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Low-Dimensional Frameworks in Solid State Chemistry of Mo_6 and Re_6 Cluster Chalcohalides

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Dedicated to Professor John D. Corbett on the occasion of his 85th birthday

Keywords: Molybdenum / Rhenium / Cluster compounds / Chalcohalides / Solid state structure / Low-dimensional compounds

The low-dimensional Mo_6 and Re_6 cluster chalcohalides synthesised from solid-state reactions at high temperature are reviewed. Their crystal structures are described in terms of interunit connectivities involving inner and apical ligands shared between adjacent cluster units. It will be shown that such architectures are controlled by the geometry of the M_6L_{14} cluster units, the steric hindrance of the ligands linked to the M_6 cluster, the specific location imposed on the halogen or chalcogen ligand and the most favourable electron count on the cluster core, considering halogen and chalcogen stoichiometries.

Introduction

Nanometric building blocks are useful for the formation of low-dimensional materials if they can be connected directionally by sharing some atoms or by using additional connectors. Such crystal engineering clearly depends on the geometry of the building block and on its ability to share some ligands with adjacent units or to connect to spacers. The latter case implies the use of complexes, organic or organometallic ligands external to the precursor building block as it is frequently the case for elaboration of nanomaterials and supramolecular compounds by solution chemistry routes, for instance in metal *cluster* (according to the well accepted definition given by F. A. Cotton[1]) chemistry.[2–8] The recent developments of the latter hybrid organic/inorganic chemistry, in regards to the considerable emergence of nanosciences in recent years, has obscured some pioneering work developed in solid-state chemistry:

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here the building blocks can be connected together directly during high temperature synthesis, starting from a stoichiometric mixture of elements and/or binary compounds. The chemistry of metal clusters is of special interest from this point of view because of the specific geometry and the ability of clusters to form a variety of different connections. This is especially the case for Mo_6 and Re_6 chalcohalides described in this microreview because the presence of both halogen and chalcogen ligands with their different electronic characteristics, linked to the M_6 octahedral core, opens the way to the control of a variety of cluster connectivities by ab initio syntheses. This then gives access to tailored low dimensionality compounds. This mechanism takes place by means of the directional in situ condensation of M_6L_{14} units in one, two or three directions in space, a situation very different from the direct condensation of metallic clusters that leads, for instance, to 1D $Tl_2Mo_6Y_6$ (Y = chalcogen)[9] which is based on chains built from the Mo_6 metal cluster sharing two opposite faces of their octahedral cores.

The $M_6L^{i}_8L^{a}_6$ Building Block

The M_6 (M = Mo, Re) chalcohalides are built from the $M_6L^i_8L^a_6$ building block –inscribable in a sphere of one nanometre in diameter– in which the octahedral cluster, consisting of six metal atoms in the d^4 state (Mo^{II} or Re^{III}) linked together by metal-metal bonds, is always bonded to 14 ligands (Figure 1): this metal cluster is face-capped by eight inner ligands (noted L^i), while six apical ligands (noted L^a) are in terminal positions. This configuration builds a square-pyramidal environment of ligands around each metal atom. 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 for the first time by H. Schäfer and H. G. von Schnering[10] and is now commonly used in metal cluster chemistry. Note that owing to the difference in valency and electronegativity between the two types of ligands, in Mo_6 and Re_6 chalcohalide chemistry, the L^a and L^{a-a} positions are occupied in priority by the halogen, while L^{i-i} and L^{i-a} are occupied in priority by the chalcogen (see Table 1). The L^i position can be occupied by either halogen or chalcogen leading frequently in the averaged structural model to a random occupancy of the inner sites by both halogen and chalcogen, often described as a "rotational disorder". Indeed, the more highly charged chalcogen prefers an environment adjacent to a positively charged metal centre when compared with the less highly charged halogen.[11,12] 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.[13] Nevertheless, it should be borne in mind that for a given compound, all the cluster units M_6L_{14} building the framework possess the same stoichiometry, due to a fixed valence electronic count (VEC, see below). Exceptions are extremely rare in solid-state synthesised compounds and correspond to the presence in the structure of two types of cluster units, each of them exhibiting a fixed halogen/chalcogen ratio: for instance in the solid solution $Cs_3Mo_6I_{14-x}Se_x$ ($1.2 < x < 1.7$) where two discrete Mo_6 cluster units, $[(Mo_6I^i_7Se^i)I^a_6]^{3-}$ and $[(Mo_6I^i_6Se^i_2)I^a_6]^{3-}$ with VEC values of 24 and 23, respectively, coexist in the structure in a ratio depending on the x value,[14] or in $Rb_{2+x}Mo_6Br_{14-x}Se_x$ ($0.2 < x < 0.7$) built from the two discrete $[(Mo_6Br^i_8)Br^a_6]^{2-}$ and $[(Mo_6Br^i_7Se^i)Br^a_6]^{3-}$ units, both with a VEC value of 24, in a ratio depending on the rubidium stoichiometry.[15]

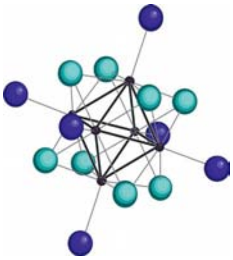

Figure 1. The $M_6L^i_8L^a_6$ cluster unit.

Table 1. Mo_6 and Re_6 chalcohalides reported in this microreview.

Compound[a]	Space group	Formula[b]	$(X\text{–}Y^i,Y^{i-i},Y^{i-a})\ Y^{a-i},X^{a-a},X^a$ [c]	Average M–M intracluster distance [Å][d]	Shorter M–M intercluster distances [Å][e]	Ref.
2-Dimensional						
$Mo_6Br_6S_3$	*Cmcm*	$[(Mo_6Br^i_4S^{i-i}_{2/2}S^{i-a}_{2/2})S^{a-i}_{2/2}Br^{a-a}_{4/2}]$	(4–0, 2, 2) 2, 4, 0	2.66	3.54; 3.53	[50]
$Re_6Se_6Cl_6$	*Cmca*	$[(Re_6\ Cl^i_2Se^i_6)Cl^{a-a}_{4/2}Cl^a_2]$	(2.6, 0, 0) 0, 4, 2	2.61	4.52; 4.52	[44]
$Re_6Se_8Cl_2$	$P\bar{1}$	$[(Re_6Se^i_4Se^{i-a}_{4/2})\ Se^{a-i}_{4/2}Cl^a_2]$	(0–4, 0, 4) 4, 0, 2	2.64	3.41; 3.44	[55]
$CsRe_6S_8Br_3$	$P2_1/n$	$[(Re_6S^i_6S^{i-a}_{2/2})S^{a-i}_{2/2}Br^{a-a}_{2/2}Br^a_2]^-$	(0–6, 0, 2) 2, 2, 2	2.60	3.25; 4.53	[63]
$TlRe_6Se_8Cl_3$	$P\bar{1}$	$[(Re_6Se^i_5Se^{i-a}_{3/2})Se^{a-i}_{3/2}Cl^a_3]^-$	(0–5, 0, 3) 3, 0, 3	2.64	3.38; 3.40; 3.46	[49]
1-Dimensional						
$Mo_6I_8Se_2$	$P6_3$	$[(Mo_6I^i_5Se^iSe^{i-i}_{2/2})I^{a-a}_{6/2}]$	(5.1, 2, 0) 0, 6, 0	2.71	3.77	[35,36]
$Re_6Se_5Cl_8$	$P\bar{1}$	$[(Re_6Cl^i_3Se^i_5)Cl^{a-a}_{2/2}Cl^a_4]$	(3.5, 0, 0) 0, 2, 4	2.61	4.47	[44]
$Cs_2Re_6S_8Br_4$	$P2_1/n$	$[Re_6(S^i_6S^{a-i}_{2/2})S^{i-a}_{2/2}Br^a_4]^{2-}$	(0–6, 0, 2) 2, 0, 4	2.60	3.25	[47]

