steps of this reaction include the attack by the selenium source (PEt_3Se) on the monosulfide ligand arising upon elimination of a sulfur atom from the disulfide ligand by free phosphine. The reaction of $[Cp_2^*V_2(\mu_2\text{-}S)_3]$ and Na_2Se_5, resulting in $[Cp_2^*V_2(\mu_2\text{-}S)_2(\mu_2\text{-}SSe)]$ (Scheme 2), which was isolated in a pure state, is likely to proceed in a similar way [31].



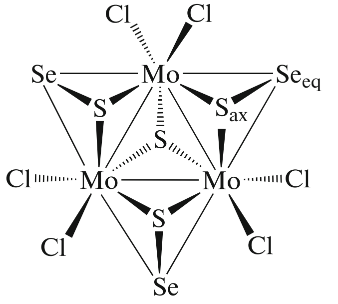
Scheme 2.

It was shown by spectroscopic methods that the reaction of the chromium monoselenide complex $[Cp(CO)_2Cr{\equiv}Se{\equiv}Cr(CO)_2Cp]$ with S_8, giving $[Cp(CO)_2Cr{\equiv}S{\equiv}Cr(CO)_2Cp]$ as the final product, involves the formation of $[Cp_2Cr_2(CO)_5(SSe)]$ and $[Cp_2Cr_2(CO)_4(SSe)]$ with the SeS^{2-} ligand, which were not isolated [32].

The trinuclear $\{M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q_2)_3\}^{4+}$ clusters (M = Mo, W; Q = S, Se, Te) are the most interesting objects for studying the selective introduction of two different chalcogen atoms into the cluster core. They contain three sorts of chalcogen atoms: an apical atom (Q_{ap} or μ_3-Q), three equatorial atoms located virtually in the M_3 plane (μ_2-Q_{eq}), and three axial atoms located above the triangle plane opposite to the apical atom (μ_2-Q_{ax}) (Fig. 1).

Thus, each μ_2-Q_2 bridging ligand can be represented as μ_2-$Q_{eq}Q_{ax}$. Therefore, in the case of two sorts of chalcogen atoms, various types are *a priori* possible for selective incorporation of one of them into any of three sites, including $\mu_2\text{-}Q'_{eq}Q''_{ax}/\mu_2\text{-}Q''_{eq}Q'_{ax}$ isomerism. The interest in selective generation of mixed-chalcogen $\{M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q_2)_3\}^{4+}$ complexes is due to the fact that physicochemical properties of complexes can be controlled by replacing one chalcogen atom by another. In particular, this is important for the design of molecular conductors based on chalcogenide clusters involving numerous specific intermolecular nonvalence Q···Q contacts, which play an important role in the electron transport [33–35]. As an example, consider the well-known semiconductor $[Mo_3S_7(Dmit)_3]$ with E_a = 12–22 meV, in which the $[Mo_3S_7(Dmit)_3]$ units are linked via the $\mu_3\text{-}S\cdots\mu_2\text{-}S_2$ contacts, thus forming conducting stacks [33]. Meanwhile, charge transfer salts based on the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Cl_6]^{2-}$ and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3Br_6]^{2-}$ cluster anions and bis(ethylenedithio)tetrathiafulvalene can be either semiconductors or insulators, which is determined by different types of chalcogen–chalcogen and chalcogen–halogen interactions [36, 37]. It is evident that the synthesis of mixed-chalcogen trinuclear clusters in which chalcogen atoms of different sorts would occupy strictly defined sites will help to better understand the contributions of each type of nonvalence contacts and the conduction mechanism and to optimize the conducting properties.

Several approaches can be used to obtain mixed-chalcogen trinuclear clusters. One of them is based on the empirical fact that the equatorial chalcogen atoms, being more reactive, are the first to be replaced in the chalcogen substitution reactions. Higher lability of chalcogen atoms in equatorial positions can be attributable to metal–chalcogen bond length, which are regularly greater for equatorial atoms than to axial atoms by up to ~0.1 Å [38]. This approach was used to prepare clusters with the $\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3\}^{4+}$ core (Scheme 3). They were identified for the first time in halide complexes, which are formed in high yields upon heating of $[Mo_3S_7X_6]^{2-}$ (X = Cl, Br) with $SePPh_3$. Selenium atoms occupy only equatorial positions. The axial and, the more so, the central sulfur atom are not displaced even with excess $SePPh_3$. The salt $(Ph_3EtP)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3Cl_6]$ is the first example of structurally characterized compound containing the SeS^{2-} ligand [39]. Later, crystal structures were determined for $(PPN)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_a\text{-}Se_{eq})_3Cl_6]$ [40] and $(TTF)(TBA)[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_a\text{-}Se_{eq})_3Br_6]$ (TTF = bis(ethylenedithio)tetrathiafulvalene, TBA = tetrabutylammonium) [36]. The latter salt was obtained by electrooxidation of TTF in the presence of the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3Br_6]^{2-}$ anions.



Scheme 3.

The aquation of $(Et_4N)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}\text{-}Se_{eq})_3Br_6]$ in 4 M HPts (*para*-toluenesulfonic acid) gives the aqua complex $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3\text{-}(H_2O)_6]^{4+}$, which reacts with water-soluble phosphine PR_3^{3-} (R = $C_6H_4SO_3$) to give quantitatively $[Mo_3S_4(H_2O)_9]^{4+}$. The rate constant of this reaction (2 M HPts) is 1.48×10^5 M^{-1} s^{-1} [41, 42]:

$$\left[Mo_3S_4Se_3\left(H_2O\right)_6\right]^{4+} + 3PR_3^{3-}$$
$$\rightarrow \left[Mo_3S_4\left(H_2O\right)_9\right]^{4+} + 3SePR_3^{3-}.$$

Similarly, the reaction of the tungsten complex $(Ph_4P)_2[W_3S_7Br_6]$ with $SePPh_3$ affords $(Ph_4P)_2[W_3\text{-}(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3Br_6]$. The complete consumption of the starting thio complex $[M_3S_7X_6]^{2-}$ is conveniently detected by Raman spectroscopy as the disappearance of the strong ν(S–S) band at 550 cm^{-1} and appearance of a new strong ν(S–Se) band at 450 cm^{-1}.

One more reagent for the introduction of selenium into the triangular cluster is potassium selenocyanate. If the reaction of $[M_3S_7X_6]^{2-}$ with KNCSe is conducted in the presence of excess KNCS, the reaction gives $[M_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3(NCS)_6]^{2-}$ (M = Mo, W; X = Cl, Br). These reactions are irreversible; even an excess of KNCS or PPh_3S does not convert $\{M_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3\}^{4+}$ back to $\{M_3S_7\}^{4+}$. In the case of tungsten, reverse reaction of selenium elimination from $[W_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3(NCS)_6]^{2-}$ takes place to afford the $\{W_3S_4\}^{4+}$ cluster. Unlike halide complexes, the dithiocarbamate complex $[Mo_3S_7(Dtc)_3]Dtc$ (Dtc = diethyldithiocarbamate) does not react with PPh_3Se, but it can be converted to $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}\text{-}Se_{eq})_3(Dtc)_3]SeCN$ by treatment with KNCSe in CH_3CN at room temperature. The structure of this salt incorporates nearly linear $(S\text{–}Se\cdots Se\cdots S\text{–}Se\cdots Se\cdots)_n$ chains formed via short (2.9–3.3 Å) cation – anion contacts. The S–Se distances in the SSe ligand are 2.16–2.23 Å [43].

A similar dithiocarbamate complex, $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3(Dtc)_3]Br$, is produced upon the reaction of $[Mo_3S_4(CH_3CN)_9]^{4+}$ with $Se(Dtc)_2$ [42]. In his case, the S^{2-} ligands are converted to SeS^{2-}.

