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Octahedral clusters in transition element chemistry

Christiane Perrin*

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Avenue du Général Leclerc, 35042 Rennes Cedex, France

Abstract

The various ways of condensation of the two different units based on Me_6 clusters, the face-capped Me_6L_{14} or the edge-capped Me_6L_{18}, are presented and illustrated by significant examples of the Mo_6 and Nb_6 chemistry, respectively. During the condensation process, the molecular character of the compounds based on Me_6L_{14} units decreases, while it is maintained in the compounds based on Me_6L_{18} units due to the important steric effects of the 18 ligands in the latter case. The physical properties of compounds based on such units are strongly dependent on the degree of their molecular character and on the filling of the electronic levels; electron deficiency may produce either metallic conductivity for compounds based on strongly interacting units, or paramagnetic behaviour due to unpaired electrons when the units are isolated. © 1997 Elsevier Science S.A.

1. Introduction

A *cluster* can be defined as an aggregate of metallic atoms with finite dimensions and high symmetry, in which the metallic atoms are linked together by metal–metal bonds. In the cluster core, the distances between the metallic atoms are close to the distances in the metal bulk. In transition element chemistry, the clusters are formed when the non-metal/metal ratio is below that needed for the preferred coordination number of the metal, when the *d*-orbitals are relatively large and when some valence electrons are available for the metal–metal bonds. The cluster is encapsulated in a shell of surrounding ligands, thus forming a unit: e.g. a Mo_4 tetrahedral cluster is bounded to four sulfur atoms, giving the Mo_4S_4 unit present in $Mo_4S_4Br_4$ [1]. These units are neutral or charged and they constitute the building blocks of a variety of crystal structures. The cohesion of the structures is made either by coulombic interactions between the countercations and the anionic units, or by ligands shared between adjacent units, or by Van der Waals interactions between the units when they are neutral. In a given structure, several of these various connections can occur simultaneously. All of these features lead to a large variety of different unit stackings in the cluster-based materials, giving original structure types with sometimes anisotropic character.

In the organometallic chemistry of transition elements the clusters are mainly formed with electron-rich elements and the ligands are frequently carbonyl or phosphine groups [2]. These clusters can be triangles, tetrahedra, octahedra or other aggregates of more complex geometry. A spherical condensation of clusters can occur giving large clusters. In contrast, in solid-state chemistry of transition elements, the clusters are formed with electron-poor elements and the ligands are frequently halogens or chalcogens; they can be also triangles, tetrahedra, octahedra or other types of relatively small clusters. The octahedra can be condensed by their apexes, edges or faces, thus giving frequently anisotropic compounds [2].

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* Corresponding author.

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Following the pioneering works of Brosset [3] and Pauling [4] on the octahedral clusters, their study has been extensively developed over the past 50 years. In this review we have chosen to focus on octahedral clusters of early transition elements in solid-state chemistry, which appear in two different types of units, and we will compare the progressive condensation of these units and the evolution of the related physical properties. For this purpose we will detail the Mo_6, Nb_6 and Ta_6 cluster chemistry and we will give some short comparisons with W_6, Re_6 and Zr_6 clusters, including both old results and more recent developments.

2. The octahedral clusters in Me_6L_{14} or Me_6L_{18} units

2.1. Differences in the formation of Me_6L_{14} or Me_6L_{18} units

In the solid state chemistry of transition elements, the octahedral clusters appear in two different units, i.e. Me_6L_{14} unit and Me_6L_{18} unit.

In the Me_6L_{14} unit, the cluster is face-capped by eight inner ligands (L^i); six additional apical ligands (L^a) are located on the quaternary axes of the octahedron (Fig. 1a). Such a unit is formed with Mo, W, Re and Tc. The highest levels occupied by the electrons are represented on the Fig. 1b; the HOMO level exhibits an e_g symmetry. These levels have a metal–metal bonding character and are fully occupied for 24 valence electrons per cluster, which corresponds to 12 two-electrons–two-centers bonds. The filling of these metal–metal bonding levels by the electrons is called VEC (Valence Electron Concentration) per Me_6 cluster. It corresponds to the number of electrons involved in the metal–metal bonding states after the charge transfer from the cations to the cluster and from the cluster to the ligands has been accounted for.

In the Me_6L_{18} unit, the cluster is edge-capped by 12 inner ligands; six additional apical ligands are located like in the Me_6L_{14} unit (Fig. 2a). These units are favored with lower *d*-electron concentration than for Me_6L_{14} units and they are formed with rare earths, Zr, Nb, Ta, Th. The highest levels occupied by the electrons in this unit are represented in Fig. 2b; the HOMO level has an a_{2u} symmetry. These levels are fully occupied by 16 valence electrons only, which corresponds to eight two-electron—three-center bonds. It must be pointed out that in the case of very poor valence electron transition elements like the rare earths, Zr and Th, an interstitial element which participates to the metal–metal bonding states, is necessary in order to stabilize the octahedral cluster. In this review, we will not consider these octahedral clusters filled with interstitial elements, except for a few significant examples taken from the zirconium chemistry.

