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Chalcogenide clusters of Group 5 – 7 metals

V E Fedorov, Yu V Mironov, N G Naumov, M N Sokolov, V P Fedin

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Abstract. The state-of-the-art and prospects of the development of chemistry of chalcogenide clusters of Group 5 – 7 metals of the Periodic Table are discussed. The main structural types, methods of synthesis, the reactivity and possible applications of vanadium, niobium, tantalum, chromium, molybdenum, tungsten and rhenium chalcogenide clusters with nuclearity of three and larger are considered. The bibliography includes 363 references.

I. Introduction

The achievements of chemistry in the second half of the 20th century are mostly associated with the foundation of basics of cluster chemistry. In 1964, F Cotton introduced the term 'cluster' for compounds the molecules of which contain a core of metal atoms linked by metal – metal bonds.[1] The development of cluster chemistry was a revolutionary step in coordination chemistry.[2] The complexes in which metal clusters are coordinated by chalcogenide or polychalcogenide ligands occupy a special place among numerous types of cluster compounds. Chalcogenide clusters are a typical example of so-called inorganic or high-valence clusters and are most characteristic of 4d- and 5d-metals of Groups 5 – 7. The present review discusses methods of synthesis, structures and properties of sulfide, selenide and telluride cluster compounds of vanadium, niobium, tantalum, chromium, molybdenum, tungsten and rhenium. The review includes only the metal clusters with nuclearity equal, to or larger than, three.

The present review is dedicated to the 50th anniversary of the A V Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences (NIIC) and it is not a coincidence: from the date of its foundation and up to now systematic studies of chalcogenide clusters of transition metals have been carried out in the Institute and several new key types of chalcogenide clusters have been discovered here. In the mid-1960s, trinuclear molybdenum complexes $Mo_3Q_7X_4$ (Q = S, Se; X = Cl, Br, I)[3,4] were synthesised in NIIC, which became a beginning of massive studies of triangular chalcogenide clusters. At the same time lower molybdenum chalcogenides of the Mo_6Q_8 (Q = Se, Te) type have been found,[5,6] which turned out to be predecessors of a group of numerous closely related ternary cluster compounds later called the Chevrel phases (these compounds were also intensively studied because of their properties as superconductors).[7] The studies of hexa- and tetranuclear rhenium clusters Re_6Te_{15},[8] $Re_6Q_4X_{10}$,[9] $Re_4Q_4(TeX_2)_4X_8$ (Ref. 10) and chalcocyanide complexes $[Re_6Q_8(CN)_6]^{4-}$ (Ref. 11) and $[Re_4Q_4(CN)_{12}]^{4-}$ (Ref. 12) should be noted among the pioneering investigations of NIIC. Recently, new types of square vanadium and tantalum clusters $V_4S_9Br_4$ (Ref. 13) and $Ta_4Q_9X_8$ (Q = S, Se; X = Br, I)[14] were discovered in NIIC and the unique 12-nuclear rhenium clusters $[Re_{12}CS_{17}(CN)_6]^{8-/6-}$ (Ref. 15) containing an interstitial carbon atom were synthesised.

Chalcogenide clusters of Group 5 – 7 transition metals are typically obtained by high-temperature synthesis. Such clusters usually possess polymeric structures and therefore they are insoluble, low-reactive and their chemical properties could not be studied for a long period. The breakthrough in this area occurred after the discovery[16] of synthetic methods of transformation of polymeric cluster complexes into soluble molecular complexes by introduction of new ligands. In addition, the substitution of atoms of the cluster core was performed, including preparation of heterometallic clusters. Inorganic ligands (SSe^{2-}, STe^{2-}, $TeCl_2$, $TeBr_2$, TeI_2, Te_6), previously unknown in coordination chemistry were discovered. Most of the studies of tellurium containing cluster complexes were also performed in NIIC.[11,17–20]

In the present review we summarise the forty years of development of chemistry of chalcogenide clusters of early transition metals. A particular attention is paid to the new advances in chemistry of this class of compounds that emerged during the last years and to the prospects of development of basic studies and practical applications of these compounds.

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II. Main structural types of chalcogenide clusters

1. Triangular clusters with the cluster core M_3Q_4

The cluster core $M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q)_3$ contains a triangular metal cluster M_3, which coordinates four chalcogenide ligands Q (one μ_3-Q and three μ_2-Q). Cluster complexes with the core M_3Q_4 are most typical of molybdenum, tungsten and rhenium, while for Group 5 metals (V, Nb, Ta) such complexes are uncommon and are represented only by sulfide clusters of vanadium $[V_3S_4(edt)_3]^{3-}$ (H_2edt is ethane-1,2-dithiol)[21] and niobium $[Nb_3SO_3(NCS)_9]^{6-}$ (Ref. 22). Numerous examples of sulfide and selenide clusters of molybdenum and tungsten are known, but so far only one telluride cluster, $\{Mo_3Te_4[(Pr^iO)_2PS_2]_3(\mu\text{-}o\text{-}NH_2C_6H_4CO_2)(PBu^n_3)\}$, has been described.[23]

Metal ions in triangular clusters with the number of valence electrons available for metal–metal bond formation (N_e) equal to 6 (*i.e.*, there are three two-electron bonds) possess d^2 electron configuration. Accordingly, the charge of the cluster core $M_3Q_4^{n+}$ is determined by the position of the metal in the Periodic Table: for V and Nb, $n = 1$, for Mo and W $n = 4$, for Re, $n = 7$. The M–M metal bond lengths correspond to those of single bonds. Besides, in the case of monodentate ligands each metal atom coordinates three ligands. Anionic complexes with single-charged anionic ligands $[M_3Q_4L_9]^{5-}$, where L is cyanide,[24] thiocyanate,[25–29] formate,[30] *etc.*, are typical examples of such clusters. There are two types of ligands L in such complexes: *cis*- and *trans*-oriented relative to the μ_3-Q ligand. The well-known aqua complexes of molybdenum and tungsten $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se) (Fig. 1)[25,31,32] are examples of cluster complexes with neutral ligands.

The cluster complexes $[Mo_3S_4(C_2O_4)_3(H_2O)_3]^{2-}$ contain simultaneously both bidentate ($C_2O_4^{2-}$) and monodentate (H_2O) ligands; the monodentate ligands in these complexes occupy only *trans*-positions relative to μ_3-Q (Fig. 2).[33–35] The complexes with chelating O-, N-, P- and S-donor ligands are most abundant among triangular cluster compounds. The complexes with oxalate,[33–35] iminodiacetate,[36] nitrilotriacetate,[25,37,38] triethylenetetraaminohexaacetate[39] and other ligands belong to this class. A number of complexes with phosphine ligands are also known. Usually the bulky monodentate phosphine ligands occupy *trans*-positions relative to the chalcogenide μ_3-ligand as, for instance, in $(HPEt_3).[Re_3S_4Cl_6(PEt_3)_3]$[40] (Fig. 3). In contrast to oxalate complexes, one phosphorus atom in complexes with bidentate phosphine ligands is in *trans*-position and another in *cis*-position relative to the chalcogenide μ_3-ligand. This results in the chirality of the cluster cations formed $[M_3S_4X_3(dmpe)_3]^+$ and $[M_3S_4X_3(dppe)_3]^+$ [M = Mo, W; X = Cl, Br; dmpe is 1,2-bis(dimethylphosphino)ethane, dppe is 1,2-bis(diphenylphosphino)ethane] (Fig. 4).[18,41]

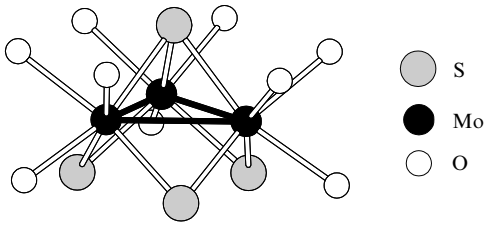


Figure 1. Structure of the complex $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(H_2O)_9]^{4+}$.

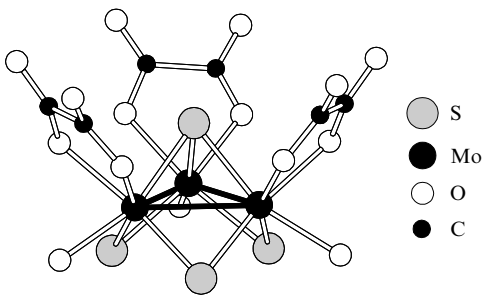


Figure 2. Structure of the complex $[Mo_3S_4(C_2O_4)_3(H_2O)_3]^{2-}$.

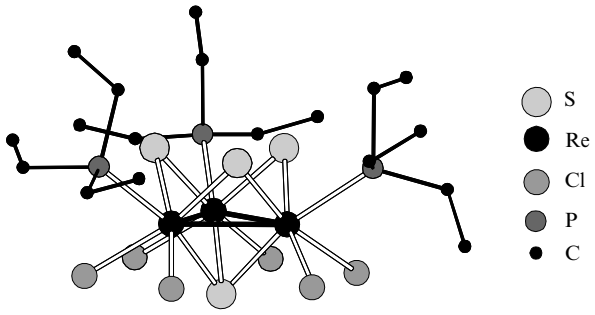


Figure 3. Structure of the complex $[Re_3S_4Cl_6(PEt_3)_3]^-$.

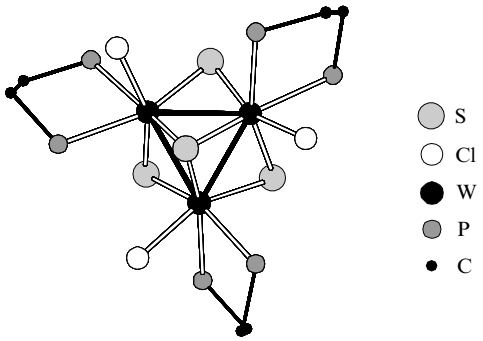


Figure 4. Structure of the complex $[W_3S_4Cl_3(dppe)_3]^+$ (the phenyl groups are omitted).

The Mo–Mo bond lengths (2.807 Å) in the cluster $Mo_3S_4^{3+}$ of the paramagnetic reduced electron-rich complex $[Mo_3S_4Cl_3(dppe)_2(PEt_3)]$ ($N_e = 7$) are slightly longer than those in its phosphine analogues with the cluster core $Mo_3S_4^{4+}$ (2.776 Å).[42,43]

There is also a significant number of compounds with S-donor ligands, including dithiophosphate, dithiolate, dithiophosphinate and dithiocarbamate complexes.[18] The tetrasulfide ligand in compound $(NH_4)_2[W_3S_4(S_4)_3(NH_3)_3]\cdot H_2O$ is bidentate and an ammonia molecule is also coordinated to the tungsten atom (Fig. 5).[44]

2. Triangular clusters with the cluster core M_3Q_7

This structural type is most typical of molybdenum and tungsten compounds; here the metal cluster M_3 coordinates one chalcogenide μ_3-ligand and three dichalcogenide μ_2-ligands $M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q_2)_3$ (Fig. 6).

Bidentate bridged dichalcogenide ligands asymmetrically coordinate metal–metal bonds according to the $\mu_2\text{-}\eta^2\text{:}\eta^2$-mode, which results in structural and chemical non-equivalence of the chalcogen atoms of these ligands. Thus, the distances Mo–S_{eq} and Mo–S_{ax} complex $(Ph_4P)_2[Mo_3S_7Cl_6]$ are equal to 2.485 and 2.391 Å, respectively.[45] The bond force

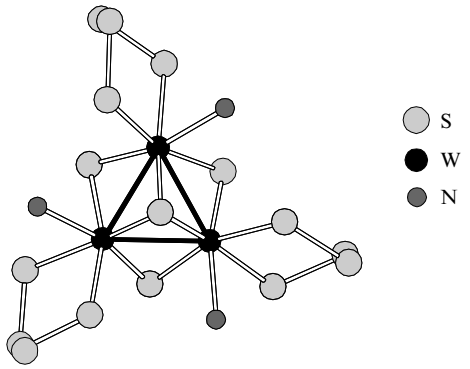


Figure 5. Structure of the complex $[W_3S_4(S_4)_3(NH_3)_3]^{2-}$.

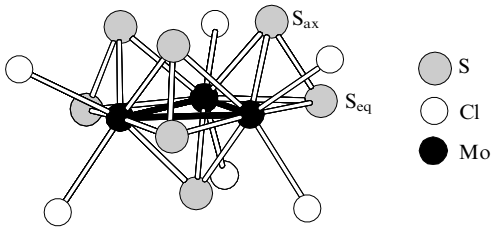


Figure 6. Structure of the complex $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Cl_6]^{2-}$.

constant of the $Mo-S_{eq}$ bond is also smaller[46] and the equatorial sulfur atoms are quite labile in chalcogen substitution and elimination reactions.[44,47–49] This makes possible their selective substitution by selenium atoms resulting in the formation of the cluster core $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}SSe)_3$.[47] Another feature of the M_3Q_7 core is its predisposition to the formation of specific non-valence interactions of the $M_3Q_7\cdots Y$ type with short contacts between axial chalcogen atoms and atom Y (Y may be a halide or chalcogenide ion). These interactions may be described as electrostatic or as a charge transfer from μ_3-Y to the σ*-orbital of the dichalcogenide ligand Y_2^{2-} (Ref. 50).

For the first time, compounds with the core M_3Q_7 were synthesised as polymeric chalcohalides $Mo_3Q_7X_4$ (Q = S, Se; X = Cl, Br, I).[3,4] The cluster cores M_3Q_7 in these compounds are linked together into infinite zigzag chains by bridging halogen atoms (Fig. 7). A number of complexes containing anions $[M_3Q_7X_6]^{2-}$ (M = Mo, W; Q = S, Se; X = Cl, Br, I, NCS) is known nowadays.[18] However, there are very few complexes with N-donor ligands. Complexes with aniline $[Mo_3S_7Br_3(PhNH_2)_3]^+$,[51] pyridine,[52] 1,10-phenanthroline $[M_3Se_7(phen)_3]^{4+}$ (Ref. 53) and ethylenediamine[54] were synthesised. On the contrary, the cluster compounds in which the cores M_3Q_7 coordinate S-donor ligands are fairly numerous and include complexes with various thio-ligands: polysulfide $[Mo_3S_7(S_2)_3]^{2-}$, dithiophosphate $[Mo_3S_7(dtp)_3]^+$, dithiocarbamate $[M_3Se_7(dtc)_3]^+$, dithiophosphinate $[Mo_3S_7(R_2PS_2)_3]^+$ (R = Et, Pr^n, Bu^n) and other.[55–58]

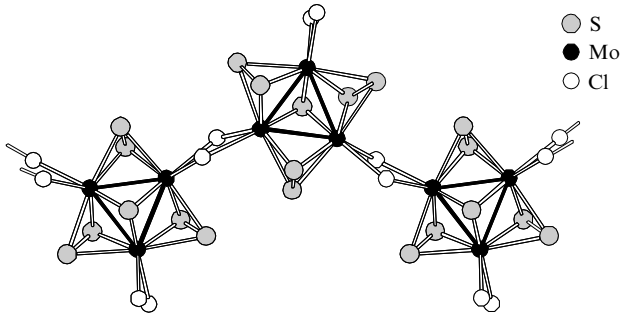


Figure 7. Structure of the polymer $Mo_3S_7Cl_4$.

Triangular clusters of molybdenum and tungsten with the core M_3Q_7 are well studied; similar complexes of vanadium and rhenium are also known. The metal–metal bond lengths in $[V_3^{III}S_7(bipy)_3]PF_6$ (Fig. 8) are equal to 2.75–2.78 Å;[59] the cluster fragment $V_3S_7^{2+}$ corresponding to the oxidised form is found in $(Et_4N)[V_3S_7(Me_2NCS_2)_3]$, where the V–V distances are slightly shorter (2.74–2.75 Å).[60]

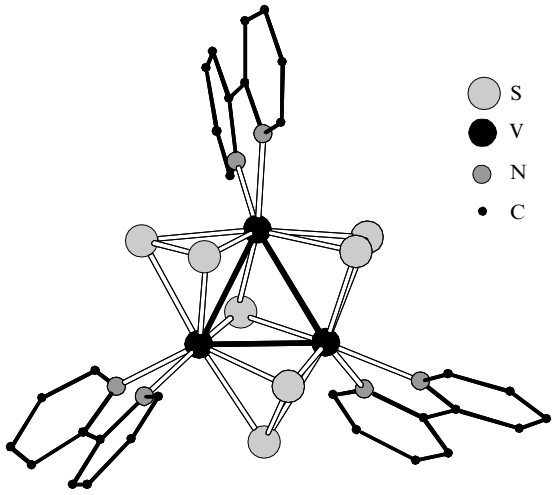


Figure 8. Structure of the complex $[V_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(bipy)_3]^+$.

A series of isostructural rhenium complexes $Re_3Q_7X_7$ (Q = S, Se; X = Cl, Br, I) were synthesised.[61–63] In these compounds, the cluster core $Re_3Q_7^{7+}$ is isoelectronic to that of $Mo_3Q_7^{4+}$, but the distance Re–Re in $Re_3S_7Cl_7$ (2.698 Å) is slightly shorter than the distance Mo–Mo in $Mo_3S_7Cl_4$ (2.758 Å) probably because of the difference in atomic radii of Re^V and Mo^{IV}.

There are very few telluride complexes M_3Q_7. The complexes $Mo_3Te_{10}I_{10}$, $[Mo_3Te_7(CN)_6]^{2-}$, $[W_3Te_7(CN)_6]^{2-}$ and $[Mo_3Te_7((EtO)_2PS_2)_3]I$ containing the $M_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3^{4+}$ core were synthesised and their structures were established.[50,64–67].

3. Other examples of triangular chalcogenide clusters

There are some mixed chalcogenide compounds among M_3Q_4 clusters.[68] In the triangular cluster $[Nb_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3.(NCS)_9]^{6-}$, only the sulfur atom occupies the μ_3-position.[22] Compounds $[M_3(\mu_3\text{-}S)(\mu_2\text{-}O)_x(\mu_2\text{-}S)_{3-x}(H_2O)_9]^{4+}$ (M = Mo, W; $x = 1-3$) and $[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}O)_x(\mu_2\text{-}Se)_{3-x}(H_2O)_9]^{4+}$ are also known.[18,69–71] Dithiophosphate derivatives of the cluster $Mo_3(\mu_3\text{-}O)(\mu_2\text{-}S)_3^{4+}$ were described as well.[72] Recently the complex $[W_3(\mu_3\text{-}Te)(\mu_2\text{-}Se)_3(CN)_9]^{5-}$ has been synthesised.[67] Mixed-chalcogen clusters M_3Q_7 are more diverse, they include $Mo_3(\mu_3\text{-}O)(\mu_2\text{-}S_2)_3^{4+}$, $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3^{4+}$, $M_3(\mu_3\text{-}S)(\mu_2\text{-}SSe)_3^{4+}$, $M_3(\mu_3\text{-}Se)(\mu_2\text{-}SSe)_3^{4+}$ (M = Mo, W), $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Te_2)_3^{4+}$, $Mo_3(\mu_3\text{-}O)(\mu_2\text{-}Te_2)_3^{4+}$ and $W_3(\mu_3\text{-}Te)(\mu_2\text{-}TeSe)_3^{4+}$ (Refs 47, 49, 50, 54, 67, 73 and 74). The substitution of the μ_3-chalcogen atom by an atom of lighter chalcogen results in significant shortening of metal–metal bonds in the M_3 triangle. This shortening corresponds approximately to the difference in size of the bridged chalcogen atoms. For example, the shortening in dithiophosphate complexes $[Mo_3Q(S_2)_3\{(EtO)_2PS_2\}_3]X$

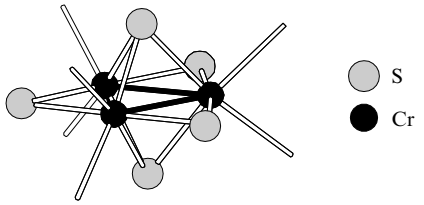


Figure 9. Cluster core in the complex $[Cr_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)_3(dmpe)_3]$ (the dmpe ligands are omitted).