The high degree of regioselectivity of these reactions was demonstrated by isotopomer experiments. The isotope exchange reactions between $(Et_4N)_2\text{-}[M_3{}^{34}S_7Br_6]$ (M = Mo, W) and $K^{32}SCN$ taken in 1 : 100 ratio give only complexes $(Et_4N)_2[M_3(\mu_3\text{-}{}^{34}S)(\mu_2\text{-}{}^{34}S_{ax}{}^{32}S_{eq})_3(NCS)_6]$ containing the ${}^{32}S_{eq}\text{–}{}^{34}S_{ax}$ ligand, as indicated by isotope shifts in the Raman spectra. The axial sulfur atoms and the μ_3-S atom are not affected by this exchange [44]:

$$\left(Et_4N\right)_2\left[M_3{}^{34}S_7Br_6\right] + 6K^{32}SCN$$
$$\rightarrow \left(Et_4N\right)_2\left[M_3(\mu_3\text{-}{}^{34}S)(\mu_2\text{-}{}^{34}S_{ax}{}^{32}S_{eq})_3\left(NCS\right)_6\right].$$

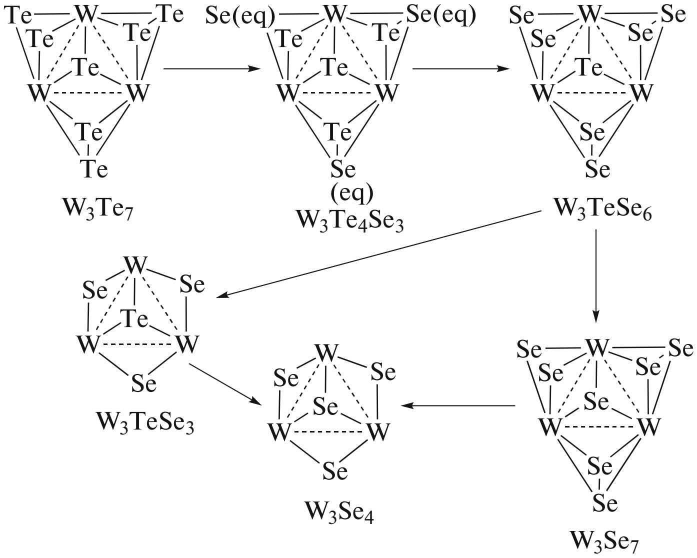
Low-melting KNCSe (T_m = 100°C, decomp.) was used in ligand exchange reactions with the $[M_3Te_7I_2I_{4/2}]^2_\infty$ cluster polymers and their sulfide and selenide analogues belonging to the same triangular cluster family. The reactions were conducted by heating solid chalcohalides in a KNCSe melt at 200°C followed by extraction into water [45]. In the case of $Mo_3Te_7I_4$, tellurium was completely displaced from the $\{Mo_3Te_7\}^{4+}$ core:

$$Mo_3Te_7I_4 + 7KCNSe$$
$$\rightarrow K_2\left[Mo_3Se_7\left(CN\right)_6\right] + 7Te + 4KI + KCN.$$

The same product is formed in the reaction of $Mo_3Se_7Br_4$ with a KCNSe melt, which is the method of choice for the preparation of $[Mo_3Se_7(CN)_6]^{2-}$. According to mass spectrometry data, the reaction of $Mo_3Te_7I_4$ with KCNSe is stepwise and gives $[Mo_3Te_4Se_3(CN)_6]^{2-}$ in an intermediate step. The chalcogen exchange in $Mo_3S_7Br_4$ in a KCNSe melt also proceeds via $[Mo_3S_4Se_3(CN)_6]^{2-}$ and $[Mo_3S\text{-}Se_6(CN)_6]^{2-}$, with $[Mo_3Se_7(CN)_6]^{2-}$ being formed as the final product.

With the assumption that the exchange of Te for Se is as regioselective, as the exchange of S for Se in the above examples, the Se atoms should first enter the equatorial positions in the $\{M_3(\mu_3\text{-}Q)(\mu\text{-}Q_{ax}\text{–}Q_{eq})_3\}^{4+}$ core. For the reaction between $W_3Te_7Br_4$ and KNCSe, the successive formation of $[W_3Te_4Se_3(CN)_6]^{2-}$,

$[W_3Te_3Se_4(CN)_6]^{2-}$, $[W_3Te_2Se_5(CN)_6]^{2-}$, $[W_3TeSe_6(CN)_6]^{2-}$, and $[W_3Se_7(CN)_6]^{2-}$ was demonstrated by mass spectrometry (Scheme 4). Unlike the molybdenum analogue, $[W_3Se_7(CN)_6]^{2-}$ easily splits off selenium from equatorial positions under the reaction conditions to give $[W_3Se_4(CN)_9]^{5-}$ as the final product [45].



Scheme 4.

By thorough control over the course of the reaction, it is possible to isolate the mixed Se/Te complex $K_3\{[W_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_{ax}Se_{eq})_3(CN)_6]Br\} \cdot 6H_2O$ (Fig. 2), in which the Se atoms are selectively located in the equatorial positions of dichalcogenide ligands. Currently, this complex is the only structurally characterized compound with the $TeSe^{2-}$ ligand.

The $W_3Se_7Br_4$ and $W_3S_7Br_4$ polymers react with a KCNSe melt to be converted to $[W_3Se_4(CN)_9]^{5-}$ and $[W_3S_4(CN)_9]^{5-}$, respectively, in agreement with the lower stability of the $\{W_3Q_7\}^{4+}$ cores, which readily lose three chalcogen atoms of the $\mu_2\text{-}Q_2$ ligands, being converted to more stable $\{W_3Q_4\}^{4+}$ clusters.

The addition of KCN to an aqueous extract of the reaction products formed from $W_3Te_7Br_4$ and KNCSe resulted in isolation of $K_5[W_3(\mu_3\text{-}Te)(\mu_2\text{-}Se)_3(CN)_9]$ [45] containing the $\{W_3(\mu_3\text{-}Te)(\mu_2\text{-}Se)_3\}^{4+}$ cluster core (Fig. 3). Presumably, the CN^- ion attacks either the Te atom in $[W_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_{ax}Se_{eq})_3(CN)_6]^{2-}$ (the $TeCN^-$ ion formed in an initial stage is unstable in aqueous solution and decomposes to CN^- and Te), or Se atom in $[W_3(\mu_3\text{-}Te)(\mu_2\text{-}Se_{ax}Se_{eq})_3(CN)_6]^{2-}$. The nucleophilic attack by the $SeCN^-$ on Te with successive replacement of tellurium by selenium cannot be ruled out either. It is known that the $\{M_3Q_4\}^{4+}$ cluster cores can (in very rare cases) be sensitive to the chalcogen exchange, as indicated by the unexpected generation of $[Mo_3(\mu_3\text{-}S)Te_3(\textit{iso}\text{-}PrO)_2PS_2)_3(PAB)(PBu_3)]$, PAB = *para*-aminobenzoate from $[Mo_3Te_7(Dtp)_3]I$ (the dithiophosphate ligand serves as the source of the sulfur atom) [46].

Apparently, this lability is caused by the fact that the M–Te bond is the weakest one out of the metal–chalcogen bonds, which enables the replacement of

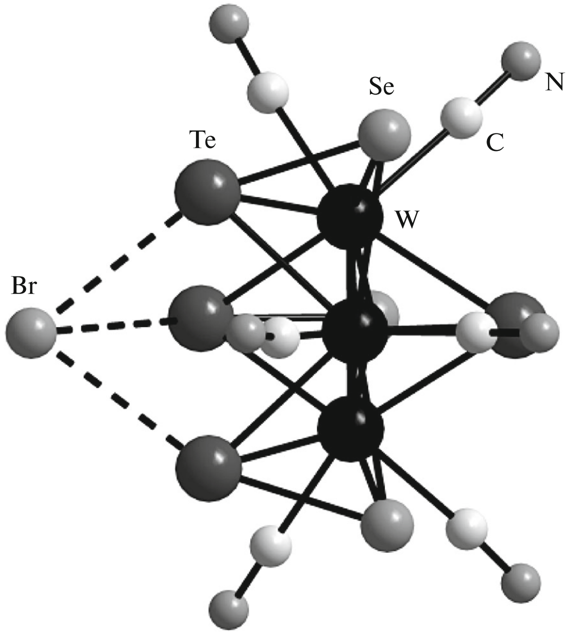


Fig. 2. Structure of the $\{[W_3Te_4Se_3(CN)_6]Br\}^{3-}$ associate in $K_3\{[W_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_{ax}Se_{eq})_3(CN)_6]Br\} \cdot 6H_2O$.

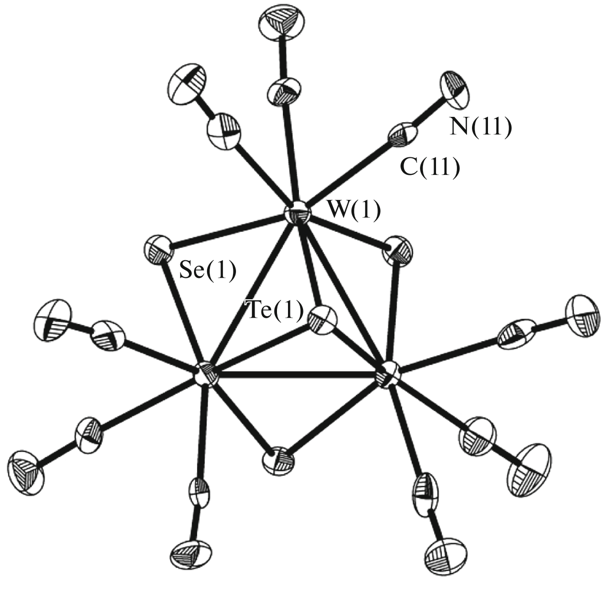


Fig. 3. Structure of $[W_3(\mu_3\text{-Te})(\mu_2\text{-Se})_3(CN)_9]^{5-}$.

tellurium by atoms of lighter chalcogens under relatively mild conditions.