2.2. Condensation of the Me_6L_{14} or Me_6L_{18} units

The Me_6L_{14} or Me_6L_{18} units can condense by

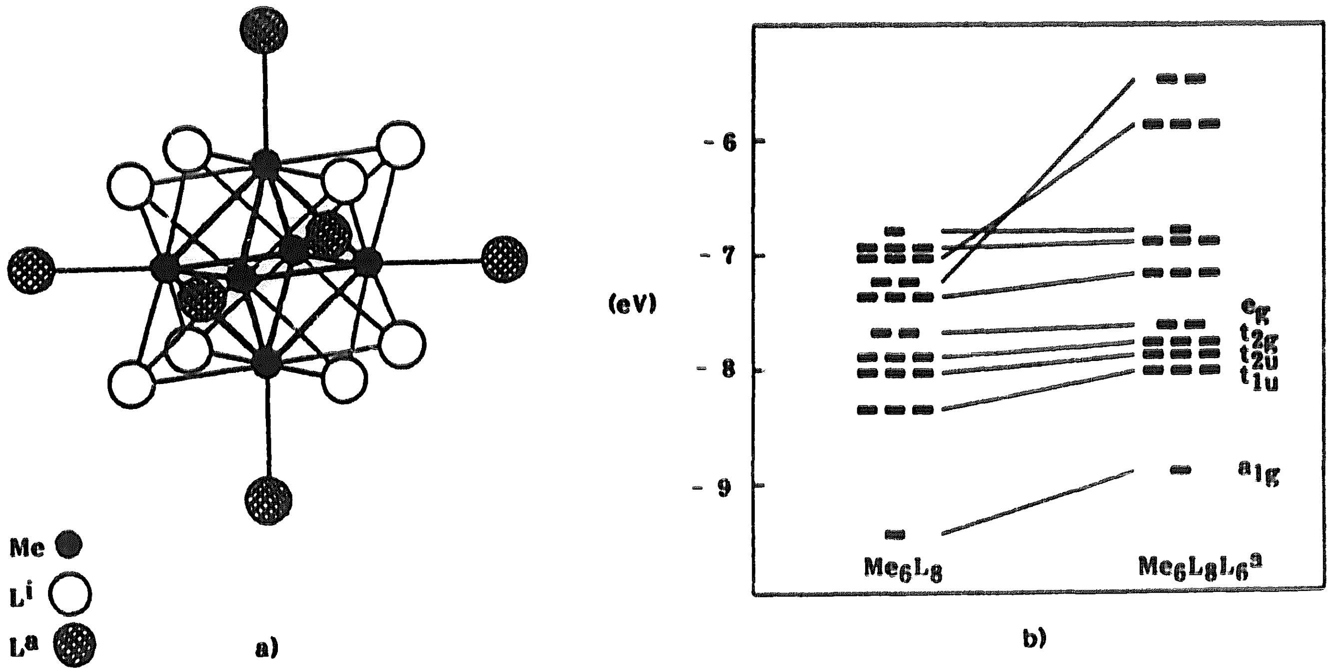


Fig. 1. (a) The Me_6L_{14} unit: representation of the inner and apical ligands. (b) Energy level diagram for the metal-centered orbitals of Me_6L_{14} unit: influence of the apical ligands. The metal–metal bonding orbitals are labelled. According to Simon et al. [5].

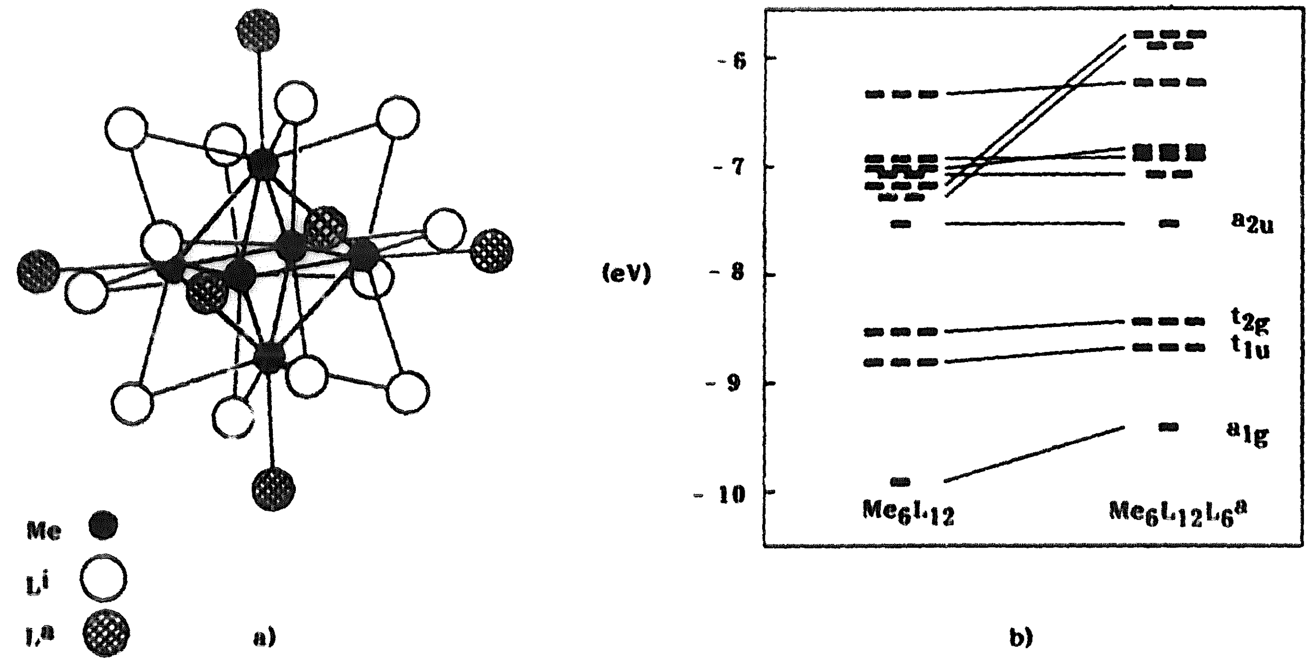


Fig. 2. (a) The Me_6L_{18} unit: representation of the inner and apical ligands. (b) Energy level diagram for the metal centered orbitals of Me_6L_{18} unit: influence of the apical ligands. The metal–metal bonding orbitals are labelled. According to Simon et al. [5].

