



Account/Revue

The molybdenum and rhenium octahedral cluster chalcogenides in solid state chemistry: From condensed to discrete cluster units

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ABSTRACT

The octahedral Mo₆ and Re₆ chalcogenides prepared by solid state routes at high temperature are reviewed from their origin to the recent period. Their crystal structures built from the face-capped M₆L₁₄ building blocks are presented according to the interunit connectivities, starting from the three-dimensional Chevrel phases and decreasing the dimensionality down to 2D, 1D and finally 0D compounds in which the cluster units are discrete. In a second step, it is shown that the solid cluster compounds are relevant precursors for more recently expanded reactions in solution or by soft chemistry, giving access to a large variety of hybrid organic/inorganic cluster materials.

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R É S U M É

Les chalcogénures à clusters octaédriques Mo₆ et Re₆ synthétisés en chimie du solide à haute température sont décrits depuis leur origine jusqu'à la période actuelle. Leurs structures cristallines formées à partir des motifs M₆L₁₄ sont présentées selon le type de connexion intermotifs, partant des phases de Chevrel tridimensionnelles et réduisant la dimensionnalité jusqu'aux phases dans lesquelles les motifs sont isolés. Il est montré comment, dans une période plus récente, les composés solides à clusters octaédriques se sont avérés d'excellents précurseurs pour des réactions en solution ou par chimie douce donnant accès à de nombreux matériaux hybrides organiques/inorganiques à clusters, constituant ainsi une thématique en rapide expansion.

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1. Introduction

The discovery in 1971 of the A_yMo₆Q₈ (Q = chalcogen, A = cation) Chevrel phases in the Solid State Chemistry Laboratory of Rennes University [1,2] was the starting point in this laboratory for a new research field on Mo₆ and Re₆ chalcogenide cluster chemistry isolated at high temperature (1000–1200 °C) by solid state routes [3,4]. Notice that before the 1970s, the molybdenum and

rhenium chalcogenides were obtained at moderate temperature – usually below 500 °C – and they were built from single cations, two-atom or triangular clusters, frequently with polysulfide groups located perpendicularly to the metal-metal bond, as in MoS₂Cl₃ or Mo₃Cl₄S₇ [5–11]. The high-critical field superconducting properties of Chevrel phases stimulated an extensive research in order to explain and to improve their superconducting behaviour [12]. Their electronic structure has been the subject of many theoretical studies, which clearly evidenced that the number of valence electrons per octahedral cluster (VEC) in the HOMO level plays the essential role in their superconducting properties considering that these phases, built up from Mo₆Q₁₄ building blocks, exhibit some

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molecular character [13]. A simple way to modify the VEC was to change the A_y cationic stoichiometry, as shown by a great number of examples [12]. Two other original routes to change the VEC were to replace divalent chalcogen by monovalent halogen, for instance in $Mo_6S_6X_2$ ($X = Br, I$) isotypical with Mo_6S_8 [14,15] or to replace a part of molybdenum (d^5s^1) in the Mo_6 cluster by rhenium (d^6s^1), as in the mixed cluster compound $Mo_2Re_4S_8$ [16]. The two last possibilities were investigated for the first time in the Rennes labs and they were the starting point of an important development of Mo_6 and Re_6 chalcogenide solid state chemistry presented below.

In this review, we will describe the crystal chemistry of Mo_6 and Re_6 chalcogenides synthesized at high temperature by solid state routes and structurally characterized by single crystal X-ray diffraction, starting from the 3D Chevrel phases in which the cluster building blocks are interconnected in the three directions, and decreasing the dimensionality to 2D, 1D architectures, down to 0D compounds built from discrete cluster units. In a second step we will show how the latter discrete units are, for several years, the object of an intensive use as individual nano-sized molecular precursors in soft chemistry for rebuilding 3D, 2D or 1D hybrid organic/inorganic cluster compounds and for the elaboration of nanocluster materials with potential applications in nanotechnology owing to their specific optical, redox and magnetic properties. As mentioned above, this review focuses essentially on chalcogenides. Nevertheless, some examples of pure halides and chalcogenides will be included when pertinent for comparison.

An aim of this article is to complete and update several previous accounts [17–25], and to remind us of a 50 year story of Mo_6 and Re_6 cluster chalcogenides in solid state chemistry. We have chosen to systematically refer to original papers, even when very old, in order to get a memory of them, because they are often forgotten by the timely used computer-assisted bibliographic tools and their users. Indeed, “if nobody remembers something, it did not ever exist” [26].

2. The $M_6L_8L^a_6$ building block

All the M_6 ($M = Mo, Re$) chalcogenides are built from the nanometer-sized $[(M_6L_8L^a_6)]$ building block in which the octahedral cluster, consisting in six metal atoms in d^4 electronic configuration (Mo^{II} or Re^{III}) linked together by metal-metal bonds, is always bonded to 14 ligands. Indeed, this metal cluster (in the sense of the restricted definition of Cotton [27]) is face-capped by eight inner ligands (noted L^i), while six apical ligands (noted L^a) are in apical positions that build a square-pyramidal environment around each metal atom (Fig. 1). A ligand shared between two units is noted L^{a-a} , L^{i-i} or L^{i-a} depending on the shared positions. This notation, which is very useful for describing schematically all the compounds built from the M_6L_{14} units, was proposed by Schäfer and von Schnering [28].

Interestingly, for mixed chalcogen/halogen $M_6L_8L^a_6$ clusters, it is worth mentioning that, owing to the difference of valence and electronegativity between

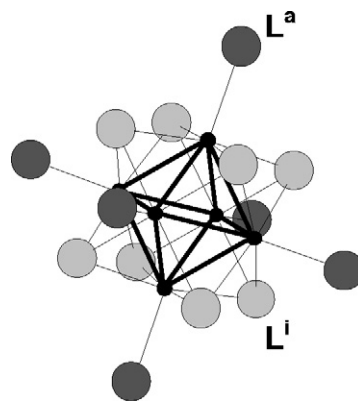


Fig. 1. The $M_6L_8L^a_6$ cluster unit.

halogen and chalcogen, L^a and L^{a-a} positions are occupied preferentially by halogens, while L^{i-i} and L^{i-a} are occupied in priority by chalcogens. The non-shared L^i positions (μ_3 - L^i) can be occupied by either halogens or chalcogens leading almost systematically in the averaged structural model to a random occupancy of the inner sites by both of them, a situation often described as a “rotational disorder” (in the following, when both Q^i and X^i appear in a developed formula it follows a Q^i/X^i disorder on the corresponding inner positions). Indeed, formal metal (donor)-halogen/chalcogen (acceptor) interactions occur to satisfy the electronic demands of the latter (Q^{2-} and X^- to obey the octet rule). Consequently, the more negatively charged chalcogens will seek to bind a larger number of positively charged metal atoms than the less negatively charged halogens [29,30]. Notice that no exception to this rule has been observed up to now in the great number of Mo_6 and Re_6 chalcogenides. Of course, in the case of pure M_6 chalcogenide chemistry, the chalcogens occupy all the ligand type positions, for instance in the Re_6 ternary chalcogenides [31].

The molecular orbital diagram of these $[(M_6L_8L^a_6)]$ units can theoretically be built from the frontier orbitals of six square-pyramidal ML_5 fragments. The 12 highest molecular orbital occupied by electrons are metal-metal bonding in character with the HOMO level formed by a doubly degenerated orbital of e_g symmetry considering an O_h symmetry for the unit. These metal-metal bonding orbitals are filled for 24 valence electrons per cluster (VEC) that constitutes the “magic number” in Mo_6 and Re_6 cluster chalcogenide chemistry [13,32–37]. Indeed, the M_6 chalcogenides obtained up to now by solid state chemistry exhibit usually a VEC value of 24, with the exception of Chevrel phases for which the VEC value can vary from 20 to 24. In the latter case the interactions between cluster units lead to a band structure giving the possibility of metallic conduction when the bands are partly filled, while the other chalcogenides with a VEC value of 24 are generally semiconducting or insulating. Notice that an extremely rare example of a compound in which coexist discrete units with VEC = 24 and 23 has been isolated in solid state chemistry (Section 3.3.2).

3. Solid state compounds

3.1. Three-dimensional M_6 chalcogenides

3.1.1. Three-dimensional Q^{i-a}/Q^{a-i} connections

The first discovered and structurally characterized 3D M_6 chalcogenides were $Mo_6Q_{8-x}X_x$ ($X = \text{halogen}$, $Q = \text{chalcogen}$ and $0 < x < 2$) [14,15], isotopic with $A_yMo_6Q_8$ ($A = \text{cations}$ with various charges) Chevrel phases built from the $[(Mo_6Q^i_2Q^{i-a}_{6/2})Q^{a-i}_{6/2}]$ three-dimensional framework [2]. In these chalcogenides the units are interconnected in the three directions by inner-apical chalcogen double bridges (Q^{i-a}/Q^{a-i}) in the same way as in Chevrel phases, while inner halogen atoms (X^i) are located on the threefold axis of the unit that builds channels developing in the three directions of the space.

When $Q = S$, definite compounds with $x = 2$ have been obtained: $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ $[(Mo_6X^i_2Q^{i-a}_{6/2})Q^{a-i}_{6/2}]$ (Fig. 2). A slight defect on Q and X positions was observed in $Mo_6I_{1.76}S_{5.96}$ [38]. While Mo_6S_8 (VEC = 20) is superconducting only at very low temperature (less than 2 K), $Mo_6S_6X_2$ (VEC = 22) is superconducting at $T_c = 13.8$ K and 14 K for $X = Br$ and I , respectively, and with high-critical field like for $PbMo_6S_8$ (VEC = 22) [14]. This VEC value of 22 corresponds to a maximum in the density of states near the Fermi level that should explain the optimal superconducting properties [39]. Notice that Mo_6S_8 (VEC = 20) is not thermodynamically stable and cannot be obtained by direct synthesis at high temperature, while $Mo_6S_6X_2$ are prepared around 1200 °C like the other $A_yMo_6Q_8$ phases and they are very stable. It was assumed that this stability is due to firstly, the addition of electrons in the metal-metal bonding orbitals and secondly, the location of two X halogens close to each other on the threefold axis leading to a van der Waals bond, partly filling the distorted vacancy at the origin of the unit-cell, that is occupied by the big A cations in $A_yMo_6Q_8$ [12]. In Mo_6S_8 the corresponding two sulfur atoms are too small to be in contact in this vacancy, leading to a poor stability of this compound. Note that, in agreement with the latter assumption, “ $Mo_6S_6Cl_2$ ”

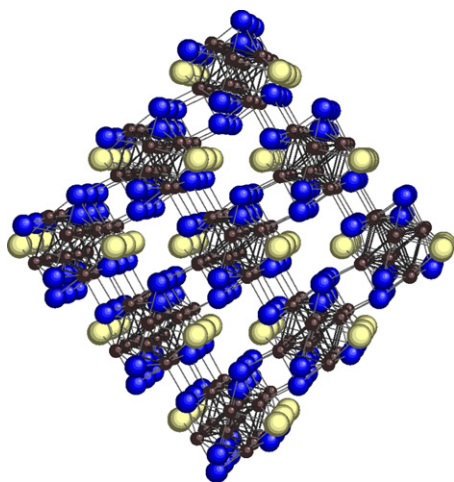


Fig. 2. Crystal structure of $Mo_6S_6Br_2$. S in blue (dark grey) Br in yellow (light grey) [15].

(VEC = 22) has never been stabilized because the origin site should be too strongly distorted to get the small chlorine atoms in contact to each other [40]. Recently, the difference between the Mo_6S_8 and $Mo_6S_6Br_2$ stability was discussed by bond valence analysis showing that lattice strain caused by anion polarization leads to instability [30]. The magnetic field penetration in nanometer-sized particles of $Mo_6S_6I_2$ has been investigated in relation with decreasing the particle size [41].

When $Q = Se$ or Te , solid solutions $Mo_6Q_{8-x}X_x$ have been evidenced ($X = Cl, Br, I$ and $0 < x < 2$) with T_c increasing correlatively with the VEC value (Fig. 3) up to 7.0 K, 7.1 K, and 7.6 K for $Q = Se$ and $X = Cl, Br$ and I , respectively. Mo_6Te_8 , not superconducting above 1 K, becomes superconducting after iodine substitution with a maximum $T_c = 2.6$ K for $Mo_6Te_6I_2$ (Fig. 3). Note that analyses of X-ray powder diffraction data and superconducting critical temperature T_c performed for $x > 2$ evidenced a saturation of both the lattice constants and T_c , indicating that the halogen should only occupy the 2c site on threefold axis, as in $Mo_6S_6Q_2$ with a maximum value $x = 2$. Thus, the various compositions of the solid solution are written as $[(Mo_6Q^{i-2-x}X^i_xQ^{i-a}_{6/2})Q^{a-i}_{6/2}]$. Indeed, as stated above, the halogen atoms should occupy only the inner sites and not the inner-apical ones.

The diffusion of small cations like Cu into the $Mo_6S_6X_2$ host structure has been carried out at low temperature (450 °C) up to the limit of 1.5 Cu for $X = Br$ [15] and 1.2 for $X = I$ [42] with a decrease of the T_c down to 4.8 K for $Cu_{1.2}Mo_6S_6I_2$, related to the increase of the VEC above the ideal value of 22. Intercalation of sodium was performed by electrochemical reactions using $Na/Mo_6Se_{8-x}I_x$ ($x = 0, 0.5, 1, 2$) test cells. Cycling data indicate that intercalation process is initially irreversible and results in compounds of formula $Na_yMo_6Se_{8-x}I_x$ with y decreasing from 1 to 0 as x increases from 0 to 2, while after the first cycle the cells are readily reversible over several cycles [43].

The first Chevrel phase discovered with rhenium was $Mo_2Re_4S_8$ built from a mixed octahedral cluster with 24 valence electrons [16]. This compound is a rare example of a semiconducting Chevrel phase, owing to the complete filling of the energy bands near the Fermi level by 24 valence electrons. Indeed, changing the Mo/Re ratio affects the VEC and, for instance, the $Mo_4Re_2Te_8$ compound (VEC = 22) turns out to be superconducting with $T_c = 3.55$ K [16]. It is also possible to change the Mo/Re ratio as well as the nature of the chalcogen and then several solid solutions were studied:

- $Mo_2Re_4Se_8$ is much easier to synthesize than the sulfur homologue, and a solid solution $Mo_2Re_4S_{8-x}Se_x$ extends over the full range $0 \leq x \leq 8$ while $Mo_2Re_4Se_{8-x}Te_x$ is severely limited to the range $0 \leq x \leq 1.2$ [16]. All these diamagnetic compounds are semiconducting, as expected (Fig. 4), but they do not follow an Arrhenius behaviour, exhibiting hopping conduction;
- as a consequence the synthesis of $Mo_2Re_4Te_8$ failed. In place $Mo_4Re_2Te_8$, with VEC = 22 was obtained [16]. This compound is, with $Mo_6Te_6I_2$, a unique example of superconducting telluride with Chevrel phase structure;

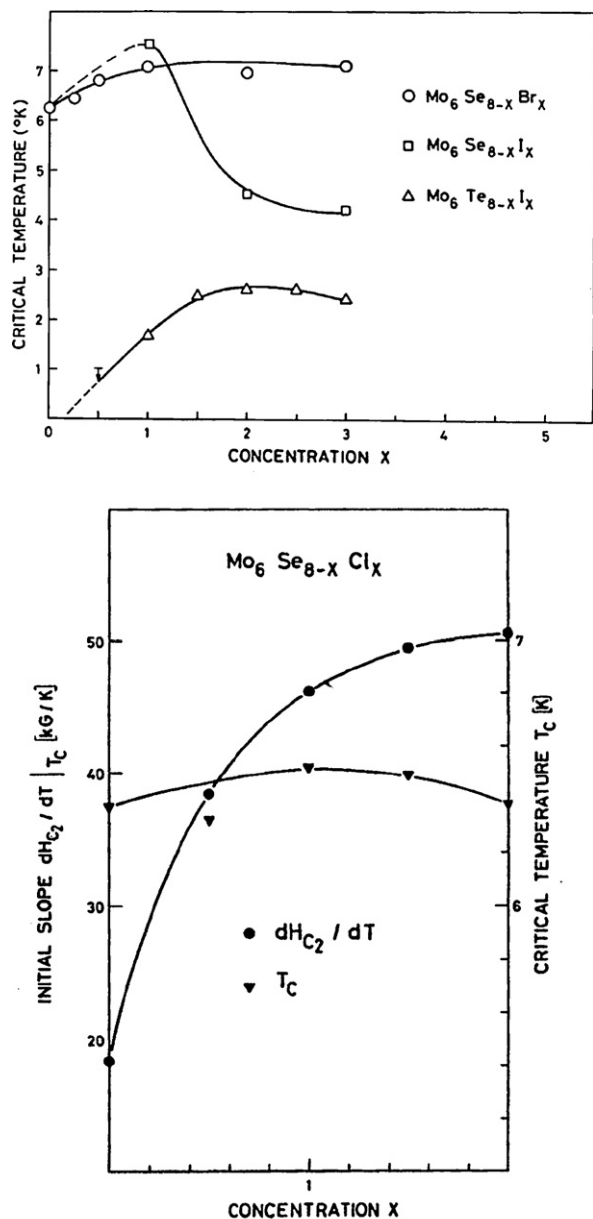


Fig. 3. Critical temperature T_c versus x stoichiometry of the superconductors $\text{Mo}_6\text{Se}_{8-x}\text{Br}_x$, $\text{Mo}_6\text{Se}_{8-x}\text{I}_x$ and $\text{Mo}_6\text{Te}_{8-x}\text{I}_x$ [14] (top). Critical temperature T_c versus x stoichiometry and initial slope of the critical field of the superconductors $\text{Mo}_6\text{Se}_{8-x}\text{Cl}_x$ [40] (bottom).

- attempts of synthesis of a solid solution like $\text{Mo}_6\text{Se}_8\text{--}\text{Mo}_2\text{Re}_4\text{Se}_8$ failed although the two extremes exhibit exactly the same structure, even if slight deviations from the 1:2 Mo:Re ratio were detected by EPMA [44] or XRD data [45]. This would be due essentially to electronic factors. In the example of the similar Mo-Ru heteroclusters, two domains of homogeneity were clearly identified, a very narrow semiconducting one close to $\text{Mo}_4\text{Ru}_2\text{Se}_8$ and a more extended metallic one at the Mo_6Se_8 border [46]. Also, this reminds us that, in Chevrel

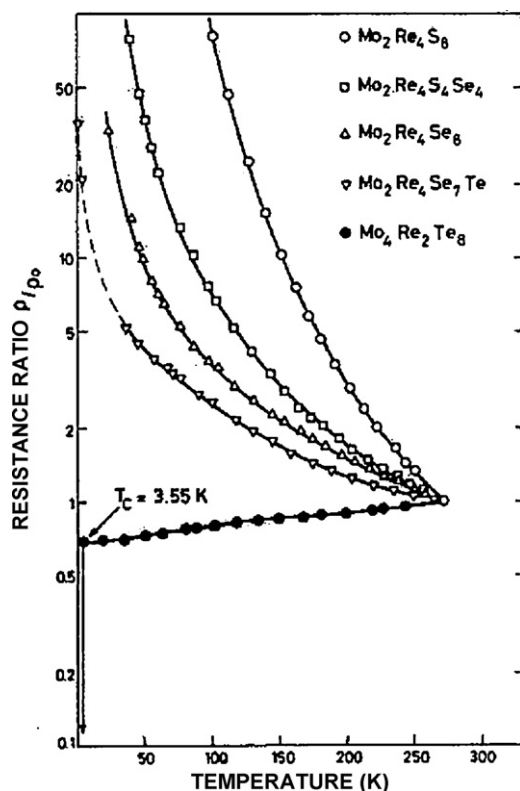


Fig. 4. Temperature dependence of the resistivity of $\text{Mo}_2\text{Re}_4\text{S}_4\text{Se}_4$, $\text{Mo}_2\text{Re}_4\text{Se}_8$, $\text{Mo}_2\text{Re}_4\text{Se}_7\text{Te}$ and $\text{Mo}_4\text{Re}_2\text{Te}_8$ [16].

phases, the 24 VEC limit (and then semiconducting compounds) is very difficult to reach actually by cationic filling of the cavities by solid state chemistry: the unique example of truly semiconducting compound seems to be $\text{Ti}_{0.9}\text{Mo}_6\text{Se}_8$ [47].

The heterometallic cluster compound $\text{Mo}_2\text{Re}_4\text{Se}_8$, as well as $\text{Mo}_4\text{Ru}_2\text{Se}_8$, was suggested as a potential material for thermoelectronic applications [44,48,49]. These compounds were also studied as catalysts for two important electrochemical reaction processes, hydrogen evolution and molecular oxygen reduction in acid medium, an important electrocatalytic reaction in polymer electrolyte membrane fuel cells, and showed significant improvement in comparison to Mo metal and Mo_6Se_8 [50]. The Mo-Ru heterometallic cluster was shown to present a catalytic behaviour comparable to platinum [51].