It should be borne in mind that the reactivity of disulfide and diselenide ligands in the $\{M_3Q_7\}^{4+}$ clusters sharply differs from that of ditelluride ligands. The bridging S_2 and Se_2 groups in $\{M_3Q_7\}^{4+}$ react with nucleophiles such as CN^-, triarylphosphines, or thiols to give $\{M_3Q_4\}^{4+}$ clusters, while the $\{M_3Te_7\}^{4+}$ clusters either remain unaffected under these conditions or require more bulky trialkylphosphines for elimination of tellurium [46, 47]. Conversely, sulfide and selenide clusters are rather stable with respect to electrophilic reagents (H^+, dihalogens) [48]. The ditelluride ligands are susceptible to electrophiles. Indeed, the reaction of $[Mo_3Te_7((EtO)_2PS_2)_3]I$ with S_2Cl_2 in 1 : 5 molar ratio results in the partial regioselective tellurium displacement by sulfur and gives $[Mo_3Te_{4.74}S_{2.26}((EtO)_2PS_2)_3]I_{0.72}Cl_{0.28}$ [49]. According to X-ray diffraction data, ~90% of Te_{ax} and~50% of Te_{eq} positions are occupied by tellurium atoms. In the mass spectrum of $[Mo_3Te_{4.74}S_{2.26}((EtO)_2PS_2)_3]I_{0.72}Cl_{0.28}$, the distribution of the $\{Mo_3Te_{7-x}S_x\}^{4+}$ cluster species varies, with x being 0 to 5. The reaction of $[Mo_3Te_7((EtO)_2PS_2)_3]I$ with a large excess of S_2Cl_2 (1 : 15 molar ratio) gives a product with the composition $[Mo_3Te_4S_3((EtO)_2PS_2)_3]I$. This is not a single compound, but a mixture of $[Mo_3Te_2S_5((EtO)_2PS_2)_3]^+$, $[Mo_3Te_3S_4((EtO)_2PS_2)_3]^+$, $[Mo_3Te_4S_3((EtO)_2PS_2)_3]^+$, and $[Mo_3Te_5S_2((EtO)_2PS_2)_3]^+$ with the S_2^{2-}, TeS^{2-}, and Te_2^{2-} ligands. Thus, the degree of displacement of axial tellurium atoms increases with increasing amount of S_2Cl_2; the μ_3-Q capping position remains invariable and corresponds to 100% Te content. The observed situation is in line with the reactivity series $Te_{eq} > Te_{ax} > \mu_3$-Te. From analysis of the Q–Q distances in the $\{M_3Q_7\}$ clusters, the expected S–Te bond length is 2.35–2.40 Å. Indeed, the S–Te distances found in both products (2.35–2.39 Å) fall in this range.

Upon the reaction of $[W_3(\mu_3\text{-Te})(\mu_2\text{-Te}_2)_3((EtO)_2PS_2)_3]Br$ with S_2Cl_2, the product $[W_3Te_{4.30}S_{2.70}((EtO)_2PS_2)_3]Br_{0.62}Cl_{0.38}$ was isolated [49]. It could have formed in the following way:

$$\left[W_3Te_7\left((EtO)_2PS_2\right)_3\right]^+ + 3S_2Cl_2$$
$$\rightarrow \left[W_3Te_4\left((EtO)_2PS_2\right)_3\right]^+ + 3\text{“TeCl}_2\text{”} + 6S,$$
$$\left[W_3Te_4\left((EtO)_2PS_2\right)_3\right]^+ + 3S$$
$$\rightarrow \left[W_3Te_4S_3\left((EtO)_2PS_2\right)_3\right]^+.$$

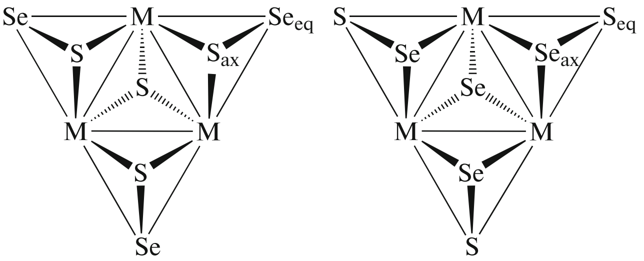
The replacement of tellurium by sulfur occurs mainly in equatorial positions: the Q_{ax} positions are predominantly occupied by Te atoms, whereas the Q_{eq} positions are occupied by both S and Te. In the mass spectra of products, peaks of $[W_3Te_4S_3((EtO)_2PS_2)_3]^+$ predominate. The spectrum exhibits medium-intensity signals for $[W_3Te_3S_4((EtO)_2PS_2)_3]^+$ and $[W_3Te_7((EtO)_2PS_2)_3]^+$ and minor signals for $[W_3Te_5S_2((EtO)_2PS_2)_3]^+$ and $[W_3Te_6S((EtO)_2PS_2)_3]^+$.

Thus, regioselectivity of substitution and elimination reactions is inherent in all clusters of the $\{M_3Q_7\}$ type (Q = S, Se, Te) for which the elimination or chalcogen exchange reactions affect mainly the equatorial positions, probably, because of weaker chalcogen binding [50].

The $[W_3(\mu_3\text{-Te})(\mu_2\text{-Te}_2)_3((EtO)_2PS_2)_3]Br$ complex does not react with soft electrophiles Ph_3PX_2 (X = Cl, Br), but reacts with Br_2 to give $[W_3Te_{4.25}S_{2.75}((EtO)_2PS_2)_3]Br$ with the TeS^{2-} ligand [49]. The formation of mixed-chalcogen $[W_3Te_4S_3((EtO)_2PS_2)_3]^+$ complex can be interpreted by the following sequence of reactions:

$$W_3Te_7^{4+} + 3Br_2 \rightarrow W_3Te_4^{4+} + 3\text{“TeBr}_2\text{,”}$$
$$2(EtO)_2PS_2^- + Br_2$$
$$\rightarrow (EtO)_2P(S)\text{–S–S–}P(S)(OEt)_2 + 2Br^-,$$
$$W_3Te_4^{4+} + 3(EtO)_2P(S)\text{–S–S–}P(S)(OEt)_2$$
$$\rightarrow W_3Te_4S_3^{4+} + 3(EtO)_2P(S)\text{–S–}P(S)(OEt)_2.$$

The $\{M_3(\mu_3\text{-Se})(\mu_2\text{-Se}_{ax}S_{eq})_3\}^{4+}$ clusters containing the $\mu_2\text{-Se}_{ax}S_{eq}^{2-}$, ligand are isomeric to those described above, because selenium atoms occupy axial positions (Scheme 5). This type of coordination of the SeS^{2-} ligand was first detected in the $[Mo_3(\mu_3\text{-S}_{0.65}Se_{0.35})(\mu\text{-Se}_{ax}S_{eq})_3((EtO)PS_2)_3]I$ complex obtained by the reaction of $[Mo_3(\mu\text{-}S_{0.65}Se_{0.35})Se_3((EtO)PS_2)_4(Py)]$ with H_2S in the presence of I_2 [51]. Selenium-containing $\{M_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_{ax}Se_{eq})_3\}^{4+}$ clusters do not undergo chalcogen exchange reactions with sulfur sources (Ph_3PS, KNCS) under mild conditions. Therefore, the reaction of selenide $\{M_3(\mu_3\text{-}Q)(\mu_2\text{-}Se)_3\}^{4+}$ clusters with sources of "active" sulfur ($H_2S + I_2$, polysulfides) proved to be appropriate for the preparation of $\{M_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_{ax}S_{eq})_3\}^{4+}$. The reaction of $[M_3Se_4(H_2O)_9]^{4+}$ with P_4S_{10} in ROH results in the selective formation of $[M_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_{ax}S_{eq})_3((RO)_2PS_2)_3]Cl$, (M = Mo, W; R = Et, *iso*-Pr) [52]. Here phosphorus sulfide acts as both the source of the $(RO)_2PS_2$ ligand (according to the equation $P_4S_{10} + 8EtOH \rightarrow 4(EtO)_2P(S)SH + 2H_2S$) and the source of "active" sulfur, which converts μ_2-Se to μ_2-$Se_{ax}S_{eq}$. Most likely, this "active" sulfur comes from a mixture of di-, tri-, and tetrasulfides, $(RO)_2P(S)S_nP(S)(OR)_2$, which is present in the products of reaction between P_4S_{10} and ROH [53].



Scheme 5.

Selective introduction of one of the chalcogen atoms into the capping μ_3-position. Since the chalcogen atom in the capping position is held most strongly, chalcogen exchange reactions are of little use for the selective preparation of $\{M_3(\mu_3\text{-}Q')(\mu_2\text{-}Q'')_3\}$ type clusters. An alternative is provided by cluster self-assembly reactions in the presence of sources of two different chalcogen atoms; in this case, one may hope that different chalcogen atoms would prefer positions with different connectivity. An example is the high-temperature syntheses of cubane rhenium clusters, $\{Re_4(\mu_3\text{-}Q)_4\}$ (Q = S, Se), from the elements in the presence of two different chalcogens (S + Te or Se + Te): the lighter chalcogen always occupies the "inner" position (μ_3-Q) in the cluster. In $Re_4S_4Te_4$ and $Re_4S_4Cl_8(TeCl_2)_4$, only sulfur atoms are involved in the formation of the $\{Re_4(\mu_3\text{-}S)_4\}$ cubane core, while tellurium atoms form the external coordination environment [54, 55]. In the structure of $Cs_4[Re_6S_{9.45}Se_{3.55}]$ obtained by heating a mixture of Re, Cs_2CO_3, H_2S, and Se at 850°C, the μ_3-positions in the $\{Re_6(\mu_3\text{-}Q)_8\}$ cluster are occupied only by sulfur atoms, whereas selenium atoms are present only in the μ-Q_2 bridges between octahedral clusters [56]. The sulfotellurochloride $Mo_2S_4Te_4Cl_{22}$, which is formed upon the reaction of $MoTe_2$ with S_2Cl_2 at 100°C is thought to have the $\{Mo_2(\mu_2\text{-}S_2)_2\}^{6+}$ cluster core containing only sulfur atoms [57]. In all of the listed cases, the cluster core consists of chalcogen atoms of only one type (sulfur or selenium).