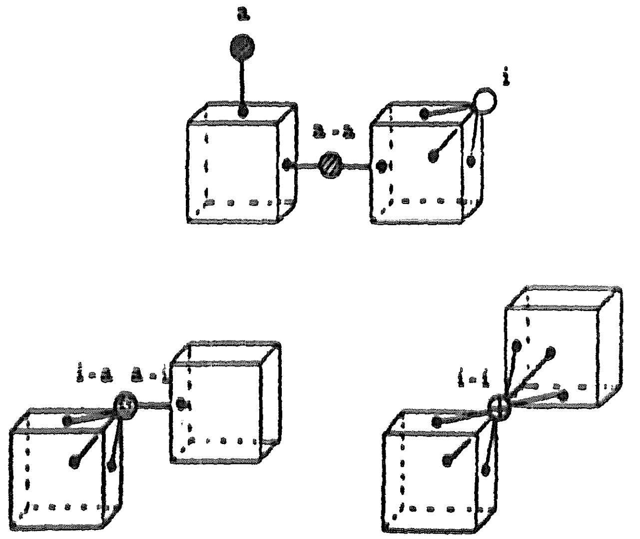


Fig. 3. Schematic representation of the unit condensation according to H. Schäfer and H.G. von Schnering notation [6].

sharing ligands (Fig. 3). A ligand in apical position or in inner position for two adjacent clusters is noted L^{a-a} or L^{i-i}, respectively; a ligand in inner position for a cluster and in apical position for the adjacent cluster is noted L^{i-a} for the first cluster and L^{a-i} for the adjacent one. This notation has been proposed for the first time by Schäfer and von Schnering [6] and is very useful for schematic description of all the structures based on these two types of units.

3. Progressive condensation of the Me_6L_{14} units in the molybdenum chemistry

In the Me_6L_{14} units, the steric effect of the inner ligand shell is not too important and it is possible to easily condense them at first by the apical ligands and then by the inner ligands. This condensation can be illustrated by significant examples taken in the molybdenum halides, chalcohalides and chalcogenides chemistry [7]. It is controlled by progressively changing the total number of anions per Mo_6 cluster (n). During this process the VEC = 24 is usually maintained. For instance, in the halides, any decrease in n is related to a decrease in the cationic charge; in the chalcohalides a decrease in n is obtained by progressively replacing two halogens by a chalcogen. But, as described above, the Mo_6 cluster remains always surrounded by 14 ligands. Then, during the condensation, an increasing number of ligands will be shared between adjacent units: at first apical ligands and then, when all the apical ligands are shared, the inner ligands start to be involved in the condensation.

3.1. *Compounds in which the molecular character is retained*

An example of the first term of this series is represented in Fig. 4: $PbMo_6Cl_{14}$ (n = 14) [8], in which the units are discrete. The next steps (Figs. 4b–d) illustrate the condensation of the Me_6L_{14} units by apical ligands (L^{a-a}) in one, two and finally three directions of the space for the typical representative compounds $AgMo_6Cl_{13}$ (n = 13) [8], Mo_6Cl_{12} (n = 12) [9] and $Mo_6Cl_{10}Se$ (n = 11) [10], respectively. When the six apical ligands are shared between adjacent units, the inner ligands (L^{i-i}) start to be involved in the condensation giving the one-dimensional $Mo_6I_8Se_2$ (n = 10)