The attempts to obtain pure Re_6 chalcogenide Chevrel phases similar to Mo_6 ones was unsuccessful because they should imply a VEC value higher than 24 (Re: d^5s^1 instead of Mo: d^5s^1) corresponding to fill antibonding metal-metal orbitals. However, the possibility to obtain mixed Mo_2Re_4 and Mo_4Re_2 octahedral clusters stimulated an intensive research to stabilize Re_6 clusters that should be obtained by replacing a part of chalcogen by halogen in Re_6L_{14} unit. It was the starting point of the development of the Re_6 chalcogenide chemistry. Note that at the same period the first example of a mixed Mo_2Re_2 tetrahedral cluster was

reported [52] that reinforced our purpose of isolating a homometallic cluster with rhenium.

3.1.2. Three-dimensional X^{a-a} connections

In M_6 chalcogenide chemistry, apical-apical interunit connections are only obtained with halogen (X^{a-a}) as expected. Some examples are found with Mo_6 and Re_6 clusters. For instance, the compounds $Mo_6X_{10}Q$ ($X = Cl, Br$ and $Q = S, Se, Te$; $X = I$ and $Q = Se, Te$) ($Pccn$ space group) [53], isotypical with Nb_6I_{11} [54], are built from $[(Mo_6X^i_7Q^j)X^{a-a}_{6/2}]$ units. The six X^{a-a} bridges that develop in the three directions of the space are different: for instance, four $Mo-Cl-Mo$ bridges of 122.8° and two of 152.9° are found in $Mo_6Cl_{10}Se$. The thioiodide member has never been isolated due to the strong difference between the ionic radii of iodine and sulfur that should distort the cluster unit too much.

A similar stacking, but more symmetrical ($R-3c$ space group), is observed in the rhenium chalcobromides $Re_6Q_7Br_4$ ($Q = S, Se$) built from $[(Re_6Q^i_7Br^j)Br^{a-a}_{6/2}]$ units [55,56]. Each cluster unit is here octahedrally surrounded by six vertex-sharing identical groups. The structure packing then derives from the ReO_3 structure but a rotation of the cluster units leads to six identical bent halogen bridges of 115° . The angle of these bridges, much smaller than in $Mo_6X_{10}Y$ leads to a more compact stacking (Fig. 5). Note that the corresponding selenochloride has a more distorted monoclinic structure [57], maybe closely related to the above mentioned molybdenum one. Unfortunately, its exact structure was not solved, due to severe twinning of the crystals.

Finally, let us mention the presence of comparable 3D Q^{a-a} connections in several compounds belonging to a rich series of Re_6 cluster-based pure chalcogenides, where Q can be the usual chalcogen, but also a dichalcogen group [58–62]. Illustrating examples are found in the structures of $Li_4Re_6S_{11}$ and $K_4Re_6S_{12}$, with the structural formulas $Li_4[(Re_6S^i_8)S^{a-a}_{6/2}]$ and $K_4[(Re_6S^i_8)S^{a-a}_{4/2}(S-S)^{a-a}_{2/2}]$, respectively. Such compounds were studied for their catalytic properties, for instance hydrogenation and dehydrogenation of cyclohexanone [63] or condensation of primary amines, dehydrogenation of secondary amines and dealkylation of ternary amines [64]. Related to this series is the structure of the neutral Re_2Te_5 , namely Re_6Te_{15} [65–67]. Here the clusters are linked in the three directions by butterfly Te_7 molecules, each of them being surrounded by 6 clusters, leading to the unit $[(Re_6Te^i_8)(Te_7)^{a-a}_{6/6}]$.

In these 3D chalcogenides, the halogen/chalcogen distribution on the inner positions leads to a VEC value of 24 for all these series of chalcogenides and, in consequence, these compounds are insulating. The studies of dielectric permittivity performed for $Mo_6X_{10}Q$ evidence dielectric relaxations. Indeed, the cluster units act locally as electrical dipoles due to the uneven halogen/chalcogen distribution around the Mo_6 cluster. This random distribution of 1Q and 7X on the eight inner positions of the cluster unit gives eight possible orientations for the dipoles with two different orientations for each of them due to the symmetry of the unit-cell and, as a result, a strong disorder of dipoles in the framework. The dielectric permittivity is

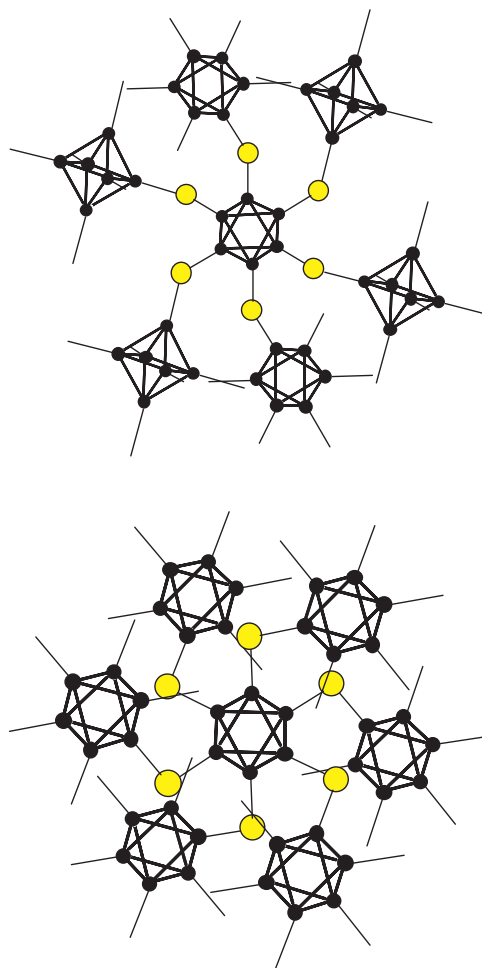


Fig. 5. Connection of a M_6L_{14} cluster unit with the six adjacent units by 3D X^{a-a} bridges in the projection of $Mo_6X_{10}Q$ (top) [53] and $Re_6Q_7Br_4$ (bottom) [55] along the pseudo threefold axis or true threefold axis, respectively.

sensitive to temperature and frequency of the applied field [53,68,69]. Namely, the maximum of permittivity versus temperature shifts towards a lower temperature as the frequency decreases (Fig. 6), that is specific of a dipole glass, the electrical analogue of spin glasses observed in disordered systems [70]. Note that in the same conditions the isotypical Nb_6I_{11} $[(Nb_6I^i_8)I^{a-a}_{6/2}]$ does not give any relaxation, due to the symmetrical arrangement of eight iodine atoms around the Nb_6 cluster that prevents the presence of permanent dipoles in the structure [40]. It was reported that $Re_6S_7Br_4$ exhibited a dielectric behaviour very close to that of $Mo_6Br_{10}S$ [69], although the detail of the dielectric relaxations were not published.

Photoelectrochemical investigations on $Re_6Se_7Br_4$ single-crystals in aqueous electrolytes [71] indicated that this compound behaves as a p-type semiconductor photoelectrode. In the visible region, it exhibits considerable cathodic photocurrents. Unfortunately, this electrode was not stable under applied potentials; the band gap (indirect) is 1.78 eV.

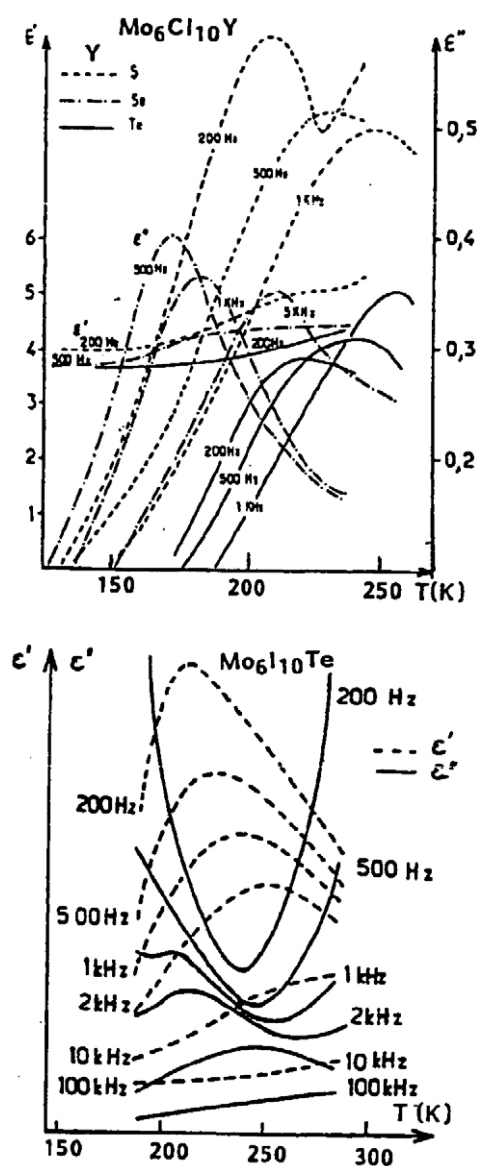


Fig. 6. Evolution of the dielectric constants ϵ' and ϵ'' versus temperature at various frequencies for $\text{Mo}_6\text{Cl}_{10}\text{Q}$ ($\text{Q} = \text{S}, \text{Se}, \text{Te}$) (top) and for $\text{Mo}_6\text{I}_{10}\text{Te}$ (bottom) [53].

3.1.3. Three-dimensional X^{a-a} and Q^{i-a}/Q^{a-i} mixed connections in Re_6 chalcocohalides

An illustrative example is given by the compounds $\text{Re}_6\text{S}_8\text{Cl}_2$, $\text{Re}_6\text{S}_8\text{Br}_2$ and $\text{Re}_6\text{Se}_8\text{Br}_2$. The crystal structures, determined in the cases of $\text{Re}_6\text{Se}_8\text{Br}_2$ [72] and $\text{Re}_6\text{S}_8\text{Br}_2$ [73] show that the cluster units are here linked in two directions of the space by bent halogen X^{a-a} bridges, similar to those encountered in $\text{Re}_6\text{Q}_7\text{Br}_4$, and in the third one by pairs of chalcogen Q^{i-a}/Q^{a-i} double bridges, similar to those present in Chevrel phases. Note that the latter were forgotten in [72], leading erroneously to some Re atoms deprived of their apical ligand [73]. Then, these compounds are in fact actually 3D and are written $[(\text{Re}_6\text{Q}_6^i\text{Q}^{i-a}_{2/2})\text{Q}^{a-i}_{2/2}\text{Br}^{a-a}_{4/2}]$. The thiochloride $\text{Re}_6\text{S}_8\text{Cl}_2$ also presents

this structure [74,75]. The photoelectrochemical behaviour of $\text{Re}_6\text{Q}_8\text{Br}_2$ ($\text{Q} = \text{S}, \text{Se}$) compounds was reported. Both of them act as p-type semiconductors and, assuming an indirect optical transition, have energy gaps of 0.84 (in good agreement with the value derived from optical absorption [72]) and 1.65 eV for the selenide and the sulphide, respectively, and appear stable in the photocathodic regime [73].

Note that the selenochloride parent $\text{Re}_6\text{Se}_8\text{Cl}_2$ exhibits a very different structure, being strongly bidimensional (Section 3.2.3).

3.2. Two-dimensional and one-dimensional M_6 chalcocohalides

These compounds reviewed recently in detail [76], will be reported very briefly here.

3.2.1. Q^{i-i} connections in 2D and 1D M_6 chalcocohalides

The inner-inner connection between two adjacent M_6L_{14} cluster units, observed in M_6 chalcocohalides, has never been obtained with Re_6 chalcocohalides. Such a type of connection corresponds to condensate the M_6L_{14} cluster units along one threefold axis of the L_8 cube to form a polymeric chain of units in which the L^{i-i} ligand is in prismatic environment of metal. Because the cluster units are rigid entities, three pairs of L^a condensate simultaneously with one pair of L^i , giving a L^{i-i} ligand surrounded by three L^{a-a} ligands (Fig. 7a).

These chains are observed in 1D $\text{M}_6\text{Br}_8\text{S}_2$, $\text{Mo}_6\text{I}_8\text{S}_2$ and $\text{Mo}_6\text{I}_8\text{Se}_2$ i.e. $[(\text{M}_6\text{X}_5\text{Q}^i\text{Q}^{i-i}_{2/2})\text{X}^{a-a}_{6/2}]$ [77,78] (Fig. 7b). They are similar to the chains found in $\text{Nb}_6\text{I}_9\text{S}$ reported later by J.D. Corbett et al., a rare example of Nb_6L_{14} chalcocohalide [79]. Van der Waals contacts between the chains ensure the (weak) cohesion of the structure. These compounds with 24 valence electrons per M_6 cluster are insulating. Single crystals of $\text{Mo}_6\text{I}_8\text{Se}_2$ oriented along or perpendicularly to the applied field exhibit a dielectric anisotropy with $\epsilon'_{\parallel}/\epsilon'_{\perp} \sim 80$ at room temperature [80].

In 2D $\text{Mo}_6\text{Br}_6\text{S}_3$ $[(\text{M}_6\text{Br}^i_4\text{S}^{i-i}_{2/2}\text{S}^{i-a}_{2/2})\text{S}^{a-i}_{2/2}\text{Br}^{a-a}_{4/2}]$ similar chains are observed, but the units are now slightly tilted along the chain axis in order to locate two inner chalcogen atoms in apical position for two clusters of two adjacent chains, building layers of chains (Fig. 7c) [81]. Between adjacent layers exist van der Waals contacts. This 24 VEC compound is semiconducting with an activation energy of 0.12 eV calculated from single crystal measurement along the growing axis of the crystal [40].

Note that such L^{i-i} connections, never observed in other M_6L_{14} chalcocohalides, were already found in M_6 and Re_6 chalcogenides like $\text{Ba}_4\text{Mo}_{12}\text{S}_{18}$ [82] and $\text{K}_8[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]$ [83] built from dimeric cluster units, the L^{i-i} position being occupied by S or C, respectively (Fig. 8). These dimeric units correspond to one link of the infinite chains observed in $\text{M}_6\text{X}_8\text{Q}_2$ fibers. However, these compounds do not grow like fibers because in $\text{Ba}_4\text{Mo}_{12}\text{S}_{18}$ $[(\text{M}_6)_2\text{S}^i_8\text{S}^{i-i}\text{S}^{i-a}_{6/2})\text{S}^{a-i}_{6/2}\text{S}^{a-a}_3]$ these dimeric units are interconnected in the three directions by sharing six $\text{S}^{i-a}/\text{S}^{a-i}$ ligands with adjacent dimeric units building large channels, while they are discrete in $\text{K}_8[\text{Re}_{12}\text{CS}_{17}\text{CN}_6]$ i.e. $[(\text{Re}_6)_2\text{S}^i_{14}\text{C}^{i-i})\text{S}^{a-a}_3(\text{CN}^a)_6]$. In $\text{Cs}_{-1}\text{Mo}_{12}\text{S}_{14}$ [84] the $[(\text{M}_6\text{S}^{i-i}_{2/2}\text{S}^{i-a}_{6/2})\text{S}^{a-i}_{6/2}]$ units are also interconnected

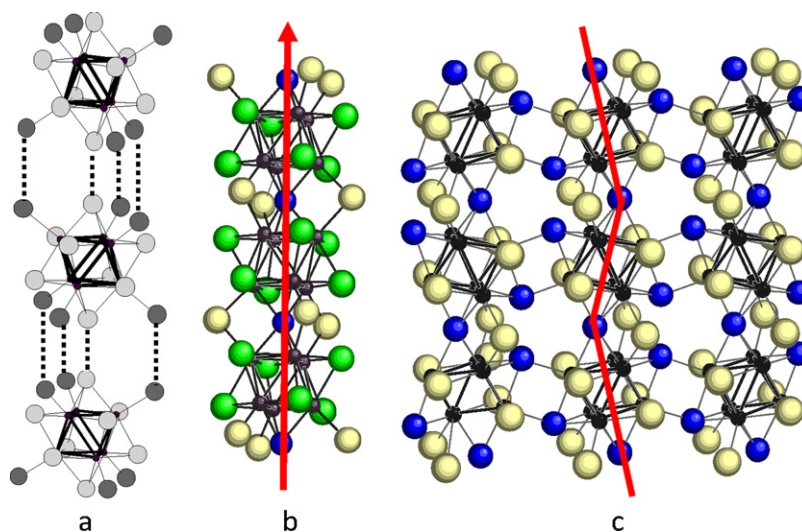


Fig. 7. a: schematic representation of the M_6L_{14} cluster unit condensation along the threefold axis. The central cluster unit is 180° rotated around the threefold axis with respect to the two others leading to the formation of L^{i-1} and L^{i-a} ligands that builds a prismatic environment of metal atoms around the L^{i-1} ligand; b: the resulting 1D chain built from $[(M_6X^i_5Q^i_{2/2}X^{i-a}_{6/2})]$ cluster units in $M_6X_8Q_2$ [77]. Q in blue (dark grey), Br in yellow (light grey), inner site randomly occupied by X and Q in green (middle grey); c: in $M_6Br_6S_3$ [81], representation of three 1D chains built from $[(M_6Br^i_4S^{i-1}_{2/2}S^{i-a}_{2/2})S^{i-1}_{2/2}Br^{i-a}_{4/2}]$ cluster units, slightly tilted in order to locate two inner ligands in apical position for clusters of adjacent chains giving a 2D structure. S in blue (dark grey) Br in yellow (light grey).

by S^{i-1} ligands, but the cluster units are now rotated around the threefold axis building an antiprismatic environment of molybdenum around S^{i-1} that prevents any condensation of the S^a ligands in the form of S^{a-a} one (Fig. 9), in contrast to the compounds reported above, while S^{i-a} ligands are now building a 3D architecture with large channels.

3.2.2. X^{a-a} connections in two-dimensional and one-dimensional Re_6 chalcogenides

The needle-shaped 1D $Re_6Se_5Cl_8$, exhibits a crystal structure based on *trans* Cl^{a-a} bridged $[(Re_6Se^i_5Cl^i_3)]$

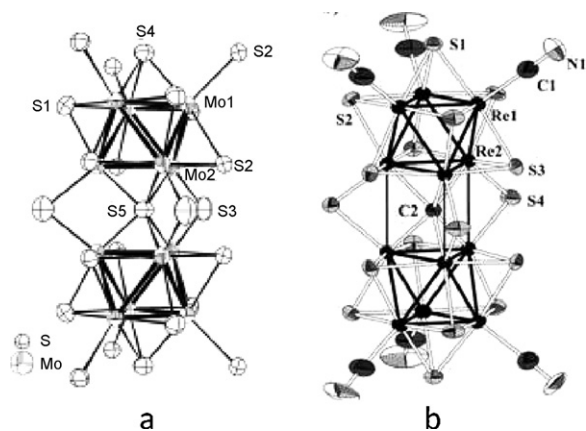


Fig. 8. a: the dimeric $[(M_6)_2S^i_8S^{i-1}_{6/2}S^{i-a}_{6/2}S^{i-1}_{6/2}S^{i-a}_{6/2}]$ cluster unit in $Ba_4Mo_{12}S_{18}$. The six S^a ligands represented on the figure are in fact S^{a-i} in the structure, and the six S^i ligand located above and below S^{i-1} are in fact S^{i-a} in the structure. From Gougeon et al. [82]; b: the dimeric $[(Re_6)_2S^{i-1}_{14}C^{i-1}_{2}S^{i-a}_{6}CN^a_6]^{6-}$ discrete unit in $Cs_6[Re_{12}CS_{17}CN_6]$. From Fedorov et al. [83].

$Cl^{a-a}_{2/2}Cl^a_4]$ cluster units. The zigzag chains are linked together only by van der Waals interactions [57]. The corresponding thiobromide was reported to present a related structure, although not isotypical, presumably related to a change in halogen bridge angle [85].

In the example of the 2D $Re_6Se_6Cl_6$, two pairs of Cl^{a-a} bridges develop in a plane, while the remaining apical ligands are terminal and point towards the third direction [55,57]. Such interunit connections build layers of units interpenetrating perpendicularly to the layer plane. This compound, that can be written $[(Re_6Se^i_6Cl^i_2)Cl^{a-a}_{4/2}Cl^a_2]$, is in fact strictly isostructural with the binary halides M_6X_{12} ($M = Mo, W$), the first examples of octahedral clusters, discovered early by C. Brosset [86] and structurally characterized by H. Schäfer et al. [87]. Note that attempts to synthesize the analogous $Re_6S_6Br_6$ have failed [85] presumably for steric reasons.

3.2.3. Q^{i-a}/Q^{a-i} connections in two-dimensional and one-dimensional Re_6 chalcogenides

Accurate structural data were obtained for the fibrous 1D $Cs_2Re_6S_8Br_4$ [88], confirming previous reports [29,85,89,90]. The cluster units are linked by *trans* Q^{i-a}/Q^{a-i} double bridges, leading to linear chains $[(Re_6Q^i_6Q^{i-a}_{2/2}Q^{a-i}_{2/2}X^a_4)]^{2-}$ interacting together by coulombic forces via Cs^+ cation.