[a] Compounds of the M_6–X–Y system, the structures of which have been determined by single-crystal X-ray diffraction. All of them exhibit a VEC value of 24. [b] Developed formula. [c] Number of ligand types per M_6L_{14} cluster unit with X = halogen and Y = chalcogen; for inner positions, the X,Y notation indicates a random halogen/chalcogen occupancy. [d] Averaged metal-metal intracluster distances. [e] 2D: shorter metal-metal intercluster distances in the layer and 1D: shorter metal-metal intercluster distances along the chain.

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Theoretical studies have been carried out by using various methods.[16–21] The molecular orbital diagram of these $M_6L^i_8L^a_6$ units is built from six ML_5 fragments in which M is in a square-pyramidal environment. The 12 highest molecular orbitals occupied by the electrons have metal-metal bonding character with a HOMO level formed by a doubly degenerated orbital with e_g symmetry, considering an ideal O_h symmetry for the M_6L_{14} unit.[16] These metal-metal bonding orbitals are completely filled for 24 valence electrons per cluster (VEC = 24) which constitutes the "magic number" in Mo_6 and Re_6 cluster chalcohalide chemistry: this number clearly corresponds to two electrons per metal-metal bond. Indeed, the M_6 chalcohalides obtained up to now by the solid-state route usually exhibit a VEC value of 24, with the exception of $Mo_6Y_{8-x}X_x$ (Y = chalcogen, X = halogen) Chevrel phase analogues for which the VEC value can be varied from 20 to 23.[22] In such compounds the quite strong interactions between the cluster units lead to a band structure causing metallic conduction when the bands are partly filled, while the other chalcohalides, in which the intercluster interactions are weaker, exhibit more discrete energy levels and then a VEC value of 24 which is associated with dielectric or semiconducting behaviour. Note that as above mentioned, extremely rare examples of compounds, in which discrete units with VEC = 24 and VEC = 23 coexist, have been isolated in solid-state chemistry. In contrast, these metal clusters, due to their oxydo-redox properties, are readily oxidised by electrochemical or soft chemical routes to give many examples of 23 VEC based compounds.[23–25]

The specific geometry and characteristics of these $M_6L^i_8L^a_6$ building blocks gave access to a great number of 3D, 2D, 1D and 0D M_6 cluster compounds widely reported in the literature: a number of review papers were published on the general chemistry of such M_6L_{14} cluster units during the last decades.[26–34] In the following discussion, we have chosen to focus on significant examples of Mo_6 and Re_6 cluster unit connectivities leading to 1D and 2D frameworks in relation to the emergence of the need for new materials in the form of nanowires or nanoplatelets for the purpose of nanotechnology research. All of them, exhibiting a VEC value of 24, have been prepared by solid-state synthesis at high temperature (800–1100 °C) and subsequently structurally characterised by single-crystal X-ray diffraction.

1D M_6 Chalcohalides

Mo_6 Chalcohalides

$Mo_6Br_8S_2$, $Mo_6I_8S_2$ and $Mo_6I_8Se_2$: Three 1D isotypical Mo_6 chalcohalides have been isolated, namely $Mo_6Br_8S_2$, $Mo_6I_8S_2$ and $Mo_6I_8Se_2$.[35,36] They are built up from $[(Mo_6X^i_5Y^iY^{i-i}_{2/2})X^{a-a}_{6/2}]$ cluster units interconnected in one direction by an inner-inner chalcogen and three associated apical-apical halogens, due to steric considerations. The six remaining inner positions are randomly occupied by one chalcogen and five halogen atoms (Figure 2). These chains are connected together by van der Waals interactions only and, in consequence, the compound crystallises in form of needles. These needles are very difficult to break along the growing axis due to the strong intercluster connections along this direction by the Y^{i-i} and X^{a-a} ligands but they are very brittle in a direction perpendicular to this axis (Figure 3).

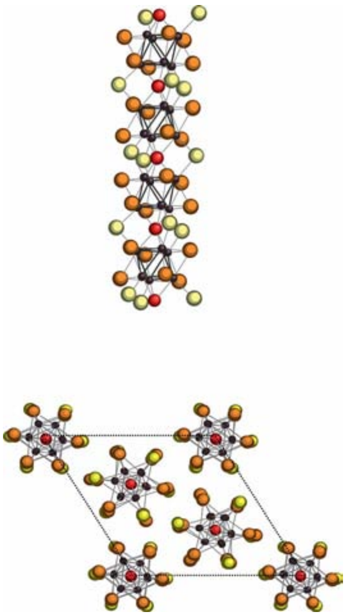

Figure 2. $Mo_6I_8Se_2$: representation of a chain of units (top) and a projection of the structure along the *c* axis (bottom). Colour code: black for Mo, red for chalcogen, yellow for halogen, orange for halogen/chalcogen in a statistical occupancy.

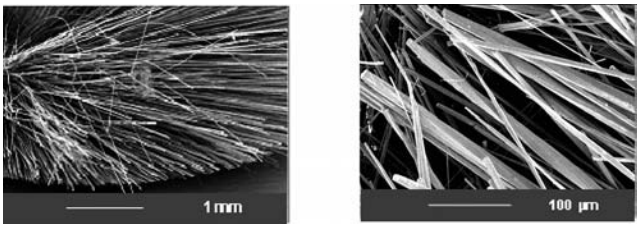

Figure 3. SEM image of $Mo_6Br_8S_2$ (left) and $Mo_6I_8S_2$ (right).