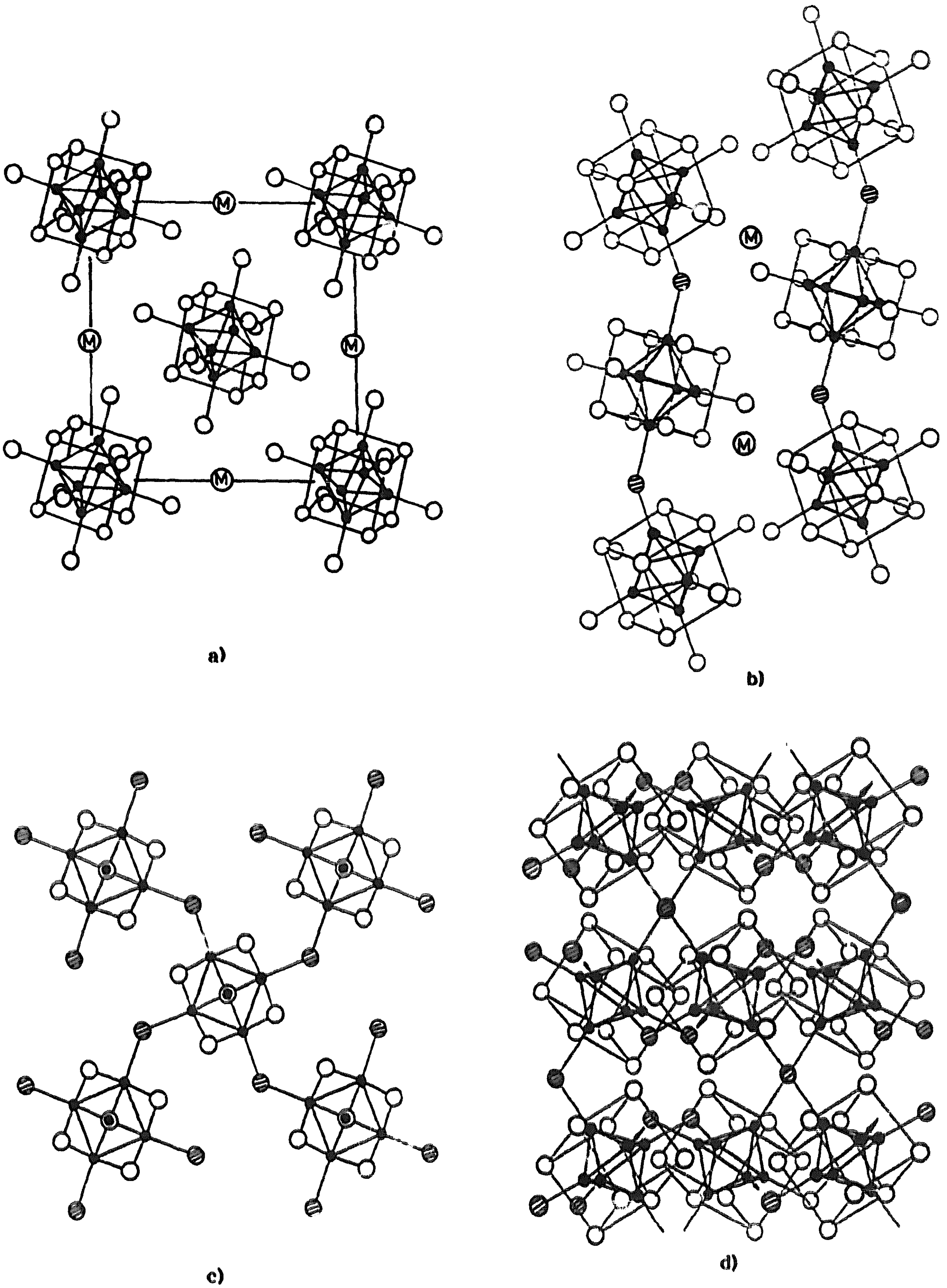


Fig. 4. Increasing condensation of the Mo_6L_{14} units via L^{a-a} ligands in Mo_6 halides and chalcohalides. Examples of: (a) $n = 14$, $PbMo_6Cl_{14}$ ($PbMo_6Cl^i_8Cl^a_6$); (b) $n = 13$, $AgMo_6Cl_{13}$ ($AgMo_6Cl^i_8Cl^a_4Cl^{a-a}_{2/2}$); (c) $n = 12$, Mo_6Cl_{12} ($Mo_6Cl^i_8Cl^a_2Cl^{a-a}_{4/2}$); and (d) $n = 11$, $Mo_6Cl_{10}Se$ ($Mo_6Cl^i_7Se^iCl^{a-a}_{6/2}$).

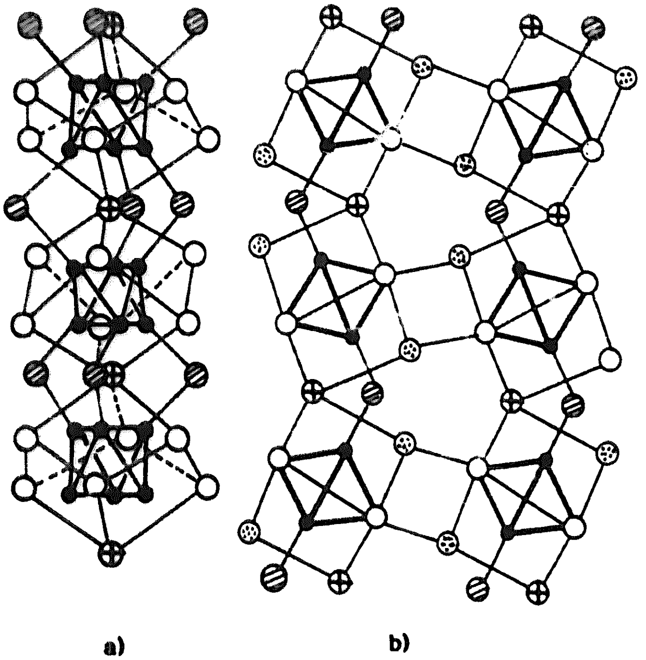


Fig. 5. Increasing condensation of the Mo_6L_{14} units via L^{a-a}, L^{i-i} and L^{i-a} ligands in Mo_6 chalcohalides. Examples of: (a) $n = 10$, $Mo_6I_8Se_2$ ($Mo_6I^i_5Se^iSe^{i-a}_{2/2}I^{a-a}_{6/2}$); and (b) $n = 9$, $Mo_6Br_6S_3$ ($Mo_6Br^i_4S^{i-i}_{2/2}S^{i-a}_{2/2}S^{a-i}_{2/2}Br^{a-a}_{4/4}$).

[11] and the two-dimensional $Mo_6Br_6S_3$ ($n = 9$) [12] compounds, both based on chains of Me_6L_{14} units, at first isolated and then connected by inner-apical ligands (L^{i-a}) in one direction of the space, respectively (Figs. 5a,b).

In all of these compounds, the clusters are far from each other and cannot interact. The molecular character is retained and these compounds are of course insulating materials. Their VEC is always 24, so the clusters are non-magnetic. When a halogen/chalcogen statistical distribution occurs, like in $Mo_6Cl_{10}Se$ (one Se occupying statistically one of the eight inner positions) or in $Mo_6I_6Se_2$ (one Se statistically located on the six available inner positions), the unit acts as a permanent dipole due to the local dissymmetry of the anionic charges around the cluster. In such cases, dielectric relaxations can be observed as illustrated in Fig. 6 for the $Mo_6Cl_{10}Y$ (Y = S, Se or Te) series, where peaks of $\epsilon'' = f(T)$ appear clearly [10].