In the structure of the 2D $Re_6Se_8Cl_2$, *trans* Se^{i-a}/Se^{a-i} double bridges define a plane where the clusters are strongly interconnected, while in the third direction are terminal apical chlorine ligands. This compound, written as $[(Re_6Se^i_4Se^{i-a}_{4/2})Se^{a-i}_{4/2}Cl^a_2]$, then exhibits a specially strong bidimensional character, the cohesion of the layers being due only to weak van der Waals contacts [91]. Transport measurements confirmed an anisotropy of the resistivity of about 10^2 [74] for this n-type semiconductor

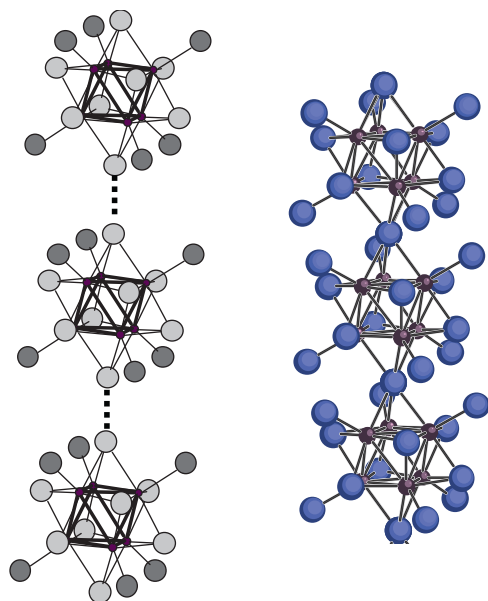


Fig. 9. Schematic representation of the cluster units condensation along the threefold axis building an antiprismatic environment of metal atoms around the L^{1-} ligand (left). Comparing with Fig. 7a, remark that all three clusters have now the same orientation. The 1D chain built from $[(Mo_6S_6^{2-})_2(S^{2-})_6]^{4-}$ cluster units in $Cs_{-1}Mo_{12}S_{14}$ (right). Redrawn from Gougeon et al. [84]. All the S^i and S^a ligands represented on the figure are in fact S^{i-a} and S^{a-i} respectively in the structure.

with a direct band gap of 1.42 eV and photoconductive properties [92]. A solid solution around $Re_6Q_8Cl_2$ was evidenced for a partial substitution of Se by S or Te [74], but a complete substitution by sulfur and/or substitution of chlorine by bromine led to the completely different three-dimensional $Re_6Q_8Br_2$ structure, described in Section 3.1.3 above. $Re_6Se_8Cl_2$ is easily exfoliated by, for instance, hydrazine [93].

3.2.4. Mixed $Q^{i-a/a-i}$ and X^{a-a} connections in two-dimensional Re_6 chalcocalides

The two-dimensional $CsRe_6S_8Br_3$ is built from rigid chains based on *trans* S^{i-a}/S^{a-i} double bridges (refer to 1D $Cs_2Re_6S_8Br_4$ above), linked together by Br^{a-a} bridges, building layers of cluster units. Then the framework is written $[(Re_6S_6^{i-a}S_2^{a-i})_2(S^{a-i})_2(Br^{a-a})_2]^-$ [94]. The structural cohesion is ensured by electrostatic interactions with Cs^+ counteranions sandwiched between the layers. This compound is isostructural with the iodine representative $CsRe_6S_8I_3$ [29].

3.3. Discrete M_6 chalcocalides

In such chalcocalides, the cluster units are not interconnected, implying a number of 14 ligands per M_6 cluster in the formula of the compound. They have been isolated long ago with Re_6 clusters, but more recently with Mo_6 ones due to the recent interest of such compounds in solution chemistry. Indeed, they act essentially as salts and, because they are soluble in many polar solvents, they

constitute the best M_6 precursors for the elaboration of hybrid organic/inorganic M_6 cluster compounds.

From a general point of view, these chalcocalides compounds lie near the halogen-rich border of the phase diagrams, because they can be written as $[(M_6X_8-xQ^i_x)X^a_6]^{n-}$, the six apical ligands being in priority halogens. Many of them present structures related to the cubic $A^{2+}M_6X_{14}$ [95–98], to the trigonal $Cs_2M_6X_{14}$ [99,100] or to the orthorhombic $Cu_2M_6I_{14}$ [98] prototypes, depending on the size of the counteranion. Note an exception, illustrated by the structure of $Cs_{10}Re_6S_{14}$ [101]. In this unique example, implying a very important anionic charge, sulfur occupies both the inner and apical positions because there is no choice, as mentioned above (in this system and related ones were reported a number of compounds, based on various organizations of apical sulfur bridges and even disulfur ones, not detailed in this report).

3.3.1. Ternary discrete M_6 chalcocalides

The family $Re_6Q_4X_{10}$ is a unique example of discrete neutral clusters in this chemistry. $Re_6Se_4X_{10}$ ($X = Cl, Br$) and $Re_6Te_4Br_{10}$ were synthesised very early in a pioneering work by Opalovskii et al. [102,103] but logically formulated at that time as $Re_3Q_2X_5$, in the absence of any structural data. Crystal structures were first determined independently in the example of $Re_6Se_4Cl_{10}$ (Fig. 10) [55,104–106]. Complete structural data were reported subsequently for several parent compounds: $Re_6S_4Br_{10}$ [85], $Re_6Se_4Br_{10}$ [107], $Re_6Te_4Cl_{10}$ [108] and $Re_6Te_4Br_{10}$ [109]. The structure of $Re_6S_4Cl_{10}$ was also solved: unit-cell and main distances were reported in the original paper [110] and structural data are given as Supplementary Material.

Briefly, the structure is built from two independent $[(Re_6Q^i_4X^i_4)X^a_6]$ units, where the eight inner positions are randomly occupied by halogens and chalcogens, with a regular distribution in the examples of $Re_6Se_4Cl_{10}$ [106] and $Re_6Te_4Cl_{10}$ [108], whereas an irregular distribution was reported for $Re_6Te_4Br_{10}$ [109]. Because the cluster

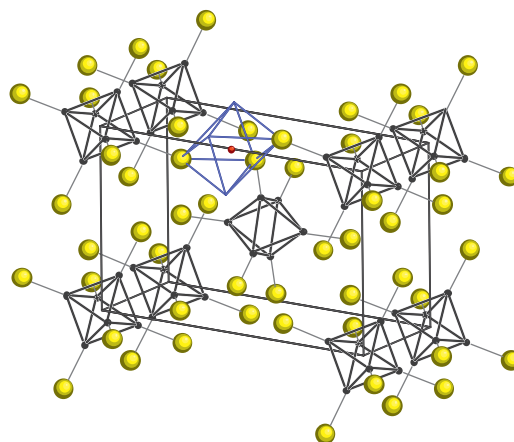


Fig. 10. Crystal structure of $Re_6Se_4Cl_{10}$ [106]. The inner ligands are omitted for clarity. One of the empty distorted octahedral site formed by the apical ligands of six adjacent cluster units is represented in blue (light grey).

units are neutral, the cohesion of the structure is done only by Q...Q or Q...X van der Waals contacts [106].

Dielectric behaviour of some of these compounds was studied in detail. $\text{Re}_6\text{Se}_4\text{Cl}_{10}$ exhibits around 120 K a phase transition (step in $\epsilon'(T)$ and λ point in $\epsilon''(T)$) strongly sensitive to applied field and frequency, suggesting the coexistence of two close energy states. Single-crystals of $\text{Re}_6\text{S}_4\text{Br}_{10}$ also show a phase transition and dielectric relaxations with a gaussian distribution of relaxation times, agreeing well with the statistical occupancy of the inner sites [106].

Note a second example of neutral cluster unit, but with some complex apical ligands, $[(\text{Re}_6\text{Te}^i_6\text{Cl}^i_2)(\text{TeCl}_2)_2\text{Cl}^a_4]$; this compound was synthesized at quite low temperature, 450 °C [111].

3.3.2. Quaternary discrete M_6 chalcobromides

For this class of compounds, only a few examples are known in the case of molybdenum, while, in contrast, it is very rich in rhenium chemistry. This is obviously related to the oxidation state of the metal (Mo II vs Re III). Indeed, even the pure molybdenum halides (for instance, $\text{A}^{2+}[\text{Mo}_6\text{Cl}_{14}]^{2-}$ [96]) are yet dianions, and any halogen-chalcogen substitution will result in increasing anionic charge in order to maintain the ideal 24 VEC value. In contrast, in rhenium chemistry, there is much space to play with such substitutions, as exemplified in the following.

With Mo_6 clusters, only quaternary OD compounds have been obtained with the general formula $\text{A}_y[(\text{Mo}_6\text{X}^i_{8-x}\text{Q}^i_x)\text{X}^a_6]$ with $0 \leq x \leq 2$. Note that the X^i/Q^i distribution on the eight inner positions is often but not systematically random, and such a distribution will be specified for the following Mo_6 compounds. Up to now, the syntheses have been performed with $\text{X} = \text{Br}$ and I , $\text{Q} = \text{S}$, Se and Te and with alkalin used as counteranion. Definite compounds and solid solutions have been isolated and structurally characterized.

The two $\text{Cs}_4\text{Mo}_6\text{Br}_{12}\text{Q}_2$ ($\text{Q} = \text{S}$, Se) chalcobromides are definite compounds with a VEC value of 24 [112]. They are built from $[(\text{Mo}_6\text{Br}^i_6\text{Q}^i_2)\text{Br}^a_6]^{4-}$ discrete units in which the eight inner positions are randomly occupied by six bromine atoms and two chalcogen atoms. Cesium cations, in complex coordination of inner and apical ligands, ensure the neutrality of the compounds.

With a rubidium cation a continuous solid solution is obtained in the Mo-Br-Se system, $\text{Rb}_{2+x}[(\text{Mo}_6\text{Br}^i_{8-x}\text{Se}^i_x)\text{Br}^a_6]$ ($0.25 < x < 0.7$) where coexist, in various ratios depending on the x value, $[(\text{Mo}_6\text{Br}^i_8)\text{Br}^a_6]^{2-}$ and $[(\text{Mo}_6\text{Br}^i_7\text{Se}^i)\text{Br}^a_6]^{3-}$ cluster units, both of them with VEC = 24. In the latter unit deduced from the average structure, the eight inner positions are randomly occupied by seven bromine atoms and one selenium atom [113]. In contrast, in the Mo-Br-Te system a definite compound, $\text{Rb}_{2.5}\text{Mo}_6\text{Br}_{13.5}\text{Te}_{0.5}$, is obtained, built from the 24 VEC cluster units $[(\text{Mo}_6\text{Br}^i_8)\text{Br}^a_6]^{2-}$ and $[(\text{Mo}_6\text{Br}^i_7\text{Te}^i)\text{Br}^a_6]^{3-}$ in 1:1 ratio. From the average structure one can deduce that in the latter unit only six of the eight inner positions are randomly occupied by bromine and tellurium atoms, while the two other inner positions located on the threefold axis of the unit are fully occupied by bromine atoms [113].

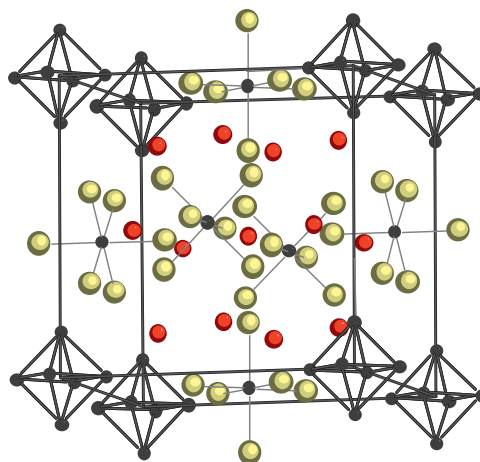


Fig. 11. Crystal structure of the double salts $\{\text{Rb}_3[(\text{Mo}_6\text{Br}_7\text{Q})\text{Br}_6]\}[\text{Rb}_3(\text{MoBr}_6)]_3$ [114]. The inner and apical ligands of the Mo_6 clusters are omitted for clarity. Br in yellow (light grey) and Rb in red (dark grey).

Increasing the rubidium ratio in the two Mo-Br-Q ($\text{Q} = \text{Se}$, Te) systems, $\text{Rb}_{12}\text{Mo}_9\text{Br}_{31}\text{Q}$ are obtained that can be written as double salts $\{\text{Rb}_3[(\text{Mo}_6\text{Br}_7\text{Q})\text{Br}_6]\}[\text{Rb}_3(\text{MoBr}_6)]_3$. They are built from the coexistence of $[\text{Mo}^{\text{III}}\text{Br}_6]^{3-}$ complex and $[(\text{Mo}_6\text{Br}_7\text{Q})\text{Br}_6]^{3-}$ (VEC = 24) cluster units in which all the eight inner positions are randomly occupied by bromine and chalcogen atoms (Fig. 11). The magnetic susceptibility measured for $\text{Rb}_{12}\text{Mo}_9\text{Br}_{31}\text{Te}$ follows a Curie law with an experimental moment consistent with molybdenum at the three oxidation state in the $[\text{MoBr}_6]^{3-}$ complex and a 24 VEC value for the cluster unit that is non magnetic [114].

In the Mo-I-Se system, with cesium atom as counteranion, the solid solution $\text{Cs}_3[(\text{Mo}_6\text{I}^i_6\text{I}^i_{2-x}\text{Se}^i_x)\text{I}^a_6]$ ($1.2 < x < 1.6$) has been isolated [115]. It is based on a mixture of $(2-x)[(\text{Mo}_6\text{I}^i_7\text{Se}^i)\text{I}^a_6]^{3-}$ and $(x-1)[(\text{Mo}_6\text{I}^i_6\text{Se}^i_2)\text{I}^a_6]^{3-}$ cluster units, in various ratios depending on x value, with VEC = 24 and 23, respectively. It constitutes an exceptional example where cluster units with two different VEC coexist in a same cluster compound. Two inner positions located on the threefold axis of the unit are randomly occupied by I and Se atoms. The 23 VEC cluster unit is magnetic due to one unpaired electron on the HOMO level of the Mo_6L_{14} molecular orbital diagram and, as a consequence, the compound is paramagnetic as evidenced by a low temperature electron paramagnetic resonance (EPR) study. Note that a similar crystal structure has been encountered for $\text{Rb}_3\text{Re}_6\text{S}_7\text{Br}_7$ (see below) and for the $\text{Cs}_3\text{Mo}_6\text{Br}_{13}\text{O}$ oxybromide, with one oxygen atom randomly distributed on the two inner positions located on the threefold axis of the cluster unit [116]. However, in the latter compound, that was the first Mo_6L_{14} compound with μ_3 -face-capping oxygen obtained by solid state chemistry, the structure is built only from one $[(\text{Mo}_6\text{Br}_7\text{O})\text{Br}_6]^{3-}$ unit in contrast to the chalcobromides reported above which contain cluster units with two different VEC values.

In the case of Re_6 clusters, the full series $[(\text{Re}_6\text{Q}^i_{4+n}\text{X}^i_{4-n})\text{X}^a_6]^{n-}$ with $0 \leq n \leq 4$ (including the neutral $[(\text{Re}_6\text{Q}^i_4\text{X}^i_4)\text{X}^a_6]$

Section 3.1.1) has been obtained, mainly with alkali counteranions [85]. The n parameter is in most cases an integer although some non-integer values were encountered in a few examples of solid solutions and half-integer ones were reported in rare cases of definite compounds.

3.3.2.1. Mono-anionic cluster units. A number of compounds $ARe_6Se_5Cl_9$ were early mentioned with $A = Li, K, Rb, Cu, Ag$ [55] and completed by some additional compounds characterized by powder X-ray diffraction [117]. The prototype structure, solved in the example of $KRe_6Se_5Cl_9$ [55,117], is cubic, isotypic with the ternary molybdenum halides like $PbMo_6Cl_{14}$ [96]. A close relationship with $Re_6Se_4Cl_{10}$ (Fig. 10) was also evidenced: a twist of the cluster units in the latter opens octahedral sites where the counteranions are located [19,55,107] (Fig. 12). The structure becomes slightly different with larger cations and/or larger apical ligands and, for instance:

- $KRe_6S_5Br_9$ is monoclinic, and the K^+ ions are in prismatic sites instead of octahedral ones, the signature of steric constraints [118];
- $CsRe_6Se_5Cl_9$ is trigonal (Fig. 13) [55], related to $Cs_2Mo_6Cl_{14}$ [99] as well as $Cs(Rb)Re_6S_5Br_9$ [85];
- $RbRe_6S_5Cl_9$ is monoclinic [110].

3.3.2.2. Di-anionic cluster units. Substituting one Se for one Cl on the randomly occupied inner positions allows the charge balance without any change in the structure and various cubic compounds with di-anionic cluster units $[Re_6Se_6Cl_8]^{2-}$, in most cases isotypic with the previous ones, were reported [55].

Note that with bromine ligands, $K_2Re_6S_6Br_8$ is not isotypic with the monoclinic parent $KRe_6S_5Br_9$, but turns again to be cubic as most of the compounds with small

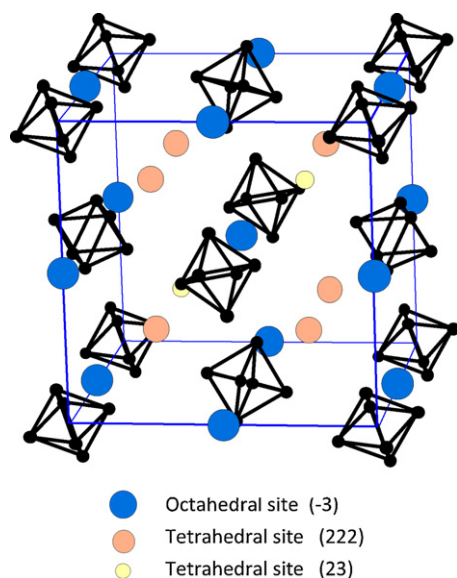


Fig. 12. Schematic representation of the octahedral and tetrahedral sites arranged by the cluster units in the $Pn-3$ structure-type.

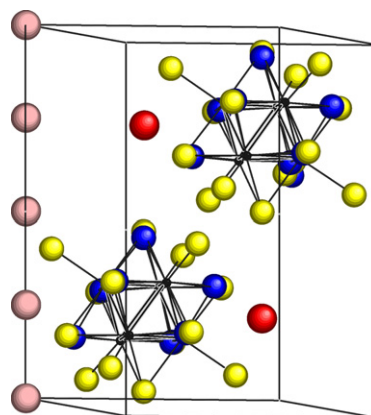


Fig. 13. Crystal structure of $Cs_{1+x}Re_6S_{5+x}Br_{9-x}$ ($0 \leq x \leq 2$). The inner positions are randomly occupied by either S or Br atom (both of them are represented on the figure). Br in yellow (light grey), S in blue (dark grey); Cs in red (large ball in dark grey) almost fills its site while the other Cs^+ ions in pink (large balls in middle grey) randomly occupy several sites delocalized along the c axis (represented only on the Oz vector for clarity) [122].

cations [119]. In fact, while the first potassium occupies the octahedral site like in $KRe_6Se_5Cl_9$, the insertion of the second potassium ion occurs in a site which was very small in the monoclinic cell but opens as a genuine tetrahedral site (222) in the cubic one (Fig. 12) (in fact, $K_2Re_6S_6Br_8$ is a point of a solid solution, see below, and the determined structure corresponded actually to 1.7 K per cluster unit). The structure of $Ag_{0.5}K_{1.5}Re_6S_6Br_8$ shows some cations ordering, as one potassium fully occupies the same tetrahedral site while 0.5 Ag and 0.5 K are distributed on the octahedral one [120]. However, $Ag_2Re_6S_6Br_8$ turns to exhibit a different triclinic structure, where the counteranions are distributed on four distorted sites (in fact there is a slight excess of silver, $Ag_{2.2}$) [120].

With divalent cations, the high temperature synthesis was reported for alkaline-earth salts $A(II)Re_6Q_6Cl_8$ ($A = Mg, Ca; Q = S, Se$) [121] and for $A(II)Re_6Se_6Cl_8$ ($A = Cr, Mn, Fe, Co, Cd, Pb, Eu$) [55] which are isotypic with the cubic prototype structure $KRe_6Se_5Cl_9$. The thiobromide $CdRe_6S_6Br_8$ also exhibits the cubic $Pn-3$ structure, but with a slight Cd deficiency, compensated by a related change in the $(Se/Br)^I$ ratio. The Cd ion occupies the octahedral site, while the tetrahedral one remains empty [120].