In the case of trinuclear clusters, self-assembly reactions may put two different chalcogens into specified positions of the cluster core. The lighter atom always occupies the μ_3-position. Indeed, the chalcohalides formed in the Re_2O_7–S–Se_2Cl_2, Re_2O_7–Se–S_2Cl_2, and OsO_4–Se–S_2Cl_2 systems (at 200°C) had the composition $Re_3S_5Se_2Cl_7$, $Re_3S_{6.5}Se_{0.5}Cl_7$, and $Os_3S_7SeCl_8$, respectively, and contained trinuclear $\{M_3(\mu_3\text{-}S)(\mu\text{-}Q_2)_3\}$ clusters (M = Re, Os; Q = S, Se) in which the μ_3-position was occupied by the sulfur atom and the μ-Q_2 groups consisted of sulfur and selenium atoms [58]. The reaction between $MoCl_3 \cdot 3H_2O$, ZnSe, and $Me_4N(S_2P(OEt)_2)$ was less selective and gave a mixture of trinuclear dithiophosphate complexes, $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3((EtO)PS_2)_3]$ and $[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3((EtO)PS_2)_3]$, from which the product $[Mo_3(\mu_3\text{-}S_{0.65}Se_{0.35})(Se_2)_3((EtO)PS_2)_3]$ was isolated [51].

In order to obtain the $\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3\}^{4+}$ and $\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3\}^{4+}$ clusters, we carried out the reaction of Mo, S, Se, and Br_2 in 3 : 1 : 6 : 2 molar ratio at 350°C, according to the stoichiometry (by analogy with the synthesis of $Mo_3S_7Br_4$ and $Mo_3Se_7Br_4$), which was expected to provide selective incorporation of sulfur into the capping position:

$$3Mo + S + 6Se + 2Br_2 \rightarrow \text{“}Mo_3SSe_6Br_4\text{.”}$$

The reaction of "$Mo_3SSe_6Br_4$" with Bu_4NBr conducted with mechanochemical activation in a vibratory mill gave $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3Br_6]^{2-}$, which was isolated as the salt $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ [59]. The Raman spectrum of $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ exhibits a band at 448 cm^{-1}, corresponding to vibrations of the Mo_3–μ_3-S group [60]. The ^{77}Se NMR spectrum of this complex shows only two signals with $\delta = 256.3$ and -132.0 ppm, corresponding to axial and equatorial selenium atoms in the μ_2-Se_2 ligand.

The aquation of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3Br_6]^{2-}$ in 4 M HPts with the subsequent addition of a stoichiometric amount of PPh_3 leads to the formation of the $[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ aqua complex [59]:

$$\begin{gathered}\left[Mo_3(\mu_3\text{-}S)(Se_2)_3Br_6\right]^{2-} + 3PPh_3 + 9H_2O \\ \rightarrow \left[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9\right]^{4+} + 3SePPh_3 + 6Br^-,\end{gathered}$$

which corresponds to the cluster core conversion from $\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3\}^{4+}$ to $\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3\}^{4+}$. In order to confirm the identity of the product, the aqua complex was allowed to react with acetylacetone (HAcac) and pyridine, which afforded $[Mo_3(\mu_3\text{-}$

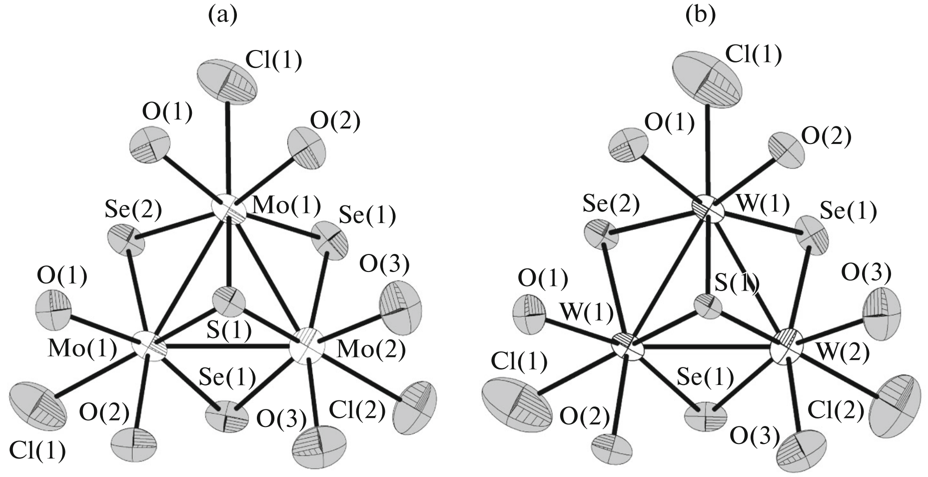


Fig. 4. Structure of (a) $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_6Cl_3]^+$ and (b) $[W_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_6Cl_3]^+$ (50% probability ellipsoids).

$S)Se_3(Acac)_3(Py)_3](PF_6)$. Electrospray ionization mass spectrum of an acetonitrile solution of the complex exhibited only a peak due to $[Mo_3(\mu_3\text{-}S)Se_3(Acac)_3(Py)_3]^+$ and peaks for pyridine elimination products down to $[Mo_3(\mu_3\text{-}S)Se_3(Acac)_3]^+$. The $\{Mo_3(\mu_3\text{-}S)Se_3\}^{4+}$ cluster core was not fragmented under these experimental conditions, thus demonstrating high strength. No peaks corresponding to a different selenium to sulfur ratio were present.

It is known that aqua complexes of the $\{M_3Q_4\}^{4+}$ clusters (M = Mo, W) form supramolecular adducts with macrocyclic cavitands, in particular, with cucurbit[6]uril (CB[6]). These adducts readily crystallize even from millimolar aqueous solutions [61]. This approach was used to prepare and structurally characterize the adduct $\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_6Cl_3]_2\text{-}CB[6]\}Cl_2 \cdot 11H_2O$ (Fig. 4a) from a solution of $[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ in 2 M HCl.

The behavior of the tungsten analogue was more intricate. The optimal method for the synthesis of the $[W_3Q_4(H_2O)_9]^{4+}$ aqua complexes (Q = S, Se) includes reactions of the $W_3S_7Br_4$ or $W_3Se_7Br_4$ polymers with H_3PO_2 in concentrated HCl [62]. Similarly, the product (or a mixture of products) with the gross composition "$W_3SSe_6Br_4$," formed in the reaction of tungsten with a mixture of sulfur, selenium and bromine, was allowed to react with H_3PO_2. The following reaction was expected to occur:

$$W_3(\mu_3\text{-}S)(Se_2)_3Br_4 + 3H_3PO_2 + 12H_2O \\ \rightarrow [W_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+} \\ + 3H_2Se + 3H_3PO_3 + 4Br^-.$$

However, all species of the series $[W_3S_xSe_{4-x}\text{-}(H_2O)_9]^{4+}$ were found among the products. This implies low selectivity of the cluster self-assembly in this case. The simultaneous presence of five species in the solution behaving in a similar way on a cation exchange resin precluded complete separation of the products [59]. The use of standard separation conditions with the Dowex resin (room temperature, elution with 2 M HCl) gives a purple (mainly $[W_3S_4(H_2O)_9]^{4+}$ according to UV/Vis data), blue, and green (major) fractions. The addition of CB[6] to the blue solution gave the crystals of $[W_3S_3Se(H_2O)_7Cl_2]_2Cl_2(CB[6]) \cdot 15H_2O$ [63]. The product $[W_3S_{1..5}Se_{2..5}Cl_{1..5}\text{-}(H_2O)_{7..5}]_2Cl_5(CB[6]) \cdot 18.5H_2O$ crystallized from the green solution [63]. In both cases, the μ_2-bridging positions are occupied by both sulfur and selenium. This means that the starting solutions comprise mixtures of aqua complexes, separation of which requires special conditions. Very slow elution with 0.5 M H_2SO_4 at 4°C resulted in the isolation of a green fraction enriched with $[W_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ (74%), but containing also $[W_3Se_4(H_2O)_9]^{4+}$ (20%) and $[W_3S_2Se_2(H_2O)_9]^{4+}$ (6%) [59]. Complete separation of these products was not attained because of their low stability during long-term elution (several days or even weeks). After elution with 0.2 M H_2SO_4 at 4°C for several weeks, the species with lower content of selenium ($[W_3S_2Se_2(H_2O)_9]^{4+}$) becomes predominant, while the fraction of $[W_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ decreases.