3.2. Compounds in which the molecular character is greatly reduced

A further condensation ($n = 8$) is obtained for $Mo_6Br_2S_6$ [13], isotypic with Chevrel phases [14], in which the units are condensed by six L^{i-a} extending in the three directions of the space (Fig. 7a). In this specific stacking of the units, the clusters are close to each other and they can interact. Then, the molecular character is greatly reduced and actual energy bands are formed (Fig. 7b) [15]. The VEC can then be varied from 20 to 24 corresponding to the filling of the e_g band. Electron deficient compounds are metallic and most of them exhibit a superconducting behaviour. In this class of compounds, there are two possibilities to change the VEC and thus influence the T_c: (i) by halogen/chalcogen substitution, i.e. $Mo_6Br_2S_6$ and $Mo_6I_2S_6$ with VEC = 22 exhibit a T_c = 13.8 K and 14 K, respectively, close to the T_c (15 K) of $PbMo_6S_8$ with the same VEC, while Mo_6S_8 with VEC = 20 has a T_c = 1.7 K [14]. In fact, in the sulfide series, VEC = 22 corresponds to a maximum of density of states which can explain the highest T_c observed for the corresponding compounds. With Se and Te the solid-solutions $Mo_6Se_{8-x}X_x$ and $Mo_6Te_{8-x}X_x$ (X = Cl, Br or I and $0 < x < 2.5$) have been obtained and T_c varies during the substitution in relation with the VEC evolution (Fig. 8) [16]. (ii) The VEC can be changed thus influencing the T_c by cationic insertion in the channels formed between the units. Indeed, it is possible to modify the nature and the stoichiometry of the cations inserted in this structure-type and then to influence the VEC and the T_c which is related to [14].

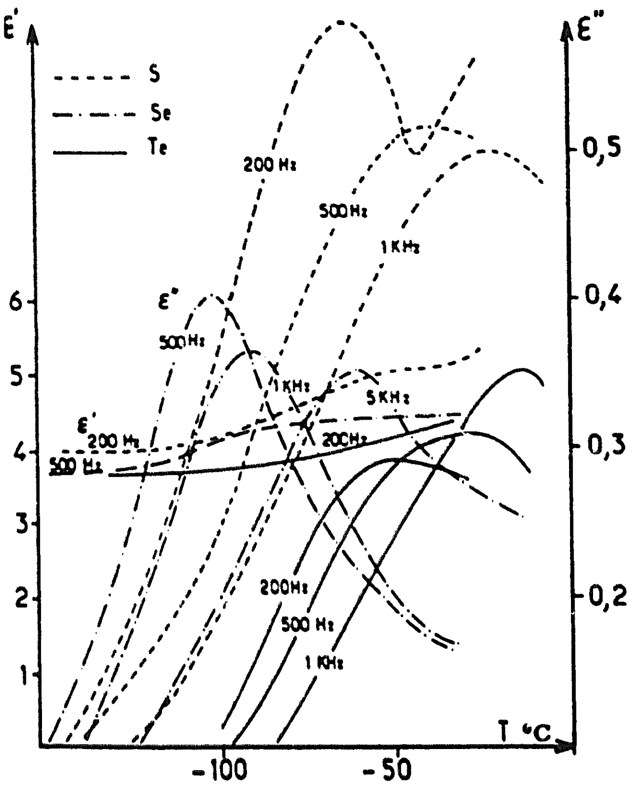
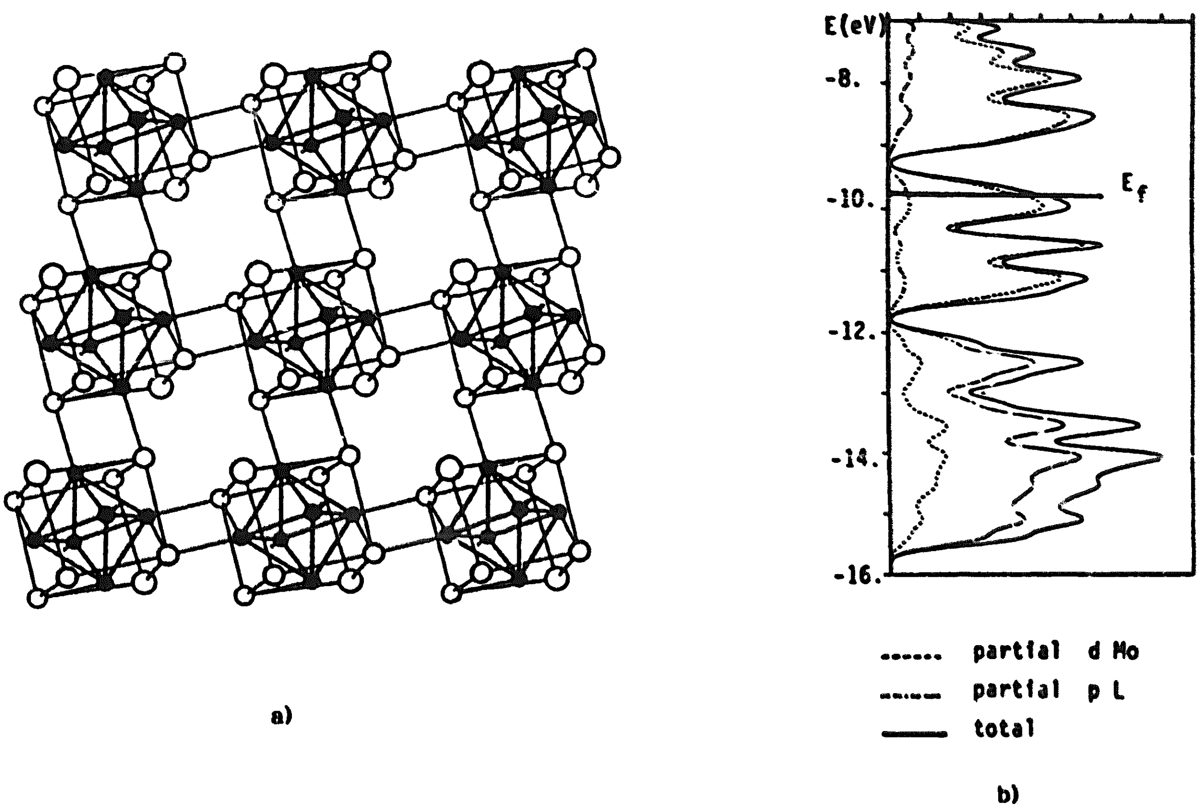