$Cs_2Re_6S_6Br_8$ is trigonal (S.G. $P31c$) like $CsRe_6S_5Br_9$ reported above and, in fact, they are the two ends of a continuous solid solution [85] (*vide infra*). One Cs^+ is sandwiched between cluster units while the second one is randomly distributed on several sites aligned on the c axis of the structure. As usual, there is some rotational disorder on the inner positions, but the two L^I ligands located on the threefold axis are ordered (one is pure Br, the second is mainly sulfur) breaking the centrosymmetry. Thanks to the acentric space group, and analysing a crystal belonging to the solid solution, it was possible, in this specific case, to determine unambiguously the actual isomers of the cluster cores $(Re_6S^I_6Br^I_2)^{4+}$ and $(Re_6S^I_5Br^I_3)^{5+}$ present in both $Cs_2Re_6S_6Br_8$ and $CsRe_6S_5Br_9$ (Fig. 14) [122]. DFT

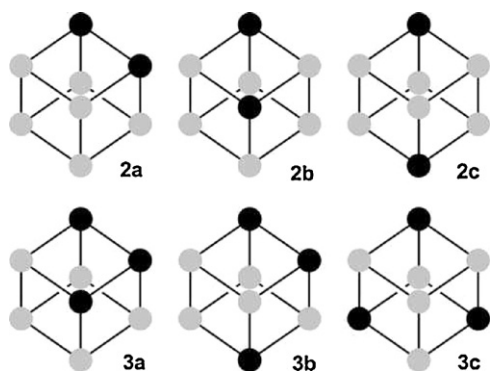


Fig. 14. Sketch of the possible isomers of the $[\text{Re}_6\text{S}_6\text{Br}_2]$ and $[\text{Re}_6\text{S}_5\text{Br}_3]$ cores (di- and tri-substituted isomers, respectively) in $\text{Cs}_{1+x}\text{Re}_6\text{S}_{5+x}\text{Br}_{9-x}$. Rhenium and bromine apical ligands were omitted for clarity. Light grey and black circles are sulfur and bromine inner ligands, respectively. From [123].

calculations were carried out for all possible isomers in this Re-S-Br system [123] as well as in the Re-S-Cl one [124]. The **2a** di-substituted and the **3b** tri-substituted isomers were computed to be the most stable in $\text{Cs}_2\text{Re}_6\text{S}_6\text{Br}_8$ and $\text{CsRe}_6\text{S}_5\text{Br}_9$, respectively [123], in full agreement with structural data [122]. In contrast, for the molybdenum compound $\text{Cs}_3\text{Mo}_6\text{I}_6^{1-}\text{I}_{2-x}\text{Se}_x^{1-}\text{I}_6^a$ it is the **2c** isomer which was found experimentally to be the most stable, again in agreement with the theoretical study by DFT which indicates that occupation of the inner position on the threefold axis by Se in this compound is energetically preferred to the other positions [115]. The structure of the rubidium parent (although less precise due to the poor quality of crystals) is similar [89].

3.3.2.3. Tri-anionic cluster units. They have been observed as definite compounds mainly for large cations, rubidium and cesium. However $\text{Na}_3\text{Re}_6\text{S}_7\text{Br}_7$ was mentioned as the upper boundary of a cubic solid solution [85], and $\text{K}_3\text{Re}_6\text{S}_7\text{Br}_7$ is thought to have been formed (with a small yield and may be not crystallized) in a mild temperature sulfidation of $\text{Re}_6\text{S}_4\text{Br}_{10}$ by KNCS [125]. This $\text{K}_3\text{Re}_6\text{S}_7\text{Br}_7$ was not detected in the systematic high temperature study of the K-Re-S-Br system [85], but was obtained later as single-crystals suitable for structure determination, after recrystallization in water, but no yield was given [126]. The most striking feature in this structure is the considerable disorder of K^+ cations, which arrange as partially occupied $(\text{K}_4)^{4+}$ tetrahedral groups and $(\text{K}_3)^{3+}$ angular groups. In the same A-Re-S-Br system, only the major structural features of the monoclinic $P2_1/n$ cesium counterpart were obtained, due to a severe twinning effect [89,120,127], while $\text{Rb}_3\text{Re}_6\text{S}_7\text{Br}_7$ (trigonal $R-3c$), which presents the same structure as $\text{Cs}_3[(\text{Mo}_6\text{I}_6^{1-}\text{I}_{2-x}\text{Se}_x^{1-})\text{I}_6^a]$ (see above), has been fully characterized as well as its tetrahydrate [127]. The main difference between the two rhenium salts is the alkalin environment, as Rb^+ fully occupies one site, while Cs^+ is distributed on three different sites. In the Cs-Re-S-Cl system was reported the compound $\text{Cs}_3\text{Re}_6\text{S}_7\text{Cl}_7$, with a space group (monoclinic, $P2_1/c$) different from the two above mentioned compounds [128].

3.3.2.4. Tetra-anionic cluster units. These compounds are well documented in the case of cesium and thallium counteranions while some examples were reported with Rb^+ [88] and K^+ [126]. In the latter case, $\text{K}_4\text{Re}_6\text{S}_8\text{Cl}_6$, the potassium ions, distributed in the voids of the cluster units packing, present a considerable disordering. $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$ [29] is monoclinic $P2_1/c$ while $\text{Cs}_4\text{Re}_6\text{S}_8\text{Br}_6$ is trigonal $P-6c2$ [88]. In the latter, the cesium ions form a very regular cuboctahedron at the center of which lies the tetra-anionic cluster unit. Such an arrangement is reminiscent in the iodide, but severely distorted (Fig. 15 a and b). However, most of the examples of tetra-anionic cluster units appear in isotypical structures $R-3c$ of general formula $\text{A}_5\text{Re}_6\text{Q}_8\text{X}_7$ ($\text{A} = \text{Rb}, \text{Cs}, \text{Tl}$; $\text{Q} = \text{S}, \text{Se}$; $\text{X} = \text{Cl}, \text{Br}$) [29,89,90,129]. As the structure contains an extra halogen (in fact half distributed on two very close positions), the compounds could be written $\text{M}_4\text{Re}_6\text{Q}_8\text{X}_6.\text{MX}$, but it happens that the A^+ ions occupy two crystallographic positions corresponding to 3 and 2 cations per cluster, respectively and, in addition, it appears clearly a triangular bipyramidal complex cation $[\text{A}_5\text{X}]^{4+}$. Then it would be better to write this series as $[\text{A}_5\text{X}]^{4+}[(\text{Re}_6\text{Q}_8)\text{X}_6]^{4-}$, leading to a very simple description of this large structure as a body centered rhombohedral stacking (Fig. 15 c and d). Note that the recrystallization of a water/HBr solution of what is thought to be $\text{Cs}_5\text{Re}_6\text{S}_8\text{Br}_7$ gives the hydrate $\text{Cs}_4\text{Re}_6\text{S}_8\text{Br}_6.2\text{H}_2\text{O}$ [130]. Finally, the even halogen richer $\text{Cs}_6\text{Re}_6\text{Se}_8\text{I}_8$ [29] is built from a cuboctahedral stacking of Cs^+ ions, like in the example of $\text{Cs}_4\text{Re}_6\text{S}_8\text{Br}_6$, but now these polyhedra are apex-sharing in their equatorial plane instead of edge-sharing, opening octahedral sites were locate the extra iodine ions (Fig. 15e).

3.3.2.5. Solid solutions and non-integer n. Most of the above mentioned structures correspond to definite compounds $\text{A}_n[(\text{Re}_6\text{Q}_{4-n}\text{X}_{4+n})\text{X}_6^a]$ ($\text{A} = \text{alkalin}$) where n is an integer. When n is non-integer, cluster units with different negative charges (but 24 VEC) coexist in the same structure as detailed above for $\text{Rb}_{2+x}[(\text{Mo}_6\text{Br}_{8-x}\text{Se}_x)\text{Br}_6^a]$ ($0.25 < x < 0.7$). Indeed, the systematic study of the quaternary A-Re-S-Br phase diagrams evidenced several solid solutions extending mainly between monoanions and dianions, but with some variations depending on the cation size [85]. For instance, the domain of homogeneity extends from Na_1 to Na_3 (cubic), $\text{K}_{1.1}$ to $\text{K}_{2.5}$ (cubic, while for $\text{K}_{1.0}$ the structure is monoclinic), Rb_1 to Rb_2 as well as Cs_1 to Cs_2 (trigonal in both cases). In the latter systems, definite compounds (non-integer n) were evidenced for $n = 0.6$ (Rb) and 0.4 (Cs), with a different structure, expected to be related to the $\text{KRe}_6\text{S}_5\text{Br}_9$ one [85]. The other systems were not so systematically studied. However note the structure determination of $\text{Rb}_{2.5}\text{Re}_6\text{S}_{6.5}\text{Cl}_{7.5}$ [110]: similarly to $\text{K}_{2.5}\text{Re}_6\text{S}_{6.5}\text{Br}_{7.5}$ [120] such composition is obtained by filling first the four octahedral sites of the $Pn-3$ unit-cell (one alkalin per cluster) and then the six tetrahedral 222 sites up to their maximum (Fig. 12). It corresponds then to the upper limit of the cubic solid solution. In fact, in the $Pn-3$ structure exist also smaller additional tetrahedral 23 sites, but they were always

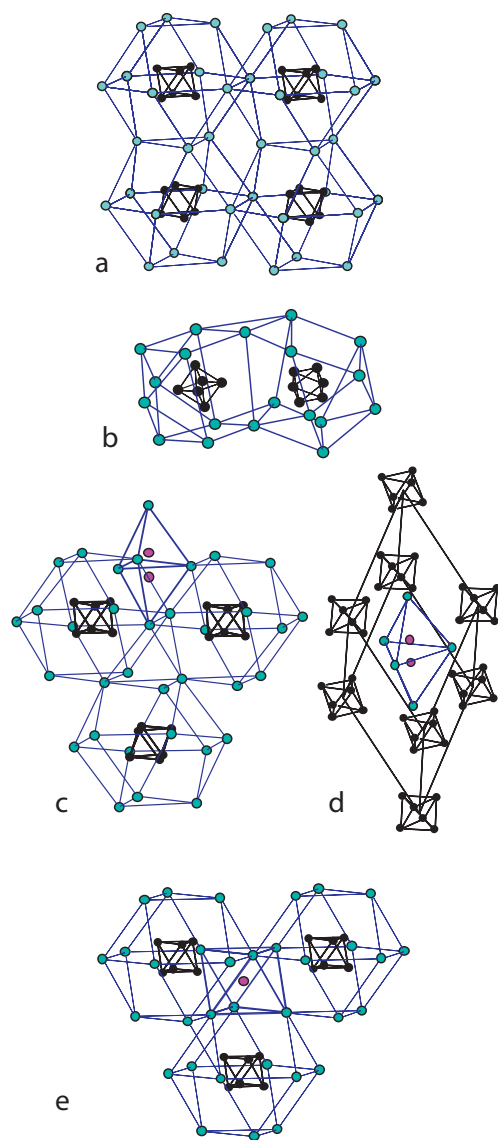


Fig. 15. Alkaline ion polyhedra surrounding the Re_6 cluster in various tetra-anionic compounds: a: in $\text{Cs}_4\text{Re}_6\text{S}_8\text{Br}_6$ [88]; b: in $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$ (redrawn from data ref. [29]); c: in $\text{Cs}_5\text{Re}_6\text{S}_8\text{Br}_7$ (redrawn from [129]); d: the rhombohedral CsCl-type pseudo unit-cell in the $\text{Cs}_5\text{Re}_6\text{S}_8\text{Br}_7$ structure evidencing the $(\text{Cs}_5\text{Br})^{4+}$ complex cation where bromine ion is splitted in two half occupied positions due to steric hindrance (redrawn from [129]); e: in $\text{Cs}_4\text{Re}_6\text{S}_8\text{I}_8$, the site of the extra iodine ions is highlighted (redrawn from [29]).

found to be vacant, even when a composition like $\text{Rb}_{2.5}\text{Li}_{0.5}\text{Re}_6\text{S}_7\text{Cl}_7$ was attempted [131].

3.3.2.6. Cationic cluster units. This case is exceptional and one can mention the examples of $[(\text{Re}_6\text{Te}^{\text{I}})_8(\text{TeX}_2)_6]X_2$ ($X = \text{Br}, \text{I}$) [111,132] prepared at mild temperatures (400–450 °C). Here the $(\text{Re}_6\text{Te}^{\text{I}})_8$ core is bounded to the tellurium of the six neutral apical ligands TeX_2 . It results large cationic units that form a distorted close packing in the voids of which are located the halogen counter-anions.

3.4. Summary of structure dimensionality and cluster interconnections

Table 1 reports the Mo_6 and Re_6 chalcogenides detailed in this review versus the dimensionality of the intercluster connections from 3D to 1D, giving the developed formula of the compounds and those for which the crystal structures were determined by single crystal X-ray diffraction.

All the shared ligand types, $\text{L}^{\text{a-a}}$, $\text{L}^{\text{i-a}}$, $\text{L}^{\text{a-i}}$ and $\text{L}^{\text{i-i}}$ are involved in these connections. $\text{L}^{\text{a-a}}$ or $\text{L}^{\text{i-a}}$ connections develop either in one, two or three directions without any other type of shared ligands or they can be associated together in a same compound. Only missing is (for 3D compounds) the “1D $\text{X}^{\text{a-a}} + 2\text{D } \text{Q}^{\text{i-a}}/\text{Q}^{\text{a-i}}$ ” combination, for instance the hypothetical 24 VEC compound “ $\text{A}[(\text{Mo}_6\text{X}^{\text{I}}_4\text{Q}^{\text{i-a}})_{4/2}\text{Q}^{\text{a-i}}]_{4/2}\text{X}^{\text{a-a}}_{2/2}$ ” has never been obtained up to now. $\text{L}^{\text{i-i}}$ connections develop only in one direction, due to strong steric hindrance, accompanied by $\text{L}^{\text{a-a}}$ connections when the $\text{L}^{\text{i-i}}$ ligand is in prismatic site of metal. One could imagine other arrangements involving several types of shared ligands and various counter cationic charges. A virtual library of all possible Re_6 chalcogenides was already reported [24]. However, such hypothetical compounds are subject to the rule concerning the specific ligand sites that can be occupied preferentially by halogen and/or chalcogen (Section 2), to a 24 VEC value (or close to 24) depending on the halogen/chalcogen stoichiometry and on the cluster unit charge, and to a reasonable steric hindrance of the ligands. They have not been obtained up to now for these reasons or because the corresponding stoichiometries were never experimentally explored. Another reason is the possibility of several connectivities for the same chemical formula, one of them being the most stable. For instance $\text{M}_6\text{Br}_8\text{S}_2$ can be written as 1D $[(\text{M}_6\text{Br}^{\text{I}}_5\text{S}^{\text{i-i}})_{2/2}\text{Br}^{\text{a-a}}]_{6/2}$ or 3D $[(\text{M}_6\text{Br}^{\text{I}}_6\text{S}^{\text{i-a}})_{2/2}\text{S}^{\text{a-i}}]_{2/2}\text{Br}^{\text{a-a}}]_{4/2}$, the former arrangement being the most stable in the case of molybdenum ($\text{Mo}_6\text{Br}_8\text{S}_2$), while the latter one was found only with rhenium in $\text{Re}_6\text{S}_8\text{Br}_2$. Other examples can be found in rhenium chemistry. For instance $\text{Re}_6\text{S}_6\text{Br}_6$ can be written either as 2D $[(\text{Re}_6\text{S}^{\text{I}}_6\text{Br}^{\text{I}}_2)\text{Br}^{\text{a-a}}]_{4/2}\text{Br}^{\text{a-a}}]_{2/2}$ or 1D $[(\text{Re}_6\text{S}^{\text{I}}_4\text{Br}^{\text{I}}_2\text{S}^{\text{i-a}})_{2/2}\text{S}^{\text{a-i}}]_{2/2}\text{Br}^{\text{a-a}}]_{4/2}$, only the first case being encountered. Similarly for $\text{A}_2\text{Re}_6\text{S}_8\text{Br}_4$ i.e. 2D $[(\text{Re}_6\text{S}^{\text{I}}_8)\text{Br}^{\text{a-a}}]_{4/2}\text{Br}^{\text{a-a}}]_{2/2}^{2-}$ or 1D $[(\text{Re}_6\text{S}^{\text{I}}_6\text{S}^{\text{i-a}})_{2/2}\text{S}^{\text{a-i}}]_{2/2}\text{Br}^{\text{a-a}}]_{4/2}^{2-}$ or for $\text{ARe}_6\text{S}_8\text{Br}_3$ i.e. 3D $[(\text{Re}_6\text{S}^{\text{I}}_8)\text{Br}^{\text{a-a}}]_{6/2}$ or 2D $[(\text{Re}_6\text{S}^{\text{I}}_6\text{S}^{\text{i-a}})_{2/2}\text{S}^{\text{a-i}}]_{2/2}\text{Br}^{\text{a-a}}]_{2/2}$ —only one of the two possible structures was obtained (the 1D and 2D, respectively). Conversely, in the case of $\text{Re}_6\text{Q}_8\text{X}_2$, the two possible connectivities 3D and 2D were known for the same general formula, but for different sets of halogen and chalcogens, probably in relation with steric constraints. Notice that the 3D $\text{X}^{\text{a-a}}$ connection is obtained for both Mo_6 and Re_6 chalcogenides while the other combinations are specific of each element.

Table 2 reports the 0D compounds $\text{A}_y[(\text{M}_6\text{X}^{\text{I}}_{8-x}\text{Q}^{\text{I}}_x)\text{X}^{\text{a}}_6]$ versus the x stoichiometry in chalcogen. Note that this x stoichiometry concerns only the cluster core, because in these discrete units the apical positions are only occupied by halogens. As expected, the smaller x values ($0 < x < 2$) were obtained for the molybdenum compounds, that is required to maintain a 24 VEC value (or close to 24) due to the smaller valence of this element when compared to

Table 1

Mo₆ and Re₆ chalcogenides reported with 3D, 2D and 1D interunit connections.

Type of connections	General formula	Developed formula	Molybdenum	Rhenium	Crystal structures reported	Space group	Ref.
3D							
3D X ^{i-a} /X ^{a-i}	M ₆ Q _{8-x} X _x	[(M ₆ Q _{2-2x} X _x ^{i-a} Q _{6/2} ^{a-i})Q ^{a-i} _{6/2}]	Mo ₆ S ₆ X ₂ (X = Br, I) Mo ₆ Se _{8-x} X _x (0 < x < 2) (X = Cl, Br, I) Mo ₆ Te _{8-x} (0 < x < 2) (X = Cl, Br, I)	–	Mo ₆ S ₆ Br ₂ Mo ₆ S _{5.96} I _{1.76}	R-3 R-3	[15] [38]
3D X ^{a-a}	M ₆ X ₁₀ Q	[(M ₆ X ₇ Q ⁱ)X ^{a-a} _{6/2}]	Mo ₆ X ₁₀ Q (X = Cl, Br; Q = S, Se, Te) (X = I; Q = Se, Te)		Mo ₆ Cl ₁₀ Se	Pccn	[53]
2D X ^{a-a} + 1D Q ^{i-a} /Q ^{a-i}	M ₆ Q ₈ X ₂	[(M ₆ Q ₆ ⁱ Q ^{i-a} _{2/2})Q ^{a-i} _{2/2} X ^{a-a} _{4/2}]		Re ₆ Q ₇ X ₄ (Q = S, Se; X = Cl, Br) Re ₆ Q ₈ X ₂ (Q = S, Se; X = Cl, Br)	Re ₆ S ₇ Br ₄ Re ₆ Se ₇ Br ₄ Re ₆ S ₈ Cl ₂ Re ₆ S ₈ Br ₂ Re ₆ Se ₈ Br ₂	R-3c R-3c P2 ₁ /n P2 ₁ /n P2 ₁ /n	[57] [56,57] [75] [73] [72]
2D							
2D X ^{a-a}	M ₆ Q ₆ X ₆	[(M ₆ Q ₆ ⁱ X ₂ ⁱ)X ^{a-a} _{4/2}]	–	Re ₆ Se ₆ Cl ₆	Re ₆ Se ₆ Cl ₆	Cmca	[57]
2D Q ^{i-a} /Q ^{a-i}	M ₆ Q ₈ X ₂	[(M ₆ Q ₄ ⁱ Q ^{i-a} _{4/2})Q ^{a-i} _{4/2} X ^a ₂]	–	Re ₆ Se ₈ Cl ₂ Re ₆ Se _{8-x} Q _x Cl ₂ (Q = S, Te)	Re ₆ Se ₈ Cl ₂	P-1	[91]
1D Q ⁱ⁻ⁱ , X ^{a-a} + 1D Q ^{i-a} /Q ^{a-i}	M ₆ X ₆ Q ₃	[(M ₆ X ₄ ⁱ Q ⁱ⁻ⁱ _{2/2} Q ^{i-a} _{2/2})Q ^{a-i} _{2/2} X ^{a-a} _{4/2}]	Mo ₆ Br ₆ S ₃	–	Mo ₆ Br ₆ S ₃	Cmcm	[81]
1D X ^{a-a} + 1D Q ^{i-a} /Q ^{a-i}	AM ₆ Q ₈ X ₃	A[(M ₆ Q ₆ ⁱ Q ^{i-a} _{2/2})Q ^{a-i} _{2/2} X ^{a-a} _{2/2} X ^a ₂]	–	ARe ₆ Q ₈ X ₃ (Q = S, Se; X = Cl, Br, I)	TlRe ₆ S ₈ Cl ₃ CsRe ₆ S ₈ Br ₃ CsRe ₆ Se ₈ I ₃	P-1 P2 ₁ /n P2 ₁ /n	[90] [94] [29]
1D							
1D X ^{a-a}	M ₆ Q ₅ X ₈	[(M ₆ Q ₅ ⁱ X ₃ ⁱ)X ^{a-a} _{2/2} X ^a ₄]	–	Re ₆ Se ₅ Cl ₈ Re ₆ S ₅ Br ₈	Re ₆ Se ₅ Cl ₈ Re ₆ S ₅ Br ₈	P-1 P-1	[57] [85]
1D Q ^{i-a} /Q ^{a-i}	A ₂ M ₆ Q ₈ X ₄	A ₂ [(M ₆ Q ₆ ⁱ Q ^{i-a} _{2/2})Q ^{a-i} _{2/2} X ^a ₄]	–	Tl ₂ Re ₆ S ₈ Cl ₄ Cs ₂ Re ₆ S ₈ Br ₄	Tl ₂ Re ₆ S ₈ Cl ₄ Cs ₂ Re ₆ S ₈ Br ₄	P-1 P2 ₁ /n	[90] [88]
1D Q ⁱ⁻ⁱ , X ^{a-a}	M ₆ X ₈ Q ₂	[(M ₆ X ₅ ⁱ Q ⁱ⁻ⁱ _{2/2})X ^{a-a} _{6/2}]	Mo ₆ Br ₈ S ₂ Mo ₆ I ₈ Q ₂ (Q = S, Se)	–	Mo ₆ I ₈ Se ₂	P6 ₃	[77,78]