Due to these characteristics, the single-crystal X-ray structure determination performed on $Mo_6I_8Se_2$ was not very accurate, but the architecture was confirmed some years later by J. D. Corbett et al. who obtained very fibrous needles of Nb_6I_9S. A reaction in the presence of RbI or CsI gave them better single-crystals of this phase allowing an accurate X-ray structure determination leading to the $[(Nb_6I^i_6S^{i-i}_{2/2})I^{a-a}_{6/2}]$ developed formula.[37] Indeed, in the latter compound, no random halogen/chalcogen distribution was present on the inner position, giving a VEC value of 19 which is typical of Nb_6 iodide chemistry[38] and a less symmetrical unit-cell, while the 24 VEC value observed for $Mo_6I_8Se_2$ is the magic number in Mo_6 chalcohalide chemistry, giving a more symmetrical unit cell, as expected. A

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theoretical study suggested Nb_6I_9S to be a semiconductor or a semimetal along the chain direction.[39] Notice that hydrogen can be inserted in the centre of the Nb_6 cluster of the Nb_6I_9S compound[37] as in other Nb_6 iodide examples, for instance in Nb_6I_{11}.[40] This gives $(H)Nb_6I_9S$ with a VEC value of 20, whereas such hydrogen insertion in Mo_6 clusters has never been observed.

The $Mo_6I_8S_2$ fibres have been recently used as nanowires. Indeed, they can be dispersed in 2-propanol after ultrasonic debundling and sedimentation[41] for use as an alternative to carbon nanotubes for applications in nanotechnology (see ref.[42] and references cited within). An original use of these fibres was reported by M. Remskar et al. who sulfurised the $Mo_6I_8S_2$ precursor under an H_2/H_2S flow in order to obtain MoS_2 nanotubes with encapsulation of MoS_2 fullerenes inside these nanotubes.[43] Recently, the "$Mo_6S_{9-x}I_x$" ($4 < x < 6$) composition was proposed for such fibres, preferentially with $x = 6$ and 4.5, assuming the absence of the L^{i-i} ligand (see ref.[42]) that is not consistent with the general rules of M_6 cluster chemistry stating that each molybdenum atom of the M_6 cluster is always located in a square-pyramidal environment. Notice, that in contrast to a "$Mo_6S_{4.5}I_{4.5}$" or "$Mo_6I_6S_3$" composition, only the $Mo_6I_8S_2$ stoichiometry provides a pure compound when used in the starting mixture. However, a slight shift with respect to the ideal $Mo_6I_8S_2$ stoichiometry, corresponding to the formula $[(Mo_6I^i_{5-y},S^i_{1+y}S^{i-i}_{2/2})I^{a-a}_{6/2}]$, something which should maintain the shape of the fibres and the square-pyramidal environment of each molybdenum atom, cannot be ruled out. Indeed, the inner positions could be randomly occupied by either a halogen or chalcogen with a VEC < 24 for $y > 0$, the other L^{i-i} and L^{a-a} positions remaining only occupied by a chalcogen or halogen respectively (see above). But, such a hypothetical solid solution, which is difficult to evidence in solid state chemistry by powder X-ray diffraction, has not been structurally characterised up to now.

Re_6 Chalcohalides

Notice that such M_6L_{10} fibres have never been observed with Re_6 clusters: indeed, such a hypothetical architecture with the maximum chalcogen amount, taking into account the M_6 chalcohalides rules for positioning halogens and chalcogens, should be $[(Re_6Y^i_6Y^{i-i}_{2/2})X^{a-a}_{6/2}]$, corresponding to a VEC value of 25. This supposes the filling of antibonding metal-metal bands. In order to stabilise such an arrangement, it would be necessary to add one counter anion in order to obtain a VEC of 24 and this would lead to a formula such as $Re_6Y_7X_{3,}X$. Such a stoichiometry effectively exists but with a tridimensional stacking and is written as $[(Re_6Y^i_7X^i)X^{a-a}_{6/2}]$.[44,45] In place, two 1D arrangements have effectively been reported in Re_6 cluster chemistry:

$Re_6Se_5Cl_8$: The needle-shaped $Re_6Se_5Cl_8$, exhibits a crystal structure based on *trans* Cl^{a-a} bridged $[(Re_6Se^i_5Cl^i_3)Cl^{a-a}_{2/2}Cl^a_4]$ cluster units, where the chains linked together by van der Waals interactions develop in a zig zag way due to the angles of the chlorine bridges (Figure 4).[44] The eight inner positions are randomly occupied by five Se atoms and three Cl ones. The corresponding thiobromide was reported to exhibit a related structure, although not isotypical, due to a change in the halogen bridge angle.[46]

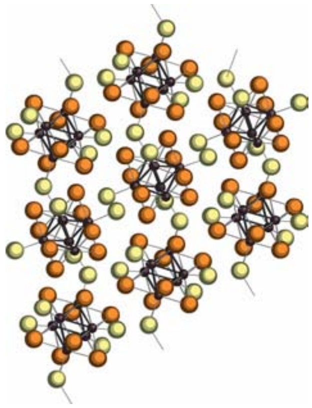

Figure 4. $Re_6Se_5Cl_8$: representation of the structure along the *c* axis. Colour code: black for Re, yellow for halogen, orange for halogen/chalcogen in a statistical occupancy.

$Cs_2Re_6S_8Br_4$: Accurate structural data were obtained for the fibrous (see Figure 5) $Cs_2Re_6S_8Br_4$[47] although it was obviously very difficult to select defect-free crystals. This structure confirms previously reported structures of $Rb_2Re_6S_8Br_4$,[46,48] $Cs_2Re_6Se_8Br_4$[11] and $Tl_2Re_6Se_8Cl_4$:[49] cluster units are linked by *trans* Y^{i-a}/Y^{a-i} double bridges, leading to linear chains $[(Re_6Y^i_6Y^{i-a}_{2/2})Y^{a-i}_{2/2}X^a_4]^{2-}$ (Figure 6) interacting together by Coulombic forces.

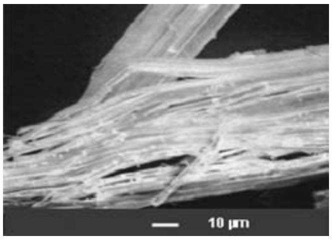

Figure 5. SEM micrograph of $Cs_2Re_6S_8Br_4$.

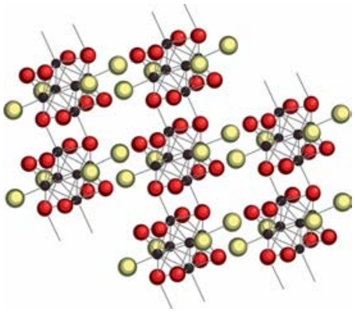

Figure 6. Representation of the chains in the structure of $Cs_2Re_6S_8Br_4$. The caesium atoms have been omitted for clarity; these atoms lie between the cluster units chains. Colour code: black for Re, red for chalcogen, yellow for halogen.