(X = Cl, I, I_3) is equal to $\sim$0.1 Å: from 2.723 Å for Q = S to 2.626 Å for Q = O.[73]

Along with most typical triangular clusters M_3Q_4 and M_3Q_7, a number of other metal chalcogenide clusters are known. The cluster $[Cr_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)_3(dmpe)_3]$ contains two μ_3-bridging chalcogen atoms (Fig. 9).[75] Similar 'double-capped' coordination was also observed in $(Et_4N)_2[Cr_3(\mu_3\text{-}Se)_2(CO)_{10}]$ and $[Re_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)_2(\mu_2\text{-}Cl)Cl_3(PEt_3)_3]$.[76,77] An equilateral triangle Nb_3 in compound $[(\eta^5\text{-}C_5EtMe_4)_3Nb_3\{\mu_3\text{-}BS_3(SH)\}(\mu_2\text{-}S)_3]$ is symmetrically 'covered' by the $[BS_3(SH)]^{4-}$ ligand.[78] Only two electrons are available for metal–metal bonding in this cluster. Very similar tantalum cluster was found in the compound $[(\eta^5\text{-}C_5EtMe_4)_3Ta_3.(\mu_3\text{-}(BS_3(H))(\mu_2\text{-}S)_3]$. In this cluster the 'cap' is represented by the hydridotrithioborato anion $[BS_3(H)]^-$.[79]

Polymeric chalcogenides of niobium and tantalum M_3QX_7 contain the cluster core $M_3(\mu_3\text{-}Q)(\mu_2\text{-}X)_3^{4+}$.[80–83] The structure consists of parallel planes containing triangular clusters Nb_3 (the Nb–Nb bond length is 2.776 Å). The triangles are linked together into a two-dimensional network by bridging halogen atoms (Fig. 10).

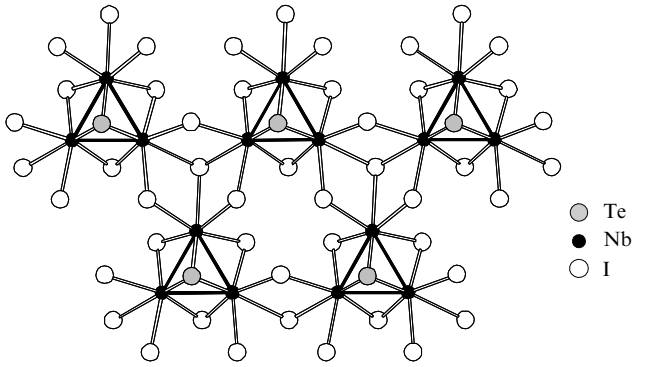


Figure 10. Fragment of the polymer Nb_3TeI_7.

4. Tetrahedral metal clusters with the core M_4Q_4

Each face of the M_4 tetrahedron in tetrahedral clusters with the core $M_4(\mu_3\text{-}Q)_4$ coordinates μ_3-chalcogen atoms in such a way that the metal and chalcogen atoms form a distorted cubane structure. The cubane clusters are topologically (and often genetically) related to previously discussed clusters of the $M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q)_3$ type, which may be regarded as defective cubane clusters (without one metal atom). Such type of cluster compounds is known for all discussed transition metals. Twelve valence electrons (N_e = 12) are required for the formation of six two-electron two-centre covalent metal–metal bonds in a tetrahedral cluster M_4. The stoichiometry of most of the stable complexes with d^3 electronic configuration of metal ions supports this rule. However, there are numerous examples of clusters where this simple model does not work and these compounds are formally electron-deficient.

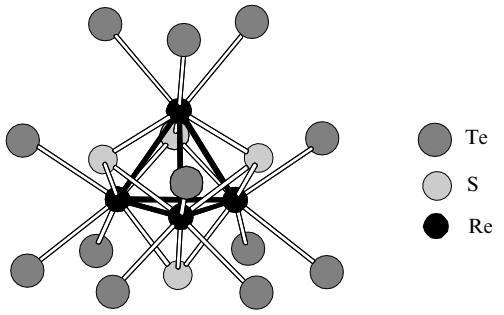


Figure 11. Structure of the cluster fragment $Re_4S_4Te_{12/3}$ in the compound $Re_4S_4Te_4$.

Polymeric ternary chalcogenides and chalcohalides of the types $M_4Q_4X_4$ (M = Nb, Mo; Q = S, Se; X = Cl, Br, I),[84–86] $Re_4S_4Te_4$ (Fig. 11)[87] and MMo_4Q_8 (M = Al, Ga)[88–91] are an abundant group of tetrahedral cluster compounds. All these compounds are isostructural and form spinel-type cubic crystal structures. The cubane cluster groups are linked into a three-dimensional framework by bridging halogen atoms or by excess chalcogen atoms according to the $[M_4Q_4X_{12/3}]_{\infty\infty\infty}$-type. Interestingly, only sulfur atoms occupy μ_3-positions in the cluster core of rhenium telluride $Re_4S_4Te_4$. Part of rhenium atoms of this cluster may be replaced by molybdenum atoms, which results in the formation of heterometallic cluster $Re_{4-x}Mo_xS_4Te_4$ ($0 \leqslant x \leqslant 1.25$).[92] The metal–metal distances in these clusters are correlated with N_e values (Table 1). The electronic and magnetic properties are determined by the successive filling of the d shell.

Table 1. Number of metal–metal bonding valence electrons and the metal–metal distances in tetrahedral metal clusters.

Compound	N_e	M–M bond length /Å
$GaNb_4Se_8$	7	3.03
$Nb_4Se_4I_4$	8	2.96
$GaMo_4Se_8$	11	2.89
$Mo_4S_4Br_4$	12	2.80
$Re_4S_4Te_4$	12	2.78

The rhenium atoms of the cluster core Re_4Q_4 of molecular rhenium chalcohalide complexes $[Re_4Q_4(TeX_2)_4X_8]$ (Q = S, Se, Te; X = Cl and Q = Te, X = Br; N_e = 12) additionally coordinate two halide ligands and the ligand TeX_2.[10,93] The tetrahedral chalcogenide clusters $[(\eta^5\text{-}C_5H_4R)_4M_4Q_4]$ with monosubstituted cyclopentadienyl ligands are known for some metals discussed: V (Q = S, R = Me),[94] Cr (Q = S, Se, Te; R = Me),[95–100] Mo (Q = S, Se; R = Pr^i).[101] The cyclopentadienyl cluster complexes of the Group 5 elements are represented only by vanadium cyclopentadienyl(thio) complexes $[(\eta^5\text{-}C_5H_4R)_4V_4S_4]$ (R = H, Me).[94] The N_e value in neutral complexes is equal to 8 for vanadium and 12 for chromium and molybdenum.

A large number of chalcocyanide cluster complexes $[M_4Q_4(CN)_{12}]^{n-}$, where M = Mo, W, Re; Q = S, Se, Te (Fig. 12) is studied in detail.[102–107] The cluster core of the complexes $[Re_4Q_4(CN)_{12}]^{4-}$ coordinates terminal cyano groups through the carbon atom. The cluster M_4 becomes electron-deficient in the corresponding molybdenum complexes $[Mo_4Q_4(CN)_{12}]^{6-}$. The cyano complexes $[M_4OTe_4(CN)_{12}]^{6-}$ containing the metal core $M_4(\mu_4\text{-}O).(\mu_3\text{-}Te)_4^{6+}$ with an interstitial oxygen atom were obtained for niobium and tantalum.[108] In these clusters, N_e = 4, and the M–M distances are significantly longer than those in the

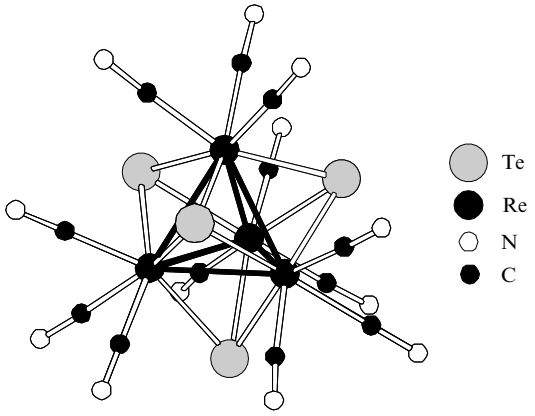


Figure 12. Structure of the complex $[Re_4Te_4(CN)_{12}]^{4-}$.

corresponding metals or in the compounds containing single M–M bond.

A series of the complexes $M_4Q_4L_{12}$ with various terminal ligands L such as H_2O (M = Mo, W; Q = S, Se),[109–111] Cl (M = Re, Q = Te; M = Mo, Q = S),[22,70,112–119] NCS (M = Re: Q = S, Se, Te; M = Mo, Q = S)[111,116,120] are known for the cubane clusters of molybdenum, tungsten and rhenium. Complexes $[Re_4S_4(S_3)_6]^{4-}$ and $[Re_4Q_4(S_3)_4(S_4)_2]^{4-}$ with polysulfide ligands are known for rhenium.[121–123] The edges of the tetrahedron Re_4 in the complex $[Re_4Se_4(S_3)_4(S_4)_2]^{4-}$ coordinate four bidentate polysulfide ligands S_3 and two S_4 ligands in *trans*-position relatively to each other (Fig. 13).

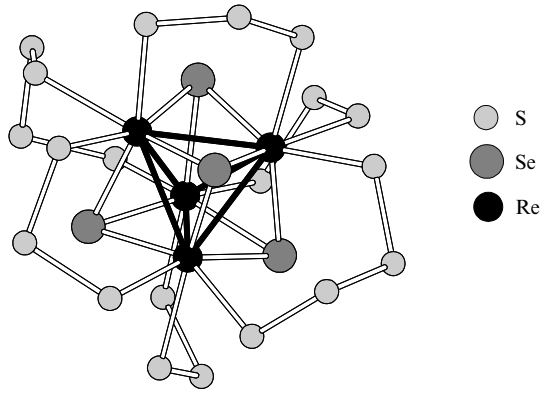


Figure 13. Structure of the complex $[Re_4Se_4(S_3)_4(S_4)_2]^{4-}$.

Sulfur-containing ligands stabilise the electron-deficient cluster core $Mo_4S_4^{6+}$ (N_e = 10): this cluster core was found in dithiophosphate $[M_4S_4(\mu_2\text{-dtp})_2(dtp)_4]$ (M = Mo, W; Q = S)[115,124] and in dithiocarbamate $[Mo_4S_4(\mu_2\text{-Et}_2NCS_2)_2.(Et_2NCS_2)_4]$[115] complexes.

A unique series of high-valence cubane clusters based on *p*-tolylimide ($tolN^{2-}$) derivatives of Mo(V) and W(V), were synthesised.[125,126] Each metal atom in the structure of $[Mo_4S_4(tolN)_4(S_2P(OEt)_2)_4]$ is bound to one terminal $=NC_6H_4Me\text{-}p$ group, to one chelating dithiophosphate and to three bridging sulfide ligands of the cluster core. Four electrons available for M–M-bonding are localised in such a way that two single Mo–Mo (2.862 Å) bonds are located at the opposite edges of the tetrahedron. The four remaining metal–metal distances are significantly longer (3.69 Å). The complex $[W_4S_4(en)_4(S)_4]S$ (en is ethylenediamine) containing a distorted metal cluster (N_e = 6; W–W 2.801–2.878 Å) is another example.[127] Alternatively, one can regard this compound as $[W_4S_4(en)_4(SH)_4]S$ with a more conventional cluster core $W_4S_4^{6+}$.

5. Square metal M_4 clusters

The complex $Li_4[Nb_4S_2(SPh)_{12}]$ in which the square metal cluster coordinates two μ_4-S-ligands was the first discovered compound of this rare type.[128] Four Nb^{III} atoms in this diamagnetic compound provide eight electrons for the formation of four metal–metal bonds with distances Nb–Nb equal to 2.83 Å. Another example is the $[Nb_4S_2(SPh)_8(PMe_2R)_4]$ complex (R = Me, Ph).[129]

The polymeric vanadium compound $V_4S_9Br_4$ contains the metal core $V_4(\mu_4\text{-S})(\mu_2\text{-S}_2)_4^{4+}$ (Fig. 14).[13] Four ligands S_2 are coordinated asymmetrically. The bridging bromine atoms link the clusters into the layer $[V_4(\mu_4\text{-S})(\mu_2\text{-S}_2)_4Br_{8/2}]_{\infty\infty}$. The vanadium oxidation state in this complex is equal to +3.5 and only two electrons take part in the metal–metal bonding (the distances V–V are equal to 3.01 Å). The remaining four non-bonded electrons are located at the metal centres (one per each metal atom), which makes the compound paramagnetic. The oxidation state of tantalum atoms in the cluster core $Ta_4(\mu_4\text{-Q})(\mu_4\text{-Q}_2)_4^{8+}$ of molecular diamagnetic compounds

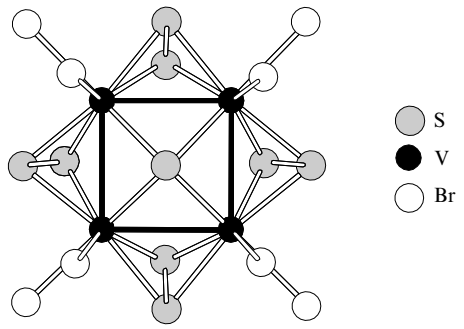


Figure 14. Structure of the cluster fragment $V_4(\mu_4\text{-S})(\mu_2\text{-S}_2)_4Br_8$ in the compound $V_4S_9Br_4$.

$Ta_4Q_9X_8$ (Q = S, Se; X = Br, I) is +4.5 and therefore only two electrons are available for bonding in the metal cluster.[14] Long distances Ta–Ta (3.30–3.39 Å) are typical of such electron-deficient square clusters.

6. Other examples of tetranuclear chalcogenide clusters

Tetranuclear complexes containing the cluster core $M_4(\mu_3\text{-S})_2(\mu_2\text{-S})_4^{2+}$ with planar arrangement of metal atoms were synthesised. The complexes $[Mo_4(\mu_3\text{-S})_2(\mu_2\text{-S})_4.(SH)_2(PMe_3)_6]$ (Fig. 15)[130] and $[W_4(\mu_3\text{-S})_2(\mu_2\text{-S})_4(SH)_2.(PMe_2Ph)_6]$ belong to this class.[131] These clusters provide ten electrons for the formation of five localised metal–metal bonds; the bond lengths lie in the narrow interval (Mo–Mo 2.83–2.85 Å; W–W 2.81–2.84 Å). The two-electron oxidation of the complex $[W_4(\mu_3\text{-S})_2(\mu_2\text{-S})_4Cl_2(PMe_2Ph)_6]$ yields the salt of double-charged cationic cluster $[W_4(\mu_3\text{-S})_2(\mu_2\text{-S})_4Cl_2.(PMe_2Ph)_6](CF_3SO_3)_2$.[131] The reduction of the same cluster by excess of sodium amalgam results in the formation of the tungsten(III) complex $[W_4(\mu_2\text{-S})_6(PMe_2Ph)_6]$, containing tetrahedral metal cluster W_4 (N_e = 12, the distances W–W are equal to 2.634 Å).[131]

The cluster M_4 core of a 'butterfly' type with two μ_3-S-ligands was found in the complex $[Mo_4(\mu_3\text{-S})_2(\mu\text{-CO})_4.(\eta^5\text{-}C_5H_4CO_2Me)_4]$; the edges also coordinate four μ_2-carbonyl groups (Fig. 16).[132]

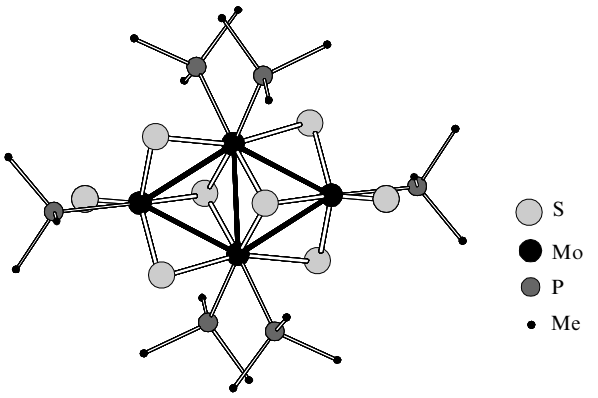


Figure 15. Structure of the complex $[Mo_4(\mu_3\text{-}S)_2(\mu_2\text{-}S)_4(SH)_2(PMe_3)_6]$.

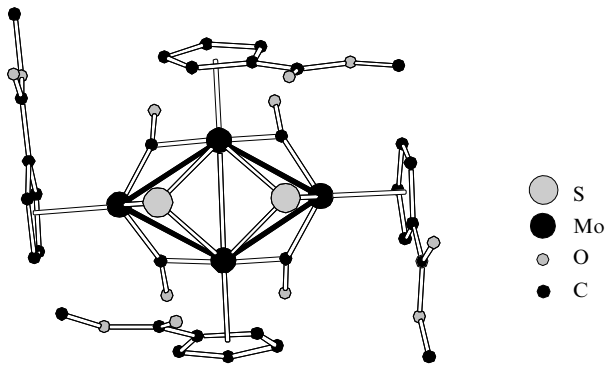


Figure 16. Structure of the complex $[Mo_4(\mu_3\text{-}S)_2(\mu\text{-}CO)_4.(\eta^5\text{-}C_5H_4CO_2Me)_4]$.

7. Octahedral clusters

The octahedral clusters (Fig. 17) are the most numerous among hexanuclear cluster complexes. The metal cluster M_6 in these complexes is surrounded by eight μ_3-L^i ligands coordinated to triangular faces of the metal octahedron. Additionally, the metal atoms coordinate the terminal ligands L^a producing a cluster complex $[\{M_6L^i_8\}L^a_6]$. [The indices i and a were introduced by Schäfer and Schnering [133] and derived from German words inner (inner) and ausser (outer); the ligands of the μ_2-L type, coordinated to the edges of metal cluster, were classified as inner.] Then the cluster core may be regarded as a combination of the metal cluster and L^i ligands. The total

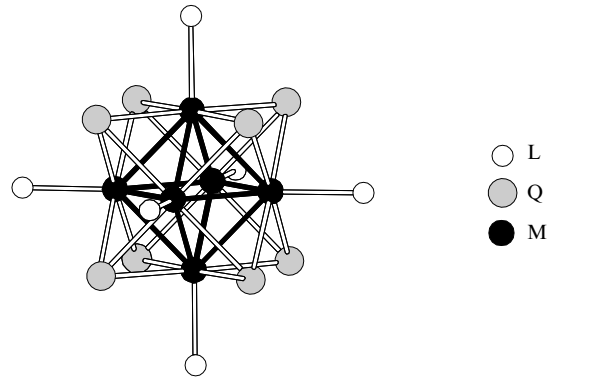


Figure 17. Structure of the octahedral cluster complex $[M_6Q^i_8]L^a_6$.

number of the ligands surrounding the M_6 octahedron is equal to 14. Accordingly, the cluster compounds with L : M = 14 : 6 possess the molecular structure with isolated cluster complexes {for example, $[Re_6S_4Br_{10}]$, $Cs_4[Mo_6S_2Br_{12}]$,[134] $[W_6S_8(py)_6]$,[135] *etc.*}. When the ratio L : M is smaller, the polymeric structures are formed. In these structures, both L^i and L^a may play the role of bridging ligands. The examples of such structures are given below.