The green crystals of $\{[W_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_7\text{-}Cl_2]_2CB[6]\}Cl_4 \cdot 12H_2O$ (Fig. 4b) were obtained by adding CB[6] to the green solution in 2 M HCl with the predominant content of $[W_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ [59]. In this compound, μ_2-bridging positions are occupied by selenium atoms, i.e., compound contains only the $\{W_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3\}^{4+}$ cluster core.

It is noteworthy that if the amount of sulfur added for the high-temperature reaction step corresponds to the "$W_3S_4Se_3Br_4$" stoichiometry, then the reaction with H_3PO_2 affords $[W_3S_4(H_2O)_9]^{4+}$ as the final product [59]. The formation of $[W_3S_4(H_2O)_9]^{4+}$ can be represented by the following equation:

$$W_3(\mu_3\text{-}S)(\mu_2\text{-}Se_{eq}S_{ax})_3Br_4 + 3H_3PO_2 + 12H_2O$$
$$\rightarrow [W_3S_4(H_2O)_9]^{4+} + 3H_2Se + 3H_3PO_3 + 4Br^-.$$

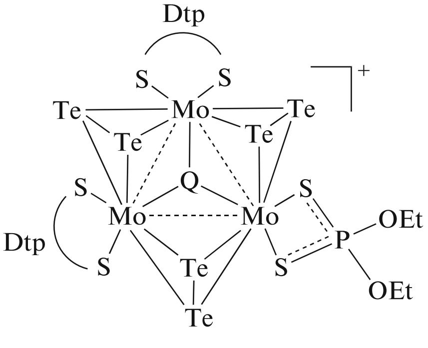
The above-considered approach for the selective introduction of sulfur into the capping position can also be used to prepare mixed-chalcogen tantalum clusters. It is known that tantalum forms the square clusters, $\{Ta_4(\mu_4\text{-}Q)(\mu_2\text{-}Q_2)_4\}^{8+}$ (Q = S, Se), a sort of higher homologues of the triangular clusters considered in the review [64, 65]. For the preparation of a mixed-chalcogen (S/Se) cluster, a mixture of Ta, S, Se, and I_2 taken in 4 : 1 : 8 : 4 molar ratio was heated; this gave the chalcoiodide $Ta_4S_{1.5}Se_{7.5}I_8$, in which the μ_4-position was occupied by only the sulfur atom [66].

$\{Mo_3(\mu_3\text{-}Q)(\mu_2\text{-}Te_2)_3\}$ (Q = O, S, Se) clusters. In the Mo–Se–Te–Br_2 and Mo–Se–Te–I_2 systems, $[Mo_3Se_7(TeBr_3)Br_2]_2[Te_2Br_{10}]$ and $[Mo_3Se_7(TeI_3)I_2]I$ chalcohalides (Fig. 5), containing the $\{Mo_3Se_7\}$ cluster core are formed at 350°C [67]. The tellurium atoms do not belong to the cluster core, but occur as TeX_3^-, ligands coordinated to molybdenum.

For introducing sulfur or selenium into the μ_3-position, we carried out the reaction between Mo, Te + Q (Q = S, Se), and Br_2 in 3 : 6 : 1 : 2 molar ratio. The products were subjected to solid-state reactions with KDtp (Dtp = diethyl dithiophosphate) with mechanical activation, which is an efficient way for "cutting out" telluride clusters from the polymeric chain [68]. This gave the dithiophosphate complexes $[Mo_3(\mu_3\text{-}Q)(\mu_2\text{-}Te_2)_3(Dtp)_3]^+$ (Scheme 6) containing a sulfur of selenium atom in the μ_3-position [69]:

$$3Mo + 6Te + Q + 2Br_2 \rightarrow \text{“}Mo_3QTe_6Br_4\text{,”}$$

$$\text{“}Mo_3QTe_6Br_4\text{”} + 4KDtp$$
$$\rightarrow [Mo_3QTe_6(Dtp)_3](Dtp) + 4KBr\ (Q = S;\ Se).$$



$[Mo_3QTe_6(Dtp)_3]^+$

Scheme 6.

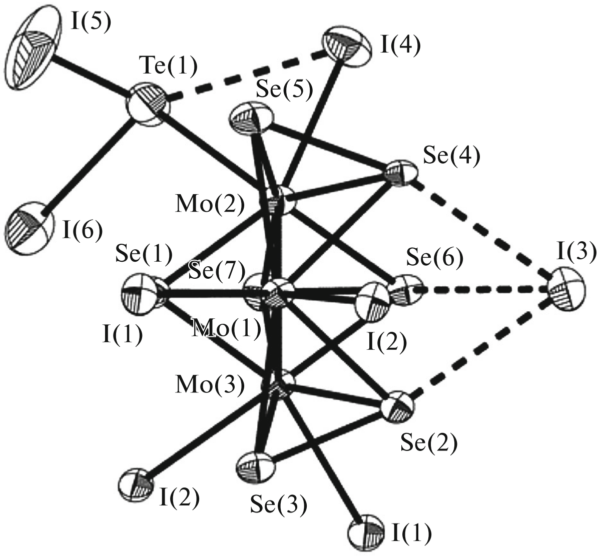
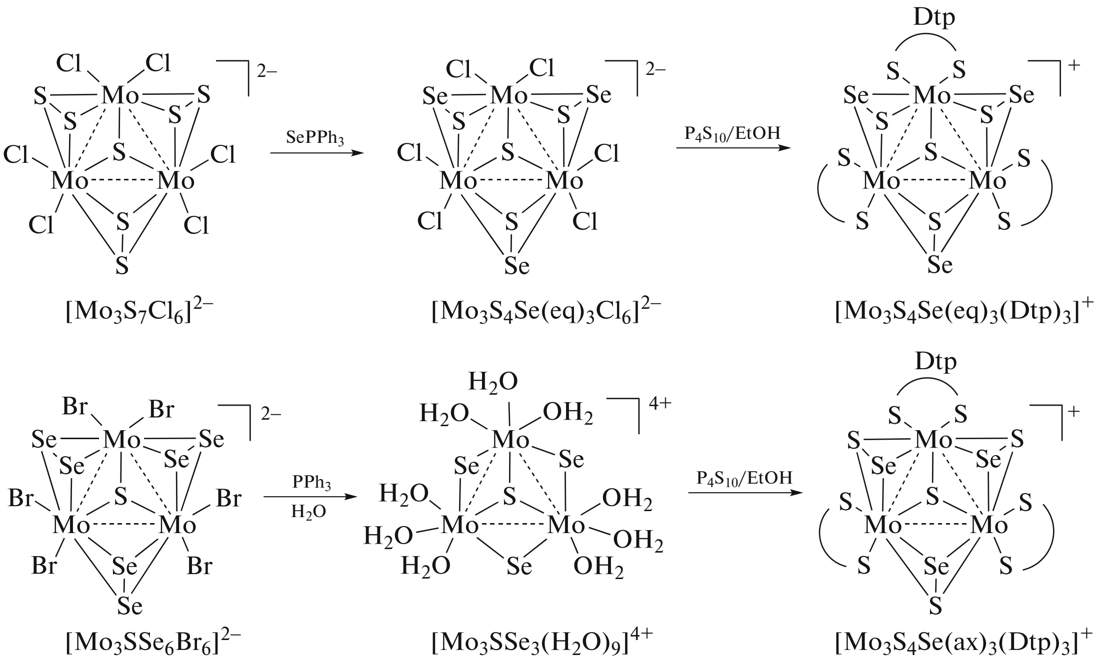


Fig. 5. Structure of $[Mo_3Se_7(TeI_3)I_2]I$. All atoms are presented as 50% probability thermal ellipsoids. The dashed lines show $Te(TeI_2)\cdots I$ and $3Se_{ax}\cdots I$ contacts.

As a side product, this reaction gave the oxo derivative $[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}Te_2)_3(Dtp)_3]^+$. This mixture could not be separated by chromatography.

Isomerism of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}SSe)_3(Dtp)_3]Cl$. Preparation of two types of isomers with different coordination modes of the μ_2-SSe ligand. The above regularities allowed us to convert $\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3\}^{4+}$ to $\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_{ax}S_{eq})_3\}^{4+}$. The latter may be regarded as a bond isomer with respect to $\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3\}^{4+}$; hence, a unique pair of the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}SSe)_3(Dtp)_3]Cl$ bond isomers differing only by the coordination mode of the μ_2-SSe ligand can be deliberately synthesized [70].

The isomer $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_{ax}S_{eq})_3(Dtp)_3]Cl$ was obtained (Scheme 7) by reacting the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_9]^{4+}$ aqua complex with a freshly prepared solution of P_4S_{10} in ethanol, similarly to the preparation of $[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_{ax}S_{eq})_3(Dtp)_3]Cl$ from $[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se)_3(H_2O)_9]^{4+}$ [52]. The second isomer was obtained by using the reaction of the $[Mo_3S_7Cl_6]^{2-}$ chloride with $SePPh_3$ giving $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}\text{-}Se_{eq})_3Cl_6]^{2-}$. The reaction with P_4S_{10} in ethanol affords the isomeric $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3(Dtp)_3]Cl$ dithiophosphate (Scheme 7) in which the sulfur atoms occupy only axial positions [70].