Table 2
Details of crystal structures for $0D A_y[(M_6X^{i}_{8-x}Q^j_x)X^a_6]$ compounds versus increasing x chalcogen stoichiometry.

x value	Molybdenum, general formula	Rhenium, general formula	Building blocks (developed formula)	Crystal structures reported	Space group	Ref.
0	$A^{2+}Mo_6X_{14}$		$[(Mo_6X^i_8)X^a_6]^{2-}$	$Rb_2Mo_6Br_{14}^a$	$C2/c$	[113]
0.5	$Rb_{2.5}Mo_6Br_{13.5}Te_{0.5}$		$0.5 [(Mo_6Br^i_8)Br^a_6]^{2-} + 0.5 [(Mo_6Br^i_7Te^i)Br^a_6]^{3-}$	$Rb_{2.5}Mo_6Br_{13.5}Te_{0.5}$	$Pn-3$	[113]
$0.25 < x < 0.7$	$Rb_{2+x}Mo_6Br_{8-x}Se_xBr_6$		$(1-x) [(Mo_6Br^i_8)Br^a_6]^{2-} + x [(Mo_6Br^i_7Se^i)Br^a_6]^{3-}$	$x = 0.25, x = 0.5, x = 0.7$	$Pn-3$	[113]
1	$[Rb_3Mo_6Br_{13}Q][Rb_3(MoBr_6)_3]$ ($Q = Se, Te$)		$[(Mo_6Br^i_7Q^i)Br^a_6]^{3-} + 3 (MoBr_6)^{3-}$	$Rb_{12}Mo_9Br_{31}Se$ $Rb_{12}Mo_9Br_{31}Te$	$Pm-3 m$ $Pm-3 m$	[114] [114]
$1.2 < x < 1.6$	$Cs_3Mo_6I_6I_{2-x}Se_xI_6$		$(2-x) [(Mo_6I^i_7Se^i)I^a_6]^{3-} + (x-1) [(Mo_6I^i_6Se^i_2)I^a_6]^{3-}$	$x = 1.2, x = 1.5, x = 1.6$	$R-3c$	[115]
2	$Cs_4Mo_6Br_{12}Q_2$ ($Q = S, Se$)		$[(Mo_6Br^i_6Q^i_2)Br^a_6]^{4-}$	$Cs_4Mo_6Br_{12}S_2$ $Cs_4Mo_6Br_{12}Se_2$	$Pbca$ $Pbca$	[112] [112]
4		$Re_6Q_4X_{10}$ ($Q = S, Se, Te; X = Cl, Br$)	$[(Re_6Q^i_4X^i_4)X^a_6]^0$	$Re_6S_4Cl_{10}$ $Re_6S_4Br_{10}$ $Re_6Se_4Cl_{10}$ $Re_6Se_4Br_{10}$ $Re_6Te_4Cl_{10}$ $Re_6Te_4Br_{10}$	$P-1$ $P-1$ $P-1$ $P-1$ $P-1$ $P-1$	[110] [85] [105,106] [107] [108] [109]
5		$A^iRe_6Q_5X_9$ ($A = Li, K, Rb, Cs, Cu, Ag; Q = S, Se; X = Cl, Br$)	$[(Re_6Q^i_5X^i_3)X^a_6]^-$	$KRe_6S_5Br_9$ $KRe_6Se_5Cl_9$	$C2/c$ $Pn-3$	[118] [117]
$5 < x < 6$		$A_{1+y}Re_6S_{5+y}Br_{9-y}$	$(1-y) [(Re_6S^i_5Br^i_3)Br^a_6]^- + y [(Re_6S^i_6Br^i_2)Br^a_6]^{2-}$	$Cs_{1.95}Re_6S_{5.82}Br_{8.19}$ $K_{1.7}Re_6S_{5.7}Br_{8.3}$ $Cd_{0.7}Re_6S_{5.5}Br_{8.5}$	$P31c$ $Pn-3$ $Pn-3$	[122] [119] [120]
6		$A^+_2Re_6Q_6X_8$	$[(Re_6Q^i_6X^i_2)X^a_6]^{2-}$	$Ag_2Re_6S_6Br_8$ $K_{1.45}Ag_{0.55}Re_6S_6Br_8$	$P-1$ $Pn-3$	[120] [120]
$6 < x < 7$		$A^+_{2.5}Re_6S_{6.5}Cl_{7.5}$	$[(Re_6S^i_6Cl^i_2)Cl^a_6]^{2-} + [(Re_6S^i_7Cl^i)Cl^a_6]^{3-}$	$Rb_{2.5}Re_6S_{6.5}Cl_{7.5}$ $K_{2.5}Re_6S_{6.5}Br_{7.5}$	$Pn-3$ $Pn-3$	[110] [120]
7		$A^+_3Re_6Q_7X_7$	$[(Re_6Q^i_7X^i)X^a_6]^{3-}$	$K_3Re_6S_7Br_7$ $Rb_3Re_6S_7Br_7$ $Cs_3Re_6S_7Cl_7$ $Cs_3Re_6S_7Br_7$	$P2_1/c$ $R-3c$ $P2_1/c$ $P2_1/n$	[126] [127] [128] [120]
8		$A^+_4Re_6Q_8X_6$	$[(Re_6Q^i_8)X^a_6]^{4-}$	$K_4Re_6S_8Cl_6$ $Cs_4Re_6Se_8I_6$ $Cs_4Re_6S_8Br_6$	$C2/m$ $P2_1/c$ $P-6c2$	[126] [29] [88]
		$A^+_5Re_6Q_8X_7$ ($A = Rb, Cs, Tl; Q = S, Se; X = Cl, Br$)	$[(Re_6Q^i_8)X^a_6]^{4-} [A_5X]^{4+}$	$Cs_5Re_6S_8Cl_7$	$R-3c$	[90]
				$Cs_5Re_6S_8Br_7$ $Tl_5Re_6S_8Cl_7$ $Tl_5Re_6Se_8Cl_7$	$R-3c$ $R-3c$ $R-3c$	[29] [90] [90]
		$A_6Re_6S_8I_8$	$[(Re_6Q^i_8)X^a_6]^{4-} (CsI)_2$	$Cs_6Re_6S_8I_8$	$Fm-3 m$	[29]

^a As an example. See also [95–100].

rhenium one. However, cyano-Mo₆ chalcogenides with $x > 2$ have been obtained by solution chemistry ([156] Section 4.3). Many of these compounds are cubic *Pn-3*, or derived from this structure-type in relation to the size of the cluster unit and of the cationic sites arranged in the cluster packing (Section 3.3.2).

4. Solid state M₆ chalcogenides as relevant precursors for soft chemistry

The [(Mo₆L₈)L^a₆] and [(Re₆L₈)L^a₆] cluster units reported above exhibit various intrinsic properties. For instance, as a rule, they are highly emissive in the red-near infrared region, the characteristics of the emission depending on the Q/X ratio and on the geometry of the unit [133–135]. They have 24 e⁻/23 e⁻ oxidation process by electrochemistry or soft chemical routes [110,133,136]; they are magnetic when the VEC = 23 that corresponds to the presence of one unpaired electron on the HOMO level of the molecular orbital diagram of the unit; they act as electrical dipole when the ligand charges are non symmetrically distributed around the M₆ cluster [53]. As a consequence such discrete cluster units are relevant candidates for the elaboration of functional hybrid cluster materials that combine the properties of both the cluster units and functional ligands, provided that they can be extracted as an individual entity from the solid state precursors and then handled for ligand substitution by functional ligands in solution or by soft chemistry.

4.1. Intrinsically soluble cluster-based compounds

Due to the strength of intercluster bonds, the polymeric 3-D to 1-D compounds are obviously not directly soluble. In contrast, many discrete anionic units are soluble in common polar solvents. For instance, for rhenium compounds this solubility strongly depends on their charge and also on the elements present in the quaternary system. As a general rule, the most important is the anionic charge, the highest is the solubility and tetra-anionic units turn out to be readily soluble in water. Table 3 gives some typical examples as an illustration [137].

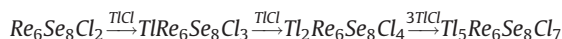
4.2. Lowering the dimensionality by chemical excision

Chemical excision is the cleavage of interunit bridges in extended solids, affording a reduction of the dimensionality. The first example in cluster chemistry is the replacement of I^{a-a} bridges in 3-D Nb₆I₁₁ (isostructural with Mo₆Cl₁₀S, Section 3.1.2) by alkyl-amines, yielding a 0-D

Table 3
Example of solubility of M₆ chalcogenides in usual solvents [137].

Compound	H ₂ O	EtOH	CH ₃ CN	CH ₂ Cl ₂
Cs ₄ Re ₆ S ₈ Br ₆ , CsBr	Soluble	Weakly soluble	Insoluble	Insoluble
Cs ₄ Re ₆ S ₈ Br ₆	Insoluble	–	–	–
Cs ₃ Re ₆ S ₇ Br ₇	Soluble	Soluble	Weakly soluble	Insoluble
Cs ₂ Re ₆ S ₆ Br ₈	Insoluble	Insoluble	Soluble	Soluble
CsRe ₆ S ₅ Br ₉	Weakly soluble	Soluble	Insoluble	Insoluble

compound [138]. The dimensional reduction formalism in solid state chemistry was extensively applied to cluster-based frameworks by the group of R.H. Holm [21,29,90,139,140]. This concept is illustrated by the following sequence of reactions where TlCl is incorporated in extended networks:



However, as emphasized by the authors, such reactions describe a ‘formalistic relationship between structures and not necessary a specific synthetic pathway’. Indeed, from an experimental point of view, they prepared intermediate and final compounds by direct synthesis and not by reaction of TlCl with a previously prepared extended solid.

4.3. Synthesis of cyano and hydroxo derivatives

In many examples (CN)⁻ groups behave like halogen anions and cyano compounds of M₆ clusters are now well documented. They are obtained in most cases by a genuine excision (associated to a substitution) process. The most usual route consists in the reaction of a presynthesized cluster compound, typically Re₆Q₈Br₂, with an excess of molten KCN at medium temperatures (530–600 °C) [141]. The same reaction, but with a KCN deficiency, produces mixed apical ligands, like [(Re₆Seⁱ₈)(CN)^a₄Br^a₂]⁴⁻ [142]. It is also conveniently possible to simply substitute (CN)⁻ for halogen in 0 D tetra-anionic species at around 635 °C [143].

An alternative preparation is the reaction of Re₆Te₁₅ (which already contains the [Re₆Te₈] core), with NaCN at 600 °C, affording the [(Re₆Teⁱ₈)(CN)^a₆]⁴⁻ ion [144,145]. When using in place thiocyanate as reagent, a core substitution (Sⁱ for Teⁱ) occurs, leading to [(Re₆Sⁱ₈)(CN)^a₆]⁴⁻ ion, more precisely [Re₆Sⁱ₆(S_{1-x}Te_x)ⁱ₂(CN)^a₆]⁴⁻. In fact this approach afforded the first example of chalcocyno compounds in this chemistry as early as 1995 (Fig. 16) [146,147]. The partial statistical disorder was studied in

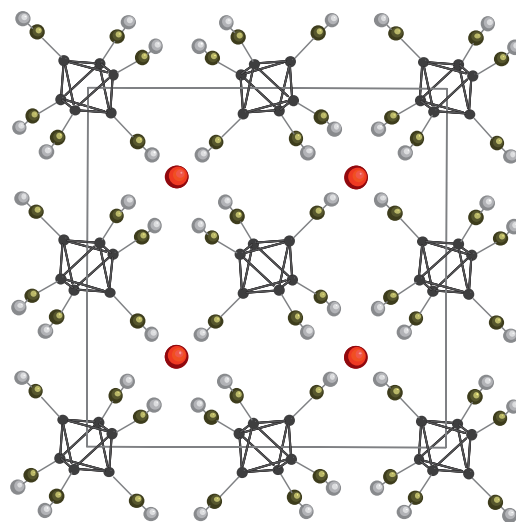


Fig. 16. Projection of the structure of KCs₃Re₆S₈(CN)₆ [147]. The inner ligands were omitted for clarity. C in dark green (dark gray), N (light gray), K/Cs in red (large balls in dark gray).

more detail later [148]. In fact, it appears not mandatory to start from a pre-existing octahedral cluster: examples are given by the reaction of the binaries ReS_2 or ReSe_2 with KCN to give $\text{K}_4[(\text{Re}_6\text{S}_8^{\text{I}})\text{S}^{2-}(\text{CN})_2^{\text{a}}]$ (layered) or $\text{K}_4[(\text{Re}_6\text{Se}_8^{\text{I}})(\text{Se}_2)^{2-}(\text{CN})_4^{\text{a}}]$ (chain) [149]. Adding an excess of CsCl in the starting mixture yields $\text{Cs}_4[(\text{Re}_6\text{S}_8^{\text{I}})\text{S}^{2-}(\text{CN})_4^{\text{a}}]$ [150].

Another route, not so explored, is the conversion of tetrahedral cluster to octahedral one: for instance, a mixture of $[(\text{Re}_5\text{MoS}_8^{\text{I}})(\text{CN})_6^{\text{a}}]^{5-}$ and $[(\text{Re}_4\text{Mo}_2\text{S}_8)(\text{CN})_6^{\text{a}}]^{5-}$ heterometallic cluster anions was obtained by reaction of $\text{Re}_3\text{MoS}_4\text{Te}_4$ and KCN at 850°C [151]. Considering the high temperature of reaction, one cannot exclude a full decomposition of the starting compound. However, an example of conversion of tetrahedral to octahedral cluster by a solvothermal route working at a temperature as low as 200°C was reported, giving access to the $[(\text{Re}_6\text{Se}_8^{\text{I}})(\text{CN})_6]^{4-}$ ion [152].

Note that the isoelectronic technetium $[(\text{Tc}_6\text{Q}_8^{\text{I}})(\text{CN})_6]^{4-}$ ion was recently reported: the structures, electronic structures and electronic transitions are very similar to those of the rhenium parents, although the energy gap is smaller in the technetium complexes [153].

The cyano derivatives of Mo_6 clusters are less documented. The early exchange of bromine apical ligands by CN ones in $\text{Mo}_6\text{Br}_{12}$ via an aqueous solution route [154] should be mentioned. On the opposite side, it was shown that the octahedral cluster-based binary Mo_6Se_8 can be excised by molten KCN in a way similar to that used in rhenium chemistry, resulting in the formation of the $[(\text{Mo}_6\text{Se}_8^{\text{I}})(\text{CN})_6]^{7-}$ and $[(\text{Mo}_6\text{Se}_8^{\text{I}})(\text{CN})_6]^{6-}$ ions [155]. In fact the starting composition can be as well a mixture of MoSe_2 and Mo, for instance, and starting from various mixtures, the above mentioned ions were obtained as well as $\text{K}_6[(\text{Mo}_6\text{Se}_8^{\text{I}})(\text{CN})_4(\text{CN})^{2-}]$, which is a chain-based compound [156]. True Mo_6 chalcocyanides have also been converted to chalcocyanides, but again by exchange in aqueous medium, giving the ions $[(\text{Mo}_6\text{Q}_8^{\text{I}}\text{Br}_6)(\text{CN})_6]^{4-}$ [112] and the $[(\text{Mo}_6\text{Se}_3\text{X}_3)(\text{CN})_6]^{5-}/[\text{Mo}_6\text{Se}_4\text{X}_4(\text{CN})_6]^{5-}$ solid solution although the intermediate chalcocyanide implied in the reaction was not actually isolated [157].

A similar strategy was used to access the corresponding hexahydroxo complexes, treating as an example $\text{Re}_6\text{Q}_8\text{Br}_2$ by molten KOH at $200\text{--}280^\circ\text{C}$, leading to the $[(\text{Re}_6\text{Q}_8^{\text{I}})(\text{OH})_6]^{4-}$ tetra-anion. Here, the hydroxo ligands are very labile, and easily back replaced by bromine ones for instance, when subjected to the action of HBr [158]. A related hexa-aqua $[\text{Re}_6\text{S}_8^{\text{I}}(\text{H}_2\text{O})_6]^{2+}$ dication was also reported: it was obtained by removing Cl^{a} apical ligands of $[\text{Re}_6\text{S}_8\text{Cl}_6]^{4-}$ by Ag^+ in perchlorate medium [159].

4.4. Quaternary ammonium salts

In order to increase the solubility in common polar organic solvents (for instance CH_3CN) it was proposed very early to use a cationic metathesis to obtain, for instance the corresponding tetrabutylammonium salt [100,110,160,161] like as an example $(\text{TBA})_2\text{Mo}_6\text{X}_{14}$ or the whole series $(\text{Bu}_4\text{N})^{n+}[\text{Re}_6(\text{S}^{4+n}\text{Cl}^{4-n})\text{Cl}^{\text{a}}]^{n-}$ used in the following as starting material for solution chemistry [110]. Note that obtaining a homogeneous series enabled to evidence a cluster core contraction when the ratio S/Cl increases [110].

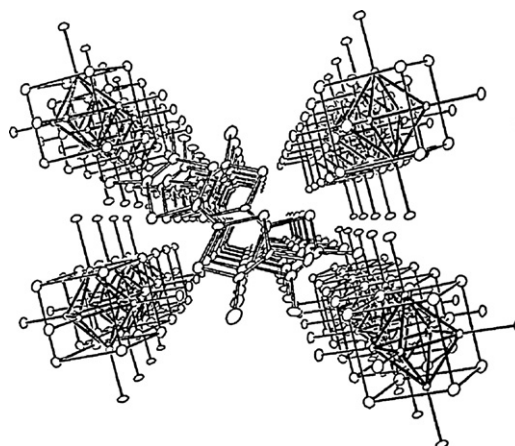


Fig. 17. Structures of $\beta\text{-(TMTTF)}_2\text{Re}_6\text{Se}_5\text{Cl}_9$ and $\beta\text{-(TMTSF)}_2\text{Re}_6\text{Se}_5\text{Cl}_9$ [160].

5. Solution chemistry of M_6 clusters

5.1. Playing with organic counteranions or ligands

5.1.1. Organic (organometallic) counteranions

In addition to the pioneering work just above mentioned, the treatment of polymeric compounds like $\text{Re}_6\text{Se}_5\text{Cl}_8$ or $\text{Re}_6\text{Se}_6\text{Cl}_6$ by an excess of R_4NCl in hot DMF or acetonitrile results in an excision reaction and the formation of R_4N^+ salts of mono- or di-anionic cluster units, respectively [139]. Mesolamellar phases were reported with long chain ($n=14\text{--}18$) alkyltrimethylammonium surfactants [162]. Several works involving tetraphenylphosphonium counteranions [125], solvates or kryptates [163,164], metal complexes [165–168] or ferrocenium [169] should also be mentioned. Cluster anions $[\text{M}_6\text{L}_{14}]^{n-}$ were combined by electrocrystallisation, very early in some examples, with various cations derived from tetrathiafulvalene TTF (Fig. 17) [160,170–175].

5.1.2. Ligand exchanges

5.1.2.1. Apical substitutions. As mentioned above, hydroxo apical ligands are very labile, and easily replaced by halogen ions, cyano ions [176] but also organic anions for instance formates [177].

Refluxing $(\text{Bu}_4\text{N})_{3-4}\text{Re}_6\text{Q}_8\text{X}_6$ with PET_3 in DMF for instance affords the $[(\text{Re}_6\text{Q}_8^{\text{I}})(\text{PET}_3)_n\text{X}^{\text{a}}_{6-n}]^{(n-4)+}$ ion ($\text{Q}=\text{Se}$, $\text{X}=\text{I}$, $n=3\text{--}6$ [178]; $\text{Q}=\text{S}$, $\text{X}=\text{Br}$, $n=2\text{--}6$ [179]; $\text{Q}=\text{S}$, $\text{X}=\text{Cl}$, $n=1\text{--}4$ [180]) (Note that $n=5$ and 6 imply the formation of the rarely encountered cationic cluster units). Similar reactions were reported with PPh_3 , AsPh_3 and SbPh_3 , although in quite stronger conditions (sealed tube, 200°C) [181,182] and also diphosphines were used as monodentate ligands [183] as well as bidentate chelating ones [184]. Some molybdenum homologues were obtained some time ago, by an indirect route using the reductive dimerization of a trinuclear molybdenum thiochloride cluster, $\text{Mo}_3\text{S}_7\text{Cl}_4$, after its reaction with triethylphosphine, to give $\text{Mo}_6\text{S}_8(\text{PET}_3)_6$ [185]. The analogous seleno derivative was synthesized in a similar way [186].