Fig. 6. Real (ϵ') and imaginary (ϵ'') part of the dielectric constant vs. temperature for the $Mo_6Cl_{10}Se$ series, for various frequencies.

Finally, in $Cs_{0.6}Mo_6S_7$ ($n = 7$) based on chains of units connected together by six L^{i-a} (Fig. 9), all the ligands are involved in the condensation and this compound constitutes the last possible step of the



a)

b)

Fig. 7. (a) Condensation of the Mo_6L_{14} units via L^{i-a} ligands in $Mo_6Br_2S_6$ ($Mo_6Br^i_2S^{i-a}_{6/2}S^{a-i}_{6/2}$). (b) Density of states (DOS) for the same compound with representation of the Fermi level, according to Certain and Lissillour [15].

Me_6L_{14} unit condensation. Like in Chevrel phases, the molecular character is greatly reduced and this compound is a superconductor with $T_c = 7.7$ K [17].

3.3. Comparison between unit condensation in Mo_6, W_6 and Re_6 chemistry

A similar condensation of the Me_6L_{14} units has been obtained with tungsten and rhenium. However, for tungsten, only the first terms of the condensation, i.e. the W_6 halides, have been obtained, probably due to a limitation of the W_6 cluster stability. Indeed, it has been recently shown that the syntheses conditions have to be drastically precise so as not to decompose the W_6 cluster and a relatively low temperature of reaction has to be used [18]. Up to now, no Chevrel phase analogue based on W_6 cluster has been isolated.

For the rhenium, a great number of compounds isostructural with molybdenum compounds have been obtained [19]. However, due to the fact that Re has seven valence electrons compared to Mo which has six, for the same n-value the chalcogen/halogen ratio is more important with rhenium than with molybdenum. This gives several compounds with original unit condensation, not found with molybdenum. For instance, in $Re_6Se_8Cl_2$ ($n = 10$) connections by four L^{i-a} appear in two directions giving a two-dimensional compound [20]; in $Re_6Se_4Cl_{10}$ ($n = 14$) the units are discrete without countercation giving a pure molecular compound, the cohesion of which being assured by Van der Waals interactions between neutral units [21]. This feature explains why Chevrel phases cannot be obtained with Re_6 cluster. Moreover, in rhenium chemistry, a number of chalcohalides exhibit Y–Y and/or Y-bridges, e.g. $K_4Re_6S_{12}$ ($K_4Re_6S^i_8S^{a-a}_{4/2}(S_2)^{a-a}_{2/2}$) [22].

4. Progressive condensation of the Me_6L_{18} units in the niobium chemistry

In the Me_6L_{18} unit the steric effect of the inner ligand shell is more important than in the Me_6L_{14} one. Only a few examples of condensation involving the inner ligands have been reported and the molecular character of the compounds based on this unit is retained. The n factor cannot be changed greatly, but the VEC can be varied from 16 to 14, which significantly differs from the Mo_6 cluster chemistry for which the VEC was always 24 for the molecular compounds. As a result, the magnetic behaviour of the cluster can be observed. Indeed, for a VEC = 15, the cluster is paramagnetic due to one unpaired electron on the a_{2u} level. In contrast, for a VEC = 14 or 16 the HOMO level is empty or filled, respectively and the cluster is non-magnetic. Illustrations of the Me_6L_{18} unit condensation will be taken from the

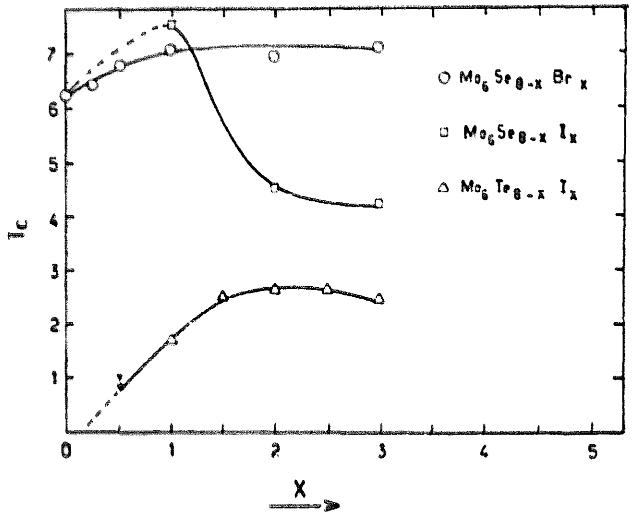


Fig. 8. T_c evolution vs. halogen substitution for the $Mo_6Se_{8-x}Br_x$, $Mo_6Se_{8-x}I_x$ and $Mo_6Te_{8-x}I_x$ solid solutions.

niobium halides and oxyhalides chemistry; tantalum gives very similar compounds.