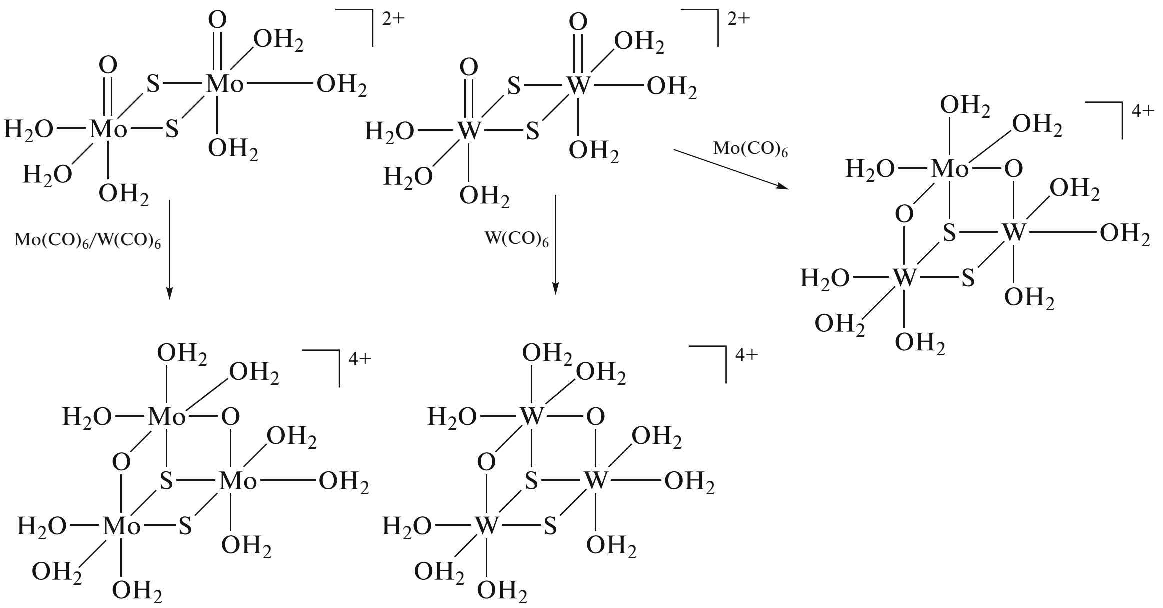
Scheme 7.

The mass spectra of both isomers are identical and show the major peak corresponding to the $[Mo_3S_4Se_3(Dtp)_3]^+$ cation. Nevertheless, the isomers can be differentiated considering the characteristic fragmentation products upon collision-induced dissociation (CID). It is known that for $\{Mo_3Q_7\}^{4+}$ type clusters, the gas-phase selective elimination of the "Q_2" molecule from equatorial positions can serve for reliable determination of the chalcogen nature in these positions [71, 72]. The CID spectrum of the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3(Dtp)_3]^+$ cation shows elimination of the Se_2 group. This confirms the fact that selenium atoms occupy equatorial positions. Conversely, the CID mass spectrum of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_{ax}S_{eq})_3(Dtp)_3]^+$ shows elimination of the S_2 group under the same conditions [70].

The ^{77}Se NMR chemical shifts proved to be quite sensitive to the positions of chalcogen atoms in $\mu_2\text{-}SSe^{2-}$. The isomer with $\mu_2\text{-}Se_{ax}S_{eq}$ exhibits a signal at 131 ppm, whereas for the isomer with $\mu_2\text{-}S_{ax}Se_{eq}$ the signal is shifted to the negative region (–107 ppm), which points to more pronounced shielding of the Se_{eq} position. The relative stabilities of the two isomers were estimated by DFT calculations. Optimization was carried out for complexes with sulfur (isomers **I** and **II**) and selenium (isomers **III** and **IV**) atoms in the capping position: $[Mo_3(\mu_3\text{-}X)(Q_{eq}Q_{ax})_3(H_2O)_6]^+$ (**I**: X = S, Q_{eq} = S, Q_{ax} = Se; **II**: X = S, Q_{eq} = Se, Q_{ax} = S; **III**: X = Se, Q_{eq} = Se, Q_{ax} = S; **IV**: X = Se, Q_{eq} = S, Q_{ax} = Se). The calculated energies for complexes **I**, **II**, **III**, and **IV** were –2.480517, –2.480518, –3.005715, and -3.005713×10^{-7} kJ/mol, respectively. Proceeding from these data, it can be concluded that for each pair, the isomer with selenium atoms in the equatorial positions is more stable [70].

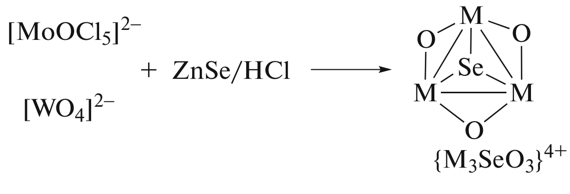
Selective introduction of an oxygen atom into triangular chalcogenide clusters. Almost simultaneously with the discovery of the $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ cluster highly stable to hydrolysis in strongly acidic media, it was proven that Mo(IV) exists in acidic aqueous solutions exclusively as a similarly constructed oxide cluster, $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ [73]. Tungsten analogues of both clusters [74, 75] and selenide clusters for both molybdenum and tungsten [62] were obtained. The preparation of intermediate, oxide sulfide and oxide selenide clusters was of obvious interest. Indeed, the reduction of the binuclear oxo-bridged Mo(V) complex, $[Mo_2O_2S_2(H_2O)_6]^{2+}$, by various reagents gave the desired products, $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ (x = 0–3) [76, 77], as a mixture, the isolation of single compounds from which was realizable, but a very labor-consuming task.

Is selective synthesis of these clusters possible? For this purpose, one can use the retrosynthetic approach well developed in organic synthesis. For example, $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)(\mu\text{-}O)_2(H_2O)_9]^{4+}$ can be regarded as the product of coordination of the $\{Mo(H_2O)_3\}^{2+}$ moiety to two sulfur atoms and one oxygen atom of the $[Mo_2O_2S_2(H_2O)_6]^{2+}$ aqua complex. The comproportionation reactions between $[Mo_2O_2(\mu\text{-}S)_2(Cys)_2]^{2-}$ and $[MoCl_6]^{3-}$, or between $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(Cys)_2]^{2-}$ and $[MoCl_6]^{3-}$ in 2 M HCl or HPts are known to give $[Mo_3O_2S_2(H_2O)_9]^{4+}$ and red $[Mo_3O_3S(H_2O)_9]^{4+}$, respectively [77]. $Mo(CO)_6$ could serve as the $\{Mo(H_2O)_3\}^{2+}$ precursor. In this case, molybdenum would be completely incorporated into the cluster, whereas in the case of hexachloromolybdate, a part of the reagent should function only as the source of electrons. Indeed, under drastic conditions (140°C, 4 M HCl), the reaction of $[Mo_2O_2S_2(H_2O)_6]^{2+}$ with $Mo(CO)_6$ gives, almost exclusively, $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)(\mu\text{-}O)_2\text{-}(H_2O)_9]^{4+}$ (Scheme 8). It is curious that under these conditions, even the metallic molybdenum powder reacts to give the same product in 90% yield. Similarly, $[W_3(\mu_3\text{-}S)(\mu\text{-}S)(\mu\text{-}O)_2(H_2O)_9]^{4+}$ was obtained (Scheme 8):



Scheme 8.