2D M_6 Chalcohalides

Mo_6 Chalcohalides

$Mo_6Br_6S_3$: With a Mo_6 cluster, a 2D architecture has been found in the Mo–S–Br system $Mo_6Br_6S_3$.[50] Up to now, no similar chalcohalide has been evidenced in the other halogen-chalcogen systems. This compound is built up from chains – similar to the ones observed in $Mo_6X_8Y_2$ – in which the $[(Mo_6Br^i{}_4S^{i-i}{}_{2/2}S^{i-a}{}_{2/2})S^{a-i}{}_{2/2}Br^{a-a}{}_{4/2}]$ cluster units are slightly tilted in order to locate two inner sulfur atoms in apical positions for the clusters of two adjacent chains giving formation of a layer by means of these S^{i-a}/S^{a-i} interunit connections (Figure 7). Cohesion of the structure is accomplished by van der Waals contacts between layers, giving to this compound a strong 2D character confirmed by its crystallisation in the shape of thin ribbons which can be easily cleaved (Figure 8). This chalcohalide could give access to platelets of nanometric thickness using a similar process reported in ref.[41]

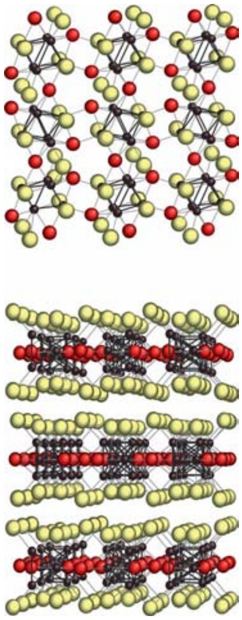

Figure 7. $Mo_6Br_6S_3$: view of a layer along the *a* axis (top) and view of three adjacent layers along the *b* axis (bottom). Colour code: black for Mo, red for chalcogen, yellow for halogen.

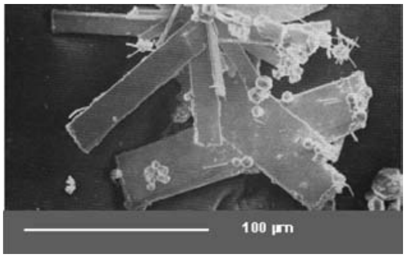

Figure 8. $Mo_6Br_6S_3$: SEM micrograph of single crystals.

This compound with a VEC value of 24 exhibits semiconducting behaviour with an activation energy of 0.02 eV calculated from resistivity measurements on a sintered pellet and 0.12 eV calculated from a single crystal measured along the direction of the growing axis of the cluster chains.[51] This difference suggests a strong anisotropy of the material.

Re_6 Chalcohalides

In place of condensation by L^{i-i} connections, unknown in Re_6 chalcohalide chemistry, three 2D Re_6 chalcohalide frameworks were evidenced based on different interunit linkages.

$Re_6Se_6Cl_6$: In the example of $Re_6Se_6Cl_6$, two pairs of Cl^{a-a} bridges develop in a plane, while the remaining apical ligands are terminal and point towards the third direction.[44,52] Such interunit connections build layers of units that are imbricated to each other perpendicularly to the layer plane (Figure 9). The eight inner positions of the cluster unit are randomly occupied by six Se and two Cl atoms. This compound, which can be written $[(Re_6Se^i{}_6Cl^i{}_2)Cl^a{}_2Cl^{a-a}{}_{4/2}]$, is in fact strictly isostructural with the binary halides M_6X_{12} (M = Mo, W) which were the first examples of octahedral clusters discovered a long time ago by C. Brosset[53] and structurally characterised by H. Schäfer et al.[54] Note that attempts to synthesise the analogous $Re_6S_6Br_6$ were unsuccessful,[46] perhaps for steric reasons.

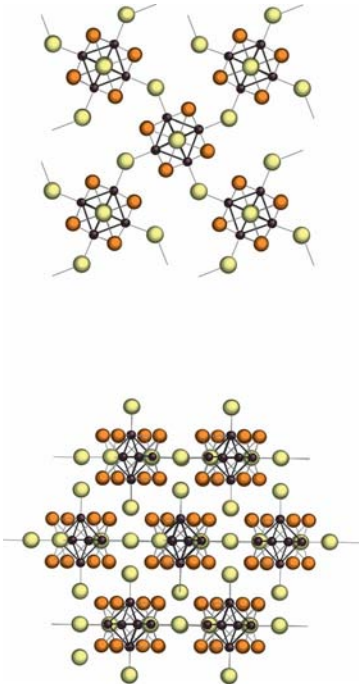

Figure 9. $Re_6Se_6Cl_6$: view of a layer along the *a* axis (top) and view of three adjacent layers along the *c* axis (bottom). Colour code: black for Re, yellow for halogen, orange for halogen/chalcogen in a statistical occupancy.

$Re_6Se_8Cl_2$: The structure of $Re_6Se_8Cl_2$ is more comparable to that of $Mo_6Br_6S_3$ while the S^{i-i} bridges are here replaced by a second pair of Se^{i-a}/Se^{a-i} bridges: it turns out that the clusters are tilted and the layers are connected only by weak van der Waals contacts implying terminal chlorines.[55] This gives to this compound, written as $[(Re_6Se^{i}_4Se^{i-a}_{4/2})Cl^{a}_2Se^{a-i}_{4/2}]$, a strong two dimensional character (Figure 10).[56]

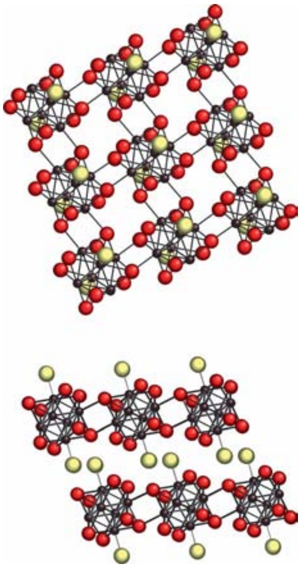

Figure 10. $Re_6Se_8Cl_2$: view of a layer (top) and view of two adjacent layers along the *c* axis (bottom). Colour code: black for Re, red for chalcogen, yellow for halogen.

Millimetre-sized single-crystals were grown (Figure 11). These are easily cleavable by the adhesive tape method and effectively exfoliated by hydrazine intercalation.[57] Transport measurements confirm an anisotropy of the resistivity of about 10^2[58] for this n type semiconductor with a direct band gap of 1.42 eV and photoconductive properties.[59]

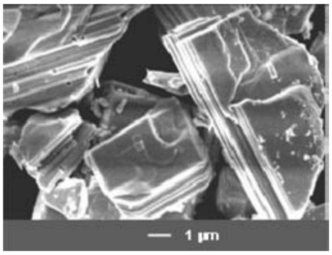

Figure 11. $Re_6Se_8Cl_2$: SEM micrograph of single crystals highlighting mica-like faces.