Due to the strong Re-P (As, Sb) bond, only the (eventually) remaining apical halogens are subsequently removable by Ag salts, giving access to cluster carbonyl [187,188], triflates [189] and solvates like, for instance, in $[(\text{Re}_6\text{Se}_8^i)(\text{PET}_3)_n(\text{MeCN})_{6-n}]^{2+}$ ($n = 0,4,5$) [178]. The latter compounds open the way to a large range of site-differentiated cluster complexes, as very labile triflates and nitriles can be in turn substituted by other ligands [190]. Alcohol reaction with acetonitrile ligand(s) activated by the cluster core afforded imino ester ligands by nucleophilic addition [191]. N_3^- azide ion (as NaN_3) does not substitute for acetonitrile, but in place undergoes an addition reaction across the nitrile triple bond, to give tetrazolato complexes [192] (note that, in contrast, N_3^- substitutes readily for halogen apical ligands, to give $[(\text{Re}_6\text{S}_8^i)(\text{N}_3)_6]^{4-}$ and $[(\text{Mo}_6\text{Br}_8^i)(\text{N}_3)_6]^{2-}$ anions [193]). On the other hand, organic azides unexpectedly form iminocomplexes with cluster-bound nitriles [194,195]. It was suggested the formation of a cluster-azido intermediate followed by a stereoselective rearrangement and the concerted photoelimination of dinitrogen [194]).

A number of examples are reported relative to the substitution of pyridine and its derivatives on the apical ligand positions [196–205]. These compounds form either by direct substitution (for a terminal halide), or via a presynthesized solvate or with the help of a silver salt, usually in reflux conditions. The hexaammine group was evidenced in the $[\text{Re}_6\text{Se}_7\text{Br}(\text{NH}_3)_6][\text{Re}_6\text{Se}_7\text{BrBr}_6] \cdot 12\text{H}_2\text{O}$ salt [206].

5.1.2.2. Core substitutions. Although the cluster core is very rigid, implying strong M-Lⁱ inner bonds, there are some restricted examples of inner ligands substitutions in “soft chemistry” conditions.

While Mo_6 chalcogenides presented in the first part of this review have been prepared at high temperature by solid state routes, several examples of $[(\text{Mo}_6\text{X}_8^i\text{Q}_x)\text{X}_6]^{n-}$ cluster units prepared in solution have been reported:

- for $x = 1$, from reaction of Mo_6X_{12} ($\text{X} = \text{Cl}, \text{Br}$) precursors with NaSH or NaSeH in pyridine [207–210];
- for $x = 1$ or coexistence of $x = 1$ and 2 in a same compound, from reaction of $(\text{H}_7\text{O}_3)_2[\text{Mo}_6\text{Cl}_{14}]$ with H_2Se generated in situ from ZnSe under hydrothermal condition [211];
- for $x = 2$ from the refluxed reaction mixture of $\text{Mo}_6\text{Cl}_{12}$, NaSeH and pyridine [212].

In these reactions the apical halogen is not substituted and the corresponding compounds crystallize as hybrid salts with organic counteranions. It is different from a reaction of Mo_6X_{12} in aqueous solution of Cs_2Se_3 and then in aqueous solution of KCN , in which the apical halogens are replaced by CN^- groups after the inner ligand substitution by chalcogen: the $[(\text{Mo}_6\text{Se}_3^i\text{Cl}_4^i)(\text{CN})_6]^{n-}$ and $[(\text{Mo}_6\text{Se}_3^i\text{Br}_4^i)(\text{CN})_6]^{n-}$ cluster units are obtained and the two compounds crystallize with Cs cation [157]. A similar example is the conversion of the $[(\text{Re}_6\text{Se}_5^i\text{Cl}_3^i)\text{Cl}_6^a]^-$ anion to $[(\text{Re}_6\text{Se}_6^i\text{Cl}_2^i)\text{Cl}_6^a]^{2-}$ one by Li_2Se in THF [140]. Exchange of two inner chlorines by hydroxo ions was evidenced by structure determination,

associated with IR spectra and mass spectroscopy, in $\text{K}[(\text{Re}_6\text{Se}_5^i\text{Cl}_3^i)\text{Cl}_6^a]$ when recrystallized at room temperature from water/ethanol mixtures [213]. In contrast, the cluster core remained unchanged when the same experiment was carried out in pure ethanol [214]. Action of water in DMF at a slightly higher temperature (60 °C) on $[(\text{Re}_6\text{Se}_4^i\text{Cl}_4^i)\text{Cl}_6^a]$ afforded the oxo-chalcogeno $[(\text{Re}_6\text{Se}_4^i\text{O}_2^i\text{Cl}_2^i)\text{Cl}_6^a]^{2-}$ anion [140]. Note that such hydrolysis was shown to work also in high temperature solid state synthesis: an example is the formation of the $[(\text{Re}_6\text{S}_5\text{OCl}_7)_2\text{O}]^{4-}$ oxo-bridged dimer with oxo-chalcogeno core at 850 °C in a sealed silica tube [215]. An efficient approach to carry out such substitutions is the use of silylated reagents $(\text{Me}_3\text{Si})_2\text{E}$ and the $[(\text{Re}_6\text{Q}_5^i\text{E}^i\text{Cl}_2^i)\text{Cl}_6^a]^{2-}$ anion was early obtained at room temperature for $\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$ [216] and subsequently for $\text{E} = \text{As}, \text{P}, \text{NH}$ [217].

A slightly different approach is the use in mild conditions of molten ligands or salts: for instance, reaction of $\text{Re}_6\text{S}_4\text{Br}_{10}$ with KNCS in a quartz ampoule at 550 °C gives access to the $[(\text{Re}_6\text{S}_7^i\text{Br}^i)\text{Br}_6^a]^{3-}$ ion which was crystallized as the hybrid salt $(\text{PPh}_4)_3[\text{Re}_6\text{S}_7\text{Br}_7]$ [125] (but in contrast, it was reported that the action of molten KNCS at 200 °C on the $[\text{Re}_6\text{S}_8\text{Cl}_6]^{4-}$ cluster anion resulted in the formation of the isocyanate complex $[\text{Re}_6\text{S}_8(\text{NCS})_6]^{4-}$ by apical substitution [218]). Similarly, action of molten 3,5-dimethylpyrazole on $[(\text{Re}_6\text{Q}_7^i\text{Br}^i)\text{Br}_6^a]^{2-}$ gave the cationic species $[(\text{Re}_6\text{Q}_7^i\text{O}^i)\text{L}_6^a]^{2+}$ ($\text{L} = 3,5\text{-Me}_2\text{PzH}$) [219].

Finally, a substitution of an organic ligand on an inner position would require ligands not only tricoordinated but also of very small dimension because of severe steric hindrance. To the best of our knowledge the only one example reported concerns the Mo_6 cluster with eight alkoxy ligands in inner positions in $\text{Na}_2[\text{Mo}_6(\text{OCH}_3)_8(\text{OCH}_3)_6]$ [220] and $\text{Na}_2[\text{Mo}_6(\text{OCH}_3)_4(\text{OC}_6\text{H}_5)_4(\text{OC}_6\text{H}_5)_6]$ [221].

5.2. Rebuilding polymeric structures from isolated building blocks

5.2.1. Connecting clusters by coordination chemistry

Taking advantage of the bidentate behaviour of the cyano ligand a number of polymeric structures were rebuilt, creating for instance transition metal complex bridges between cluster units [143,222]. This approach is illustrated, for instance, by the formation of discrete dimers $\{[\text{Cu}(\text{en})_2][\text{Re}_6\text{Te}_8(\text{CN})_6]_2\}^{6-}$ (Fig. 18), 1-D $[\text{Ni}(\text{NH}_3)_2(\text{en})_2]_2\{[\text{Ni}(\text{NH}_3)_4]\text{Re}_6\text{Se}_8(\text{CN})_6\}\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (linear chains) or 1-D $\{[\text{Mn}(\text{H}_2\text{O})(\text{en})_2][\text{Mn}(\text{en})_2\text{Re}_6\text{Te}_8(\text{CN})_6], 3\text{H}_2\text{O}$ (zigzag chains) and 2-D $(\text{NH}_4)_2\{[\text{Ni}(\text{en})_2]_3[\text{Re}_6\text{Te}_8(\text{CN})_6]_2\} \cdot 6\text{H}_2\text{O}$ (wavy layers) [223]. Three-dimensional frameworks are illustrated for instance by $\text{Na}[\text{Mn}(\text{salen})_3][\text{Re}_6\text{Se}_8(\text{CN})_6]$ [224] or $(\text{Me}_4\text{N})_4\{[\text{Mn}(\text{H}_2\text{O})_2]_{1.5}\text{Mo}_6\text{Se}_6(\text{CN})_6\} \cdot 8\text{H}_2\text{O}$ [225]. The reaction of $[\text{Re}_6\text{Te}_8(\text{CN})_6]^{4-}$ ion with Fe^{3+} cations in aqueous solution results in the synthesis of the porous expanded Prussian Blue analogue $\text{Fe}_4[\text{Re}_6\text{Te}_8(\text{CN})_6]$ [226]. In many other examples the 3-D structures can be described as deriving from Prussian Blue [227–229]. A specific example with Mo_6 chalcogenide core is $\text{A}(\text{Et}_4)_{11}[(\text{Mo}_6\text{Br}_6\text{S}_2)(\text{CN})_6]_3 \cdot 16\text{H}_2\text{O}$ ($\text{A} = \text{mixed alkalis Cs/K}$), but here alkalin ions in octahedral environment of

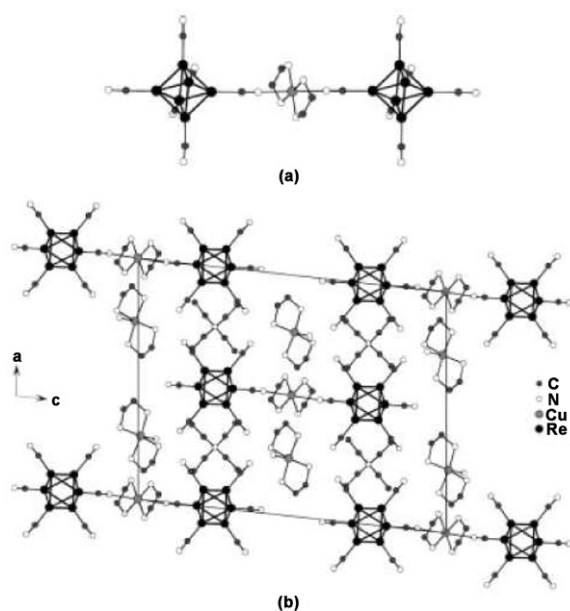


Fig. 18. Structure of anionic dimer $[\text{Cu}(\text{en})_2]_2[\text{Re}_6\text{Te}_8(\text{CN})_6]^{6-}$ (a) and view along [010] of the crystal packing in $(\text{Et}_4\text{N})_2[\text{Cu}(\text{NH}_3)(\text{en})_2]_2[\text{Re}_6\text{Te}_8(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ (b). All hydrogen and tellurium atoms and water molecules have been omitted for clarity [223].

(CN) replace transition element complexes, leading to an even more porous framework [112]. This approach of cyano-based coordination chemistry was subsequently widely developed and more details can be found in a recent review [230]. The first coordination polymers based on hexahydroxo rhenium clusters anions and alkaline-earth metal cations were published more recently: they include discrete molecular structures, 1-D chains and two types of 2-D layered structures [231].

5.2.2. Creating self organized structures using organic spacers

Generating site-differentiated species $[\text{Re}_6\text{Q}_8(\text{PET}_3)^a_{6-x}\text{X}^a_x]^{2-x}$ and subsequently substituting labile MeCN for halogen offers the possibility of assembling new molecular species, provided that the number (and isomer geometry) of solvate ligands and the nature of grafted ligands are well chosen. For instance, assembling $[\text{Re}_6\text{Q}_8(\text{PET}_3)^a_5(\text{MeCN})^a]^{2+}$ with bipyridines gives discrete bridged diclusters, and even triclusters (with the use of *trans*- $[\text{Re}_6\text{Q}_8(\text{PET}_3)^a_4(\text{MeCN})^a_2]^{2+}$) [197], while with tri and tetradentate pyridil-based ligands, star-shaped (three- and tetra armed) multiclusters were obtained [232]. Using the *cis*- $[\text{Re}_6\text{Q}_8(\text{PET}_3)^a_4(\text{MeCN})^a_2]^{2+}$ isomer instead of the *trans*-one afforded the first examples of cluster-based molecular squares *cyclo*- $[\text{Re}_6\text{Q}_8(\text{PET}_3)^a_4\text{L}^{a-2/2}]_4^{8+}$ with various lengths of the organic spacer [233].

Within this approach, supramolecular arrays were obtained via three routes:

- the mediation of *trans*- $[\text{Re}_6\text{Q}_8(\text{PET}_3)^a_4(\text{dipyridyl})^a_2]^{2+}$ with transition metal ions (Co^{2+} , Cd^{2+} , Zn^{2+} as nitrates) gave sinusoidal and zigzag chains and porous structures

[234] while the use of the *cis*- isomer resulted in the formation of one-dimensional chain of corner-sharing squares [235];

- the use of hydrogen bonding involving ligands like nicotinamides [236], giving again dimers, linear and zigzag chains;
- the use of halogen bonding between the nitrogen of a cyano ligand and the iodine of a TTF derivative [237] or a bis iodoethynyl benzene [238].

6. Conclusion: recent trends in M_6 cluster chemistry and perspectives

In conclusion, we would like to emphasize the recent use of the M_6L_{14} cluster units – obtained by solid state chemistry – as building blocks for the elaboration of nano-sized materials. Indeed, they are ideal candidates for elaboration of such materials due to their molecular size, their various intrinsic properties (magnetism, luminescence, oxido-redox, electrical dipolar) and the possibility of apical ligand exchange for functional one. Up to now, these cluster materials were obtained with $(\text{Mo}_6\text{X}_8^i)$ or (Re_6Q_8) cluster cores starting from Mo_6 halides or Re_6 chalcogenides. However, due to their potential applications in catalysis, in biology, or in optoelectronic it is worth thinking about their future extension towards chalcogenides $(\text{Mo}_6\text{X}_8^i\text{-xQ}_x^i)$ or $(\text{Re}_6\text{Q}_8^i\text{-xX}_x^i)$ cluster cores, because the presence of mixed Q/X ligands on the cluster core modifies the intrinsic properties of the cluster units that could be used for specific applications. In the following we briefly report some examples of such cluster nano assemblies or nanomaterials.

In $[\text{n-Bu}_4\text{N}]_2[(\text{Mo}_6\text{Br}_8^i)(\text{CF}_3\text{SO}_3^a)_6]$, the substitution of the six apical triflate ligands by the organometallic pyridine ligands $[\text{RuCp}(\text{PPh}_3)_2(\eta^1\text{-C}_2\text{-4-pyridinyl})]$, the tri-silylferrocenyl phenolate dendron $p\text{-NaO-C}_6\text{H}_4\text{C}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{Me})_2\text{Fc})_3$, or the dendronic pyridine

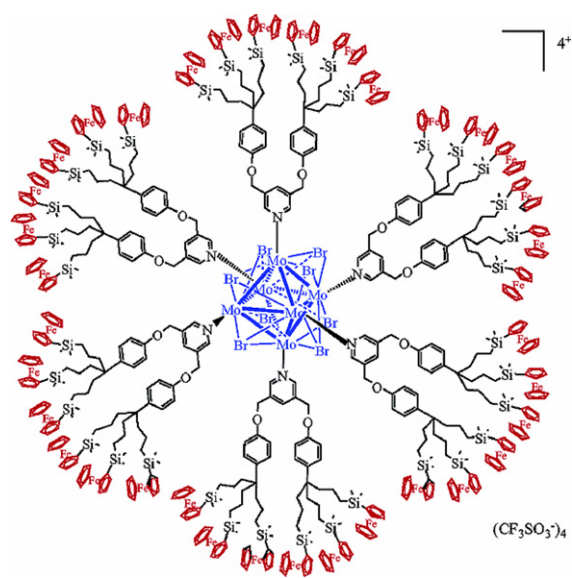


Fig. 19. Mo_6 cluster-dendrimer assembling with 36 ferrocenyl endings [239].

3,3'-{CH₂O-*p*-C₆H₄C(CH₂CH₂CH₂SiMe₂C₅H₅FeCp)₃}₂Py, gives new cluster-dendrimer assemblings. The two latter ones with 18 or 36 ferrocenyl endings (Fig. 19), respectively, can recognize biologic molecules by cyclic voltametry. [239,240]. The hexa arm dendrimer based on the Mo₆Cl₈ core [241] should also be mentioned. In the solvated [(Re₆Seⁱ₈)(CH₃CN)^a]₆(SbF₆)₂ compound the apical ligands can be replaced by a variety of functionality-bearing dendrons to give cluster-dendrimer assemblings [190,200,242,243], with luminescence properties [242]. In another approach, [(Re₆Seⁱ₈)(OH)^a]₆⁴⁻ units have been encapsulated and released in maltose-decorated polypropylene amine dendrimer, showing the interest of such assemblings for therapeutic treatment [244].

Other cluster nanomaterials have been obtained, like, for instance:

- luminescent liquid crystals after the grafting of mesogenic ligands in apical position of (Mo₆Brⁱ₈) [245,246] cluster cores or after using mesogenic counteranions [247,248];
- silica nanoparticles Cs₂Mo₆Br₁₄@SiO₂ [249], (nBu₄N)₂[Mo₆I₈(CF₃CO₂)₆] [250] and γ-Fe₂O₃-Cs₂Mo₆Br₁₄@SiO₂ [251] in which the [Mo₆L₁₄]²⁻ units are well-dispersed inside the silica matrix, while γ-Fe₂O₃ is located at the center of the particle. They are luminescent in the red and near infrared region under UV excitation and additionally magnetic for the latter bifunctional ones, and thus they are promising candidates for applications in biotechnology. Similar luminescent nanoparticles were elaborated from rhenium cluster compounds [252,253]. Characterization of photonic colloidal crystals from silica spheres with incorporated luminescent [Mo₆Br₁₄]²⁻ cluster units was also reported [254];
- nanocolloids and nanocomposites, [(n-C₄H₉)₄N]₂Mo₆Br₁₄@ZnO, with [Mo₆Br₁₄]²⁻ cluster units immobilized on the ZnO nanocrystal surface. Depending on the excitation wavelength, the visible emission of either ZnO or the cluster units is observed, giving them properties of tunable emission [255];
- [Mo₆I₈(CF₃SO₂)^a]₆²⁻ units anchored in apical position on *n*- and *p*- type Si(111) surfaces through alkyl monolayers end-capped by pyridine, previously covalently bound to hydrogen terminated Si(111) [256,257] and *trans*-[(Re₆Seⁱ₈)(TBP)^a]₄(OH)^a cluster units (TBP = 4-terbutylpyridine) immobilized on Si(111) surfaces through alkyl spacers [258]. Such assemblings provide new types of molecular junctions the electronic properties of which being influenced by the presence of metal clusters;
- [(Re₆Seⁱ₈)(TBP)^a]₄(MAC)^a neutral cluster units embedded into polymeric matrices after copolymerization with methyl metacrylate to give cluster-polymer materials that combine the processability of the polymeric matrix with luminescent properties, keeping their properties even after several months of ageing and with a small amount of cluster units embedded in the polymer [259]. Another way was to copolymerize the cluster complex [(Re₆Seⁱ₈)(PEt₃)^a]₅(4-vinylpyridine)^a(SbF₆)₂ with styrene via the polymerizable 4-vinylpyridine ligand [199]. With molybdenum clusters, the properties of the photoactive composite materials of

(nBu₄N)₂[Mo₆I₈(CF₃CO₂)₆] in polyurethane nanofibers have been reported [250];

- Mo₆I₈S₂ [77,78] fibers dispersed in isopropanol after ultrasonic debundling and sedimentation [260] for use as an alternative to carbon nanotubes for applications in nanotechnology. These fibers were sulfurized under argon-H₂/H₂S flow in order to obtain MoS₂ nanotubes with encapsulation of MoS₂ fullerenes inside them [261] or, according to a similar process, using the Mo₆S₄I₆ [262,263] fibers strongly related to Mo₆I₈S₂ fibers [264]. These Mo₆I₈S₂ nanofibers have been also used as precursors for the elaboration of new composite films based on MoO_{3-x} nanowires aligned in a liquid single crystal elastomer matrix [265]. Other nanofibers in the Mo-S-I system have been used for elaboration of various electronic devices, but no precise crystal structure was reported for such fibers [266].