Twenty-four valence electrons (N_e = 24) are required for the filling of 12 bonding molecular orbitals (MO) corresponding to metal – metal bonds in a metal cluster M_6. This situation exists in compounds in which the metal ions possess the d^4 electron configuration, for instance, in the octahedral Re^{III} complexes that contain the $Re_6Q_8^{2+}$ cluster core.[136] Compounds with electron-deficient cluster cores (N_e = 20 – 22) are stable in the case of chromium, molybdenum and tungsten chalcogenide complexes; the most spectacular examples of such compounds are molybdenum chalcogenides, Mo_6Se_8 (N_e = 20) and $PbMo_6S_8$ (N_e = 22).

The octahedral chalcogenide clusters of the Group 5 metals are virtually unknown, probably, because of the considerable deficit of electrons required for the formation of the M – M bonds in the cluster. The complex $[V_6Se_8(O)(PMe_3)_6]$ (Fig. 18), in which the metal cluster V_6 contains an interstitial (μ_6) oxygen atom, is the only example of such chalcogenide clusters.[137] The octahedral geometry of this electron-deficient cluster (N_e = 12) is retained due to the formation of V – O bonds.

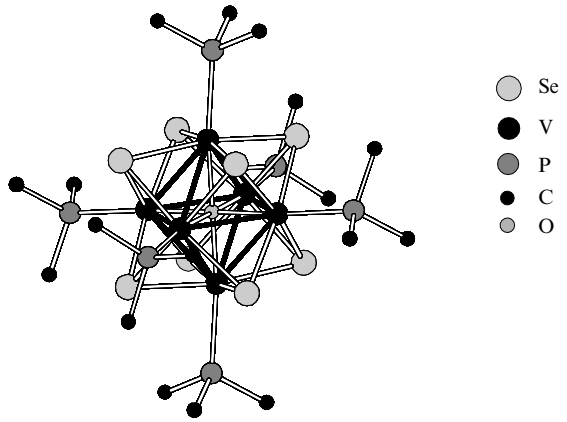


Figure 18. Structure of the complex $[V_6Se_8(O)(PMe_3)_6]$.

Isocharged or non-isocharged substitution of chalcogenide ligands in the cluster core M_6Q_8 results in the formation of isomers which are very hard to separate. Thus in the case of $M_6Q_6Q'_2$ three geometric isomers are possible (Fig. 19), and in the case of $M_6Q_4Q'_4$ the number of isomers is six. Typically, the heteroatoms in the solid state structure of the clusters with mixed ligands are disordered over all possible positions. However, there are some examples of ordered structures. These compounds are usually formed in the cases of significant difference in atomic radii of the ligands L^i: Te and Cl in $Re_6Te_8Cl_{10}$ (Ref. 138) or Se and O in $[Re_6Se_4O_4Cl_6]^{4-}$.[139] The metal cluster Re_6 in compound $Cs_{11}(H_3O).[Re_6Se_4O_4Cl_6]_3 \cdot 4\,H_2O$ is surrounded by four oxygen atoms and four selenium atoms, localised at the opposite faces of the Se_4O_4 cube (Fig. 20).[139] Such ligand environment results in a significant distortion of the metal cluster and the Re – Re distances in this compound vary from 2.46 Å (in the faces coordinating the μ_3-oxygen atoms) to 2.62 Å (in the faces coordinating the μ_3-selenium atoms).

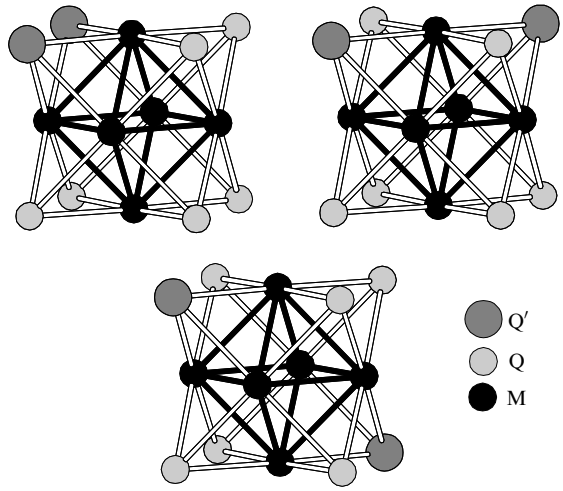


Figure 19. Geometrical isomers of the cluster core $[M_6Q_6Q'_2]$.

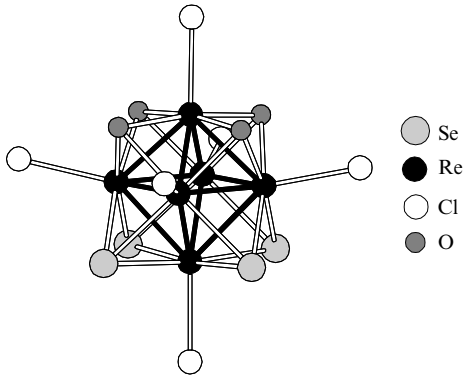


Figure 20. Structure of the complex $[Re_6Se_4O_4Cl_6]^{4-}$.

There are several examples of heterometallic octahedral clusters: $Mo_{6-x}M_xQ_8$ (M = Re: Q = S, Se, Te, $x = 4$; M = Ru: Q = Se, Te, $0 \leqslant x \leqslant 2$; M = Rh, Q = Te, $x = 0.5$, 1.33),[140] $Nb_{6-x}Ru_xTe_8$ ($2.50 \leqslant x \leqslant 3.17$),[141] $Cs_5[Re_{6-x}Mo_xS_8(CN)_6]$,[142] $Cs_3[Re_5OsS_{11}]$,[143] $Cs_3[Re_{6-x}Os_xSe_8Cl_6]$ ($x = 1$, 2) and $K_2[Re_3Os_3Se_8Cl_6][Re_4Os_2Se_7Cl_7]$.[144] The phosphine and cyanide complexes were studied for rhenium – osmium clusters.[144, 145]

A great number of molecular complexes of molybdenum, tungsten and rhenium with the cluster core M_6Q_8 were studied. Ions (halides, cyanide, thiocyanate, hydroxide) or neutral molecules (phosphines, pyridines, *etc.*) play the role of ligands L^a in these complexes.[19, 135, 136, 139, 146–178] Usually, the terminal ligands are coordinated in a monodentate mode or as bridging ligands linking adjacent clusters. The study of coordination of diphosphine $Ph_2P(CH_2)_nPPh_2$ with octahedral rhenium clusters has shown that the chelate complexes are formed if $n \geqslant 6$.[153]

8. Miscellaneous hexanuclear clusters

The metal cluster V_6 in compound $(Et_4N)_3[V_6S_4(edt)_6(O)_2]$ is essentially planar. Nine valence electrons take part in the formation of five V – V bonds (2.82 – 2.86 Å) (Fig. 21).[179] Four triangles Mo_3 with shared edges in the topologically related hexanuclear molybdenum clusters $[Mo_6S_{10}(SH)_2.(PEt_3)_6]$ coordinate four μ_3- and six μ_2-chalcogen atoms (Fig. 22).[130] There are 14 electrons per nine Mo – Mo bonds in this cluster, which results in the shortening (in comparison with the vanadium structure) of the distances Mo – Mo (2.73 – 3.06 Å). Similar structure of the cluster core was also observed in compounds $[Mo_6Q_8Cl_6(PEt_3)_6]$.[180]

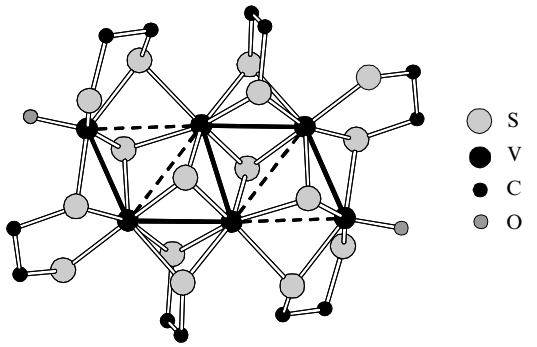


Figure 21. Structure of the complex $[V_6(\mu_3\text{-}S)_4(edt)_6(O)_2]^{3-}$.

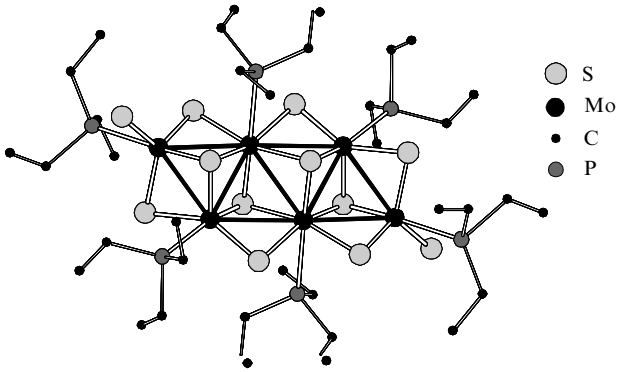


Figure 22. Structure of the complex $[Mo_6(\mu_3\text{-}S)_4(\mu\text{-}S)_6(SH)_2(PEt_3)_6]$.

The metal cluster Mo_6 in an unusual complex $[Mo_6S_6(CN)_{16}]^{8-}$ (Fig. 23) may be represented by two edge-sharing tetrahedrons. Four edges coordinate sulfur atoms according to the μ_3-type and two pairs of fused faces (*i.e.* those with the shared edge) coordinate sulfur atoms according to the μ_4-type.[181]

Two triangles Nb_3 in the hexanuclear cluster $[Nb_6SBr_{17}]^{3-}$ (Fig. 24) are linked together by a μ_6-sulfur atom.[182] The Nb – Nb bond lengths in the triangles are in the range of 2.95 – 2.98 Å, the distances between the triangles are longer and equal to 3.276 Å.

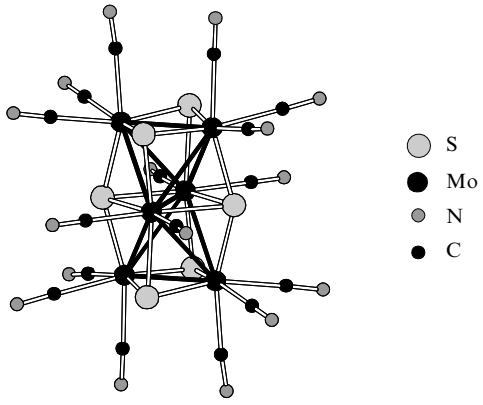


Figure 23. Structure of the complex $[Mo_6S_6(CN)_{16}]^{8-}$.

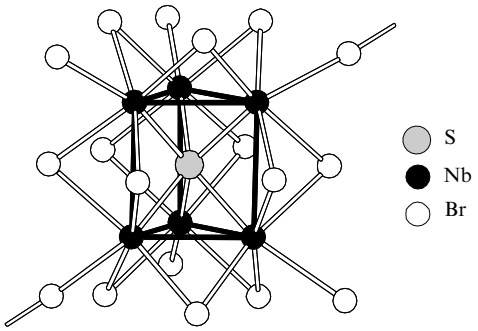


Figure 24. Structure of the complex $[Nb_6SBr_{17}]^{3-}$.

9. Compounds based on polymeric octahedral cluster complexes

The decrease of the number of ligands in molecular complexes $[M_6L^i_8]L^a_6$ results in the formation of polymeric-bridged structures. According to Schäfer,[133] the inter-cluster bridging ligands are designated as L^{a-a}, L^{i-a} and L^{a-i} depending on their structural role in each of the metal clusters linked by them.

a. Linking of the octahedral cluster cores through bridging halide ligands L^{a-a}

One of the most common methods of linking of cluster cores $M_6L^i_8$ into polymeric chains, layers and frameworks (when the ratio L : M is decreasing) is the linking through apical halide ligands which become bridging between two cluster cores (Table 2). If all six apical ligands are bridging, then the compounds form 3D frameworks (Fig. 25), if four equatorial ligands are bridging then layered 2D polymers are formed and in the case of two bridging ligands 1D chains are formed.

The ternary systems Re–Q–Y (Q = S, Se; Y = Cl, Br) are models in the studies of the influence of the number of shared ligands on the polymeric structure type. Depending on the ratio Q : Y, all possible types of structures are formed in these systems: the frameworks in $\{(Re_6Q^i_7Y^i)Y^{a-a}_{6/2}\}$,[184] the layers in $\{(Re_6Q^i_6Y^i_2)Y^i_2Y^{a-a}_{4/2}\}$,[184] the chains in $\{(Re_6Q^i_5Y^i_3)Y^a_4Y^{a-a}_{2/2}\}$[184] and isolated cluster complexes in $(Re_6Q^i_4Y^i_4)Y^a_6$.[186–190] The structures and properties of these compounds are discussed in details in reviews.[16, 136, 191]

Table 2. Octahedral clusters with inter-cluster halide ligands.

Compound	Structural type	Crystallochemical formula	Ref.
Mo_6QCl_{10}	framework (3D)	$\{(Mo_6Q^iCl^i_7)Cl^{a-a}_{6/2}\}$; Q = S, Se, Te	183
$Re_6Q_7X_4$	"	$\{(Re_6S^i_7Br^i)Br^{a-a}_{6/2}\}$	184
$Re_6Q_6X_6$	layer (2D)	$\{(Re_6Se^i_6Cl^i_2)Cl^a_2Cl^{a-a}_{4/2}\}$, $\{(Re_6S^i_6Br^i_2)Br^a_2Br^{a-a}_{4/2}\}$	184
$Re_6Q_5X_8$	chain (1D)	$\{(Re_6Se^i_5Cl^i_3)Cl^a_4Cl^{a-a}_{2/2}\}$, $\{(Re_6S^i_5Br^i_3)Br^a_4Br^{a-a}_{2/2}\}$	184
$AgRe_6Se_6Cl_7$	"	$Ag\{(Re_6Se^i_6Cl^i_2)Cl^a_4Cl^{a-a}_{2/2}\}$	185
$ZnRe_6Se_7Cl_6$	"	$Zn\{(Re_6Se^i_7Cl^i)Cl^a_4Cl^{a-a}_{2/2}\}$	185

b. Linking of the octahedral cluster cores through chalcogenide and polychalcogenide inter-cluster ligands

The compounds with bridging chalcogenide and polychalcogenide ligands were obtained only for rhenium and technetium;[192] some crystal data on these compounds are listed in Table 3. The examples of the compounds with unusual bridging ligands, *viz*., spiro-Te_7^{2-} and Te_6, are shown in Figs 26 and 27.[8, 206]

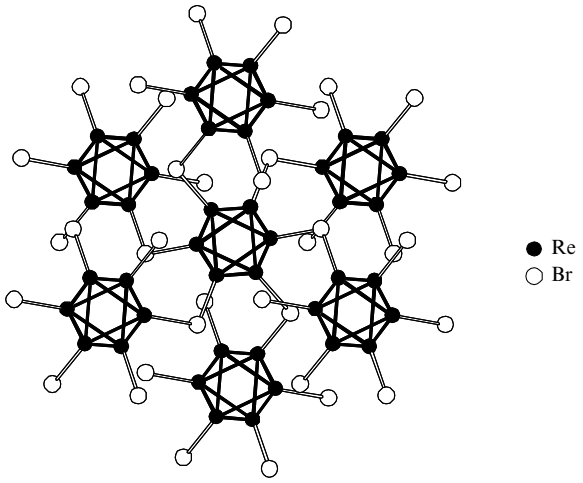


Figure 25. Fragment of the structure of $Re_6Se_7Br_4$ (the 'inner' ligands are omitted).

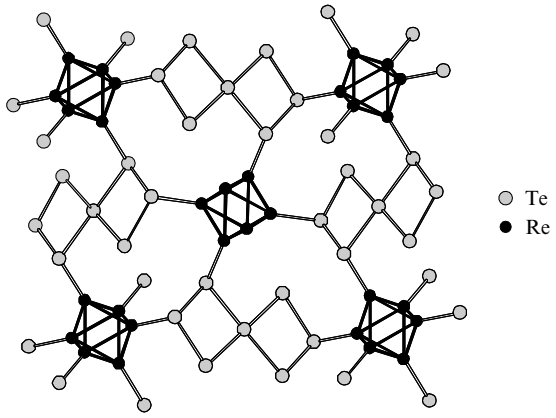


Figure 26. Linking of the metal clusters Re_6 through Te_7 ligands in the structure of Re_6Te_{15}.

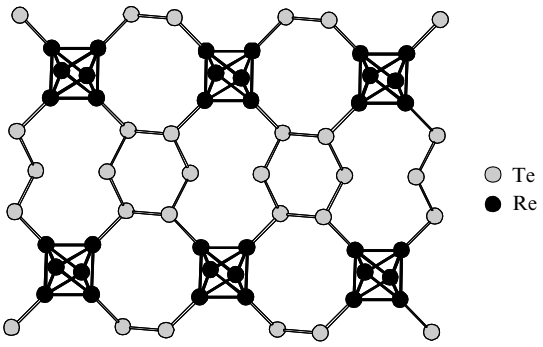


Figure 27. Linking of the metal clusters Re_6 through Te_6 ligands in the structure of $Re_6Te_{16}Cl_{18}$.

Linking of the cluster cores into layered or 3D-framework structures through chalcogen atoms is typical of ternary rhenium sulfides and selenides. The cluster cores in $Cs_4[(Re_6Se^i_8)Se^{a-a}_{2/2}(Se_2)^{a-a}_{4/2}]$ are linked together by two selenide and four diselenide bridges yielding a 3D structure (Fig. 28).[201]

Recently, octahedral rhenium chalcocyanide complexes with bridging chalcogenide ligands have been obtained: the layered structure of $K_4[Re_6S_{10}(CN)_2]$ and chain structures of

Table 3. Octahedral clusters with chalcogenide and polychalcogenide inter-cluster ligands.