A solid solution was evidenced for a partial substitution of Se by S or Te[58] but a complete substitution by sulfur and/or substitution of chlorine by bromine led to a completely different structure.[60,61] The cluster units here are linked in two directions in space by halogen X^{a-a} bridges and in the third by pairs of chalcogen Y^{i-a}/Y^{a-i} double bridges. Note that the latter were omitted in ref.[60], leading erroneously to some Re atoms deprived of their apical ligand.[61] These compounds, then, are in fact actually 3D. The thiochloride $Re_6S_8Cl_2$ also exhibits this structure.[58,62]

$CsRe_6S_8Br_3$: This compound 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 forming layers of cluster units. The framework is then written $[(Re_6S^{i}_6S^{i-a}_{2/2})S^{a-i}_{2/2}Br^{a-a}_{2/2}Br^{a}_2]^-$ (Figure 12).[63] The Cs^+ counter cations are sandwiched between two layers, ensuring the structural cohesion in the third direction by electrostatic interactions. This compound is isostructural with the iodine representative $CsRe_6S_8I_3$.[11]

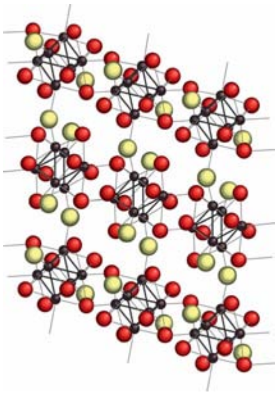

Figure 12. $CsRe_6S_8Br_3$: representation of a layer. Cs^+ counter cations lying between adjacent layers were omitted for clarity. Colour code: black for Re, red for chalcogen, yellow for halogen.

Discussion

The Mo_6 and Re_6 chalcohalides described in this review are gathered together in Table 1 with their developed formulae, the number of ligand types per cluster unit as well as the intra- and intercluster metal-metal distances observed in each compound.

We can see the diversity of interunit connections giving access to these 2D and 1D architectures which involve all the possible L^{i-i}, L^{i-a}, L^{a-i} and L^{a-a} ligands shared between adjacent units. However, owing to the geometry of the M_6L_{14} cluster units, the steric hindrance of the ligands linked to the M_6 cluster, the specific position imposed on the halogen or chalcogen ligand and the most favourable VEC of the compound considering halogen and chalcogen stoichiometries, the number of possible architectures are quite limited. All the possibilities have been systematised by A. Perricone et al.[46] albeit restricted to the case of symmetrical bridges, by J. R. Long et al.[11] in the limited case of the $(Re_6Y^{i}_8)$ cluster core and by P. Batail et al.[31] in a very general case of cluster cores. Both the latter include the possibility of odd numbers of bridges. Note that only few Mo_6 chalcohalides of low dimensionality have been isolated, while the Re_6 chalcohalide chemistry is richer due to larger possibilities of halogen/chalcogen combinations per Re_6L_{14} unit in relation to a higher number of valence electrons of the Re element when compared with Mo one (seven instead of six).

The double L^{i-a}/L^{a-i} bridge connecting two M atoms of two adjacent M_6 clusters with a short M–M intercluster distance (see Table 1) found in these chalcohalides is the same as the interunit bridges found in $A_xMo_6Y_8$ Chevrel

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phases with the $[(Mo_6Y^i_2Y^{i-a}_{6/2})Y^{a-i}_{6/2}]$ framework (A = wide variety of differently charged cations), the first cluster compounds discovered with such interunit connectivity.[64] This is different from the arrangement of the simple L^{i-a} and L^{a-i} bridges observed in several M_6L_{18} cluster compounds built from edge-bridged M_6 clusters, for instance in Nb_6Cl_{14}[65] or $CsZr_6I_{14}$,[66] that give longer M–M intercluster distances (> 4 Å).

Notice that the unit condensation by the L^{i-i} inner-inner bridge observed in the two reported Mo_6 chalcohalides is rare and, up to now, unknown in rhenium chalcohalide chemistry. However, in M_6 chalcogenide chemistry we can recall the two examples of S^{i-i} ligands in $Cs_{1.15}Mo_{12}S_{14}$ built from infinite chains connected to each other in the two other directions by S^{i-a}/S^{a-i} ligands $\{[(Mo_6S^{i-i}_{2/2}S^{i-a}_{6/2})S^{a-i}_{6/2}]$ framework$\}$[67] and in $Ba_4Mo_{12}S_{18}$ built from dimers of cluster units interconnected by S^{i-a}/S^{a-i} ligands $\{[\{(Mo_6)_2S^i_8S^{i-i}S^{i-a}_{6/2}\}S^{a-i}_{6/2}S^{a-a}_3]$ framework$\}$.[68] In Re_6 chalcogenide chemistry, the uniquely related example is $K_8[Re_{12}CS_{17}CN_6]$ in which two Re_6 clusters are connected by one C^{i-i} ligand leading to a dimeric unit.[69] This unusual compound, at the border of the scope of this microreview, is obviously zero dimensional but one can speculate on the possible formation of chains such as $(Re_6C^{i-i}_{2/2}Y^i_6)X^{a-a}_{6/2}$ in hypothetical compounds that could be formulated, for instance $ARe_6CY_6X_3$ (A = monovalent cation).

Concerning the 1D chalcohalides, the three possible connections in one direction by 2 L^{i-i}, 2 L^{a-a} or 2 (L^{i-a}/L^{a-i}) which build chains of units have been observed in $Mo_6I_8Se_2$, $Re_6Se_5Cl_8$ and $Cs_2Re_6S_8Br_4$. In all these compounds, two identical L ligands are located in the *trans* position of the cluster unit. In contrast, ligands of different types in the *trans* position have not yet been encountered, such as in the hypothetical compound "$[(M_6L^i_7L^{i-a}_{1/2})L^{a-i}_{1/2}L^{a-a}_{1/2}L^a_4]$" giving for instance $Mo_6I_{11.5}S$ or $Re_6S_8I_{4.5}$ with VEC values equal to 22.5 and 21.5, respectively. In 2D compounds, similar arrangements could be speculated. Nevertheless, the interunit connections are almost always built by pairs of identical ligands located in a *trans* position of the cluster unit. This observation is in agreement with the systematisation of J. R. Long et al. on the possible connectivities between M_6 cluster units which indicates that mainly chalcohalides with pairwise connectivity have been experimentally observed.[11] However, an exception should be reported: the 2D $TlRe_6Se_8Cl_3$ built from layers $[(Re_6Se^i_5Se^{i-a}_{3/2})Se^{a-i}_{3/2}Cl^a_3]^-$ in which one cluster unit is linked to three others by three Se^{i-a}/Se^{a-i} bridges (Figure 13).[49]

These three bridges are located on one side of the cluster unit while the three apical chlorines are located on the opposite side giving a *fac* geometry to this arrangement which is very rare in M_6 cluster solid-state chemistry. However, few examples of *fac* isomers have been reported in the literature in hybrid organic/inorganic Re_6 cluster compounds, for instance in $[(n\text{-}C_4H_9)_4N][fac\text{-}Re_6Se^i_8(PEt_3)^a_3I^a_3]$,[70] *fac*-$Re_6S^i_7Br^i(PPh_3)^a_3Br^a_3$[71] or in *fac*-$Re_6Y^i_7Br^i(Pyz)^a_3Br^a_3\cdot xH_2O$ (Y = S, Se).[72] However it is noteworthy that all these compounds were obtained by "soft" chemistry.