4.1. Unit condensation in the niobium halides

Several niobium halides exist with discrete units ($n = 18$) and monovalent or divalent countercations. Important examples are $K_4Nb_6Cl_{18}$ [23], $In_2Li_2Nb_6Cl_{18}$ [24], $Ba_2Nb_6Cl_{18}$ [25], $Cs_2EuNb_6Br_{18}$ [26] with VEC = 16. With trivalent countercations like rare earths an important series, $MRENb_6X_{18}$ (M = monovalent cation, RE = rare earth, X = Cl, Br) has been obtained. An additional monovalent countercation is present in the structure, which again gives a VEC of 16 [27,28]. These compounds crystallize in two structure-types ($R\bar{3}$ or $P\bar{3}1c$) depending on the size of the monovalent cation. For a large cation like Cs^+ the units form a pseudo-hexagonal stacking ($P\bar{3}1c$) (Fig. 10a) and for smaller monovalent cations they form a *f.c.c.* stacking ($R\bar{3}$) (Fig. 10b). In the latter case the monovalent site is only half occupied; this site can be emptied without destroying the structural skeleton giving the ternary compounds $RENb_6X_{18}$ with the quite unusual VEC = 15. This example is of first interest because it is possible to control the VEC in exactly the same structure-type ($R\bar{3}$) and to compare the magnetism of the cluster in quaternary compounds with VEC = 16 and ternary compounds with a VEC = 15. With a non-magnetic rare earth like Lu the magnetism of the cluster can be clearly quantified by comparing $KLuNb_6Cl_{18}$ (VEC = 16) and $LuNb_6Cl_{18}$ (VEC = 15): it corresponds to a paramagnetism due to one unpaired electron in the latter case, while a nearly temperature independent behaviour is observed for the quaternary compound (Fig. 11). For $LuNb_6Cl_{18}$, a maximum of susceptibility at 2.5 K has been attributed to interactions between magnetic clusters [29].

The first step of unit condensation is obtained for $n = 16$ in $Li_2Nb_6Cl_{16}$ [30] in which the units are

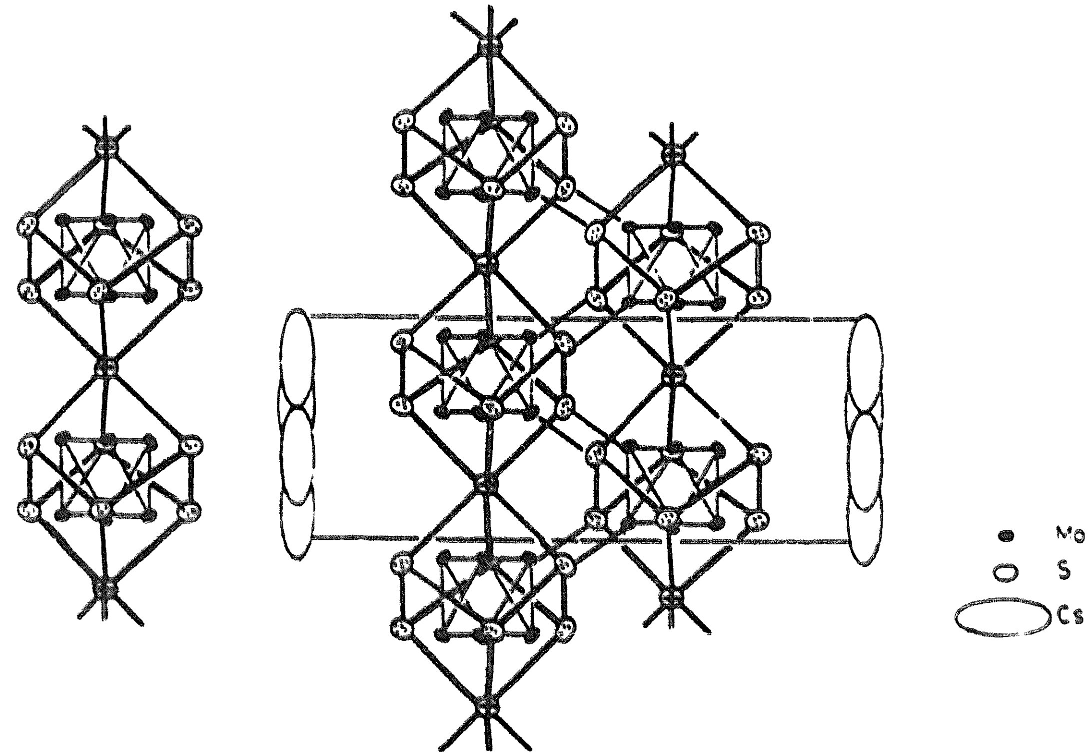


Fig. 9. Structure of $Cs_{0.6}Mo_6S_7$ ($Cs_{0.6}Mo_6S^{i}_{2}S^{i-a}_{6/2}S^{a-i}_{6/2}$) ($n = 7$) according to Gougeon et al. [17].