Scheme 8 ($[M_2O_2S_2(H_2O)_6]^{2+}$ + source of M' (M' = Fe, Co, Ni, Pd, Pt, Cu, etc.) in a low oxidation state) can, in principle, be used for the synthesis of heterometallic clusters. Indeed, $[W_2O_2S_2(H_2O)_6]^{2+}$ and $Mo(CO)_6$ gave $[W_2Mo(\mu_3\text{-}S)(\mu\text{-}S)(\mu\text{-}O)_2(H_2O)_9]^{4+}$, which was isolated and structurally characterized as $[W_2Mo(\mu_3\text{-}S)(\mu\text{-}S)(\mu\text{-}O)_2(Acac)_3(Py)_3]PF_6$. It is noteworthy that other combinations of reactants ($[M_2O_2S_2\text{-}(H_2O)_6]^{2+}$ + $Cr(CO)_6$ or $[Mo_2O_2S_2(H_2O)_6]^{2+}$ + $W(CO)_6$) afford only homometallic triangular clusters, $[M_3(\mu_3\text{-}S)(\mu\text{-}S)(\mu\text{-}O)_2(H_2O)_9]^{4+}$, with the metal coming only from the binuclear complex [78]. Unexpectedly, it turned out that the $[Mo_2O_2S_2(H_2O)_6]^{2+}/Re(CO)_5Cl$ combination gives the monosulfide $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ cluster [79]. The pathway of these transformations is obscure, but remarkably, only one trinuclear cluster rather than a mixture is formed. One can expect that similar reactions of the binuclear monosulfide clusters $[M_2O_2(\mu\text{-}O)(\mu\text{-}S)(H_2O)_6]^{2+}$ with appropriate carbonyls should give triangular $[M_3(\mu_3\text{-}S)(\mu\text{-}O)_3(H_2O)_9]^{4+}$. The feasibility of Scheme 8 is indirectly supported by the preparation of selenide clusters $[M_3(\mu_3\text{-}Se)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ via self-assembly of mononuclear $[MoOCl_5]^{2-}$ or WO_4^{2-} and H_2Se (Scheme 9). Hydrogen selenide is a strong reducing agent (E^0 Se/H_2Se −0.4 V). Presumably, binuclear $[M_2O_2(\mu\text{-}O)(\mu\text{-}Se)(H_2O)_6]^{2+}$ is formed at a certain stage; metal atom coordination to this complex followed by reduction affords $[M_3(\mu_3\text{-}Se)(\mu\text{-}O)_3(H_2O)_9]^{4+}$, which was previously hardly accessible (the known synthesis of the Mo cluster gave a 3% yield, while the tungsten cluster was unknown). Attention is attracted by high selectivity of these reactions, which give no triangular clusters with a different oxygen : chalcogen ratio; and the isolation of the target product does not cause difficulties. This made it possible to perform a number of ligand exchange reactions and to study the electrochemical behavior of molybdenum and tungsten oxosulfide and oxoselenide clusters [80, 81].



Scheme 9.

The same approach can be extended to Group 5 metal clusters. In particular, the reduction of $NbCl_5$ in the presence of ZnSe/HCl gives only one product with the $\{Nb_4(\mu_4\text{-}Se)(\mu_2\text{-}O)_5\}^{4+}$ cluster core [82]. Thus, the Se^{2-} anion probably plays a key role in cluster self-assembly reactions, functioning as the ligand with the highest connectivity: μ_3 for trinuclear Mo and W clusters and μ_4 for tetranuclear Nb clusters.

Mixed-metal $\{Mo_xW_{3-x}Q_4\}$ and $\{Mo_xW_{4-x}Q_4\}$ clusters ($Q = S, Se$). The only synthetic route to mixed clusters of this type is the reduction of an equimolar mixture of $(NH_4)_2WS_4$ and $[Mo_2O_2(\mu\text{-}S)_2(Cys)_2]^{2-}$ with excess $NaBH_4$. This gives a mixture of products, chromatographic separation of which results in green $[Mo_2WS_4(H_2O)_9]^{4+}$ (17%) and gray $[MoW_2S_4(H_2O)_9]^{4+}$ (3%) [83]. It is obvious that this procedure cannot considered as a preparative method. The problem of selective preparation of $\{Mo_xW_{3-x}Q_4\}$ ($Q = S$, Se) proved to be closely connected with the preparation of the $\{Mo_xW_{4-x}Q_4\}$ cubane clusters and their selective degradation.

We demonstrated that the cubane clusters can be obtained in a high yield by triangular cluster "completion" reaction (Scheme 10):

$$\left[W_3Q_4(H_2O)_9\right]^{4+} + \left[Mo_2Cl_8\right]^{4-} \\ \to \left[MoW_3S_4(H_2O)_{12}\right]^{5+},$$

$$\left[W_3Q_4(H_2O)_9\right]^{4+} + W(CO)_6 + 2H^+ \\ \to \left[W_4Q_4(H_2O)_{12}\right]^{6+} + H_2 + 6CO\ (2\,\text{M HCl}, 140°\text{C}).$$

This reaction is based on the fact that the triangular and cubane clusters are closely related both structurally and chemically. Three bridging chalcogen atoms of the triangular cluster can be considered as ligands able to coordinate the metal atom and thus to "complete" the triangular cluster to a cube. On heating of solutions of cubane aqua complexes in air, the reverse reaction takes place, namely, oxidative degradation of clusters to give trinuclear complexes; in the case of heterometallic clusters, the tungsten rather than molybdenum atom is always selectively lost. Thus, the $[W_2MoQ_4(H_2O)_9]^{4+}$ clusters ($Q = S$, Se) become available (Scheme 10):

$$\left[W_3MoQ_4(H_2O)_{12}\right]^{5+} + O_2 \to \left[W_2MoQ_4(H_2O)_9\right]^{4+}.$$

It is notable that this cycle can be repeated

$$\left[W_2Mo_2Q_4(H_2O)_{12}\right]^{5+} \to \left[WMo_2Q_4(H_2O)_9\right]^{4+},$$

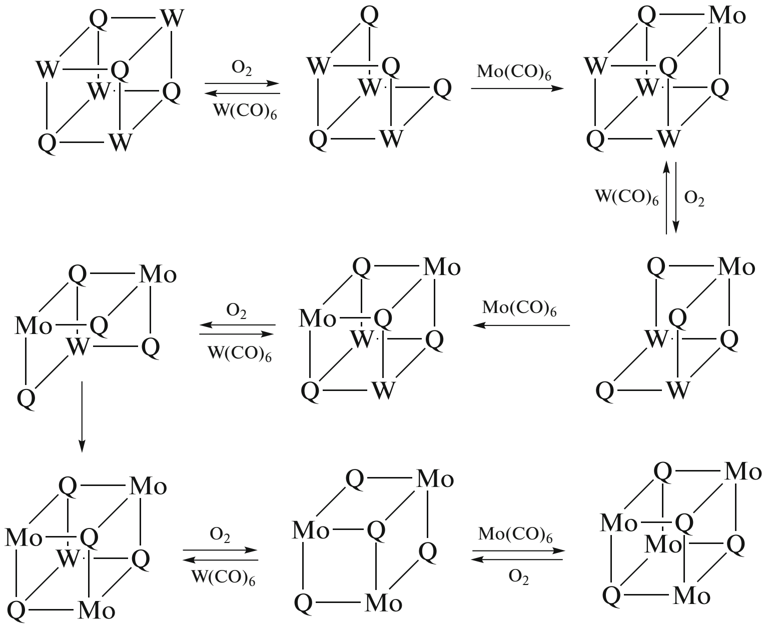
$$\left[W_2MoQ_4(H_2O)_9\right]^{4+} + \left[Mo_2Cl_8\right]^{4-}\left(Mo(CO)_6\right) \\ \to \left[Mo_2W_2Q_4(H_2O)_{12}\right]^{5+},$$

$$\left[W_2Mo_2Q_4(H_2O)_{12}\right]^{5+} + O_2 \to \left[WMo_2Q_4(H_2O)_9\right]^{4+},$$

and even the following stage can be performed

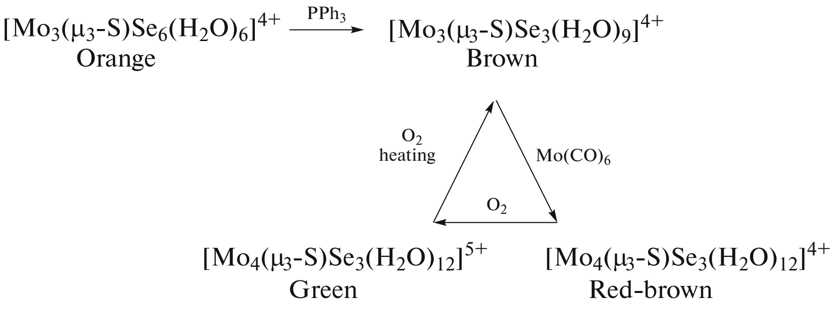
$$[Mo_2WQ_4(H_2O)_9]^{4+} \\ \to [Mo_3WQ_4(H_2O)_{12}]^{5+} \to [Mo_3Q_4(H_2O)_{12}]^{5+}.$$

It is of interest successive implementation of all three completion–degradation stages starting from triangular tungsten clusters finally gives the triangular molybdenum cluster, which is thus successively assembled on the matrix of sulfur atoms. This can be considered as a unique example of transfer of structural information upon complete replacement of one metal in the cluster by another one [84, 85].



Scheme 10.

The mixed-chalcogen triangular cluster $[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ reacts with $Mo(CO)_6$ at 130°C in an HCl solution in a sealed tube to give the red-brown $[Mo_4(\mu_3\text{-}S)(\mu_3\text{-}Se)_3(H_2O)_{12}]^{4+}$ complex, which is oxidized in air to green $[Mo_4(\mu_3\text{-}S)(\mu_3\text{-}Se)_3(H_2O)_{12}]^{5+}$ (Scheme 11). Heating of a solution of $[Mo_4(\mu_3\text{-}S)(\mu_3\text{-}Se)_3(H_2O)_{12}]^{5+}$ in air induces degradation of the complex and gives the initial $[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ complex identified using the UV/Vis spectra [59].



Scheme 11.

The degradation of the cubane cluster can follow two pathways. First, the Mo_4SSe_3 cube can lose one vertex via either Mo–S or Mo–Se bond cleavage. This should give the Mo_3SSe_3 cluster in which one sulfur atom occupies the μ_2-position (this cluster is unknown). Second, cleavage of three Mo–Se bonds is possible. This would give the initial Mo_3SSe_3 cluster, which is actually observed in our case. The latter fragmentation pathway is preferred, probably, due to the relative ease of the Mo–Se bond cleavage [59].