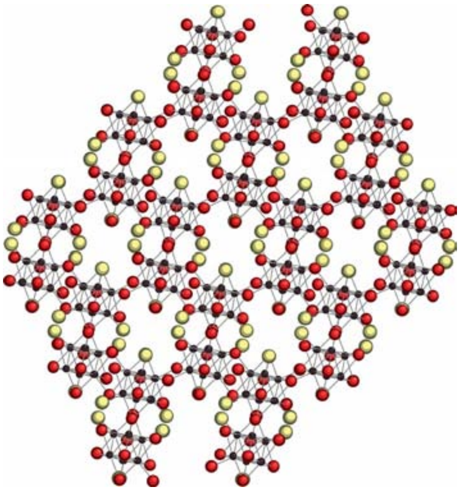

Figure 13. $TlRe_6Se_8Cl_3$: representation of a layer (redrawn from ref.[49]). Colour code: black for Re, red for chalcogen, yellow for halogen.

Table 1 also gives the average M–M intracluster distances for the given structures. All of them correspond to a Pauling bond order PBO[73] close to 1. The matrix effect, defined by J. D. Corbett as metal-metal separation being dictated by ligand-ligand contact distance[74] is then quite small in these M_6L_{14} clusters. In fact, the cluster deformability was calculated to be about 2% in the example of Mo_6L_{14} clusters when going from smaller (Cl^-) to a larger (I^-) inner ligand.[12]

Intercluster M–M distances are obviously strongly dependent on the connectivity mode: they are in the range 3.2–3.5 Å for double Y^{i-a}/Y^{a-i} bridges and around 4.5 Å for X^{a-a} bridges depending of course on the ligand size. Y^{i-i} associated with X^{a-a} ligands is a special case: values as different as 3.54 and 3.77 Å are obviously related to different ligand sizes. M–M distances between chains or layers are typically about 6 Å or even more. Other significant distances, namely M–X^i and M–Y^i are not discussed here, due to the wide distribution of examples. Notice that there is a general trend for M–X^a distances to increase significantly with the anionic charge of $[M_6L_{14}]^{n-}$ unit, as calculated[12,75] and observed[75,76] in a wide series of Re_6 chalcohalides.

Conclusions

In this microreview, restricted to 1D and 2D Mo_6 and Re_6 octahedral cluster chalcohalides, we have gathered the various possibilities of building chains or layers of cluster units by sharing different ligand types between the units considered as building blocks. Obviously, the mode of connectivity is limited by the general rules governing the architecture of individual cluster units, the preference for a given ligand to form a specific bridge and also by steric hindrance of ligands. In summary, 1D compounds can be built either from L^{a-a}, L^{i-a} or L^{i-i} bridges: all the corresponding examples are already known. In the case of 2D connectivity, the possibilities are larger:

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– two pairs of $L^{a–a}$ bridges
– one pair of $L^{a–a}$ and one pair of $L^{i–a}$
– two pairs of $L^{i–a}$
– one pair of $L^{i–i}$ (associated to intrachain $L^{a–a}$) and one pair of $L^{i–a}$.
– one pair of $L^{i–i}$ and one pair of $L^{a–a}$

All these connectivities were reported with the exception of the last one and this is because, due to unit geometry, the formation of a $L^{i–i}$ bridge implies the associated creation of $L^{a–a}$ bonds along the chain. As a general rule, all these interconnections are symmetrical and then involve an even number of identical ligands. Exceptions are very rare in solid-state chemistry and are more often encountered in solution chemistry.

Based on these observations, a number of formulae can be imagined. Examining for instance the data reported by Perricone et al.[46] (given for the example of the A–Re–S–Br system; A = alkaline) a number of expected phases have been reported. However, some additional observations can be made: i) several compositions (calculated from valency balance and VEC number) lead to isomers, refer for instance to $ARe_6S_8Br_3$ which could be written either as 1D $[(Re_6S_8)Br^{a–a}{}_{6/2}]^-$ or 2D $[(Re_6S^i{}_6S^{i–a}{}_{2/2})S^{a–i}{}_{2/2}Br^{a–a}{}_{2/2}Br^a{}_2]^-$. Only the second connectivity was reported. Similar behaviour was observed for $A_2Re_6S_8Br_4$. These two examples suggest that the $S^{i–a}/S^{a–i}$ double bridges could be more stable than the $Br^{a–a}$ simple bridge; ii) compounds $ARe_6Y_6X_7$ and $A_2Re_6Y_7X_6$, for which only a developed formula based on $X^{a–a}$ bridges can be written, have not been fully structurally characterised although they have been detected a long time ago in $AgRe_6Se_6Cl_7$ and $ZnRe_6Se_7Cl_5$;[77] iii) the compounds $ARe_6Y_7X_5$ (2D or 1D according to two possible developed formulae) have not been observed for reasons not yet understood.

Finally, all the compounds reported here originate from solid-state chemistry and were synthesised ab initio from elements and/or binary compounds. An alternative approach to control the dimensionality of such cluster based materials, based on solution chemistry, has quickly emerged in recent years. The general idea is to start from (soluble) 0D compounds, eventually obtained by dimensional reduction[11,30] (or excision) of solid-state condensed compounds, to functionalise some apical ligands and treat them with a well chosen bidentate ligand in order to rebuilt polymeric species. Prominent examples involve inorganic chemistry or organic ligands in order to rebuilt 1D or 2D compounds – many polymeric species were reported by V. E. Fedorov et al.[78] and J. R. Long et al.[79] starting mainly from cyano functionalised clusters coordinated to transition metal complexes. This approach is illustrated, for instance, by 1D $[Ni(NH_3)_2(en)_2]_2[\{Ni(NH_3)_4\}Re_6Se_8(CN)_6]Cl_2,2H_2O$ (linear chains) or 1D $[\{Mn(H_2O)(\mathit{en}_2)\}][Mn(\mathit{en}_2)Re_6Te_8(CN)_6],3H_2O$ (zig zag chain) and 2D $(NH_4)_2[\{Ni(\mathit{en})_2\}_3\{Re_6Te_8(CN)_6\}_2]$, $6H_2O$ (wavy layers).[80] A comparable polymerisation scheme occurs from hexahydroxo rhenium clusters.[81]