Compound	Structural type	Crystallochemical formula	Ref.
Compounds containing only the chalcogenide bridges			
$Cs_4Re_6S_9(CN)_4$	chain (1D)	$Cs_4\{(Re_6S_8^i)(CN)_4^a(S)_{2/2}^{a-a}\}$	193
$K_4Re_6S_{10}(CN)_2$	layer (2D)	$K_4\{(Re_6S_8^i)(CN)_2^a(S)_{4/2}^{a-a}\}$	194
$Cs_6Re_6S_{12}$	"	$Cs_6\{(Re_6S_8^i)S_{4/2}^{a-a}S_2^a\}$	195
$Li_4Re_6S_{11}$	framework (3D)	$Li_4\{(Re_6S_8^i)S_{6/2}^{a-a}\}$	196
$M_2Re_6S_{11}$, M = Sr, Ba, Eu	"	$M_2\{(Re_6S_8^i)S_{6/2}^a\}$	197, 198
Compounds containing polychalcogenide bridges			
$K_4Re_6Se_{10}(CN)_4$	chain (1D)	$K_4\{(Re_6S_8^i)(CN)_4^a(Se_2)_{2/2}^a\}$	194
$M_4Re_6S_{12}$, M = Na, K, Rb	framework (3D)	$M_4\{(Re_6S_8^i)S_{4/2}^{a-a}(S_2)_{2/2}^{a-a}\}$	199, 200
$M_4Re_6Se_{12}$, M = K, Rb	"	$M_4\{(Re_6Se_8^i)Se_{4/2}^{a-a}(Se_2)_{2/2}^{a-a}\}$	201
$M_4Re_6S_{13}$, M = (K,Rb), Rb, Cs	"	$M_4\{(Re_6S_8^i)S_{2/2}^{a-a}(S_2)_{4/2}^{a-a}\}$	201, 202
$Cs_4Re_6Se_{13}$	"	$Cs_4\{(Re_6Se_8^i)Se_{2/2}^{a-a}(Se_2)_{4/2}^{a-a}\}$	201
$Cs_4Re_6S_{13.5}$	"	$Cs_4\{(Re_6S_8^i)S_{2/2}^{a-a}(S_2)_{3/2}^{a-a}(S_3)_{1/2}^{a-a}\}$	202, 203
$Cs_6Re_6S_{15}$	"	$Cs_4\{(Re_6S_8^i)(S_2)_{6/2}^{a-a}\}\cdot Cs_2S$	204
$Cs_6Re_6Se_{15}$	"	$Cs_4\{(Re_6Se_8^i)(Se_2)_{6/2}\}\cdot Cs_2Se$	205
Re_6Te_{15}	"	$\{(Re_6Te_8^i)(Te_7)_{6/6}^a\}$	8
$Re_6Te_8(Te_8Cl_{18})$	"	$\{(Re_6Te_8^i)(Te_8Cl_{18})_{6/6}^a\}$	206
$Re_6Te_8(Te_6)(TeCl_3)_2$	layer (2D)	$\{(Re_6Te_8^i)(TeCl_3)_2^a(Te_6)_{4/4}^a\}$	206

$K_4[Re_6Se_{10}(CN)_4]$ and $Cs_4[Re_6S_9(CN)_4]$ contain bridging sulfide and diselenide ligands (Fig. 29).[193, 194]

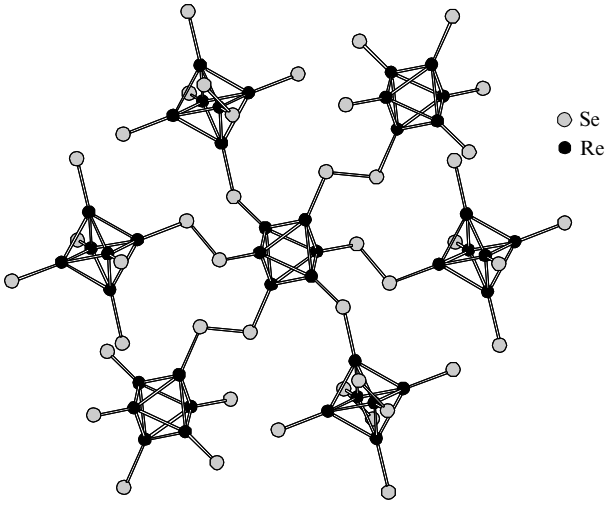


Figure 28. Fragment of polymer layer $[\{Re_6Se_8^i\}Se_{2/2}^{a-a}(Se_2)_{4/2}^{a-a}]_{\infty\infty}^{4-}$ in the structure of $Cs_4[Re_6Se_{13}]$ (the μ_3-Se ligands are omitted).

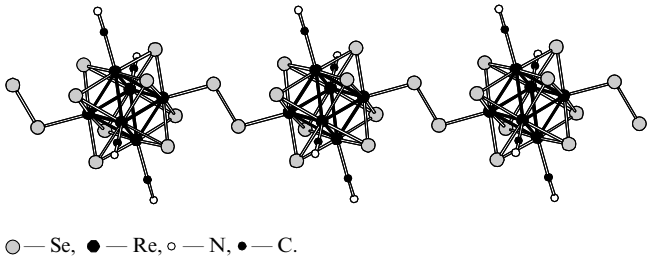


Figure 29. Fragment of polymer chain $[\{Re_6Se_8\}(Se_2)_{2/2}(CN)_4]_{\infty}^{4-}$ in the structure of $K_4[Re_6Se_{10}(CN)_4]$.

c. Linking of the octahedral cluster cores through 'inner' ligands

The metal coordination sphere of lower chalcogenides contains the ligands of an adjacent cluster core which thus become the inter-cluster bridges. The less is the L : M ratio the more 'inner' ligands are involved in the formation of these inter-cluster bridges. Examples of such compounds are given in Table 4.

Each molybdenum atom in the compound Mo_6Se_8 is bonded to the inner ligand of the adjacent cluster, which thus may be regarded as an apical ligand.[213, 214] As a result, the clusters are strongly linked together due to the formation of rhombic fragments $Mo_2Se_2^i$ (Fig. 30) and the Mo – Mo distances between the molybdenum atoms of the neighbouring metal clusters are shortened (3.266 Å).

Other compounds with strong inter-cluster bridges are represented by rhenium chalcohalides $Re_6S_8Cl_2$, $Re_6Se_8Cl_2$, $Re_6S_8Br_2$ and $Re_6Se_8Br_2$.[207 – 209] The cores $Re_6S_8^i$ in crystals of $Re_6S_8Cl_2$ are linked in chains by two centrosymmetrical Re – S

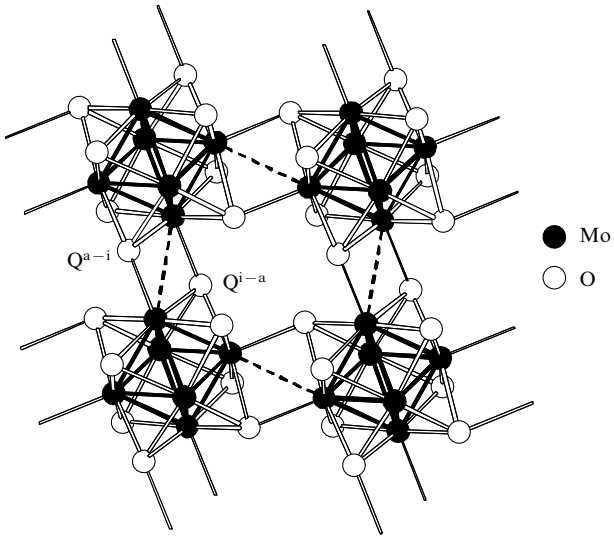


Figure 30. Fragment of the structure of Mo_6Q_8 in the Chevrel phases. The inter-cluster Mo – Mo contacts are shown by dashed lines.

Table 4. Octahedral clusters with additional coordination of the 'inner' ligands of cluster core.

Compound	Structural type	Crystallochemical formula	Ref.
$Re_6S_8Cl_2$, $Re_6S_8Br_2$, $Re_6Se_8Br_2$	framework (3D)	$\{(Re_6Q^i_6Q^{i-a}_{2/2})Q^{a-i}_{2/2}Y^{a-a}_{4/2}\}$; Q = S, Se; Y = Cl, Br	207 – 209
$Re_6Se_8Cl_2$	layer (2D)	$\{(Re_6Se^i_4Se^{i-a}_{4/2})Se^{a-i}_{4/2}Cl^a_2\}$	210
$Cs_2Re_6Se_8Br_4$	chain (1D)	$Cs_2\{(Re_6Se^i_6Se^{i-a}_{2/2})Br^a_4Se^{a-i}_{2/2}\}$	211
$TlRe_6Se_8Cl_3$	layer (2D)	$Tl\{(Re_6Se^i_5Se^{i-a}_{3/2})Cl^a_3Se^{a-i}_{3/2}\}$	212
$CsRe_6Se_8I_3$	"	$Cs\{(Re_6Se_6Se^{i-a}_{2/2})I^a_2I^{a-a}_{2/2}Se^{a-i}_{2/2}\}$	211
$M_2Re_6Q_8Cl_4$, M = Tl: Q = S, Se; M = Cs, Q = S	chain (1D)	$M_2[Re_6Q_6Q^{i-a}_{2/2}]Cl^a_4Q^{a-i}_{2/2}$	211, 212
$Re_4Os_2Se_8Cl_4$	framework (3D)	$\{(Re_4Os_2Se^i_8)Se^{a-i}_{2/2}Cl^a_2Cl^{a-a}_{2/2}(Re_4Os_2Se^i_6Se^{i-a}_{2/2})Cl^a_4Cl^{a-a}_{2/2}\}$	144
Mo_6Q_8	"	$\{(Mo_6Q^i_2Q^{i-a}_{6/2})Q^{a-i}_{6/2}\}$; Q = S, Se	213, 214
$Mo_6S_6Br_2$	"	$\{(Mo_6Br^i_2S^{i-a}_{6/2})S^{a-i}_{6/2}\}$	215
$Mo_6I_8Se_2$	"	$\{(Mo_6I^i_5Se^iSe^{i-i}_{2/2})I^{a-a}_{6/2}\}$	216
Nb_6I_9S	chain (1D)	$\{Nb_6I^i_6S^{i-i}_{2/2}I^{a-a}_{6/2}\}$	217

bonds. The chains are combined into a 3D structure by $Re-Cl^{a-a}-Re$ bridges. The rhombic bridges Re_2Q_2 were also found in some other compounds. The structure $TlRe_6.Se_8Cl_3$, *i.e.* $Tl[(Re_6Se^i_5Se^{i-a}_{3/2})Se^{a-i}_{3/2}Cl^a_3]$, consists of layers linked by three Re_2Se_2 bridges.[212] The cores Re_6Se_8 in crystals of $Cs_2Re_6Se_8Br_4$ are *trans*-linked in chains by rhombuses Re_2Se_2 (Fig. 31).[211]

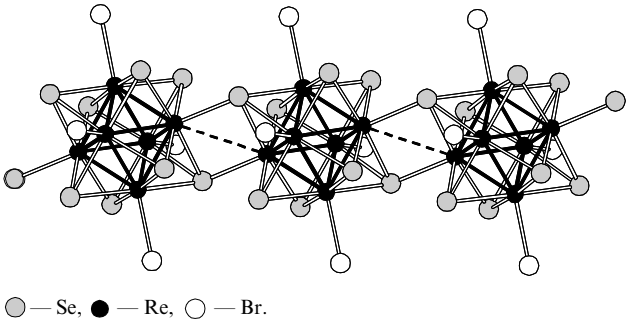


Figure 31. Fragment of polymer chain $\{Re_6Se_8Br_4\}^{2-}_{\infty}$ in the structure of $Cs_2Re_6Se_8Br_4$.

The complex Nb_6I_9S containing the electron-deficient 19-electron cluster core $Nb_6I^i_6S^i_2$ occupies a special place among the polymeric chalcogenides. The sulfide ligands L^i in this compound are shared between adjacent clusters (Fig. 32). In addition, the apical iodine atoms also make bridges between the clusters; this results in the formation of unusual linear chains $[Nb_6I^i_6S^{i-i}_{2/2}I^{a-a}_{6/2}]$.[217]

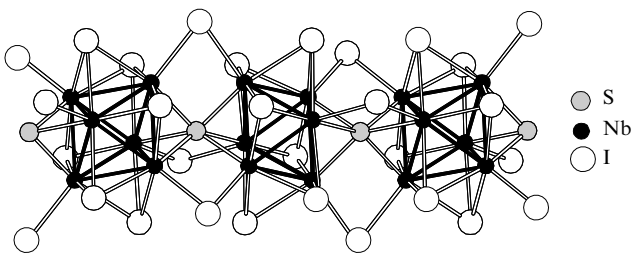


Figure 32. Fragment of a polymeric chain $\{Nb_6I^i_6S^{i-i}_{2/2}I^{a-a}_{6/2}\}$ in the structure of Nb_6I_9S.

10. High nuclearity clusters

A homological series of the clusters $Mo_{6+3x}Q_{8+3x}$ (Q = S, Se; $x = 1-3$), which was found in ternary molybdenum chalcogenides, may be described as a product of the progressive condensation of triangles Mo_3. The first member of the series, Mo_9Se_{11}, contains a dioctahedral metal cluster Mo_9.[218] Eight selenium atoms are bonded to the metal cluster according to the μ_3-mode, and three selenium atoms, which are located in the plane of the middle Mo_3 triangle, are μ_4-mode coordinated. The metal atoms of the outer triangles Mo_3 of the cluster core Mo_9Q_{11} in a crystal are additionally coordinated by six bridging Se atoms, which link together the adjacent cluster fragments Mo_9Q_{11}. The structures of clusters Mo_9Q_{11}, $Mo_{12}Q_{14}$ and $Mo_{15}Q_{17}$ are shown in Fig. 33.[218–221] The condensation continues up to joining together 11 octahedra in the structure of $Rb_{10}Mo_{36}S_{38}$.[222] The ultimate case of the condensation of the triangles Mo_3 is represented by compounds $M[Mo_3Q_3]$ (M = Li, In, Tl; Q = Se, Te) containing infinite chains $[Mo_3Q_3]^-_{\infty}$.[223]

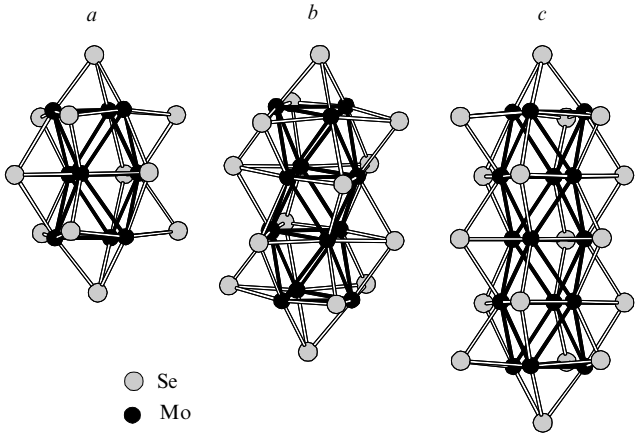


Figure 33. Structures of the cluster cores Mo_9Se_{11} (*a*), $Mo_{12}Se_{14}$ (*b*), $Mo_{15}Se_{18}$ (*c*).

The mixed-valence cluster complex $[Re_9Se_{11}Br_6]^{2-}$ consists of eight Re^{III} atoms and one Re^{II} atom. This is the only example of a rhenium cluster in the family of condensed octahedral clusters.[224] The complex contains a cluster core similar to that of the Mo_9Se_{11} and only the bromine ligands occupy terminal positions.

The unique twelve-nuclear cluster complex $[Re_{12}CS_{17}(CN)_6]^{8-}$ (Fig. 34) consists of two Re_6 octahedra

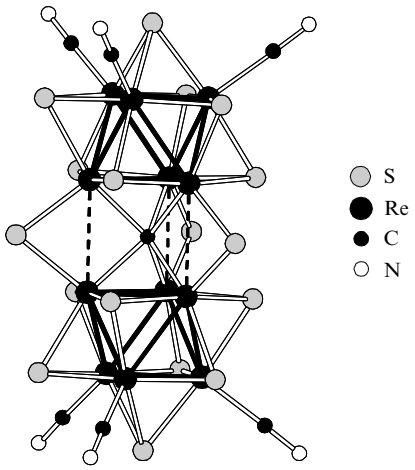


Figure 34. Structure of the complex $[Re_{12}CS_{17}(CN)_6]^{8-}$.

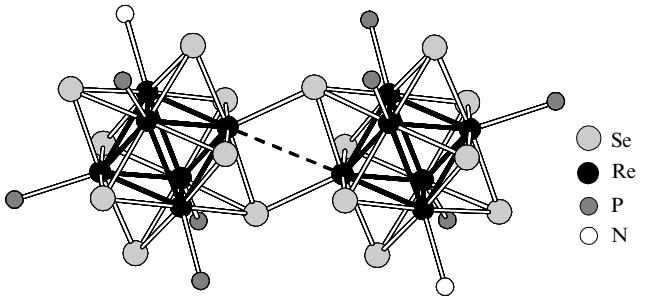


Figure 35. Structure of the complex *trans*-$[Re_{12}Se_{16}(PEt_3)_8(MeCN)_2]^{4+}$ (the ethyl and MeC groups are omitted).

linked by three μ_2-S-bridges and a μ_6-carbon atom.[15] Each Re_6-cluster coordinates seven μ_3-S-atoms and a μ_6-C-ligand attaining environment typical of octahedral Re clusters Re_6Q_8. The Re_6 prism formed by 'inner' triangles and centred by the μ_6-carbon atom is an important part of the structure. The mean distance between metal clusters in the anion $[Re_{12}CS_{17}.(CN)_6]^{8-}$ is equal to 3.17 Å. This distance is very sensitive to the charge of the cluster anion and decreases to 2.90 Å after two-electron oxidation of the cluster.[15] The cluster $Mo_{12}S_{18}$, which was found in the compound $Ba_4Mo_{12}S_{18}$, possesses a similar structure.[225]

The dodecanuclear clusters of a different type are formed in the condensation of the octahedral clusters with labile apical ligands. Thus thermolysis of *cis*-$[Re_6Se_8(PEt_3)_4(MeCN)_2]$ containing two labile MeCN ligands results in the formation of dimers of *trans*-$[Re_{12}Se_{16}(PEt_3)_8(MeCN)_2]^{4+}$ (Fig. 35).[152, 226]

III. Methods of synthesis of chalcogenide clusters

The methods of synthesis of the cluster compounds may be divided into two main groups: the high-temperature synthesis, which is carried out in closed systems (usually, in sealed evacuated tubes), and the solution synthesis. The high-temperature reactions are extremely important for the synthesis of clusters of the Group 5–7 metals because quite often a chalcogenide cluster core, especially a high-nuclear one, cannot be formed in solution. Further chemical modifications of a cluster compound obtained by high-temperature synthesis may be carried out in solutions or in melts.

1. High-temperature synthesis

The method is based on the fact that a phase that is thermodynamically stable under certain experimental conditions may be obtained from different starting compounds taken in the appropriate ratio. The elements and compounds (for example, metal halides, chalcogenides and chalcohalides) are used as the starting compounds in the synthesis of chalcogenide clusters. In addition to the ratio of the starting compounds in the reaction mixture, the right choice of temperature of the synthesis is very important. A standard procedure for the synthesis of cluster chalcogenides is as follows: a quartz tube is loaded with starting compounds and then evacuated and sealed. If necessary, the tube is cooled down by liquid nitrogen prior to evacuation in order to avoid the loss of volatile components. The sealed tube is placed into a furnace and heated according to the chosen protocol. The reaction mixture is kept at certain temperature for the required period, usually from several tens of hours up to several days, in order to complete the reaction. Such processes, particularly in the case of chalcohalide systems, are accompanied sometimes by mass-transfer processes, which results in the concentration of a solid phase in a cool area. Usually, such gas-transport reactions produce crystals of high quality suitable for X-ray crystallographic and other physicochemical studies.

The chalcohalides of niobium Nb_3QX_7 (Q = S, Se, Te; X = Cl, Br, I)[80, 83, 227] and tantalum Ta_3QI_7 (Q = Se, Te),[228] Ta_3SBr_7,[82] Ta_4SI_{11},[229] $Ta_4S_9Br_8$, $Ta_4Se_9I_8$ (Ref. 14) were obtained from the elements at 450–550 °C.

Trinuclear molybdenum and tungsten complexes $M_3Q_7X_4$ (Q = S, Se, Te; X = Cl, Br, I) were synthesised at 350–400 °C. The choice of this temperature interval is caused by both kinetic and thermodynamic factors because these compounds are unstable at higher temperatures. Wide variety of compounds that ensure the correct stoichiometry may be used as the starting components: elementary compounds, lower halides ($MoCl_3$ or Mo_6Cl_{12}, W_6Cl_{12}) with sulfur or selenium, sulfides MS_3 (M = Mo, W) with PCl_5 as well as other systems.[3, 230, 231]

High-temperature synthesis affords the telluride complexes $[Mo_3Te_7(TeI_3)_3]$,[66] $[Mo_3Te_7(TeI_3)_3]_2(TeI_3)I$, $[Mo_3Se_7(TeI_3)I_2]I$ and $[Mo_3Se_7(TeBr_3)Br_2]_2[Te_2Br_{10}]$ as single crystals in which the cluster fragments are coordinated by TeX_3^- ligands.[232] The triangular clusters $Re_3Q_7X_7$ (Q = S, Se; X = Cl, Br) were synthesised from ReX_4 or $ReOCl_4$, elemental sulfur or selenium and the corresponding sulfur and selenium halides Q_2X_2 or SeX_4 (Q = S, Se; X = Cl, Br) at 130–250 °C.[61] Compounds $Re_3S_7Br_7$ and $[Re_3S_7Cl_6][AlCl_4]$ were obtained in the reaction of Re_2O_7 with S_2Br_2 and with the solution of $AlCl_3$ and S_2Cl_2, respectively.[62, 63]

The high-temperature synthesis is used for the preparation of various types of tetranuclear cluster compounds: rhombic, square and tetrahedral clusters. The rhenium dichalcogenides ReQ_2 (Q = S, Se) containing rhombic clusters were obtained by the high-temperature synthesis from elements at 600–800 °C.[233, 234] The vanadium and tantalum chalcogenides $V_4S_9Br_4$ (Ref. 13) and $Ta_4Q_9X_8$ (Q = S, Se)[14, 235] containing square clusters were synthesised by the same method but at lower temperatures (400–450 °C).