Chalcogen-containing polyoxometallates (POMs) are polynuclear complexes whose structures are based on transition metal atoms (Mo, W, V, Nb, Ta) in higher oxidation states connected through bridging oxygen atoms. As a rule, the replacement of oxygen atoms by chalcogen atoms causes complete degradation of the POM structure. A rare exception is provided by reactions of niobium-substituted polytungstates ($[W_5O_{18}\{NbO\}]^{3-}$, $[PW_{11}O_{39}\{NbO\}]^{3-}$) with sulfur or selenium sources ($(Me_3Si)_2S$, $(Me_3Si)_2Se$, $R_2P_2S_4$), resulting in selective replacement of oxygen at the niobium atom by chalcogens with the retention of POM structure [86]. An alternative approach to the synthesis of hybrid chalcogen-containing POMs was proposed in [87]. The authors prepared the sulfur analogue of $\gamma\text{-}[SiW_{12}O_{40}]^{4-}$ by the reaction of $\gamma\text{-}[SiW_{10}O_{36}]^{8-}$ with binuclear $[Mo_2S_2O_2(H_2O)_4]^{2+}$. In this simple and elegant reaction, the silicotungstate

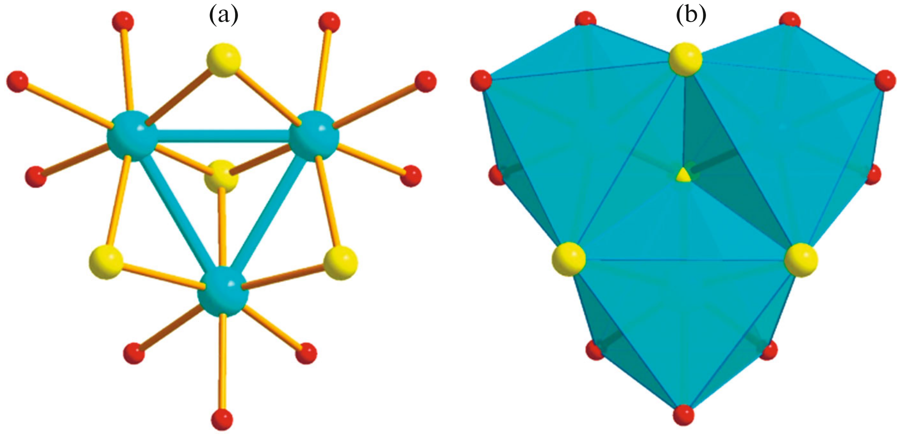

(a) (b)

Fig. 6. Structural analogy between (a) $[Mo_3S_4(H_2O)_9]^{4+}$ and (b) $[W_3O_{13}]^{8-}$.

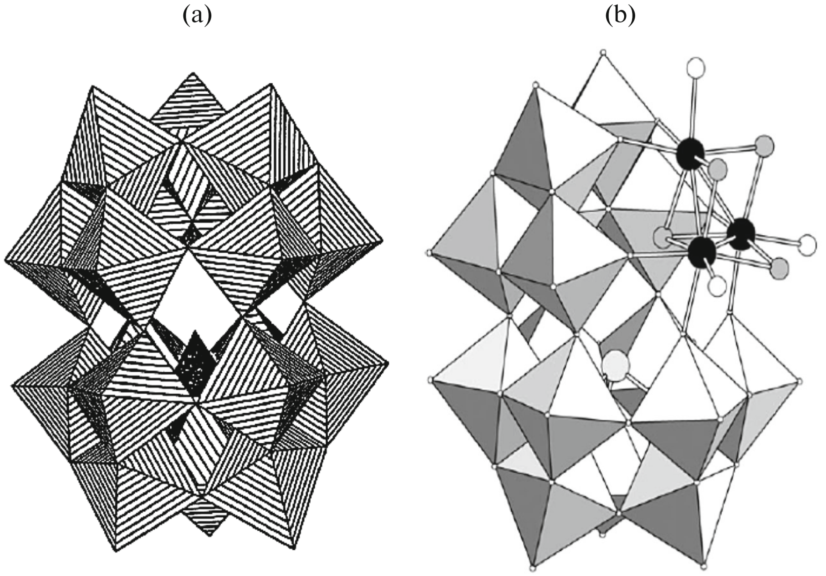

(a) (b)

Fig. 7. (a) Structure of $EW_{15}O_{60}{}^{9-}$ (E = As, Sb) and $TeW_{15}O_{60}^{8-}$, with the lower half corresponding to the starting anions expanded to a 15-nuclear anion by three $\{W_3O_{13}\}$ groups; and (b) the same structure with one $\{W_3O_{13}\}$ group being replaced by the structurally equivalent $\{Mo_3S_4(H_2O)_3O_6\}$ group.

acts as a tetradentate ligand, which replaces four water molecules in the binuclear thio cation. We paid attention to one more potential building block: the $[Mo_3S_4(H_2O)_9]^{4+}$ aqua complex and its analogues [88]. Their structural analogy with the $[W_3O_{13}]^{8-}$ moiety, the key building blocks of many Keggin and Dawson type polyoxometallates, is obvious (Fig. 6).

In practice, the insertion of $[Mo_3S_4(H_2O)_9]^{4+}$ was implemented in the following way. Trilacunary anions, $EW_9O_{33}^{9-}$ (E = As, Sb) and $TeW_9O_{33}^{8-}$, can be expanded in the presence of excess tungstate to form larger $EW_{15}O_{60}^{9-}$ (E = As, Sb) and $TeW_{15}O_{60}^{8-}$ anions (Fig. 7).

We were able to synthesize $[AsW_{15}Mo_3S_4(H_2O)_3O_{53}]^{9-}$, $[SbW_{15}Mo_3S_4(H_2O)_3O_{53}]^{9-}$, and $[TeW_{15}Mo_3S_4(H_2O)_3O_{53}]^{8-}$ by adding the necessary amount of the tungstate and $[Mo_3S_4(H_2O)_9]^{4+}$ to As(III), Sb(III), and Te(IV) nonatungstate derivatives. The resulting hybrid chalco-polyoxometallates (chalco-POMs) correspond to the highest currently attained degree of oxygen replacement by chalcogen in the POM structure. The introduction of sulfur atoms sharply changes the POM reactivity and, hence, enables the coordination of soft metal ions such as Cu(I) or Au(I). Indeed, $[AsW_{15}Mo_3S_4(H_2O)_3O_{53}]^{9-}$ reacts with CuCl to give the heterometallic $[AsW_{15}Mo_3(CuCl)S_4(H_2O)_3O_{53}]^{9-}$ cluster, which was isolated

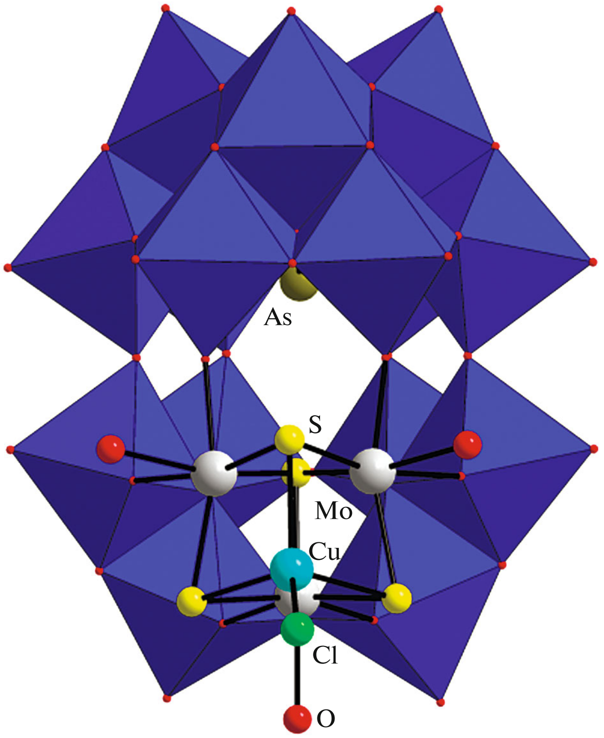


Fig. 8. Structure of $[AsW_{15}Mo_3(CuCl)S_4(H_2O)_3O_{53}]^{9-}$.

and structurally characterized as the cesium salt (Fig. 8) [89, 90].

Thus, we demonstrated the possibility and necessity of rational design of the synthetic approaches to complex clusters and polynuclear compounds. This was illustrated mainly by molybdenum and tungsten cluster complexes with chemically different chalcogen atoms in the core. For these clusters, targeted synthetic routes to mixed chalcogenide and oxide chalcogenide clusters and polynuclear complexes were developed. The synthesis of these compounds not only stimulates the strategy towards complex (mixed-ligand, polynuclear and cluster) coordination compounds, but is also suitable for step-by-step modification of physical and chemical properties, which is undoubtedly important for the design of functional materials with predictable properties.

FUNDING

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