Organic ligands were extensively used by Z. Zheng et al.[82] and can act by means of hydrogen bonding {example of linear 1D $[(M_6Se_8)(PEt_3)_4(\text{isocotinamide})_2]^{2+}$[82]} or can be mediated by secondary metal coordination, as above, in the example of 4,4′-dipyridyl ligands.[82] Although dimers based on the *trans* linkage of two clusters by ditopic 4-pyridyl, for instance $[\{Re_{12}Se_{16}(PEt)_3\}_{10}(4,4'\text{-bpy})]^{4+}$, were reported,[25] we have no knowledge of extended polymerisation that would produce 1D chains by direct linkage by such bidentate organic ligands. Maybe the reason is purely technical, as such species are expected to quickly precipitate from solution without allowing the growth of single crystals suitable for structure determination.

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[1] F. A. Cotton, *Inorg. Chem.* **1964**, *3*, 1217–1220.
[2] M. P. Shores, L. G. Beauvais, J. R. Long, *Inorg. Chem.* **1999**, *38*, 1648–1649.
[3] N. G. Naumov, S. B. Artemkina, A. V. Virovets, V. E. Fedorov, *J. Solid State Chem.* **2000**, *153*, 195–204.
[4] H. D. Selby, Z. Zheng, T. G. Gray, R. H. Holm, *Inorg. Chim. Acta* **2001**, *312*, 205–209.
[5] S. Jin, F. J. DiSalvo, *Chem. Mater.* **2002**, *14*, 3448–3457.
[6] H. Zhou, A. Lachgar, *Cryst. Growth Des.* **2006**, *6*, 2384–2391.
[7] Z. Zheng, X. Tu, *CrystEngComm* **2009**, *11*, 707–719.
[8] Y. Molard, F. Dorson, V. Circu, T. Roisnel, F. Artzner, S. Cordier, *Angew. Chem.* **2010**, *122*, 1–6.
[9] M. Potel, R. Chevrel, M. Sergent, *Acta Crystallogr., Sect. B* **1980**, *36*, 1545–1548.
[10] H. Schäfer, H. G. von Schnering, *Angew. Chem.* **1964**, *76*, 833–849.
[11] J. R. Long, L. S. McCarty, R. H. Holm, *J. Am. Chem. Soc.* **1996**, *118*, 4603–4616.
[12] E. Levi, D. Aurbach, *Chem. Mater.* **2011**, *23*, 1901–1914.
[13] W. Bronger, C. Koppe, D. Schmitz, *Z. Anorg. Allg. Chem.* **1997**, *623*, 239–242.
[14] K. Kirakci, S. Cordier, A. Shames, B. Fontaine, O. Hernandez, E. Furet, J.-F. Halet, R. Gautier, C. Perrin, *Chem. Eur. J.* **2007**, *13*, 9608–9616.
[15] K. Kirakci, S. Cordier, O. Hernandez, T. Roisnel, C. Perrin, *J. Solid State Chem.* **2005**, *178*, 3117–3129.
[16] T. Hugbanks, R. Hoffmann, *J. Am. Chem. Soc.* **1983**, *105*, 1150–1162.
[17] A. Deluzet, H. Duclusaud, P. Sautet, S. A. Borshch, *Inorg. Chem.* **2002**, *41*, 2537–2542.
[18] T. G. Gray, C. M. Rudzinski, E. E. Meyer, R. H. Holm, D. G. Nocera, *J. Am. Chem. Soc.* **2003**, *125*, 4755–4770.
[19] T. G. Gray, *Chem. Eur. J.* **2009**, *15*, 2581–2593.
[20] H. Honda, T. Noro, K. Tanaka, E. Miyoshi, *J. Chem. Phys.* **2001**, *114*, 10791–10797.
[21] B. Fontaine, R. Gautier, G. Pilet, S. Cordier, C. Perrin, A. Perrin, Yu. V. Mironov, *J. Cluster Sci.* **2009**, *20*, 145–151.
[22] M. Sergent, O. Fischer, M. Decroux, C. Perrin, R. Chevrel, *J. Solid State Chem.* **1977**, *22*, 87–92.

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[23] N. G. Naumov, E. V. Ostanina, A. V. Virovets, M. Schmidtman, A. Müller, V. E. Fedorov, *Russ. Chem. Bull., Int. Ed.* **2002**, *51*, 866–871.

[24] J.-C. P. Gabriel, K. Boubekeur, P. Batail, *Inorg. Chem.* **1993**, *32*, 2894–2900.

[25] Z. Zheng, T. G. Gray, R. H. Holm, *Inorg. Chem.* **1999**, *38*, 4888–4895.

[26] A. Simon, *Angew. Chem.* **1988**, *100*, 163; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 159–183.

[27] S. C. Lee, R. H. Holm, *Angew. Chem.* **1990**, *102*, 868; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 840–856.

[28] T. G. Gray, *Coord. Chem. Rev.* **2003**, *243*, 213–235.

[29] T. Saito, *J. Chem. Soc., Dalton Trans.* **1999**, 97–105.

[30] E. G. Tulsky, J. R. Long, *Chem. Mater.* **2001**, *13*, 1149–1166.

[31] J.-C. P. Gabriel, K. Boubekeur, S. Uriel, P. Batail, *Chem. Rev.* **2001**, *101*, 2037–2066.

[32] C. Perrin, M. Sergent, *J. Less-Common Met.* **1986**, *123*, 117–133.

[33] A. Perrin, M. Sergent, *New J. Chem.* **1988**, *12*, 337–356.

[34] A. Perrin, C. Perrin, M. Sergent, *J. Less-Common Met.* **1988**, *137*, 241–267.

[35] C. Perrin, M. Sergent, *J. Chem. Res. Synop.* **1983**, *2*, 38–39.

[36] C. Perrin, M. Sergent, *J. Chem. Res. Miniprint* **1983**, 449–464.

[37] H.-J. Meyer, J. D. Corbett, *Inorg. Chem.* **1991**, *30*, 963–967.

[38] A. Simon, H. G. von Schnering, H. Schäfer, *Z. Anorg. Allg. Chem.* **1967**, *355*, 295–310.

[39] H.-J. Meyer, J. D. Corbett, *Inorg. Chem.* **1992**, *31*, 4276–4280.

[40] H. Imoto, A. Simon, *Inorg. Chem.* **1982**, *21*, 308–319.