The cubane clusters form the most abundant group of tetranuclear chalcogenide clusters. A series of Mo and Nb chalcohalides $M_4Q_4X_4$ (Q = S, Se; X = Cl, Br, I) was obtained by high-temperature synthesis (880–1000 °C) from various starting compounds providing the required proportion of the metal, chalcogen and halogen.[84, 85] The isostructural rhenium mixed chalcogenide $Re_4S_4Te_4$ was synthesised by heating a stoichiometric mixture of metallic rhenium, sulfur and tellurium for three weeks at 900 °C.[87] A series of ternary chalcogenides AM_4Q_8 (A = Al, Ga; M = Mo, Nb, Ta; Q = S, Se), $GaMo_4(Q,Q')_8$ (Q,Q′ = S, Se, Te) and $MMo_2Re_2S_8$ (M = Zn,

Ni, Co, Fe) belong to the same group of compounds (Refs 88–91, 236–238).

The synthesis of $Re_4Te_4(TeBr_2)_4Br_8$ from elements at 550 °C was also described.[93] The tetrahedral cluster-type rhenium chalcohalides $Re_4Q_4(TeCl_2)_4Cl_8$ were obtained from $ReCl_5$ by the reaction either with tellurium or with a mixture S–Te or Se–Te at 350–400 °C:[10]

$$4\,ReCl_5 + 4\,Q + 5\,Te \longrightarrow Re_4Q_4(TeCl_2)_4Cl_8 + TeCl_4.$$

Chalcocyanide cluster complexes can also be prepared by high-temperature synthesis. The niobium and tantalum tellurocyanide tetrahedral complexes $[M_4OTe_4(CN)_{12}]^{6-}$ are formed in the reaction of higher tellurides $NbTe_4$ and $TaTe_4$ with KCN at 440–460 °C and 340–360 °C, respectively.[108, 239] The tetrahedral tellurocyanides $[Mo_4Te_4(CN)_{12}]^{7-}$ and $[W_4Te_4(CN)_{12}]^{6-}$ were obtained from the ditellurides of these metals by heating with KCN at 400 °C.[102] Interestingly, the interaction of trinuclear chalcohalides $M_3Q_7X_4$ (M = Mo, W) with KCN at 400 °C also yields the clusters $[M_4Q_4(CN)_{12}]^{n-}$ of higher nuclearity.[102]

The high-temperature synthesis is the main method for the preparation of octahedral chalcogenide clusters of Mo, W, Re. The binary and ternary molybdenum chalcogenides Mo_6Q_8 (Q = Se, Te) and $M_xMo_6Q_8$ (M is a transition or post-transition metal) as well as phases with condensed clusters containing two, three, four and more fused octahedra up to the phase MMo_3Q_3 (M is an alkali metal), which consists of infinite chains $(Mo_3Q_3)^-$, were synthesised from the simple compounds.[214, 223] The temperature of the synthesis of these compounds is in the range of 900–1500 °C. The synthesis of clusters of higher nuclearity usually requires higher temperatures. The octahedral chalcogenide complexes of the type $A_4M_6S_x$ (A is an alkali metal or thallium; M = Tc, Re; x = 11, 12, 13, 13.5) were synthesised at 800–1400 °C. Hydrogen sulfide or hydrogen selenide were used as sources of chalcogen, which were passed over the mixture of a powder metallic rhenium with an alkali metal carbonate.[192, 196, 197, 199, 201, 203, 240] The cluster-type rhenium telluride Re_6Te_{15} was obtained by heating metallic rhenium with tellurium for two weeks at 900 °C.[8] The reaction rate increases significantly if highly reactive highly-dispersed rhenium powder is used. The chalcohalides $Re_6Q_{8-n}X_{2+2n}$, where Q = S, Se; n = 1, 2, 3, 4, were synthesised from elements or from the corresponding compounds at 800–900 °C. $ReCl_5$ is typically used as a source of chlorine in the synthesis of chalcochlorides.[136] The tellurohalide complexes $Re_6Te_8(Te_8Cl_{18})$, $Re_6Te_8(Te_6)(TeCl_3)_2$ and $Re_6Te_8(TeBr_2)_6Br_2$ with unusual ligands TeX_2, Te_6, $Te_8Cl_{18}^{2-}$ were obtained from $ReCl_5$ or Re_3Br_9 at 450–500 °C.[138, 189, 206, 241] It should be noted that the octahedral rhenium chalcohalides are formed exclusively in the high-temperature reactions. Besides the synthesis from simple compounds, the octahedral rhenium chalcohalides are formed in the condensation of triangular clusters: in the reaction of rhenium bromide Re_3Br_9 with cadmium or lead chalcogenides at 500–550 °C.[190] The nonanuclear dioctahedral complex $[Re_9Se_{11}Br_6]^{2-}$ is also formed.[224] The dodecanuclear sulfidocarbide cluster $[Re_{12}S_{17}C(CN)_6]^{8-/6-}$ was obtained by the reaction of ReS_2 with KCN at 750 °C.[15]

2. Methods of solution synthesis

The methods of synthesis in aqueous solutions or in organic solvents are mainly used for chemical modifications of cluster-type complexes obtained by high-temperature synthesis. The reactions in solutions used specially for the synthesis of chalcogenide clusters are significantly less common, as the yields in these reactions are usually low and are well developed only for a limited number of clusters. Solution syntheses are used most often for the preparation of thio complexes, less often for seleno complexes and only in very few cases for telluro complexes. Mononuclear tetrathiometallate complexes, metal halides or organometallic compounds are used as starting components of these reactions. In some cases, reductive condensation of bi- or trinuclear complexes into cluster complexes of higher nuclearities are also carried out in solutions.

a. Synthesis of triangular cluster complexes

At present, trinuclear vanadium complexes are obtained only in solutions. Usually, VCl_3 or $(NH_4)_3VS_4$ are used as the starting compounds. For instance, the compound $(Et_4N)[V_3S_7(Me_2NCS_2)_3]$ was obtained in low yield in the reaction of $(NH_4)_3VS_4$ with CuCl, PhSNa, $Na(Me_2NCS_2)$ and Et_4NCl in DMF,[60] and the complex $(Et_4N)[V_3S_7.(Et_2NCS_2)_3]$ was synthesised from $(NH_4)_3VS_4$, $Na(Et_2NCS_2)$ and Et_4NCl in methanol with passage of H_2S through the reaction mixture.[242] The reaction of $[V(SPh)_2(bipy)_2]PF_6$ with sulfur in MeCN furnishes $[V_3S_7(bipy)_3]PF_6$ in 35%–40% yield.[59] The unique cluster-type complex $(Et_4N)_3[V_3S_4.(edt)_3]\cdot 2\,MeCN$ with the core $V_3S_4^{3+}$ was isolated in 20% yield from a multicomponent reaction mixture containing $Na_2(edt)$, Et_4NBr, VCl_3 and sulfur.[21]

The cluster-type niobium complex $[Nb_3SO_3(NCS)_9]^{6-}$ was obtained by dissolution of $[Nb_2Cl_6(THT)_3]$ (THT is tetrahydrothiophene) in hydrochloric acid followed by treatment with NH_4NCS.[22] The triangular complex $[Cr_3S_5(dmpe)_3]$ was synthesised in the reaction of anhydrous $CrCl_2$ with NaSH (78 °C, methanol) with subsequent addition of the phosphine.[75] The selenide cluster $(Et_4N)_2[Cr_3(\mu_3\text{-}Se)_2(CO)_{10}]$ was obtained in 52% yield by the reaction of SeO_2 with $Cr(CO)_6$ in a methanolic alkaline solution with subsequent addition of Et_4NBr.[76]

The cluster aqua complexes, obtained preliminarily by reductive condensation of mono- or binuclear chalcogenide complexes, are used in the synthesis of triangular Mo and W complexes. In most cases these reactions are non-selective and result in mixtures of products that can be separated by chromatography with difficulty. Thus, the aqua complex $[Mo_3S_4(H_2O)_9]^{4+}$ was obtained in 15% yield alongside with $[Mo_4S_4(H_2O)_{12}]^{5+}$ (20%) in the reaction of $[Mo(CO)_6]$ with anhydrous Na_2S in acetic anhydride.[35] The cluster $[Mo_3S_4(H_2O)_9]^{4+}$ was synthesised with the yield of 20% by the reduction of $(NH_4)_2[Mo_2(S_2)_2Cl_8]$ with Pb or In in concentrated HCl.[243] The compound $(NH_4)_2MoS_4$ can be reduced with $NaBH_4$ in aqueous hydrochloric acid yielding $[Mo_4S_4(H_2O)_{12}]^{5+}$. Oxidation of the latter with atmospheric oxygen results in $[Mo_3S_4(H_2O)_9]^{4+}$ isolated by ion-exchange chromatography in 50% yield.[25] The selenium analogue $[Mo_3Se_4(H_2O)_9]^{4+}$ is difficult to obtain and it was synthesised by the reduction of $[Mo_2O_2Se_2(cys)_2]^{2-}$ (cysH is L-cysteine) with $NaBH_4$ in a solution of hydrochloric acid. Cation-exchange chromatography afforded a mixture of species, *viz.*, $[Mo_3O_2Se_2(H_2O)_9]^{4+}$, $[Mo_3OSe_3(H_2O)_9]^{4+}$, $[Mo_3Se_4.(H_2O)_9]^{4+}$ and $[Mo_4Se_4(H_2O)_{12}]^{5+}$ in a total yield of 10%. The cluster $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ was obtained in 70% yield by the reaction of $[Mo_2O_2Se_2(cys)_2]^{2-}$ with $[MoCl_6]^{3-}$ (90 °C, 1 h, 1 M HCl), and the complex $[Mo_3O_3Se(H_2O)_9]^{4+}$ was synthesised by electrochemical reduction of $[Mo_2O_4(cys)_2]^{2-}$ in the presence of grey selenium powder in 3% yield or by treatment of $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ with a 30-fold excess of $NaBH_4$.[28, 29] The cationic complex $[W_3S_4(H_2O)_9]^{4+}$ was obtained in the reduction of a solution of $(NH_4)_2[WS_4]$ with $NaBH_4$ in the presence of HCl. The reaction produces a mixture of complexes, *viz.*, $[W_3O_2S_2(H_2O)_9]^{4+}$ (0.3%), $[W_3OS_3(H_2O)_9]^{4+}$ (5%) and $[W_3S_4(H_2O)_9]^{4+}$ (25%).[25] The complex $(NH_4)_2[Mo_3S_7(S_2)_3]$, which is a starting compound in the synthesis of other $Mo_3S_7^{4+}$ derivatives, was obtained by the reaction of $(NH_4)_6[Mo_7O_{24}]$ with $(NH_4)_2S_x$ at 90 °C,[244] and the selenide analogue $[Mo_3Se_7(Se_2)_3]^{2-}$, by the hydrothermal

synthesis from Mo or MoO_3 and a polyselenide.[245] The cluster $[Mo_3O(Te_2)_3 .(en)_3]In_2Te_6$ was synthesised by heating the mixture of Li_2Te, K_2Te, $MoCl_5$, $InCl_3$ and Te in ethylenediamine (180 °C, 7 days).[54]

b. Synthesis of tetranuclear cluster complexes

The solution synthesis is extremely important for the preparation of vanadium and chromium tetrahedral complexes because the high-temperature methods of synthesis of these compounds are yet to be developed. The vanadium cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_4R)_4V_4S_4]$ were obtained from the corresponding mononuclear vanadium complexes by the reactions with thiols (as a source of sulfur) in hydrocarbon solvents. Thus refluxing of $[(\eta^5\text{-}C_5H_4Me)_2V]$ with Bu^tSH in heptane yields $[(\eta^5\text{-}C_5H_4Me)_4V_4S_4]$ (with a small amount of pentanuclear $[(\eta^5\text{-}C_5H_4Me)_5V_5S_6]$).[246] The compound $[Cp_4V_4S_4]$ was obtained from the vanadocene and MeC(S)SH or H_2S.[247, 248] The cluster $V_4S_4^{5+}$ was isolated as the dithiocarbamate complex $(Et_4N)[V_4S_4(C_4H_8NCS_2)_6]$ in 67% yield from $(NH_4)_3VS_4$, ammonium pyrrolidinodithiocarbamate and PPh_3 in the presence of Et_3N.[249]

Tetranuclear vanadium clusters can be synthesised by reductive dimerisation of binuclear complexes. For example, the complex $[(\eta^5\text{-}C_5H_4Me)_4V_4S_4]$ was obtained by the reaction of $[(\eta^5\text{-}C_5H_4Me)_2V_2S_4]$ with Bu^n_3P.[247] The selenide $[Cp_2V_2Se_5]$ also reacts with PBu^n_3 in CH_2Cl_2 yielding $[Cp_4V_4Se_4]$ (72% yield).[94] The tellurides $[(\eta^5\text{-}C_5H_4R)_4V_4Te_4]$ (R = H, Me) were obtained by thermolysis of $[(\eta^5\text{-}C_5H_4R)_2V_2(CO)_4(\mu\text{-}Te)_2]$ in toluene at 50–60 °C in virtually quantitative yields. [94]

Only the cyclopentadienyl derivatives of the cubane-type clusters $Cr_4Q_4^{n+}$ ($n = 4$, 5) are known. The compounds $[(\eta^5\text{-}C_5H_4R)_4Cr_4S_4]$ (R = H, Me) were obtained from the corresponding chromocenes $[(\eta^5\text{-}C_5H_4R)_2Cr]$ and elemental sulfur or Bu^tSH by heating in high-boiling organic solvents.[250, 251] Thermolysis of $[Cp_2Cr_2(\mu\text{-}S)_2(CO)_5]$ in toluene at 100 °C yields $[Cp_4Cr_4S_4]$.[95–97] The cluster $[(\eta^5\text{-}C_5H_4Me)_4 .Cr_4S_4]$ was obtained upon thermolysis of $[(\eta^5\text{-}C_5H_4Me)_2 .Cr_2(SBu^t)_2S]$ or upon its reaction with $CuBr_2$ in THF in the presence of triethylamine.[252] The complexes $[(\eta^5\text{-}C_5H_4R)_4 .Cr_4Se_4]$ (R = H, Me) were formed upon heating $[Cp_2Cr_2(CO)_6]$ or $[(\eta^5\text{-}C_5H_4Me)_2Cr]$ with grey selenium.[95, 97] The reaction of $[(\eta^5\text{-}C_5H_4Me)_2Cr]$ with H_2Se in toluene produces complex $[(\eta^5\text{-}C_5H_4Me)_4Cr_4Se_4]$ in the yield of 90%.[252, 253] The cluster $[Cp_4Cr_4Se_4]$ was obtained from $[Cp_2Cr_2(CO)_6]$ and Ph_2Se_2.[98, 99] For tellurium, only mixed oxide-telluride clusters $[Cp_4Cr_4Te_3O]$, $[Cp_4Cr_4Te_2O_2]$ and $[Cp_4Cr_4TeO_3]$, obtained by thermolysis of $[CpCr(CO)_3TePh]$, are known.[100]

In contrast to the derivatives of the Group 5 metals and chromium, the tetrahedral clusters of Mo and W are so resistant against oxygen and water that they can also be obtained in aqueous solutions. Mononuclear carbonyls, halides or chalcogenides are used as the starting compounds. Reductive condensation of binuclear chalcogenide complexes and the addition of a mononuclear fragment to a triangular cluster are also potentially very important as the synthetic methods. The methods of synthesis of tetrahedral Mo and W complexes are numerous, well developed and described in detail in several reviews.[18, 19] It should be noted that in most cases the solution syntheses of the cubane-type cluster are nonselective and afford complex mixtures of products requiring laborious separations.

There is an example of synthesis of the complex $[W_4S_4(en)_4(S)_4]S$ by a reaction of $[W(CO)_6]$ with K_2S_4 in supercritical ethylenediamine at 300 °C.[127] The complex $[(\eta^5\text{-}C_5H_4Pr^i)MoCl_2]_2$ reacts with LiHS or LiHSe producing $[(\eta^5\text{-}C_5H_4Pr^i)_4Mo_4Q_4]$ (Q = S, Se) in high yield.[101, 253]

A unique method of synthesis of $Cs_6[Mo_4S_4(S_x)_6]$ ($x = 3$, 4) by the reaction of Mo_6Br_{12} with Cs_2S_3 in water was found. So far this is the only example of the transformation of a hexanuclear halide cluster into a tetranuclear chalcogenide cluster.[254]

The tetrahedral polysulfide cluster complex $[Re_4(\mu_3\text{-}S)_4 .(\mu\text{-}S_3)_6]^{4-}$ was obtained by heating a solution of NH_4ReO_4 with an aqueous solution of ammonium polysulfide.[122, 123] The cyanide complex $[Re_4S_4(CN)_{12}]^{4-}$ was prepared by the reaction of trinuclear thiobromide $Re_3S_7Br_7$ with KCN in aqueous solution at room temperature.[104]

c. Synthesis of octahedral cluster complexes

The molecular octahedral vanadium complex $[V_6Se_8(O)(PMe_3)_6]$ with an interstitial oxygen atom was obtained from $[CpVCl_2(PMe_3)_2]$ and $(Me_3Si)_2Se$.[137] Octahedral clusters with the $Cr_6(\mu_3\text{-}Te)_8$ core were synthesised by either the reaction of $[CrCl_2(PEt_3)_2]$ with alkyl magnesium chloride and $TePEt_3$ (the source of tellurium) or the reaction of bis(2,4-dimethylpentadienyl)chromium with $TePEt_3$ in the presence of excess PEt_3.[255] The reaction of anhydrous $CrCl_2$ with Na_2Se or NaSH followed by treatment with PEt_3 in methanol yields a mixture of complexes $[Cr_6Q_8(PEt_3)_6]$ and $[Cr_6Q_8(H)(PEt_3)_6]$.[256]

The first molecular octahedral molybdenum clusters $[Mo_6S_8(PEt_3)_6]$ and $[Mo_6Se_8(PEt_3)_6]$ stable in air were obtained by the reductive dimerisation of trinuclear clusters $[Mo_3Q_4Cl_4(PEt_3)_x]$ ($x = 3$, 4; Q = S, Se) with Mg.[257–259] The substitution of halogen atoms in octahedral molybdenum dihalide is yet another approach to the synthesis of chalcogenide clusters. The cluster $[Mo_6S_8(py)_6]$ was obtained by the reaction of Mo_6Cl_{12} with NaSH and $NaOBu^t$ in pyridine,[176] and complexes $Cs_5[Mo_6Se_{3.6}Cl_{4.4}(CN)_6]$ and $Cs_5[Mo_6Se_{3.4} .Br_{4.6}(CN)_6]$, by refluxing metal dihalides and Cs_2Se_3 in water followed by the addition of KCN to the reaction mixture.[260]

The methods of solution synthesis are particularly important for the preparation of octahedral chalcogenide tungsten clusters. The reaction of W_6Cl_{12} with NaSH and $NaOBu^t$ in pyridine yields $[W_6S_8(py)_6]$ *via* complexes $[W_6Cl_6S_2Cl_2(py)_6]$ and $[W_6S_6Cl_2(py)_6]$.[135] The octahedral tungsten telluride clusters $[Na(py)_6][W_6Te_8(py)_6]\cdot py$ and $[W_6Te_8(pip)_6]\cdot 6(pip)$ were obtained by the reaction of Na_2Te with W_6Cl_{12} [3 days, refluxing in pyridine (py) or piperidine (pip)].[175, 178]

IV. Reactivity of chalcogenide clusters

Diverse chemical transformations of the chalcogenide cluster complexes may be divided into two large groups, *viz*., transformations occurring with and without changes in the metal chalcogenide cluster core. The reactions of the former type for the clusters of various nuclearity have much in common but the changes in cluster cores are highly specific for different types of clusters.