Finally, all the recent examples above mentioned evidence the great potentiality of cluster compounds as precursors in the new field of nanotechnology. This short review that covers the Mo₆ and Re₆ chalcogenides in solid state chemistry since the origin to recent period, evidences that a number of cluster compounds with chalcogenide cluster cores could be also used as precursors for elaboration of cluster nanomaterials, that opens in the future a promising and exciting way of wide investigations. Curiosity, perseverance and determination are required to develop such a research field, that were the qualities of the pioneer researchers who have started – sometimes in difficult conditions – the transition metal cluster chemistry a very long time ago [28,86].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.crci.2012.07.004>.

The supplementary materials contain: experimental, crystal data, atomic positions, refined multiplicities, interatomic distances and angles, general displacement parameters β 's and root mean-square amplitudes of anisotropic displacement for $K_{2.5}Re_6S_{6.5}Br_{7.5}$ (Tables 1–6), $Ag_{0.5}K_{1.5}Re_6S_6Br_8$ (Tables 7–12), $Ag_2Re_6S_6Br_8$ (Tables 13–18), $CdRe_6S_6Br_8$ (Tables 19–24) and $Cs_3Re_6S_7Br_7$ (Tables 25–30).

References

- [1] R. Chevrel, M. Sergent, J. Prigent, *J. Solid State Chem.* 3 (1971) 515.
- [2] O. Bars, J. Guillevic, D. Grandjean, *J. Solid State Chem.* 6 (1973) 335.
- [3] C. Perrin, M. Sergent, J. Prigent, *C.R. Acad. Sci. Paris, Ser. C* 277 (1973) 465.
- [4] A. Perrin, M. Sergent, *Bull. Soc. Chim. Fr.* 11–12 (1980) 66.
- [5] N.S. Fortunatov, N.I. Timoshchenko, *Ukr. Khim Zh. Russ. Ed.* 31 (1965) 1078.
- [6] J.P. Rannou, M. Sergent, *C.R. Acad. Sci. Ser. C* 265 (1967) 734.
- [7] A.A. Opalovski, V.E. Fedorov, *Dokl. Chem. Engl. Transl.* 176 (1967) 810.
- [8] A.A. Opalovski, V.E. Fedorov, K.A. Khaldoyanidi, *Dokl. Chem. Engl. Transl.* 182 (1968) 907.
- [9] C. Perrin-Billot, A. Perrin, J. Prigent, *Chem. Comm.* (1970) 676.
- [10] J. Marcoll, A. Rabenau, D. Mootz, H. Wunderlich, *Rev. Chim. Min.* 11 (1974) 607.
- [11] D. Britnell, G.W.A. Fowles, D.A. Rice, *J. Chem. Soc. Dalton Trans.* (1974) 2191.
- [12] R. Chevrel, M. Sergent, *Topics in Current Physics Superconductivity*, in: Ø. Fischer, M.B. Maple (Eds.), *Ternary Compounds I*, Springer-Verlag, Berlin, Heidelberg, New-York, 1982, p. 25.
- [13] T. Hugbanks, R. Hoffmann, *J. Amer. Chem. Soc.* 105 (1983) 1150.
- [14] M. Sergent, Ø. Fischer, M. Decroux, C. Perrin, R. Chevrel, *J. Solid State Chem.* 22 (1978) 87.
- [15] C. Perrin, R. Chevrel, M. Sergent, Ø. Fischer, *Mat. Res. Bull.* 14 (1979) 1505.
- [16] A. Perrin, M. Sergent, Ø. Fischer, *Mat. Res. Bull.* 13 (1978) 259.
- [17] C. Perrin, M. Sergent, *J. Less Common Met.* 123 (1986) 117.
- [18] A. Perrin, M. Sergent, *New J. Chem.* 12 (1988) 337.
- [19] A. Perrin, C. Perrin, M. Sergent, *J. Less Common Met.* 137 (1988) 241.
- [20] A. Simon, *Angew. Chem. Int. Ed. Engl.* 29 (1988) 159.
- [21] S.C. Lee, R.H. Holm, *Angew. Chem. Int. Ed. Engl.* 29 (1990) 840.
- [22] C. Perrin, *J. Alloys Comp.* 229 (1997) 10.
- [23] T. Saito, *J. Chem. Soc. Dalton Trans.* (1999) 97.
- [24] J.-C.P. Gabriel, K. Boubekour, S. Uriel, P. Batail, *Chem. Rev.* 101 (2001) 2037.
- [25] T.G. Gray, *Coord. Chem. Rev.* 243 (2003) 213.
- [26] R. Nakamura, *Serial Experiments Lain*, Manga Cartoon, Tokyo, 1998.
- [27] F.A. Cotton, *Inorg. Chem.* 3 (1964) 1217.
- [28] H. Schäfer, H.G. von Schnering, *Angew. Chem.* 20 (1964) 833.
- [29] J.R. Long, L.S. McCarty, R.H. Holm, *J. Am. Chem. Soc.* 118 (1996) 4603.
- [30] E. Levi, D. Aurbach, *Chem. Mater.* 23 (2011) 1901.
- [31] W. Bronger, C. Koppe, D. Schmitz, *Z. Anorg. Allg. Chem.* 623 (1997) 239.
- [32] F.A. Cotton, T.E. Haas, *Inorg. Chem.* 3 (1964) 10.
- [33] L.F. Mattheis, C.F. Fong, *Phys. Rev. B* 15 (1977) 1760.
- [34] D. Certain, R. Lissilour, *Z. Phys. D* 3 (1986) 411.
- [35] T. Hugbanks, *Prog. Solid State Chem.* 19 (1989) 329.
- [36] Z. Lin, I.D. Williams, *Polyhedron* 15 (1996) 3277.
- [37] R. Gautier, J.F. Halet, J.Y. Saillard, *Computational methods: transition metals clusters*, in: E.I. Solomon, R.A. Scott, R.B. King (Eds.), *Computational Inorganic and Bioinorganic Chemistry*, John Wiley and Sons, Chichester, 2009, pp. 539–550.
- [38] V.F. Shamrai, G.M. Leitus, A.Y. Musatenko, *Kristallografiya* 33 (1988) 1289.
- [39] Ø. Fischer, *Appl. Phys.* 16 (1978) 1.
- [40] C. Perrin, *Dissertation: Doctorat d'Etat es Sciences Physiques*, Rennes (1981).
- [41] M. Rangus, A. Omerzu, A. Mrzel, D. Vengust, D.D. Mihailovic, *AIP Conf. Proc.* 786 (2005) 378.
- [42] F.J. Culetto, F. Pobell, *Mat. Res. Bull.* 14 (1979) 473.
- [43] J.M. Tarascon, G.W. Hull, P. Marsh, L. Ter Haar, *J. Solid State Chem.* 66 (1987) 204.
- [44] T. Caillat, J.P. Fleurial, *J. Phys. Chem. Solids* 49 (1988) 1139.
- [45] W. Hönle, H.D. Flack, K. Yvon, *J. Solid State Chem.* 49 (1983) 157.
- [46] A. Perrin, R. Chevrel, M. Sergent, Ø. Fisher, *J. Solid State Chem.* 33 (1980) 43.
- [47] C. Roche, R. Chevrel, A. Jenny, P. Pêcheur, H. Scherrer, S. Scherrer, *Phys. Rev. B* 60 (1999) 16442.
- [48] T. Caillat, J.P. Fleurial, G.J. Snyder, *Solid State Sci.* 1 (1999) 535.
- [49] R.W. Nunes, I.I. Mazin, D.J. Sing, *Phys. Rev. B* 59 (1999) 7969.
- [50] N. Alonso Vante, B. Schubert, H. Tributsch, A. Perrin, *J. Catalysis* 112 (1988) 384.
- [51] N. Alonso Vante, H. Tributsch, *Nature* 323 (1986) 431.
- [52] C. Perrin, R. Chevrel, M. Sergent, *J. Solid State Chem.* 19 (1976) 305.
- [53] C. Perrin, M. Sergent, F. Le Traon, A. Le Traon, *J. Solid State Chem.* 25 (1978) 197.
- [54] A. Simon, H.G. von Schnering, H. Schäfer, *Z. Anorg. Allg. Chem.* 355 (1967) 295.
- [55] L. Leduc, A. Perrin, M. Sergent, *C. R. Acad. Sci. Paris, Ser. II* 296 (1983) 961.
- [56] C.B. Pinheiro, N.L. Speziali, H. Berger, *Acta Cryst. C* 53 (1997) 1178.
- [57] A. Perrin, L. Leduc, M. Sergent, *Eur. J. Solid State Inorg. Chem.* 28 (1991) 919.
- [58] W. Bronger, M. Spangenberg, *J. Less Common Met.* 76 (1980) 73.
- [59] W. Bronger, H.J. Miessen, *J. Less Common Met.* 83 (1982) 29.
- [60] W. Bronger, H.J. Miessen, D. Schmitz, *J. Less Common Met.* 95 (1983) 275.
- [61] W. Bronger, H.J. Miessen, P. Muller, R. Neugroschel, *J. Less Common Met.* 105 (1985) 303.
- [62] W. Bronger, H.J. Miessen, R. Neugroschel, D. Schmitz, M. Spangenberg, *Z. Anorg. Allg. Chem.* 525 (1985) 41.
- [63] S. Kamiguchi, S. Nagashima, T. Chihara, *Chem. Lett.* 36 (2007) 1340.
- [64] S. Kamiguchi, N. Ikeda, S. Nagashima, H. Kurokawa, H. Miura, T. Chihara, *J. Clust. Sci.* 20 (2009) 683.
- [65] F. Klaiber, W. Petter, F. Hulliger, *J. Solid State Chem.* 46 (1983) 112.
- [66] D.W. Bullett, *Solid State Comm.* 51 (1984) 51.
- [67] V.E. Fedorov, N.V. Podbereskaya, A.V. Mischenko, G.F. Khudorozko, I.P. Azanov, *Mater. Res. Bull.* 21 (1986) 1335.
- [68] J.C. Pilet, F. Le Traon, A. Le Traon, C. Perrin, A. Perrin, L. Leduc, M. Sergent, *Surf. Sci.* 156 (1985) 359.
- [69] F. Le Traon, J.C. Pilet, A. Le Traon, C. Perrin, A. Perrin, L. Leduc, M. Sergent, *Proc. 7th Coll. Hertzian Optics and Dielectrics*, in: Y. Servant (Ed.), Bordeaux, 1984.
- [70] B.E. Vugmeister, M.D. Glinchuk, *Rev. Mod. Phys.* 62 (1990) 993.
- [71] A. Aruchamy, H. Tamaoki, A. Fujishima, H. Berger, N.L. Speziali, F. Levy, *Mater. Res. Bull.* 29 (1994) 359.
- [72] N.L. Speziali, H. Berger, G. Leicht, R. Sanjinés, G. Chapuis, F. Lévy, *Mat. Res. Bull.* 23 (1988) 1597.
- [73] C. Fisher, N. Alonso-Vante, S. Fiechter, H. Tributsch, G. Reck, W. Schulz, *J. Alloys Comp.* 178 (1992) 305.
- [74] L. Leduc, J. Padiou, A. Perrin, M. Sergent, *J. Less Common Met.* 95 (1983) 73.
- [75] C. Fischer, S. Fiechter, H. Tributsch, G. Reck, B. Schultz, *Berichte der Bunsengesellschaft fuer Physikalische Chemie* 96 (1992) 1652.
- [76] A. Perrin, C. Perrin, *Europ. J. Inorg. Chem.* (2011) 3848.
- [77] C. Perrin, M. Sergent, *J. Chem. Res. (S)* 2 (1983) 38.
- [78] C. Perrin, M. Sergent, *J. Chem. Res. (M)* (1983) 449.
- [79] H.-J. Meyer, J.D. Corbett, *Inorg. Chem.* 30 (1991) 963.
- [80] C. Perrin, M. Sergent, A. Sadok, J.C. Pilet, F. Le Traon, A. Le Traon, *Proceeding of the Second European Workshop on Charge Density Waves*, CDW, Aussois, 1987.
- [81] C. Perrin, M. Potel, M. Sergent, *Acta Cryst.* 39C (1983) 415.
- [82] D. Salloum, R. Gautier, M. Potel, P. Gougeon, *Angew. Chem. Int. Ed.* 44 (2005) 1363.
- [83] Yu.V. Mironov, N.G. Naumov, S.G. Kozlova, S.J. Kim, V.E. Fedorov, *Angew. Chem. Int. Ed.* 44 (2005) 6867.
- [84] P. Gougeon, D. Salloum, J. Cuny, L. Le Pollès, M. Le Floch, R. Gautier, M. Potel, *Inorg. Chem.* 48 (2009) 8337.
- [85] A. Perricone, A. Slougui, A. Perrin, *Solid State Sci.* 1 (1999) 657.
- [86] C. Brossat, *Arkiv. Kem. Mineralog.* 7 (1945) A20.
- [87] H. Schäfer, H.G. von Schnering, J. Tillack, F. Khunen, H. Wöhrle, H. Baumann, *Z. Anorg. Allg. Chem.* 353 (1967) 281.
- [88] G. Pilet, A. Perrin, *Solid State Sci.* 6 (2004) 109.
- [89] A. Slougui, *PhD Dissertation*, Rennes, France (1998).
- [90] J.R. Long, A.S. Williamson, R.H. Holm, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 226.
- [91] L. Leduc, A. Perrin, M. Sergent, *Acta Cryst.* C39 (1983) 1503.
- [92] N. Lenagard, A. Perrin, M. Sergent, C. Levy-Clément, *Mat. Res. Bull.* 20 (1985) 835.
- [93] D. Dorignac, Z.G. Li, A. Perrin, *J. Microsc. Spectrosc. Electron.* 11 (1986) 27a.
- [94] G. Pilet, O. Hernandez, A. Perrin, *Z. Kristallogr. NCS* 217 (2002) 11.
- [95] H.G. von Schnering, *Z. Anorg. Allg. Chem.* 385 (1971) 85.
- [96] M. Potel, C. Perrin, A. Perrin, M. Sergent, *Mat. Res. Bull.* 21 (1986) 1239.
- [97] S. Bösch, H.L. Keller, *Z. Kristallogr.* 200 (1992) 305.
- [98] A. Peppenhorst, H.L. Keller, *Z. Anorg. Allg. Chem.* 622 (1996) 663.