[41] D. Mc Carthy, V. Nicolosi, D. Vengust, D. Mihailovic, G. Compagnini, W. J. Blau, J. N. Coleman, *J. Appl. Phys.* **2007**, *101*, 014317–1–6.

[42] D. Mihailovic, *Prog. Mater. Sci.* **2009**, *54*, 309–350.

[43] M. Remskar, A. Mrzel, M. Virsek, A. Jesih, *Adv. Mater.* **2007**, *19*, 4276–4278.

[44] A. Perrin, L. Leduc, M. Sergent, *Eur. J. Solid State*, *Inorg. Chem.* **1991**, *28*, 919–931.

[45] C. B. Pinheiro, N. L. Speziali, H. Berger, *Acta Crystallogr., Sect. C* **1997**, *53*, 1178–1180.

[46] A. Perricone, A. Slougui, A. Perrin, *Solid State Sci.* **1999**, *1*, 657–666.

[47] G. Pilet, A. Perrin, *Solid State Sci.* **2004**, *6*, 109–116.

[48] A. Slougui, *PhD Thesis*, Rennes, France, **1998**.

[49] J. R. Long, A. S. Williamson, R. H. Holm, *Angew. Chem.* **1995**, *107*, 248; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 226–229.

[50] C. Perrin, M. Potel, M. Sergent, *Acta Crystallogr., Sect. C* **1983**, *39*, 415–418.

[51] C. Perrin, *Doctorat d'Etat ès Sciences Physiques*, Rennes, **1981**.

[52] L. Leduc, A. Perrin, M. Sergent, *C. R. Acad. Sci.* **1983**, *II-296*, 961–966.

[53] C. Brosset, *Arkiv. Kem. Mineralog. A* **1945**, *20*, no. 7.

[54] H. Schäfer, H. G. von Schnering, J. Tillack, F. Khunen, H. Wöhrle, H. Baumann, *Z. Anorg. Allg. Chem.* **1967**, *353*, 281–310.

[55] L. Leduc, A. Perrin, M. Sergent, *Acta Crystallogr., Sect. C* **1983**, *39*, 1503–1506.

[56] D. Dorignac, Z. G. Li, B. Jouffrey, L. Leduc, A. Perrin, M. Sergent, *J. Microsc. Spectrosc. Electron.* **1984**, *9*, 6a.

[57] D. Dorignac, Z. G. Li, A. Perrin, *J. Microsc. Spectrosc. Electron.* **1986**, *11*, 27a.

[58] L. Leduc, J. Padiou, A. Perrin, M. Sergent, *J. Less-Common Met.* **1983**, *95*, 73–80.

[59] N. Lenagard, A. Perrin, M. Sergent, C. Levy-Clément, *Mater. Res. Bull.* **1985**, *20*, 835–843.

[60] N. L. Speziali, H. Berger, G. Leicht, R. Sanjinés, G. Chapuis, F. Lévy, *Mater. Res. Bull.* **1988**, *23*, 1597–1604.

[61] C. Fisher, N. Alonso-Vante, S. Fiechter, H. Tributsh, G. Reck, W. Schulz, *J. Alloys Compd.* **1992**, *178*, 305–314.

[62] C. Fischer, S. Fiechter, H. Tributsch, G. Reck, B. Schultz, *Ber. Bunsen Ges. Phys. Chem.* **1992**, *96*, 1652–1658.

[63] G. Pilet, O. Hernandez, A. Perrin, *Z. Kristallogr. New Cryst. Struct.* **2002**, *217*, 11–12.

[64] R. Chevrel, M. Sergent, *Topics in Current Physics Superconductivity in Ternary Compounds I* (Eds.: M. B. Maple, O. Fischer), Springer-Verlag, Berlin, Heidelberg, New York, **1982**, chapter 2.

[65] A. Simon, H.-G. von Schnering, H.-G. Wöhrle, H. Schäfer, *Z. Anorg. Allg. Chem.* **1965**, *339*, 155–170.

[66] D. H. Guthrie, J. D. Corbett, *Inorg. Chem.* **1982**, *21*, 3290–3295.

[67] P. Gougeon, D. Salloum, J. Cuny, L. Le Pollès, M. Le Floch, R. Gautier, M. Potel, *Inorg. Chem.* **2009**, *48*, 8337–8341.

[68] D. Salloum, R. Gautier, M. Potel, P. Gougeon, *Angew. Chem.* **2005**, *117*, 1387; *Angew. Chem. Int. Ed.* **2005**, *44*, 1363–1365.

[69] Yu. V. Mironov, N. G. Naumov, S. G. Kozlova, S.-J. Kim, V. E. Fedorov, *Angew. Chem.* **2005**, *117*, 7027; *Angew. Chem. Int. Ed.* **2005**, *44*, 6867–6871.

[70] Z. Zheng, J. R. Long, R. H. Holm, *J. Am. Chem. Soc.* **1997**, *119*, 2163–2171.

[71] M. A. Shestopalov, Yu. V. Mironov, K. A. Brylev, S. G. Kozlova, V. E. Fedorov, H. Spies, H.-J. H. Pietzsch, H. Stephan, G. Geipel, G. Bernhard, *J. Am. Chem. Soc.* **2007**, *129*, 3714–3721.

[72] M. A. Shestopalov, S. Cordier, O. Hernandez, Y. Molard, C. Perrin, A. Perrin, V. E. Fedorov, Yu. V. Mironov, *Inorg. Chem.* **2009**, *48*, 1482–1489.

[73] L. Pauling, *The Nature of The Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, N. Y., **1960**, pp. 403–410.

[74] J. D. Corbett, *J. Solid State Chem.* **1981**, *37*, 335–351.

[75] S. Uriel, K. Boubaker, P. Batail, J. Orduna, E. Canadell, *Inorg. Chem.* **1995**, *34*, 5307–5313.

[76] A. Slougui, A. Perrin, M. Sergent, *J. Solid State Chem.* **1999**, *147*, 358–365.

[77] L. Leduc, *PhD Thesis*, Rennes, **1983**.

[78] N. G. Naumov, A. V. Virovets, V. E. Fedorov, *J. Struct. Chem.* **2000**, *41*, 499–520.

[79] L. G. Beauvais, M. P. Shores, J. R. Long, *Chem. Mater.* **1998**, *10*, 3783–3786.

[80] K. A. Brylev, G. Pilet, N. G. Naumov, A. Perrin, V. E. Fedorov, *Eur. J. Inorg. Chem.* **2005**, *3*, 461–466.

[81] Yu. V. Mironov, V. E. Fedorov, H. Bang, S. J. Kim, *Eur. J. Inorg. Chem.* **2006**, *3*, 553–557.

[82] H. D. Selby, B. K. Roland, Z. Zheng, *Acc. Chem. Res.* **2003**, *36*, 933–944.

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