1. Substitution of terminal ligands

Similarly to the classic coordination chemistry, the reactions of ligand substitution in clusters are the most abundant and allow an access to compounds with virtually any cluster–ligand combinations. In the present review, we will discuss general features of these reactions for each cluster type, specially highlighting only the most important or unusual cases.

The substitution of halide or aqua ligands proceeds most easily. Therefore, it is not surprising that the chemistry of clusters stable in such environment is the most well studied. Three main classes of compounds belong to such clusters: the triangular chalcogenide clusters M_3Q_4 and M_3Q_7 (M = Mo, W), the tetrahedral clusters M_4Q_4 (M = Mo, W, Re) and the octahedral clusters M_6Q_8 (M = Mo, Re). However, in some cases as, for example, for $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}Cl)_3Cl_6]^{2-}$,[18] such studies have not been carred out yet. The octahedral clusters $[M_6S_8L_6]$ containing highly labile inorganic (hydroxide and

halide) and organic (acetonitrile, amines, *etc*.) ligands that can easily be substituted by other ligands (for example, phosphines) are quite perspective in studies of the ligand substitution reactions.[18]

a. Triangular clusters M_3Q_4

The substitution of water molecules in aqua complexes $[M_3Q_4(H_2O)_9]^{4+}$ is studied in detail.[261] The exchange of the coordinated water in $[Mo_3S_4(H_2O)_9]^{4+}$ was studied by ^{17}O NMR spectroscopy. Different exchange rates were observed for the ligands in non-equivalent positions. The exchange rate of the molecules in *trans*-positions relative to the μ_3-sulfur atom (*c*-H_2O) is approximately 10^5 times slower than that for the water molecules in the *cis*-position relative to μ_3-S and therefore in the *trans*-position relative to the bridging sulfur atom (*d*-H_2O). It was suggested that the conjugated base $[Mo_3S_4(H_2O)_8(OH)]^{3+}$ is formed in which the positions *d* rather than *c* are activated. The dissociation constant value (K_a) of $[Mo_3S_4(H_2O)_9]^{4+}$ was equal to 0.18 mol litre^{-1} (25 °C, ionic strength I = 2.00 mol litre^{-1}) when the formation of this conjugated base was taken into account.[261] Depending on the concentration of HCl in the solution, equilibrium mixtures of aqua chloride complexes are produced up to $[Mo_3S_4.(H_2O)_2Cl_7]^{3-}$, which can be isolated by the formation of supramolecular systems of hydrogen bonds with the macrocyclic cavitands cucurbit[*n*]urils. So far, all attempts to isolate the complexes with completely substituted anions $[M_3Q_4Cl_9]^{5-}$ were unsuccessful.[262] The small value of the formation constant for the complex $[Mo_3S_4(H_2O)_8Cl]^{3+}$ (3.0) indicates low competitiveness of the chloride ligands in aqueous solutions.[262]

The substitution of thiocyanate for coordinated water was studied in detail for a series of complexes $[Mo_3O_xQ_{4-x}(H_2O)_9]^{4+}$ and $[W_3O_xQ_{4-x}(H_2O)_9]^{4+}$. The following regularities were found: the substitution of μ_3-S and further of μ_3-Se for μ_3-O in the series from $[Mo_3O_4(H_2O)_9]^{4+}$ to $[Mo_3Se_4(H_2O)_9]^{4+}$ decreases the rate of *d*-ligand, substitution by 6 and 11 orders of magnitude for S and Se, respectively. At the same time, the substitution of μ_2-bridging ligands increases the substitution rate by 10 (for S) and 20 (for Se) orders of magnitude per bridging atom.[69] In the mixed-metal complexes $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$, the substitution of the ligands bonded to the molybdenum atom is faster than of those bonded to the tungsten atom.[264] The kinetic data of the reaction of $[W_3S_4(H_2O)_9]^{4+}$ with NCS^- were explained by the formation of an intermediate complex with S-coordinated thiocyanate ligand and its subsequent transformation into more stable N-bonded isomer.[263] The complexes $[M_3Q_4(NCS)_9]^{5-}$ are easily formed upon the treatment of thiocyanate aqua complexes, and in all isolated solid products the ligand is coordinated by nitrogen atom.[25–28, 265, 266] The substitution of formate for water results in the formation of η^1-formate complexes, which were isolated and structurally characterised in the form of salts $K_4[Mo_3S_4(HCO_2)_8(H_2O)]$ and $K_6[W_3S_4(HCO_2)_9](HCO_2)\cdot 3H_2O$.[30] No complexes of this type with other carboxylate ligands are known. The anion pts^- in the known toluene-*p*-sulfonates is always located in the outer coordination sphere as follows from structural studies of the corresponding aqua complexes $[M_3Q_4(H_2O)_9](pts)_4\cdot x\,H_2O$.[31, 118, 267] The cyclopentadienyl derivatives $[Cp_3M_3S_4](pts)$ and their analogues with substituted cyclopentadienyl ligands were synthesised from the complex $Mo_3S_4(pts)_4\cdot x$THF obtained *in situ* by its reaction with TlCp and Tl(η^5-C_5H_4Me).[268]

The substitution of oxalate or acetylacetonate for water molecules yields the complexes $[M_3Q_4(C_2O_4)_3(H_2O)_3]^{2-}$ and $[M_3Q_4(acac)_3L_3]^+$ (L = py, NH_3; M = Mo, W; Q = S, Se), respectively.[33, 34] The complexes $[Mo_3S_4(dtp)_3(\mu\text{-dtp})(H_2O)]$ and $[Mo_3OS_3(dtp)_3(\mu\text{-dtp})(H_2O)]$ (dtp is diethyldithiophosphate) are formed in the reactions of the corresponding aqua complexes with $(EtO)_2PS_2H$. The remaining water molecule is easily substituted by other neutral ligands and the bridging diethyl dithiophosphate, by carboxylate.[269, 270] A number of complexes obtained from $[Mo_3S_4(dtp)_3(\mu\text{-dtp})(H_2O)]$ and related compounds by substitution of various (predominantly, nitrogen-containing heterocycles and carboxylates) ligands for coordinated water and bridging dithiophosphate have been described.[18] The complex $[Mo_3Se_4(dtp)_3(\mu\text{-AcO})(py)]$ was obtained from the aqua complex $[Mo_3Se_4(H_2O)_9]^{4+}$ similarly.[271] The attempt to synthesise the dithiophosphate complexes $[M_3Se_4(\mu\text{-dtp})(dtp)_3(H_2O)]$ (M = Mo, W) from solutions of $[M_3Se_4(H_2O)_9]^{4+}$ in hydrochloric acid by the addition of P_4S_{10} in the corresponding alcohol yielded the complexes $[M_3(\mu_3\text{-Se})(\mu\text{-}Se_{eq}Se_{ax})_3(dtp)_3]Cl$ as a result of sulfur addition to the cluster core $M_3(\mu_3\text{-Se})(\mu\text{-}Se_{ax})_3^{4+}$.[271]

Quite complicated molecules can be obtained on the basis of polynuclear carboxylates, such as the complexes $[\{Mo_3S_4(dtp)_3L\}_2(\mu\text{-}COO(CH_2)_nCOO)]$ (n = 3, 4) containing two cluster units linked by bridging glutarate or adipinate ligands.[272] Two bridging ligands, glutarate and 1,3-bis(4-pyridyl)propane, link simultaneously two cluster units in $[\{Mo_3(\mu_3\text{-O})S_3(dtp)_3\}_2(\mu\text{-}COO(CH_2)_3COO)(\mu\text{-py}'(CH_2)_3\text{py}')]$ (py′ is 4-pyridyl).[273]

The tridentate ligand diethylenetriamine (dien) reacts with $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3OS_3(H_2O)_9]^{4+}$ yielding $[Mo_3S_4.(dien')(dien)_2]Cl_3\cdot 4H_2O$ and $[Mo_3OS_3(dien')(dien)_2]Cl_3\cdot 3H_2O$ where one of three ligands (dien) is deprotonated (dien′).[274] The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3OS_3(H_2O)_9]^{4+}$ with $KHB(pz)_3$ (pz is pyrazolo) results in the formation of the corresponding pyrazoloborate complexes $[Mo_3Q_4\{HB(pz)_3\}_3]^+$.[275] Due to partial hydrolysis of the ligand, the compound $[\{(HB(pz)_3)_2Mo_3S_4\}_2(\mu\text{-O})(\mu\text{-pz})_2]$ is also formed. Two cluster fragments of this compound are linked by a bridging oxygen atom and two pyrazolyl ligands.[276]

Of the ligands containing both nitrogen oxygen donor atoms only polyaminocarboxylates were the subject of fairly detailed studies. A series of iminodiacetate (H_2ida) and nitrilotriacetate (H_3nta) complexes $[Mo_3S_xO_{4-x}(ida)_3]^{2-}$ and $[M_3S_xO_{4-x}(Hnta)_3]^{2-}$ were synthesised.[18] The nitrilotriacetate is a tridentated ligand leaving one CH_2COOH group free. In all cases, the nitrogen atoms occupy the *trans*-positions with respect to the μ_3-sulfur atom. Complexes of $W_3S_4^{4+}$ and $W_3O_3S^{4+}$ with polyaminocarboxylate ligands [ethylenedioxybis(ethylenenitrilo)tetraacetate, triethylenetetramine hexaacetate, oxybis(ethylenenitro)tetraacetate, 1,4-butylenediaminotetraacetate, 1,3-propylenediaminotetraacetate and its 2-methyl-, 2-methoxy- and 2-carboxymethyl derivatives] were suggested as X-ray contrast diagnostic agents of a new generation.[39, 277, 278]

Complexes of $Mo_3S_4^{4+}$ with 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) and its hexa-*N*-methyl derivative were synthesised. Three bond isomers with ligands coordinated in the N,N,N-, N,N,O-, and N,O,O-mode are present in aqueous solution of $[Mo_3S_4(taci)_3]^{4+}$.[279]

The lacunar anions $[SiW_{11}O_{39}]^{6-}$ and $[P_2W_{17}O_{61}]^{10-}$ can also serve as the ligands to form, with $[Mo_3S_4(H_2O)_9]^{4+}$, nanosized hybrid polyoxometallate cluster complexes $[\{(SiW_{11}O_{39})Mo_3S_4(H_2O)_3(\mu\text{-OH})\}_2]^{10-}$ and $[\{(P_2W_{17}O_{61}).Mo_3S_4(H_2O)_3(\mu\text{-OH})\}_2]^{14-}$. In these structures, the polyoxymetallate ligands are coordinated around the central core, which consists of two fragments $Mo_3S_4(H_2O)_3^{4+}$ linked by two hydroxyl bridges (both are in the *cis*-positions with respect to μ_3-S). These complexes are stable in solutions in the pH range of 1–7, but in more acidic solutions form $[Mo_3S_4(H_2O)_9]^{4+}$ quantitatively.[280]

The halide ligands in the phosphine complexes $[W_3Q_4Cl_3(dmpe)_3]^+$ and $[W_3Q_4Br_3(dppe)_3]^+$ may be substituted by the hydride by the reaction with $NaBH_4$ to yield the

salts $[W_3Q_4H_3(dmpe)_3]^+$ and $[W_3Q_4H_3(dppe)_3]^+$.[276] The halide complexes can be recovered upon treatment with hydrohalide acids. According to the kinetic data, in the presence of water the reaction proceeds through several stages and the dihydrogen complex $[W_3Q_4(H_2)H_2(dmpe)_3]^+$ is formed initially. In the absence of water, this does not happen and the bond H···H is formed between the hydride complex and the dimer $(HCl)_2$.[281 – 283] The reaction with NaOH in acetonitrile yields $[W_3Q_4(OH)_3(dmpe)_3]^+$.[281, 283]

b. Triangular clusters M_3Q_7

In the presence of sources of halide ions, the coordination polymers $M_3Q_7X_4$ can be transformed into discrete anionic complexes $[M_3Q_7X_6]^{2-}$ under rather drastic conditions: in melt, upon mechanochemical treatment or upon radiolysis.[45, 53, 231, 284, 285] The salts $[M_3Q_7X_6]^{2-}$ in turn can be transformed into aqua complexes $[M_3Q_7(H_2O)_6]^{4+}$ that are quite stable in an aqueous solution of TsOH, but could not be isolated in the solid state.[24, 32] The rate constants of substitution of the halide ion for the coordinated water in the molybdenum aqua complexes $[Mo_3Q_7(H_2O)_6]^{4+}$ do not depend on $[H^+]$ [for Cl^-: 1.83×10^{-4} (Q = S); 6.7×10^{-4} (Q = Se); for Br^-: 2.07×10^{-4} (Q = S); 33×10^{-4} litre · mol^{-1} s^{-1} (Q = Se)].[32] The observed kinetic data agree with the suggestion that the replacement of the water molecule in *cis*-position relative to μ_3-Q proceeds in one step yielding $[Mo_3Q_7Cl_3(H_2O)_3]^+$. The halide complexes $[M_3Q_7Br_6]^{2-}$ are convenient starting materials for the synthesis of other $Mo_3S_7^{4+}$ derivatives by the ligand substitution reactions. The complexes $[Mo_3Q_7(NCS)_6]^{2-}$ [Q = S,[51, 286] Se (Ref. 44)] are formed in the reactions with thiocyanate and the reaction with aniline furnishes the complex $[Mo_3S_7Br_3(PhNH_2)_3]Br \cdot Et_4NBr$.[51, 286] The ligand exchange reactions were used for the synthesis of dithiocarbamates $[Mo_3S_7(Et_2NCS_2)_3]X$, $[Mo_3S_7(pdtc)_3]X$ (pdtc is piperidine-1-dithiocarboxylate), dithiophosphates and diselenophosphates.[53, 287 – 290] The compounds $[Mo_3Q_7\{N(QPPh_2)_2\}_3]Br$ containing six-membered chelate rings were synthesised from $(Et_4N)_2[Mo_3Q_7Br_6]$ and $K[\{Ph_2P(Q)\}_2N]$ (Q = S, Se).[287, 291] The complex $(Et_4N)_2$. .$[Mo_3S_7(MeC_6H_3S_2)_3]$ with toluene-3,4-dithiolate as a ligand was synthesised and its structure was studied. [292] Catecholate complexes are also known.[293, 294] Trischelate complexes of Mo_3S_7 with bidentate ligands [2-mercaptosuccinic acid (H_3msa), *meso*-2,3-dimercaptosuccinic acid (H_4dsa), 2-mercaptobenzoic acid, 3,4-dihydroxybenzoic acid, 8-hydroxyquinoline and 6-mercaptopurine] were obtained by exchange reactions from $(Et_4N)_2[Mo_3S_7Br_6]$ in acetonitrile or DMF.[293 – 295] Although the presence of only one isomer of the compound $(Et_3NH)_2[Mo_3S_7(Hmsa)_3]$ in which the sulfur atoms of the three ligands are coordinated in *cis*-positions with respect to μ_3-S was established, the results of potentiometric titration of $[Mo_3S_7(dsa)_3]^{2-}$ better correspond to the behaviour of less symmetric isomer in which two chelate rings are closed through the sulfur atoms (S,S′) and the third one through the S and O atoms.[293] The coordination of the redox-active ligands 4,5-dimercapto-1,3-dithiole-2-thione (dmit) and dimercaptomaleonitrile (mnt) results in the complexes $[Mo_3S_7(dmit)_3]^{2-}$ and $[Mo_3S_7(mnt)_3]^{2-}$.[296, 297]

The oxalate complexes $[M_3Q_7(C_2O_4)_3]^{2-}$ (M = Mo: Q = S, Se; M = W, Q = S) were obtained by mechanochemical synthesis from the corresponding coordination polymers and potassium oxalate or the solution synthesis from the bromide complexes and oxalate.[34, 297] The oxalate ligands can subsequently coordinate ions of other transition metals, lanthanides and actinides yielding in some cases nanosized complexes and porous coordination polymers.[298]

Melting of selenobromides $M_3Se_7Br_4$ (M = Mo, W) with 1,10-phenanthroline produces very stable complexes $[M_3Se_7(phen)_3]^{4+}$ isolated as salts with anions X^- or ZnX_4^{2-} (X = Cl, Br) after the extraction of the melt with hot concentrated solutions of HCl or HBr.[53]

The chalcohalides $Mo_3Te_7I_4$ and $W_3Te_7Br_4$ produce the cyanide complexes $[M_3Te_7(CN)_6]^{2-}$ when heated with aqueous solution of KCN. The cluster $[Mo_3Te_7(TeI_3)_3]I$ forms $[Mo_3Te_7\{(RO)_2PS_2\}_3]I$ in a solid-state reaction with dithiophosphates $KS_2P(OR)_2$ (R = Et, Pr^i) at 100 °C. The mechanochemical reactions of $Mo_3Te_7I_4$ or $W_3Te_7Br_4$ with $(EtO)_2PS_2K$ also result in the 'cutting out' of the M_3Te_7 cluster fragment and formation of $[Mo_3Te_7\{(EtO)_2PS_2\}_3]I$ or $[W_3Te_7((EtO)_2PS_2)_3]Br$ in low yields.[50, 64, 67, 299, 300]

c. Cubane-type clusters M_4Q_4

The cubane-type molybdenum aqua complexes $[Mo_4S_4(H_2O)_{12}]^{n+}$ exist in three oxidation states with $n = 4$, 5 (the most stable state) and 6. The chloride ion is weakly coordinated to $[Mo_4S_4(H_2O)_{12}]^{5+}$ ($K_1 = 1.98$, which is approximately 1000 times less than the corresponding value for thiocyanate). According to the kinetic data, the rate of substitution of thiocyanate for water molecule increases by several orders of magnitude in the series $5+ < 4+ < 6+$. The substitution of Se for S in the aqua complex $[Mo_4S_4(H_2O)_{12}]^{5+}$ increases the rate of substitution approximately tenfold. In all cases, the full substitution is accompanied by oxidation of the cluster core to the state $M_4Q_4^{6+}$ and the formation of isothiocyanate complexes $[M_4Q_4(NCS)_{12}]^{6-}$, although the kinetic data indicate probability of the intermediate formation of an S-coordinated isomer.[70] The salts $[Mo_4S_4(NCS)_{12}]^{6-}$, $[Mo_4Se_4(NCS)_{12}]^{6-}$, $[W_4Q_4(NCS)_{12}]^{6-}$, $[MoW_3Q_4$. .$(NCS)_{12}]^{6-}$ (Q = S, Se), $[Mo_3WS_4(NCS)_{12}]^{6-}$ were synthesised and their structures were studied.[22, 116 – 118] The oxidation of the cluster $M_4Q_4^{5+}$ into $M_4Q_4^{6+}$ also occurs upon addition of the dithiophosphates $(RO)_2PS_2^-$ (R = Et, Pr^i) to solutions of aqua complexes in HCl. This results in the dithiophosphate complexes $[M_4Q_4(dtp)_6]$, which exist in the form of two isomers $[M_4Q_4(\mu\text{-dtp})_2(dtp)_4]$ and $[M_4Q_4(\mu\text{-dtp})_3(dtp)_3]$.[116] Similarly to the triangular clusters M_3Q_4, the bridging dithiophosphate ligand in $[Mo_4S_4(\mu\text{-dtp})_2(dtp)_4]$ is rather labile and can be easily replaced by other bidentate ligands such as, for example, acetate or benzoate. As a result, the paramagnetic complexes $[Mo_4S_4(\mu\text{-OOCR})_2(dtp)_4]$ are formed.[114, 124] The bridging dithiocarbamate ligands can be selectively substituted by xanthate producing a mixture of $[Mo_4S_4(\mu\text{-}Et_2NCS_2)$. .$(\mu\text{-EtOCS}_2)(Et_2NCS_2)_4]$ and $[Mo_4S_4(\mu\text{-EtOCS}_2)_2$. .$(Et_2NCS_2)_4]$.[115] On the contrary, treatment of the aqua complex $[Mo_4S_4(H_2O)_{12}]^{5+}$ with concentrated aqueous ammonia results in the reduction of the cluster core and formation of the complex $[Mo_4S_4(NH_3)_{12}]^{4+}$.[113] Reaction of the aqua complex $[Mo_4S_4(H_2O)_{12}]^{5+}$ with potassium tris(pyrazolo)borate proceeds without any redox processes in the cluster core and yields $[Mo_4S_4\{HB(pz)_3\}_4(pz)]$.[301] An attempt to coordinate oxalate to $[Mo_4S_4(H_2O)_{12}]^{5+}$ resulted in the isolation of the triangular cluster $[Mo_3S_4(C_2O_4)_3(H_2O)_3]^{2-}$ as the only product.[35]