- [99] P.C. Healy, D.L. Kepert, D. Taylor, A.H. White, J. Chem. Soc. Dalton Trans. (1973) 646.
- [100] K. Kiracki, S. Cordier, C. Perrin, Z. Anorg. Allg. Chem. 631 (2005) 411.
- [101] W. Bronger, M. Kanert, M. Loevenich, D. Schmitz, Z. Anorg. Allg. Chem. 619 (1993) 2015.
- [102] A.A. Opalovskii, V.E. Fedorov, E.U. Lobkov, Z. Neorg. Khim. 16 (1971) 1494.
- [103] A.A. Opalovskii, V.E. Fedorov, E.U. Lobkov, B.G. Erenburg, Z. Neorg. Khim. 16 (1971) 3175.
- [104] V.E. Fedorov, A.V. Mishchenko, B.A. Kolesov, S.P. Gubin, Y.L. Slovo-khotov, Y.T. Struchkov, Izvestiya Akademii Nauk SSSR Ser. Khim. 9 (1984) 2159.
- [105] V.E. Fedorov, A.V. Mishchenko, B.A. Kolesov, S.P. Gubin, Y.L. Slovo-khotov, Y.T. Struchkov, Koord. Khim. (English Transl.) 11 (1985) 980.
- [106] L. Leduc, A. Perrin, M. Sergent, F. Le Traon, J.C. Pilet, A. Le Traon, Mater. Lett. 3 (1985) 209.
- [107] S.F. Solodovnikov, Y.V. Mironov, S.S. Yarovoi, A.V. Virovets, V.E. Fedorov, Chem. Sustainable Dev. 8 (2000) 115.
- [108] Y.V. Mironov, J.A. Cody, J.A. Ibers, Acta Cryst. C52 (1996) 281.
- [109] S.S. Yarovoi, Y.I. Mironov, Y.V. Mironov, A.V. Virovets, V.E. Fedorov, U.H. Paek, S.C. Shin, M.L. Seo, Mater. Res. Bull. 32 (1997) 1271.
- [110] J.C. Gabriel, K. Boubekeur, P. Batail, Inorg. Chem. 32 (1993) 2894.
- [111] Yu.V. Mironov, M.A. Pell, J.A. Ibers, Inorg. Chem. 35 (1996) 2709.
- [112] S. Cordier, N.G. Naumov, D. Salloum, F. Paul, C. Perrin, Inorg. Chem. 43 (2004) 219.
- [113] K. Kiracki, S. Cordier, O. Hernandez, T. Roisnel, F. Paul, C. Perrin, J. Solid State Chem. 178 (2005) 3117.
- [114] K. Kiracki, S. Cordier, C. Perrin, Chem. Eur. J. 12 (2006) 6419.
- [115] K. Kiracki, S. Cordier, A. Shames, B. Fontaine, O. Hernandez, E. Furet, J.F. Halet, R. Gautier, C. Perrin, Chem. Eur. J. 13 (2007) 9608.
- [116] K. Kiracki, S. Cordier, C. Perrin, C. R. Chimie 8 (2005) 1712.
- [117] A. Perrin, L. Leduc, M. Potel, M. Sergent, Mat. Res. Bull. 25 (1990) 1227.
- [118] A. Slougui, A. Perrin, M. Sergent, Acta Cryst. C48 (1992) 1917.
- [119] A. Slougui, S. Ferron, A. Perrin, M. Sergent, J. Clust. Sci. 8 (1997) 349.
- [120] A. Slougui, A. Perrin, unpublished data. Refer to Supplementary Material for crystal data; details can be found in [88].
- [121] S. Uriel, K. Boubekeur, J.C. Gabriel, P. Batail, J. Orduña, Bull. Soc. Chim. Fr. 133 (1996) 783.
- [122] G. Pilet, S. Cordier, C. Perrin, A. Perrin, J. Struct. Chem. 48 (2007) 680.
- [123] B. Fontaine, R. Gautier, G. Pilet, S. Cordier, C. Perrin, A. Perrin, Y.V. Mironov, J. Clust. Sci. 20 (2009) 145.
- [124] A. Deluzet, H. Duclausaud, P. Sautet, S.A. Borshch, Inorg. Chem. 41 (2002) 2537.
- [125] V.P. Fedin, H. Imoto, T. Saito, V.E. Fedorov, Y.V. Mironov, S.S. Yarovoi, Polyhedron 15 (1996) 1229.
- [126] S.F. Solodovnikov, S.S. Yarovoi, Y.V. Mironov, A.V. Virovets, V.E. Fedorov, J. Struct. Chem. 45 (2004) 865.
- [127] A. Slougui, A. Perrin, M. Sergent, J. Solid State Chem. 147 (1999) 358.
- [128] C.B. Guilbaud, J.C.P. Gabriel, K. Boubekeur, P. Batail, C. R. Acad. Sci. Paris, Ser. IIC 1 (1998) 765.
- [129] A. Slougui, S. Ferron, A. Perrin, M. Sergent, Eur. J. Solid State Inorg. Chem. 33 (1996) 1001.
- [130] S.S. Yarovoi, S.F. Solodovnikov, Y.V. Mironov, V.E. Fedorov, J. Struct. Chem. 44 (2003) 318.
- [131] J.C. Gabriel, PhD Dissertation, Orsay (1993).
- [132] V.P. Fedin, V.E. Fedorov, H. Imoto, T. Saito, Polyhedron 16 (1997) 1615.
- [133] A.W. Maverick, J.S. Najdzionek, D. MacKenzie, D.G. Nocera, H.B. Gray, J. Am. Chem. Soc. 105 (1983) 1878.
- [134] T.G. Gray, C.M. Rudzinski, E.E. Meyer, R.H. Holm, D.G. Nocera, J. Am. Chem. Soc. 125 (2003) 4755.
- [135] T. Yoshimura, A. Matsuda, Y. Ito, S. Ishizaka, S. Shinoda, H. Tsukube, N. Kitamura, A. Shinohara, Inorg. Chem. 49 (2010) 3473.
- [136] N.G. Naumov, E.V. Ostanina, A.V. Virovets, M. Schmidtman, A. Müller, V.E. Fedorov, Russ. Chem. Bull. Int. Ed. 51 (2002) 866.
- [137] G. Pilet, PhD Dissertation, Rennes (2003).
- [138] F. Stollmaier, A. Simon, Inorg. Chem. 24 (1985) 168.
- [139] E.G. Tulsky, J.R. Long, Chem. Mater. 13 (2001) 1149.
- [140] O.M. Yaghi, M.J. Scott, R.H. Holm, Inorg. Chem. 32 (1992) 4778.
- [141] N.G. Naumov, A.V. Virovets, N.V. Podberezskaya, V.E. Fedorov, J. Struct. Chem. 38 (1997) 857.
- [142] S.B. Artemkina, N.G. Naumov, A.V. Virovets, V.E. Fedorov, J. Struct. Chem. 43 (2002) 689.
- [143] L.G. Beauvais, M.P. Shores, J.R. Long, Chem. Mater. 10 (1998) 3783.
- [144] Y.V. Mironov, J.A. Cody, T.E. Albrecht-Schmitt, J.A. Ibers, J. Am. Chem. Soc. 119 (1997) 493.
- [145] H. Imoto, N.G. Naumov, A.V. Virovets, T. Saito, V.E. Fedorov, J. Struct. Chem. 39 (1998) 720.
- [146] Y.V. Mironov, A.V. Virovets, V.E. Fedorov, N.Y. Podberezskaya, O.V. Shishkin, Y.T. Struchkov, Polyhedron 14 (1995) 3171.
- [147] A. Slougui, Y.V. Mironov, A. Perrin, V.E. Fedorov, Croat. Chem. Acta 68 (1995) 885.
- [148] N.V. Podberezskaya, A.V. Virovets, Y.V. Mironov, L.P. Kozeeva, N.G. Naumov, V.E. Fedorov, J. Struct. Chem. 40 (1999) 436.
- [149] Y.V. Mironov, V.E. Fedorov, C.C. McLaughlan, J.A. Ibers, Inorg. Chem. 39 (2000) 1809.
- [150] N.G. Naumov, S.J. Kim, A.V. Virovets, Y.V. Mironov, V.E. Fedorov, Bull. Korean Chem. Soc. 27 (2006) 635.
- [151] N.G. Naumov, K.A. Brylev, Y.V. Mironov, A.V. Virovets, D. Fenske, V.E. Fedorov, Polyhedron 23 (2004) 599.
- [152] M. Emirdag-Eanes, J.A. Ibers, Inorg. Chem. 41 (2002) 6170.
- [153] T. Yoshimura, T. Ikai, T. Takayama, T. Sekine, Y. Kino, A. Shinihara, Inorg. Chem. 49 (2010) 5876.
- [154] M.K. Simsek, D. Dublitz, W. Preetz, Z. Anorg. Allg. Chem. 623 (1997) 1885.
- [155] Y.V. Mironov, A.V. Virovets, N.G. Naumov, V.N. Ikorskii, V.E. Fedorov, Chem. Eur. J. 6 (2000) 1361.
- [156] C. Magliocchi, X. Xie, T. Highbanks, Inorg. Chem. 39 (2000) 5000.
- [157] Y.V. Mironov, V.N. Ikorskii, V.E. Fedorov, J.A. Ibers, Eur. J. Inorg. Chem. 2005 (2005) 214.
- [158] S.S. Yarovoi, Y.V. Mironov, D.Y. Naumov, Y.V. Gatilov, S.G. Kozlova, S.J. Kim, V.E. Fedorov, Eur. J. Inorg. Chem. 2005 (2005) 3945.
- [159] V.P. Fedin, A.A. Virovets, A.G. Sykes, Inorg. Chim. Acta 271 (1998) 228.
- [160] P. Batail, L. Ouahab, A. Pénicaud, C. Lenoir, A. Perrin, C. R. Acad. Sci. Ser. II 304 (1987) 1111.
- [161] W. Preetz, H. Harder, H.G. von Schnering, G. Kliche, K. Peters, J. Alloys Comp. 183 (1992) 413.
- [162] M.J. Suh, S. Huh, Y. Kim, S.J. Kim, Eur. J. Inorg. Chem. 2008 (2008) 686.
- [163] G. Pilet, S. Cordier, C. Perrin, A. Perrin, Inorg. Chim. Acta 350 (2003) 537.
- [164] S. Perruchas, F. Simon, S. Uriel, N. Avarvari, K. Boubekeur, P. Batail, J. Organometallic Chem. 643–644 (2002) 301.
- [165] Y. Kim, S. Kim, S.-J. Kim, M.K. Lee, M. Kim, H. Lee, C.S. Chin, Chem. Comm. (2004) 1692.
- [166] S.A. Gromilov, K.V. Ysenko, E.A. Shusharina, J. Struct. Chem. 48 (2007) 899.
- [167] M.A. Shestopalov, Z.S. Kozhomuratova, A.I. Smolentsev, Y.V. Mironov, A. Perrin, C. Perrin, V.E. Fedorov, J. Siberian Fed. Univ. Chem. 1 (2009) 81.
- [168] A. Brylev, N.G. Naumov, G. Peris, R. Llusar, V.E. Fedorov, Polyhedron 22 (2003) 3383.
- [169] G. Pilet, K. Kiracki, F. De Montigny, S. Cordier, C. Lapinte, C. Perrin, A. Perrin, Eur. J. Inorg. Chem. 2005 (2005) 919.
- [170] L. Ouahab, P. Batail, C. Perrin, C. Garrigou-Lagrange, Mat. Res. Bull. 21 (1986) 1223.
- [171] S. Perruchas, K. Boubekeur, E. Canadell, Y. Misaki, P. Auban-Senzier, C. Pasquier, P. Batail, J. Am. Chem. Soc. 130 (2008) 3335.
- [172] A. Deluzet, P. Batail, Y. Misaki, P. Auban-Senzier, E. Canadell, Adv. Mater. 12 (2000) 436.
- [173] A. Pénicaud, K. Boubekeur, P. Batail, E. Canadell, P. Auban-Senzier, D. Jerome, J. Am. Chem. Soc. 115 (1993) 4101.
- [174] A. Pénicaud, P. Batail, C. Coulon, A. Perrin, Synth. Met. 32 (1989) 25.
- [175] K. Kiracki, H. Hosoda, S. Cordier, C. Perrin, G. Saito, J. Solid State Chem. 179 (2006) 3628.
- [176] Y.V. Mironov, K.A. Brylev, S.J. Kim, S.G. Kozlova, N. Kitamura, V.E. Fedorov, Inorg. Chim. Acta 370 (2011) 363.
- [177] K.A. Brylev, Y.V. Mironov, S.G. Kozlova, V.E. Fedorov, S.J. Kim, H.J. Pietzsch, H. Stephan, A. Ito, S. Ishizaka, N. Kitamura, Inorg. Chem. 48 (2009) 2309.
- [178] Z. Zheng, J.R. Long, R.H. Holm, J. Am. Chem. Soc. 119 (1997) 2163.
- [179] M.W. Willer, J.R. Long, C.C. McLaughlan, R.H. Holm, Inorg. Chem. 37 (1998) 328.
- [180] L.F. Szczepura, D.L. Cedeno, D.B. Johnson, R. McDonald, S.A. Knott, K.M. Jeans, J.L. Durham, Inorg. Chem. 49 (2010) 11386.
- [181] M.A. Shestopalov, Y.V. Mironov, K.A. Brylev, S.G. Kozlova, V.E. Fedorov, H. Spiess, H.J. Pietzsch, H. Stephan, G. Geipel, G. Bernhard, J. Am. Chem. Soc. 129 (2007) 3714.
- [182] M.A. Shestopalov, Y.V. Mironov, K.A. Brylev, V.E. Fedorov, Russ. Chem. Bull. Int. Ed. 57 (2008) 1644.
- [183] Z.N. Chen, T. Yoshimura, M. Abe, K. Tsuge, Y. Sasaki, S. Ishizaka, H.B. Kim, N. Kitamura, Chem. Eur. J. 7 (2001) 4447.
- [184] Z.N. Chen, T. Yoshimura, M. Abe, Y. Sasaki, S. Ishizaka, H.-B. Kim, N. Kitamura, Angew. Chem. Int. Ed. 40 (2001) 239.
- [185] T. Saito, M. Yamamoto, T. Yamagata, H. Imoto, J. Am. Chem. Soc. 110 (1988) 1646.
- [186] T. Saito, M. Yamamoto, T. Nagase, T. Tsuboi, K. Kobayashi, T. Yagamata, H. Imoto, K. Unoura, Inorg. Chem. 29 (1990) 764.
- [187] P.J. Orto, G.S. Nichol, R. Wang, Z. Zheng, Inorg. Chem. 46 (2007) 8436.
- [188] P.J. Orto, G.S. Nichol, N. Okumura, D.H. Evans, R. Arratia-Perez, R. Ramirez-Tagle, R. Wang, Z. Zheng, Dalton Trans. (2008) 4247.

- [189] D.H. Johnston, D.C. Gaswick, M.C. Lonergan, C.L. Stern, D.F. Shriver, *Inorg. Chem.* 31 (1992) 1869.
- [190] R. Wang, Z. Zheng, *J. Am. Chem. Soc.* 121 (1999) 3549.
- [191] P. Orto, H.D. Selby, D. Ferris, J.R. Maeyer, Z. Zheng, *Inorg. Chem.* 46 (2007) 4377.
- [192] L.F. Szczepura, M.K. Oh, S.A. Knott, *Chem. Commun.* (2007) 4617.
- [193] G. Pilet, S. Cordier, S. Golhen, C. Perrin, L. Ouahab, A. Perrin, *Solid State Sci.* 5 (2003) 1263.
- [194] X. Tu, E. Boroson, H. Truong, A. Munoz-Castro, R. Arratia-Perez, G.S. Nichol, Z. Zheng, *Inorg. Chem.* 49 (2010) 380.
- [195] X. Tu, H. Truong, E. Alster, A. Munoz-Castro, R. Arratia-Perez, G.S. Nichol, Z. Zheng, *Chem. Eur. J.* 17 (2011) 580.
- [196] Z. Zheng, R.H. Holm, *Inorg. Chem.* 36 (1997) 5173.
- [197] Z. Zheng, T.G. Gray, R.H. Holm, *Inorg. Chem.* 38 (1999) 4888.
- [198] T. Yoshimura, K. Umakoshi, Y. Sasaki, A.G. Sykes, *Inorg. Chem.* 38 (1999) 5557.
- [199] B.K. Roland, W.H. Flora, M.D. Carducci, N.R. Armstrong, Z. Zheng, *J. Clust. Sci.* 14 (2003) 449.
- [200] B.K. Roland, W.H. Flora, H.D. Selby, N.R. Armstrong, Z. Zheng, *J. Am. Chem. Soc.* 138 (2006) 6620.
- [201] B.K. Roland, H.D. Selby, J.R. Cole, Z. Zheng, *Dalton Trans.* (2003) 4307.
- [202] M.A. Shestopalov, S. Cordier, O. Hernandez, Y. Molard, C. Perrin, A. Perrin, V.E. Fedorov, Y.V. Mironov, *Inorg. Chem.* 48 (2009) 1482.
- [203] F. Dorson, Y. Molard, S. Cordier, B. Fabre, O. Efreanova, D. Rondeau, Y. Mironov, V. Circu, N. Naumov, C. Perrin, *Dalton Trans.* (2009) 1297.
- [204] S.J. Hilsenbeck, V.G. Young, R.E. McCarley, *Inorg. Chem.* 33 (1994) 1822.
- [205] G. Prabusankar, Y. Molard, S. Cordier, S. Golhen, Y. Le Gal, C. Perrin, L. Ouahab, S. Kahlal, J.F. Halet, *Eur. J. Inorg. Chem.* (2009) 2153.
- [206] Y.V. Mironov, N.G. Naumov, S.S. Yarovi, S. Cordier, C. Perrin, V.E. Fedorov, *Russ. Chem. Bull. Int. Ed.* 51 (2002) 1919.
- [207] B. Michel, R.E. McCarley, *Inorg. Chem.* 21 (1982) 1864.
- [208] M. Ebihara, K. Toriumi, K. Saito, *Inorg. Chem.* 27 (1988) 13.
- [209] M. Ebihara, K. Isobe, Y. Sasaki, K. Saito, *Inorg. Chem.* 31 (1992) 1644.
- [210] M. Ebihara, T. Imai, T. Kawamura, *Acta Crystallogr. C51* (1995) 1743.
- [211] P.A. Abramov, M.N. Sokolov, A.V. Virovets, E.V. Peresyphkina, C. Vicent, V.P. Fedin, *J. Clust. Sci.* 20 (2009) 83.
- [212] M. Ebihara, K. Toriumi, Y. Sasaki, K. Saito, *Gazz. Chim. It.* 125 (1995) 87.
- [213] A. Perrin, *New J. Chem.* 14 (1990) 561.
- [214] S. Uriel, K. Boubekeur, P. Batail, J. Orduna, A. Perrin, *New J. Chem.* 25 (2001) 737.
- [215] F. Simon, K. Boubekeur, J.C.P. Gabriel, P. Batail, *Chem. Commun.* (1998) 845.
- [216] S. Uriel, K. Boubekeur, P. Batail, J. Orduna, E. Canadell, *Inorg. Chem.* 34 (1995) 5307.
- [217] A. Decker, F. Simon, K. Boubekeur, D. Fenske, P. Batail, *Z. Anorg. Allg. Chem.* 626 (2000) 309.
- [218] T. Yoshimura, Z.N. Chen, A. Itasaka, M. Abe, Y. Sasaki, S. Ishizaka, N. Kitamura, S.S. Yarovi, S.F. Solodovnikov, V.E. Fedorov, *Inorg. Chem.* 42 (2003) 4857.
- [219] Y.V. Mironov, M.A. Shestopalov, K.A. Brylev, S.S. Yarovi, G.R. Romanenko, V.E. Fedorov, H. Spies, H.J. Pietzsch, H. Stephan, G. Geipel, G. Bernhard, W. Krauss, *Eur. J. Inorg. Chem.* 2005 (2005) 657.
- [220] P. Nannelli, B.P. Block, *Inorg. Chem.* 7 (1968) 2423.
- [221] P. Nannelli, B.P. Block, *Inorg. Chem.* 8 (1969) 1767.
- [222] N.G. Naumov, A.V. Virovets, V.E. Fedorov, *J. Struct. Chem.* 41 (2000) 499.
- [223] K.A. Brylev, G. Pilet, N.G. Naumov, A. Perrin, V.E. Fedorov, *Eur. J. Inorg. Chem.* 3 (2005) 461.
- [224] Y. Kim, S.M. Park, S.J. Kim, *Inorg. Chem. Comm.* 5 (2005) 592.
- [225] K.A. Brylev, N.G. Naumov, A.V. Virovets, S.J. Kim, V.E. Fedorov, *J. Clust. Sci.* 20 (2009) 165.
- [226] M.P. Shores, L.G. Beauvais, J.R. Long, *J. Am. Chem. Soc.* 121 (1999) 775.
- [227] M.V. Bennett, L.G. Beauvais, M.P. Shores, J.R. Long, *J. Am. Chem. Soc.* 123 (2001) 8022.
- [228] N.G. Naumov, D.V. Soldatov, J.A. Ripmcester, S.B. Artemkina, V.E. Fedorov, *Chem. Comm.* (2001) 571.
- [229] N.G. Naumov, A.V. Virovets, M.N. Sokolov, S.B. Artemkina, V.E. Fedorov, *Angew. Chem. Int. Ed.* 37 (1998) 1943.
- [230] Y. Kim, V.E. Fedorov, S.J. Kim, *J. Mater. Chem.* 19 (2009) 7178.
- [231] Y.V. Mironov, V.E. Fedorov, H. Bang, S.J. Kim, *Eur. J. Inorg. Chem.* 3 (2006) 553.
- [232] B.K. Roland, H.D. Selby, M.D. Carducci, Z. Zheng, *J. Am. Chem. Soc.* 124 (2002) 3222.
- [233] H.D. Selby, Z. Zheng, T.G. Gray, R.H. Holm, *Inorg. Chim. Acta* 312 (2001) 205.
- [234] H.D. Selby, P. Orto, Z. Zheng, *Polyhedron* 22 (2003) 2999.
- [235] H.D. Selby, P. Orto, M.D. Carducci, Z. Zheng, *Inorg. Chem.* 41 (2002) 6175.
- [236] H.D. Selby, B.K. Roland, M.D. Carducci, Z. Zheng, *Inorg. Chem.* 42 (2003) 1656.
- [237] A. Ranganathan, A. El-Ghayoury, C. Mézière, E. Harté, R. Clérac, P. Batail, *Chem. Comm.* (2006) 2878.
- [238] A.L. Barrès, A. El-Ghayoury, L.V. Zorina, E. Canadell, P. Auban-Senzier, P. Batail, *Chem. Comm.* (2008) 2194.
- [239] D. Mery, L. Plault, C. Ornelas, J. Ruiz, S. Nlate, D. Astruc, J.C. Blais, J. Rodrigues, S. Cordier, K. Kiracki, C. Perrin, *Inorg. Chem.* 45 (2006) 1156.
- [240] D. Mery, C. Ornelas, M.C. Daniel, J. Ruiz, D. Astruc, S. Cordier, K. Kiracki, C. Perrin, *C. R. Chimie* 8 (2005) 1789.
- [241] C.B. Gorman, W.Y. Su, H. Jiang, C.M. Watson, P. Boyle, *Chem. Commun.* (1999) 877.
- [242] T.L. Chasse, J.C. Yohannan, N.K.Q. Li, Z. Li, C.B. Gorman, *Tetrahedron* 59 (2003) 3853.
- [243] B.K. Roland, C. Carter, Z. Zheng, *J. Am. Chem. Soc.* 124 (2002) 6234.
- [244] M. Kubeil, H. Stephan, H.J. Pietzsch, G. Geipel, D. Appelhans, B. Voit, J. Hoffmann, B. Brutschy, Y.V. Mironov, K.A. Brylev, V.E. Fedorov, *Chem. Asian J.* 5 (2010) 2507.
- [245] Y. Molard, F. Dorson, V. Circu, T. Roisnel, F. Artzner, S. Cordier, *Angew. Chem. Int. Ed.* 49 (2010) 3351.
- [246] A.S. Mocanu, M. Amela-Cortes, Y. Molard, V. Circu, S. Cordier, *Chem. Comm.* 47 (2011) 2056.
- [247] J. Bäker, S. Mihm, B. Mallick, M. Yang, G. Meyer, A.V. Mudring, *Eur. J. Inorg. Chem.* 2011 (2011) 4089.
- [248] Y. Molard, A. Ledneva, M. Amela-Cortes, V. Circu, N.G. Naumov, C. Meriadec, F. Artzner, S. Cordier, *Chem. Mater.* 23 (2011) 5122.
- [249] F. Grasset, F. Dorson, S. Cordier, Y. Molard, C. Perrin, A.M. Marie, T. Sasaki, H. Haneda, Y. Bando, M. Mortier, *Adv. Mater.* 20 (2008) 143.
- [250] K. Kiracki, P. Kubát, M. Dušek, K. Fejfarová, V. Šicha, J. Mosinger, K. Lang, *Eur. J. Inorg. Chem.* 2012 (2012) 3107.
- [251] F. Grasset, F. Dorson, Y. Molard, S. Cordier, V. Demange, C. Perrin, V. Marchi-Artzner, H. Haneda, *Chem. Commun.* (2008) 4729.
- [252] T. Aubert, A.Y. Ledneva, F. Grasset, K. Kimoto, N.G. Naumov, Y. Molard, N. Saito, H. Haneda, S. Cordier, *Langmuir* 26 (2010) 18512.
- [253] L. Gao, M.A. Peay, T.G. Gray, *Chem. Mater.* 22 (2010) 6240.
- [254] J.F. Dechézelles, T. Aubert, F. Grasset, S. Cordier, C. Barthou, C. Schwob, A. Maître, R.A.L. Vallée, H. Cramail, S. Ravaine, *Phys. Chem. Chem. Phys.* 12 (2010) 11993.
- [255] F. Grasset, Y. Molard, S. Cordier, F. Dorson, M. Mortier, C. Perrin, M. Guilloux-Viry, T. Sasaki, H. Haneda, *Adv. Mater.* 20 (2008) 1710.
- [256] B. Fabre, S. Cordier, Y. Molard, C. Perrin, S. Ababou-Girard, C. Godet, *J. Phys. Chem. C* 113 (2009) 17437.
- [257] S. Ababou-Girard, S. Cordier, B. Fabre, Y. Molard, C. Perrin, *Chem. Phys. Chem.* 8 (2007) 2086.
- [258] S. Cordier, B. Fabre, Y. Molard, A.B. Fadje-Djomkam, N. Tournerie, A. Ledneva, N.G. Naumov, A. Moreac, P. Turban, S. Tricot, S. Ababou-Girard, C. Godet, *J. Phys. Chem. C* 114 (2010) 18622.
- [259] Y. Molard, F. Dorson, K.A. Brylev, M.A. Shestopalov, Y. Le Gal, S. Cordier, Y.V. Mironov, N. Kitamura, C. Perrin, *Chem. Eur. J.* 16 (2010) 5613.
- [260] M. Carthy, V. Nicolosi, D. Vengust, D. Mihailovic, G. Compagnini, W.J. Blau, J.N. Coleman, *J. Appl. Phys.* 101 (2007) 014317-1-6.
- [261] M. Remskar, A. Mrzel, M. Virsek, A. Jesih, *Adv. Mater.* 19 (2007) 4276.
- [262] D.V. Drobot, V.V. Starkov, E.A. Pisarev, Z. Neorg. Khim. 30 (1985) 1668.
- [263] V.V. Starkov, D.V. Drobot, E.A. Pisarev, Z. Neorg. Khim. 32 (1987) 557.
- [264] M. Remskar, A. Mrzel, M. Virsek, M. Godec, M. Krause, A. Kolitsch, A. Singh, A. Seabaugh, *Nanoscale Res. Lett.* 6 (2011) 26.
- [265] V. Domenici, M. Conradi, M. Remskar, M. Viršek, B. Zupančič, A. Mrzel, M. Chambers, B. Zalar, *J. Mater. Sci.* 46 (2011) 3639.
- [266] D. Mihailovic, *Prog. Mater. Sci.* 54 (2009) 309.