The molecular complexes $[Re_4Q_4(TeCl_2)_4Cl_8]$ (Q = S, Se, Te) are very convenient starting compounds in the chemistry of tetranuclear rhenium complexes:[121] the coordinated $TeCl_2$ molecules and chloride ions can easily be substituted for other ligands.[106, 107, 120, 302 – 304]

d. Octahedral clusters Re_6Q_8

The halide complexes $[Re_6S_8X_6]^{4-}$ ($N_e = 24$) and $[Re_6Se_8I_6]^{3-}$ ($N_e = 23$) are the most common starting compounds for the substitution reactions.[136] The substitution rarely proceeds completely and even in the excess of the ligand di- and trisubstituted products are often formed. The addition of Ag^+ ions for binding of the halide ions allows complete substitution of the terminal ligands. This method was used for the synthesis of the complexes $[Re_6S_8(H_2O)_6]^{2+}$ (from $[Re_6S_8X_6]^{4-}$ and $AgClO_4$ in $HClO_4$),[147] $[Re_6Se_8(MeCN)_6]^{2+}$

(from $[Re_6Se_8Br_6]^{3-}$ and $AgBF_4$ in MeCN; in this case the substitution is accompanied by the cluster reduction).[146] The reaction of $Cs_3[Re_6(S_7Br)Br_6]$ (the 'inner' ligands L^i of the cluster complex are given in parentheses) with aqueous ammonia results in step-by-step substitution of NH_3 for all terminal ligands and in the formation of $[Re_6(S_7Br)(NH_3)_6]^{3+}$.[148] The reactions of $[Re_6S_8Cl_6]^{3-}$ with pyridine affords a mixture of *cis*- and *trans*-isomers of $[Re_6S_8Cl_4(py)_2]^{2-}$ as well as faceial isomers of trisubstituted complexes $[Re_6S_8Cl_3(py)_3]^{n-}$ ($n = 0, 1$).[149, 150] In the case of phosphines, more complete substitution is possible. Thus in the reaction of $[Re_6Se_8I_6]^{3-}$ with PEt_3 the following complexes were obtained: *fac*- and *mer*-$[Re_6Se_8(PEt_3)_3I_3]^{-}$, *cis*- and *trans*-$[Re_6Se_8(PEt_3)_4I_2]$, $[Re_6Se_8(PEt_3)_5I]^{+}$ and completely substituted $[Re_6Se_8.(PEt_3)_6]^{2+}$. The reaction of $[Re_6Se_8I_6]^{3-}$ with a bidentate 1,6-bis(diphenylphosphino)hexane ligand also results in the monochelate, *cis*- and *trans*-bischelate and trischelate complexes and is accompanied as usual, by one-electron reduction of the cluster core.[153] The remaining unsubstituted halogen atoms in the mixed-ligand phosphine complexes can be substituted by other ligands. For example, the solvolysis of $[Re_6Se_8(PEt_3)_4I_2]$ in donor solvents yields cationic complexes $[Re_6Se_8(PEt_3)_4L_2]^{2+}$ (L = MeCN, DMF, DMSO).[152, 154] The bicluster derivatives $\{[Re_6Se_8(PEt_3)_5]_2(L-L)\}^{4+}$ were obtained from $[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$ using the bidentate bridging (ditopic) ligands [4,4′-bipyridyl and 1,2-disubstituted ethane, ethylene and acetylene with 4-pyridyl substituents (L–L).[154] These reactions with $[Re_6Se_8(PEt_3)_4(MeCN)_2]^{2+}$ result in the formation of tetrakiscluster complexes in which the clusters and bipyridyl bridges form molecular squares.[155] The substitution of 4-(3,4,6-tribenzyloxy)benzyloxypyridine for acetonitrile molecules in the complex $[Re_6Se_8(MeCN)_6]^{2+}$ is the first step in the synthesis of dendrimers based upon redox-active sixnuclear clusters.[146]

Highly nucleophilic cyanide ion is able of substituting all bridging ligands even in the three-dimensional structures $[Re_6Q_8Br_2]$ (Q = S, Se) and Re_6Te_{15} yielding $[Re_6Q_8(CN)_6]^{4-}$ (Refs 156, 157 and 305). Similarly compound $[Re_6Q_8(OH)_8]^{4-}$ is formed in a melt of KOH.[158] In the case of $[Re_6Se_8Br_2]$, the reaction can also result in partial substitution of oxide bridges for the selenide yielding $Re_6Se_4O_4^{2+}$ derivatives. Remarkably, the selective substitution of selenium atoms of just one face of the Se_8 cube takes place.[139] Another method for the synthesis of hexacyanide complexes is based on the reactions of the salts $[Re_6Se_8I_6]^{4-}$ and $[Re_6S_8Br_6]^{4-}$ with a melt of NaCN.[306] The telluride $[Re_6Te_8(Te_7)]$ forms $[Re_6Te_8(CN)_6]^{4-}$ in the cyanide melt.[163] Similarly, the chalcogenides $ZnMo_6S_8$ and Mo_6Se_8 give $[Mo_6S_8(CN)_6]^{7-}$ and $[Mo_6Se_8(CN)_6]^{7-}$ in a sodium cyanide melt, the latter complex is readily oxidised to $[Mo_6Se_8(CN)_6]^{6-}$.[162, 307]

The interaction of the cluster complexes $Cs_4[Re_6S_8Br_6]\cdot 2H_2O$, $Cs_3[Re_6S_8Br_6]\cdot 2H_2O$, $Cs_3[Re_6(Q_7Br)Br_6]\cdot H_2O$ and $K_2[Re_6(S_6Br_2)Br_6]$ with the melts of 3,5-dimethylpyrazole (3,5-Me_2pzH) and triphenylphosphine results in complete or partial substitution of the halide ligands. The complexes $[Re_6Q_8(3,5\text{-}Me_2pzH)_6]Br_2\cdot 2(3,5\text{-}Me_2pzH)$, $[Re_6(Q_7O)(3,5\text{-}Me_2pzH)_6]Br_2\cdot(3,5\text{-}Me_2pzH)$ (with the substitution of μ_3-O for μ_3-Br), *trans*-$[Re_6Q_8(PPh_3)_4Br_2]$, *fac*-$[Re_6(Q_7Br)(PPh_3)_3Br_3]$, *cis*-$[Re_6(S_6Br_2)(PPh_3)_2Br_4]$ and *trans*-$[Re_6(S_6Br_2)(PPh_3)_2Br_4]\cdot 4H_2O$ were isolated and their structures were studied.[159–161]

2. Redox reactions

Cyclic voltammetry (CV) of triangular clusters $M_3Q_4^{4+}$ shows two waves of reduction, which can be explained as sequential reduction $M_3^{IV}O_4^{4+} \rightarrow M_2^{IV}M^{III}Q_4^{3+} \rightarrow M^{IV}M_2^{III}Q_4^{2+}$. The reduction ability decreases in the series $Mo_3S_4^{4+} > Mo_3Se_4^{4+} > W_3Se_4^{4+} > W_3S_4^{4+}$ (Refs 24, 38, 269 and 308). In some cases the one-electron reduction products may be isolated and their structures can be established.[42, 309, 310] Usually, the reduction of the clusters $Mo_3S_7^{4+}$ is irreversible and is accompanied by elimination of sulfur yielding $Mo_3S_4^{4+}$ (Ref. 293).

Cyclic voltammetry revealed the possibility of reversible one-electron reduction (to $n = 4$) and oxidation (to $n = 6$) of the clusters $[Mo_xW_{4-x}Q_4(H_2O)_{12}]^{n+}$ ($x = 0-4$).[116, 117] For both of the pairs 5+/4+ and 6+/5+, the value of half-wave potential ($E_{1/2}$) almost linearly decreases with the increase in the number of tungsten atoms in the cluster: each additional tungsten atom causes a negative potential shift of approximately 0.2 V. It reflects the predisposition of tungsten to higher oxidation states. The effect of the substitution of selenium for sulfur in the cluster core is less pronounced: the substitution of four Se atoms for S decreases the potential by less then 0.1 V.[116, 117] Two waves of one-electron reduction of the cyanide clusters $[M_4Q_4(CN)_{12}]^{6-}$ (M = Mo, W; Q = S, Se, Te) were also observed by CV. Interestingly, the substitution of the cyanide ions for coordinated water molecules results in a significant positive shift of the potentials (0.6–0.7 V), which makes possible the reduction of $[W_4Q_4(CN)_{12}]^{7-}$ to $[W_4Q_4(CN)_{12}]^{8-}$ (Q = S, Se, Te). The cyanide ligands damp the effect of the metal change on the electrode potential: while for the pair $[Mo_4S_4(H_2O)_{12}]^{6+}/[W_4S_4(H_2O)_{12}]^{6+}$ $\Delta E_{1/2}$ is equal to 825 mV, it is only 411 mV for the pair $[Mo_4S_4(CN)_{12}]^{6-}/[W_4S_4(H_2O)_{12}]^{6-}$. Presumably, this is caused by the participation of the cyanide ion π-orbitals in the charge redistribution within the cluster core. The transition from Q = S to Se and Te regularly (by approximately 100 mV) decreases the redox potential stabilising the most oxidised state of the cluster ($M_4Q_4^{6+}$).[102] However, in the case of $[Mo_4Q_4(edta)_2]^{n-}$ ($n = 2-4$), the substitution of Se for S does not affect the $E_{1/2}$ value.[311] The reversible two-electron oxidation was also observed in the case of cyclopentadienyl clusters $[(\eta^5\text{-}C_5H_4Pr^i)_4Mo_4Q_4]$ (Q = S, Se); the selenium clusters undergo oxidation at significantly more negative potentials.[101, 253] In contrast to the molybdenum and tungsten analogues, no reversible redox transformations were observed for rhenium tetrahedral clusters.

One-electron oxidation proceeds relatively easily in the case of the chalcogenide clusters Re_6Q_8 ($N_e = 24$).[136] The reversible one-electron reduction at the negative potentials was detected by CV for the compounds $[Re_6(Q_5Cl_3)Cl_6]^{-}$ (Q = S, Se), but no oxidation occurs.[188] Such behaviour is in keeping with both the increase in the negative charge of the cluster anion with the increase in the number of chalcogen atoms in the cluster core and lower electronegativity of the chalcogen atoms. In some cases, stable oxidation products, such as $(Bu^n_4N)_3[Re_6S_8Cl_6]$, $(Ph_4P)_3[Re_6S_8(CN)_6]$ $(Ph_4P)_2(H).[Re_6Se_8(CN)_6]\cdot 8H_2O$ and $(Et_4N)_2(H)[Re_6Te_8(CN)_6]\cdot 2H_2O$, can be isolated.[312, 313] It was found that the oxidation potential of complexes with heterocyclic amines increases in accord with the basicity of the ligand. The reduction of heterocyclic ligands takes place in the region of negative potentials and the electronic interaction of two heterocyclic ligands through the cluster was observed.[149] The oxidation of the cyanide complexes $[Re_6Q_8(CN)_6]^{4-}$ occurs at significantly lower potential than that of their halide analogues. The transition from a sulfide cluster to the telluride drastically (by 0.5 V) reduces the oxidation potential.[314]

Both reversible one-electron reduction and one-electron oxidation are possible for the electron-deficient molybdenum clusters $[Mo_6Q_8(PEt_3)_6]$ (Q = S, Se; $N_e = 20$). In spite of a strong electron-deficient character of the clusters, reduction occurs at highly negative potentials. Both electrode processes occur at virtually the same potentials for sulfide and selenide clusters.[259] On the contrast, the monochalcogenide clusters $[Mo_6(QX_7)X_6]^{3-}$ (Q = S, Se; X = Cl, Br) can reversibly loose one or two electrons. The introduction of the second chalcogen atom results in a strong negative shift of the potentials, as in the

case of the cyanide clusters $[Mo_6Q_2X_6(CN)_6]^{4-}$ (Q = S, Se).[134] It should be noted that there is virtually no difference in $E_{1/2}$ values for $[Mo_6(QCl_7)X_6]^{3-/2-}$, whereas for two geometrical isomers of $[Mo_6(Se_2Cl_6)Cl_6]^{4-/3-/2-}$, the difference in $E_{1/2}$ values is as large as ~0.1 V.[164, 165]

3. Clusters of clusters, coordination polymers and supramolecular compounds

Cyanide derivatives of chalcogenide clusters attract attention as 'building blocks' in the synthesis of coordination polymers, particularly those with big cavities and high porosity. Both tetrahedral clusters $M_4Q_4(CN)_{12}$ and octahedral clusters $M_6Q_8(CN)_6$ (M = Mo, W, Re; Q = S, Se, Te) are used for these purposes.[11, 12, 315–330] Recently, coordination polymers based on the aqua complexes $[Re_6Q_8(OH)_6]^{4-}$ (Q = S, Se) have been synthesised.[331]

The condensation of clusters takes place during thermolysis of $[Re_6Se_8(PEt_3)_5(MeCN)_2]^{2+}$ and *cis*-$[Re_6Se_8(PEt_3)_4.(MeCN)_2]^{2+}$. Here, the labile acetonitrile molecules are substituted by the μ_3-Se atom of the other cluster core yielding $[Re_{12}Se_{16}(PEt_3)_{10}]^{4+}$ and *trans*-$[Re_{12}Se_{16}(PEt_3)_8(MeCN)_2]^{4+}$ (Ref. 152). Similar process resulting in the formation of $[Mo_{12}Q_{16}(PEt_3)_{10}]$ was observed in the elimination of coordinated triethylphosphine from the complex $[Mo_6Q_8(PEt_3)_6]$ under the action of sulfur.[332]

Due to the formation of complementary bonds between the carbonyl groups of the macrocyclic cavitand cucurbit[6]uril and water molecules of aquachloride complexes, the isolation of the cluster complexes $[M_3Q_4(H_2O)_{9-x}Cl_x]^{(4-x)+}$ ($x = 1-3$) in the form of supramolecular adducts with cucurbit[6]uril from solutions in 2–4 M HCl and studies of their structures become possible. The size and the symmetry of six carbonyl groups of cucurbituril correspond well to six aqua ligands in *cis*-positions with respect to μ_3-bridging chalcogen atom in the triangular cluster aqua complexes. In the case of bulkier and less water-soluble cucurbit[8]uril, the aquachloride complexes with higher chloride content (up to $x = 7$) were isolated in spite of the loss of complementarity, because the cluster aquachloride complexes occupied the voids between differently packed large cucurbit[8]uril molecules and the hydrogen bonds provided additional stabilisation of the structure.[262, 333, 334]

4. Substitution of 'inner' bridging ligands

The reactions of the sulfohalides $[M_3S_7X_6]^{2-}$ with PPh_3Se or KNCSe result in the selective substitution of selenium for the equatorial sulfur atom of the disulfide ligand. This reaction is irreversible and even the excess of KNCS or PPh_3S does not transform the clusters $Mo_3S(SSe)_3^{4+}$ back into $Mo_3S_7^{4+}$. The synthesis of the compound $[Mo_3S_4Se_3(Et_2NCS_2)_3]^+$ from $[Mo_3S_7(Et_2NCS_2)_3]^+$ and KNCSe in MeCN at room temperature is an example of such reaction.[47, 49] High lability of the equatorial sulfur atom was confirmed by selective isotope exchange in the reaction of $(NH_4)_2[Mo_3S_7(S_2)_3]$ with a solution of ammonium polysulfide containing the isotope ^{34}S.[44, 48] The substitution of chalcogen atoms of $Mo_3S_7Br_4$ in KNCSe melt at 200–220 °C proceeds further *via* $[Mo_3S_4Se_3(CN)_6]^{2-}$ and $[Mo_3(\mu_3\text{-}S)Se_6(CN)_6]^{2-}$ and yields finally $[Mo_3Se_7(CN)_6]^{2-}$.[67] The relative lability of the chalcogen atoms in three different positions of the cores $M_3(\mu_3\text{-}Q)(\mu\text{-}Q_{ax}Q_{eq})_3^{4+}$ decreases in following order $Q_{eq} > Q_{ax} > \mu_3\text{-}Q$. Seleno cyanate serves simultaneously as a source of selenium for the formation of selenide clusters and a source of cyanide ions. A similar order of substitution of Se for Te was found in the reaction of $M_3Te_7Br_4$ with KNCSe. The complex $[W_3(\mu_3\text{-}Te).(\mu_2\text{-}TeSe)_3(CN)_6]^{2-}$, containing a new inorganic ligand $TeSe^{2-}$ was isolated and its structure was studied.[67] The molten KNCS transforms the chalcobromides $W_3S_7Br_4$ and $W_3Se_7Br_4$ into $[W_3S_4(NCS)_9]^{5-}$ *via* $[W_3S_xSe_{4-x}(NCS)_9]^{5-}$ ($x = 1-3$).[335] The transformation of the cluster $Mo_3Se_7^{4+}$ into Mo_3S_74+ was also observed in the reaction of $Mo_3Se_7Br_4$ with $(NH_4)_2S_x$ under hydrothermal conditions.[44]

The substitution of ions Q^{2-} (Q = O, S, Se, Te), NR^{2-}, P^{3-}, As^{3-} for μ_3-bridging halogen atoms is typical of octahedral rhenium complexes. This reaction proceeds more easily in the case of the most halogen-rich cluster cores. Thus $[Re_6(Se_4O_2Cl_2)Cl_6]^{2-}$ is formed upon mere heating of the compound $[Re_6(Se_4Cl_4)Cl_6]$ in wet DMF, both isomers, which differ in mutual position of the oxygen atoms, being isolated. $[Re_6(S_7Br)Br_6]^{3-}$ is one of the products of a complex reaction of the sulfobromide $[Re_6(S_4Br_4)Br_6]$ with KNCS in a melt.[336]

The clusters $[Re_6(Q_5Cl_3)Cl_6]^-$ (Q = S, Se) are studied in most details. They readily form the complexes $[Re_6(Q_5Q'Cl_2)Cl_6]^{2-}$ (Q′ = O, S, Se, Te) in the reactions with the silylated chalcogen carriers $[(Me_3Si)_2Q]$.[337] With the silylamide reagents $[(Me_3Si)_2NR$, where R = H, Me, $Bu^n]$, the complexes $[Re_6(Q_5EX_2)Cl_6]^{2-}$ (E = $NSiMe_3$, NMe, NBu^n) are formed. The trimethylsilyl group can be removed by treatment of the reaction mixture with Bu^n_4NF yielding $[Re_6\{Q_5(NH)X_2\}Cl_6]^{2-}$. The nitrogen atom in this cluster remains nucleophilic and can be alkylated by butyl chloride in the presence of a base yielding the complex $[Re_6\{Q_5(NBu^n)X_2\}Cl_6]^2$.[338] In the case of the oxide cluster, the substitution of one of the terminal chloride ligands also takes place and the complex $[\{Re_6(S_5OCl_2)Cl_5\}_2O]^{4-}$ is formed.[339] The substitution of O, S, NH for two μ_3-chlorine atoms in the chalcogenide clusters $[Re_6(S_6Cl_2)Cl_6]^{2-}$ is possible in the reactions with silyl reagents. The clusters $[Re_6(S_6E_2)(PPr_3)_6]^{2+}$ (E = P, As) containing μ_3-atoms of Group 15 elements in the cluster core were obtained when $PhAs(SiMe_3)_2$ or $P(SiMe_3)_3$ were used.[136]

The bridging chalcogenide ligands are less labile and can be substituted only under drastic conditions. For instance, the reaction of $[Re_6Te_8(Te_7)]$ with a melt of KNCS results in the substitution of sulfur for μ_3-tellurium atoms and produces a mixture of $[Re_6S_8(CN)_6]^{4-}$ and $[Re_6S_6Te_2(CN)_6]^{4-}$.[163, 340] The formation of the mixed-chalcogen clusters was confirmed by ^{77}Se and ^{125}Te NMR spectroscopy.[341] The reaction of $[Re_6Te_8(Te_7)]$ with bromine yields $[Re_6(Te_4Br_4)Br_6]$.[8, 187] Iodine, being a weaker oxidant, transforms the *spiro*-anion Te_7^{2-} into the ligand TeI_2 without affecting the cluster core to give the cluster $[Re_6Te_8(TeI_2)_6]I_2$.[342]

In the series of the octahedral molybdenum chalcogenide clusters Mo_6Q_8 (Q = S, Se, Te), the telluride possesses the highest reactivity and can be transformed into Mo_6Cl_{12} with chlorine or other chlorinating reagents. The experiments with isotopomeric compounds have shown that the octahedron of Mo_6 remains intact.[343, 344]

5. Elimination of chalcogens from the clusters M_3Q_7

A well studied transformation of triangular clusters M_3Q_7 into M_3Q_4 in the reaction with such reagents as cyanide ion or phosphines belongs to this class of processes.[18] It was shown by isotope exchange method that it is the equatorial atom of dichalcogenide ligand that is eliminated.[46, 48] The selenium atom is eliminated from the clusters $Mo_3(\mu_3\text{-}S).(\mu\text{-}S_{ax}Se_{eq})_3^{4+}$.[32, 47] The proneness to chalcogen elimination decreases in the order $Mo_3S_7 > Mo_3Se_7 > Mo_3Te_7$. In the case of telluride clusters, no elimination of tellurium atom in reactions with cyanides or phosphines usually occurs. The only exception is the reaction of $[Mo_3Te_7\{(Pr^iO)_2PS_2\}_3]I$ with tributylphosphine (in the presence of benzoic acid), which results in the formation of the complex $[Mo_3Te_4.\{(Pr^iO)_2PS_2\}_3(\mu\text{-}C_6H_4CO_2)(PBu^n_3)]$.[23]

The aqua complex $[Mo_3S_7(H_2O)_6]^{4+}$ quantitatively yields $[Mo_3S_4(H_2O)_9]^{4+}$ in the reaction with water-soluble phosphine PR_3^{3-} (R = $C_6H_4SO_3$). The following equation describes the dependence of the rate of this reaction on $[H^+]$

$$k = k_1[H^+] + k_{-1}[H^+]^{-1}$$

($k_1 = 3.14 \times 10^4$ litre^2 mol^{-2} s^{-1}; $k_{-1} = 2.78 \times 10^4$ s^{-1}). It was thus suggested that both the μ-S_2-protonated form of $[Mo_3S_5(HS_2)(H_2O)_6]^{5+}$ and the conjugated base $[Mo_3S_7.(H_2O)_5(OH)]^{3+}$ are involved. The rate of this reaction in the case of the selenide complex $[Mo_3Se_7(H_2O)_6]^{4+}$ is approximately 1000 times lower than for the sulfide analogue.[32] The reactions with cyanide and phosphines usually produce the corresponding cyanide or phosphine complexes.[18, 24, 308, 345] Even coordination polymers react in this way.[24, 53] The complexes $[M_3Q_4(dmpe)_3X_3]^+$ obtained in the reaction with dmpe are convenient starting compounds for the synthesis of heterometallic cubane-type clusters.[346] Recently, complexes with chiral phosphines have been obtained.[347] The isotope labelling studies suggest that the formation of $[Mo_3S_7(S_2)_3]^{2-}$ from $Mo_3S_7Br_4$ and $(NH_4)_2S_x$ proceeds as the elimination–addition in the equatorial position, *i.e.*, *via* the cluster Mo_3S_4.[44, 48] In the case of $W_3S_7Br_4$ and $(NH_4)_2S_x$ the complex $[W_3S_4(S_4)_3(NH_3)_3]^{2-}$ is the reaction product.[44, 231] Generally, the tungsten clusters $W_3Q_7^{4+}$ are less stable and readily eliminate three chalcogen atoms yielding the clusters $W_3Q_4^{4+}$, for example, in the synthesis of oxalate complexes.[33] The complex $[W_3S_7Br_6]^{2-}$ yields $[W_3S_4(NCS)_9]^{5-}$ even upon heating with KNCS in acetonitrile.[231] The sulfobromide $Mo_3S_7Br_4$ eliminates sulfur atoms from the disulfide ligands in a melt of KHF_2 furnishing $[Mo_3S_4F_7(FHF)_2]^{5-}$.[348]

The reaction of $[Re_3S_7Cl_6]Cl$ with an ionic liquid (a mixture of 1-ethyl-3-methyl-imidazolium bromide and $AlBr_3$) results in the formation of the anionic complex $[Re_3S_4Br_9]^{2-}$.[349] The reactions with phosphines are accompanied by reduction and transformation of the cluster core.[350]

6. Reactions with the change in of the number of metal atoms

The incorporation of Group 6–15 metals (more than 20 elements) in low oxidation states into the cluster core is typical of triangular clusters M_3Q_4 and results in the formation of heterometallic cubane-type clusters. These reactions were intensively studied and the results were summarised in several reviews.[18, 19, 346] In the case of a transition metal (Cr, Mo, W, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu) that is incorporated, this is involved in bonding Mo (W) to form a metallotetrahedron. Group 12–15 metals do not form metal–metal bonds. In the case of transition metals, the clusters in which the total number of valence electrons (NVE) including those provided by the ligand is equal to 60 are the most stable. This corresponds to the scheme of MO of tetrahedral clusters. The derivatives of $Mo_3CuQ_4^{4+}$ (NVE = 61), $Mo_3CoQ_4^{4+/3+}$ (NVE = 58 and 59), $Mo_3FeS_4^{4+}$ (NVE = 58) are exceptions to the rule. When an atom of post-transition element is incorporated, the heterometallic clusters are formed only if the metal is in the formally zero oxidation state (Zn, Cd, Hg, In, Tl, Ge, Sn, Pb, As, Sb, Bi) or possesses a lone pair of electrons (Ga^I, In^I, Ge^{II}, Sn^{II}, Pb^{II}, Sb^{III}, Bi^{III}). The tendency towards the formation of heterometallic clusters decreases in the order $Mo_3S_4^{4+} > Mo_3Se_4^{4+} > W_3Se_4^{4+} > W_3S_4^{4+}$, *i.e.* similarly to the order of decrease in the rate of cluster core reduction.[18, 19, 346]

Oxidation of heterometallic cubane-type clusters recovers readily the starting triangular clusters $M_3Q_4^{4+}$.[19] The ease of oxidation increases in the same order as the tendency to reduction of a triangular cluster decreases. In the case of heterocubane clusters $[Mo_xW_{4-x}Q_4(H_2O)_{12}]^{6+}$ ($x = 1-3$), oxidation always proceeds with elimination of the tungsten atom. This reaction can be used for selective synthesis of otherwise hardly accessible mixed heterometallic triangular clusters $[Mo_xW_{3-x}Q_4(H_2O)_9]^{4+}$ (Q = S, Se; x = 1, 2).[116, 117] The first heterometallic clusters Re_3MS_4 (M = Ni, Co, Cu) were obtained.[40, 351, 352]

In some cases the cubane-type clusters M_4S_4 are formed from triangular clusters as a result of complicated reactions in attempted reduction or ligand exchange reactions. Thus, the reduction of the aqua complex $[Mo_3S_4(H_2O)_9]^{4+}$ affords a mixture of a cubane-type and a heptanuclear bis-cubane clusters $[Mo_4S_4(H_2O)_{12}]^{4+}$ and $[Mo_7S_8(H_2O)_{18}]^{8+}$,[353] and an attempt to synthesise Re_3S_4 derivatives from $[Re_3S_7Cl_6]Cl$ by the reaction with KCN unexpectedly yields $[Re_4S_4(CN)_{12}]^{4-}$.[87] The cyanide cluster complexes $[M_4Q_4(CN)_{12}]^{6-}$ were obtained by high-temperature reactions of triangular coordination polymers $M_3Q_7X_4$ (Q = S, Se, Te; X = Br, I) with KCN.[102]

The reduction of phosphine complexes $[Mo_3Q_4.(PEt_3)_{3-4}X_4(MeOH)_{1-2}]$ (Q = S, Se) with magnesium results in the reductive fusion of two metal triangles into an octahedron and the formation of phosphine cluster complexes $[Mo_6Q_8(PEt_3)_6]$, which are molecular analogues of the Chevrel phases.[257] Formally, octahedral clusters M_6Q_8 are the dimerisation products of reduced triangular clusters M_3Q_4. If the reaction takes place at low temperatures, then the dimerisation of two triangular clusters happens at the stage of one-electron reduction. This reaction affords the compounds $[Mo_6Q_8Cl_6.(PEt_3)_6]$ in which two metal triangles are linked by one metal–metal bond.[179] The cluster $[Mo_6S_{10}(SH)_2(PEt_3)_6]$ of a similar structure was obtained from $(NH_4)_2[Mo_3S_7(S_2)_3]$ and triethylphosphine.[130]

The cases of transformation of tetrahedral clusters into octahedral clusters are extremely rare. One example is the formation (simultaneously with the chalcogen atom replacement in the cluster core) of the complex $[Re_6Se_8(CN)_6]^{4-}$ from $[Re_4Te_4(TeCl_2)_4Cl_8]$ and KNCSe (the latter is the reducing agent as well as the source of selenium and cyanide ions) in acetonitrile at 200 °C. The cluster $Re_4S_4Te_4$ reacts with KCN at 850 °C yielding the octahedral cluster complex $[Re_6S_6(S_{0.34}Te_{0.66})_2(CN)_6]^{4-}$. This reaction was used for the synthesis of heterometallic clusters $[Re_5MoS_8(CN)_6]^{5-}$ and $[Re_4Mo_2S_8(CN)_6]^{5-}$ from $Re_3MoS_4Te_4$.[142]

V. Potential applications of chalcogenide clusters

The progress in chemistry of chalcogenide clusters of early transition metal is very important for better understanding of the processes that occur in living systems with involvement of transition metals. It is well known that at least seven metals (V, Mo, W, Fe, Ni, Cu and Zn) in living systems are bonded quite often to sulfur (and/or selenium) atoms and are vital for various biological functions. Among the early transition metals, molybdenum is particularly important as a part of different enzymes. Tungsten is the heaviest element with reliably determined biological role. Chalcogenide clusters are also of interest as models of solid-state metal chalcogenides; besides they are used in the synthesis of new catalysts and advanced materials (superconductors, X-ray contrast diagnostic agents and nonlinear optic materials).

Catalysis. Supported transition metal sulfides are catalysts of hydrorefining of crude oil.[354] CoMoS and NiMoS supported onto alumina are widely used in industry for desulfurisation. Traditionally they are prepared by impregnation of γ-Al_2O_3 with ammonium heptamolybdate and cobalt or nickel nitrate with subsequent calcination and transformation of oxides into sulfide phases by heating in an atmosphere of H_2S and H_2 at 400 °C. More effective catalysts were obtained in the reactions of the sulfide cluster $[Mo_3S_{13}]^{2-}$ with various salts, including those with complex nickel- or cobalt-containing cations.[355] The metal ratio in the heterometallic cubane-type clusters M_3NiS_4 and M_3CoS_4 corresponds to the composition

of the best hydrorafining catalysts and the coordination of heterometal is thought to be similar to that of cobalt or nickel atom in the active site of such catalysts.[356] The triangular and heterometallic cubane-type cationic aqua complexes $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ were incorporated into zeolites by an ion-exchange reaction.[357–359] It was shown that the activity of such catalysts in hydrogenation of thiophene strongly depends on the zeolite type. The complex $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ incorporated into the zeolite cavity catalyses also the synthesis of ethane and ethylene in the hydrogenation of CO.

The triangular pentamethylcyclopentadienyl cluster $[Cp^*_3Mo_3S_4]^+$ reacts with $[Ni(cod)_2]$ (cod is cycloocta-1,5-diene) in dichloromethane at room temperature yielding the cubane-type heterometallic cluster $[(Cp^*_3Mo_3NiS_4)_2(cod)]^{2+}$, which is a highly effective catalyst of intramolecular cyclisation of alkynoic acids into the corresponding enollactones in the presence of Et_3N. Presumably, an intermediate nickel alkyne complex is formed in this reaction.[360]

The 1,4,7-triazacyclononane (tacn) heterometallic cluster $[Mo_3(PdCl)S_4(tacn)]^{3+}$ possesses a unique ability of coordinating and activating such π-acidic ligands as CO, isonitriles, alkenes and alkynes under very mild conditions. Thus the solution reaction with CO proceeds even at room temperature and yields the brown complex $[Mo_3(PdCO)S_4(tacn)_3]^{3+}$. Activated alkynes (for example, $HC{\equiv}CCO_2Me$ and $MeO_2CC{\equiv}CCO_2Me$) also coordinate only the palladium atom of the cluster, but form very labile complexes, which could not be isolated. However, selective nucleophilic addition of methanol to methyl propiolate result in (*Z*)-$MeOCH{=}CHCO_2Me$ in virtually quantitative yield takes place in the presence of methanol. It is important that the reactions of nucleophilic addition are catalytic processes and more effective than the catalytic reactions of mononuclear palladium complexes.[361]

Unique catalysts possessing a chiral metal chalcogenide cores can be obtained from chalcogenide clusters.[347] Each diphosphine ligand in the triangular molybdenum and tungsten diphosphine complexes $[M_3Q_4(diphospine)_3X_3]^+$ (M = Mo, W; Q = S, Se; X = Cl, Br) links to only one metal atom, while the phosphorus atoms are located in *cis*- and *trans*-positions with respect to the μ_3-chalcogen atom. These diphosphine clusters are chiral. From the chiral diphosphine (+)-1,2-bis[(2*R*,5*R*)-2,5-(dimethylphospholan-1-yl)]ethane [(*R*,*R*)-MeBPE], the chiral triangular cluster $[Mo_3S_4\{(R,R)\text{-MeBPE}\}_3Cl_3]^+$ and heterometallic derivative $[Mo_3CuS_4\{(R,R)\text{-MeBPE}\}_3Cl_3]^+$ were obtained. This heterometallic cluster turned out to be an effective catalyst of two reactions: the intramolecular cyclisation of 1-diazohex-5-en-2-one and the intermolecular cyclopropanation of styrene or 2-phenylpropene with ethyl diazoacetate. The reactions proceed in high yields of the corresponding cyclopropanes (up to 95%), the enantiomeric excess being in the range from 12% to 25%.[347]

Conductors and superconductors. A unique substance was obtained by two-electron oxidation of the anionic molybdenum cluster $[Mo_3S_7(dmit)_3]^{2-}$.[362] Electrochemical oxidation of its *tert*-butylammonium salt yields deep-violet needle-shaped crystals stable in air. Chemical oxidation with iodine in dichloromethane is yet another method of its synthesis in quantitative yield. The neutral cluster molecules crystallise in a hexagonal space group and the structure is built of chains. The molecules in the chains are linked by short S···S contacts between axial sulfur atoms of the bridging disulfide ligands and μ_3-sulfur atoms. The S···S contacts between the sulfur atoms of the cluster complexes of different chains combine the chains into honeycomb-like framework with spacious vacant channels ~10 Å in diameter. The room-temperature conductivity measurements have shown that $[Mo_3S_7(dmit)_3]$ is a quazi-one-dimensional semiconductor with a very low value of activation energy. The magnetic susceptibility measurements reveal the presence of antiferromagnetic exchange interactions between unpaired electrons of the neutral clusters $[Mo_3S_7(dmit)_3]$. It is expected that chemical modification of this unique cluster (for example, by the replacement of the metal, chalcogen or redox-active ligand) and application of high pressure will eventually result in the stabilisation of the metal state.

Non-linear optical properties. The triangular molybdenum and tungsten chalcogenide clusters and their heterometallic cubane derivatives were systematically studied in this respect. All triangular clusters $[M_3Q_4L_3X_4]^+$ (M = Mo, W; Q = S, Se; L = dmpe, dppe) and their copper-containing cubane-type derivatives $[M_3CuQ_4L_3X_4]^+$ turned out to be promising optical limiters and the value of threshold limiting flux decreases on going from the cubane-type clusters to triangular ones and from tungsten clusters to molybdenum analogues.[296, 308, 346]

X-Ray contrast agents. The cluster-type tungsten thio complexes ($W_3S_4^{4+}$ derivatives) represent a new class of X-ray contrast diagnostic agents. The cluster compounds of heavy metals ($Z > 50$) possess a high X-ray absorption coefficient, which results in a significant improvement of the image quality and/or reduction of X-ray irradiation dose. Triangular tungsten thio clusters are highly soluble in water, do not hydrolyse in aqueous solutions and form stable chelate complexes with various ligands. It is very important that the $W_3S_4^{4+}$ derivatives are significantly less toxic in comparison with water-soluble tungsten heteropolyanions.[363]

VI. Conclusion

The data presented show that the chemistry of chalcogenide cluster complexes of Group 5–7 metals is extensive and diverse. Many specific properties of cluster compounds are determined by the structure, geometry and electronic features of the cluster core. The possibility of modifying the cluster core by isovalent and non-isovalent substitution of both 'inner' ligands and metal atoms allows one to change the properties of cluster complexes. Such approach underlies the directed synthesis of materials with preset properties in which the cluster complexes are used as building blocks with predetermined spatial, electronic, optical or magnetic characteristics. The list of useful properties of chalcogenide cluster compounds is already quite remarkable and will undoubtedly be extended with the further studies of this class of compounds. More and more, not only synthetic chemists, but also physicists, theoreticians, materials scientists are involved in these studies and, owing to their efforts, the first steps towards the design of new materials and better understanding of the principles which control the properties of these compounds are being made.

The data presented show the progress in the studies of cluster chalcogenide complexes of transition metals. Quite interesting is the evolution of studies of such systems. Whereas after the discovery of the key compounds, they were studied predominantly by the methods of solid state chemistry the set of which was rather small, nowadays the main attention is paid to the chemistry of solutions due to the development of methods of transformation of polymeric cluster compounds into molecular complexes. New research groups became involved into this field of chemistry, which increases the ability to detect specific properties of cluster complexes.

At the first glance, it seems that, as a result of intensive studies, the chemistry of chalcogenide cluster complexes of Group 5–7 metals has been exhausted. However, recent syntheses of cluster metal complexes of unexpected types, such as square vanadium $V_4S_9Br_4$ and tantalum $Ta_4Q_9X_8$ (Q = S, Se) clusters, dodecanuclear rhenium complexes $[Re_{12}CS_{17}(CN)_6]^{8-/6-}$ with interstitial carbon atom, indicate that further discoveries are awaiting.

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