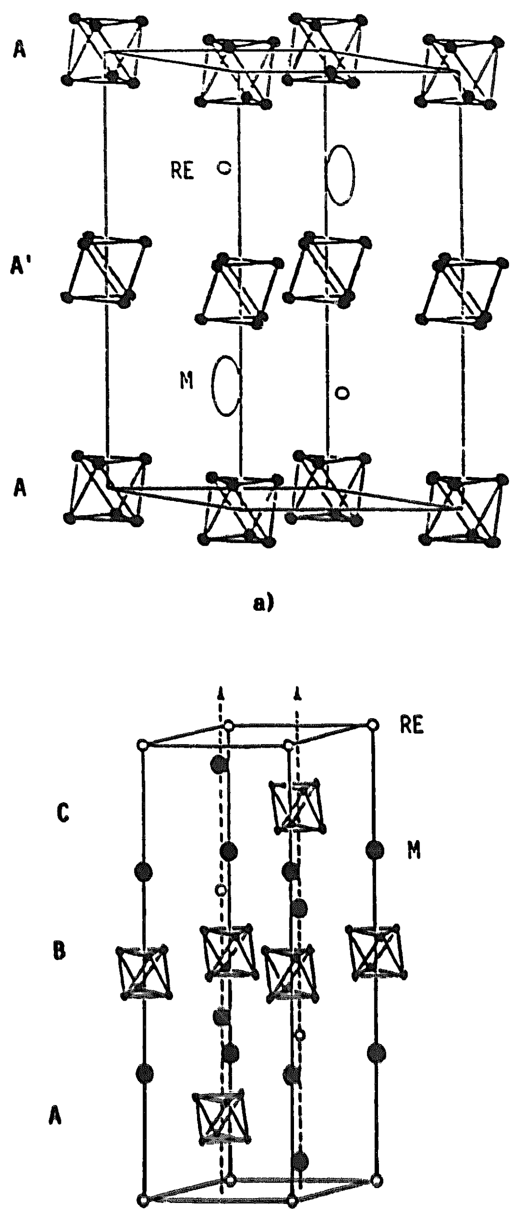


Fig. 10. Unit-cell representation of the two $MRENb_6X_{18}$ ($MRENb_6X^i_{12}X^a_6$) structure-types ($n = 18$): (a) $P\bar{3}1c$; and (b) $R\bar{3}$. For clarity the halogens are not represented.

condensed in two directions by four apical–apical ligands (Fig. 12a). No intermediate step corresponding to $n = 17$ has been reported up to now. For $n = 15$, the units are connected in the three directions by six apical–apical ligands forming halogen bridges which are linear in Nb_6F_{15} (Fig. 12b) [31] and bent in Ta_6Cl_{15} (Fig. 12c) [32] or $NaNb_6Cl_{15}$ [33]. In the last step, Nb_6Cl_{14} ($n = 14$), the inner ligands start to be involved in the condensation: the units are condensed by four Cl^{a-a} and two Cl^{i-a} (Fig. 12d), but due to the important steric effect of the 18 ligands, the $Nb–Cl^{i-a}$ distance is large ($Nb–Cl^i = 2.41$ Å, $Nb–Cl^{a-a} = 2.58$ Å, $Nb–Cl^{i-a} = 3.01$ Å) and the clusters cannot get closer [34]. It appears that the Me_6L_{18} condensation by inner ligands is difficult, which explains that n cannot be decreased greatly in the Me_6L_{18} based compounds.

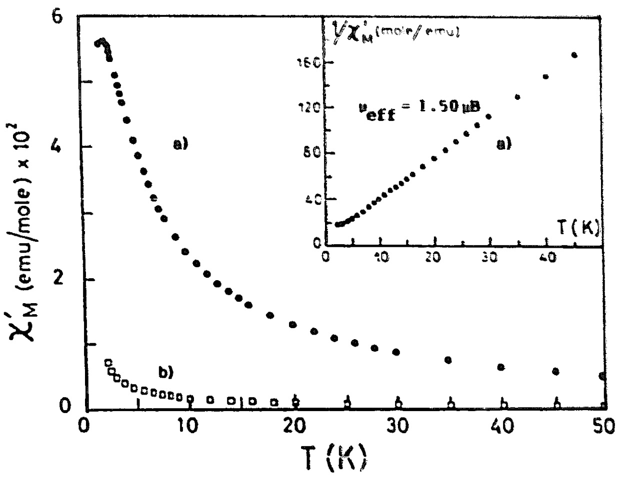


Fig. 11. Magnetic susceptibility vs. temperature for: (a) $LuNb_6Cl_{18}$ single crystals; and (b) $KLuNb_6Cl_{18}$ powder. Insert: inverse of the magnetic susceptibility of $LuNb_6Cl_{18}$.

4.2. Unit condensation in the niobium oxyhalides

An alternative possibility to produce interactions between the clusters is to reduce the size of the Me_6L_{18} units by introducing a small ligand like oxygen around the cluster. Then, three series of oxyhalides have been recently isolated and they constitute a unique example of oxyhalides based on Me_6 cluster obtained up to now in solid state chemistry.

For $n = 18$ two series have been obtained, $M_2RENb_6Cl_{17}O$ ($R\bar{3}$) (VEC = 16) [35] and $M_2RENb_6Cl_{15}O_3$ ($P\bar{3}1c$) (VEC = 14) [36], respectively isotypical or strongly related to the two structures of the $MRENb_6Cl_{18}$ chlorides ($R\bar{3}$ and $P\bar{3}1c$) described above. In the first compound the oxygen is statistically distributed on the 12 inner positions which does not influence greatly the size of the unit, while in the second one three oxygens are ordered on inner positions. In the latter case the size of the unit is significantly reduced, but no interaction can occur between the clusters because the units are still discrete (Fig. 13a). In the third series $RENb_6Cl_{13}O_3$ (VEC = 14) [37], three oxygens are again ordered in inner position like in the previous compound, but the main difference is that now they are in *cis*-position with respect to the Nb_6 cluster, producing now a strong distortion. The units are condensed by four L^{a-a} and, due to the great deformation of the units, this connection produces helices of units (Fig. 13b). Now the clusters are relatively close to each other due to the smaller size of the units induced by the three oxygens and to the type of their condensation.

However, these three series of oxyhalides remain

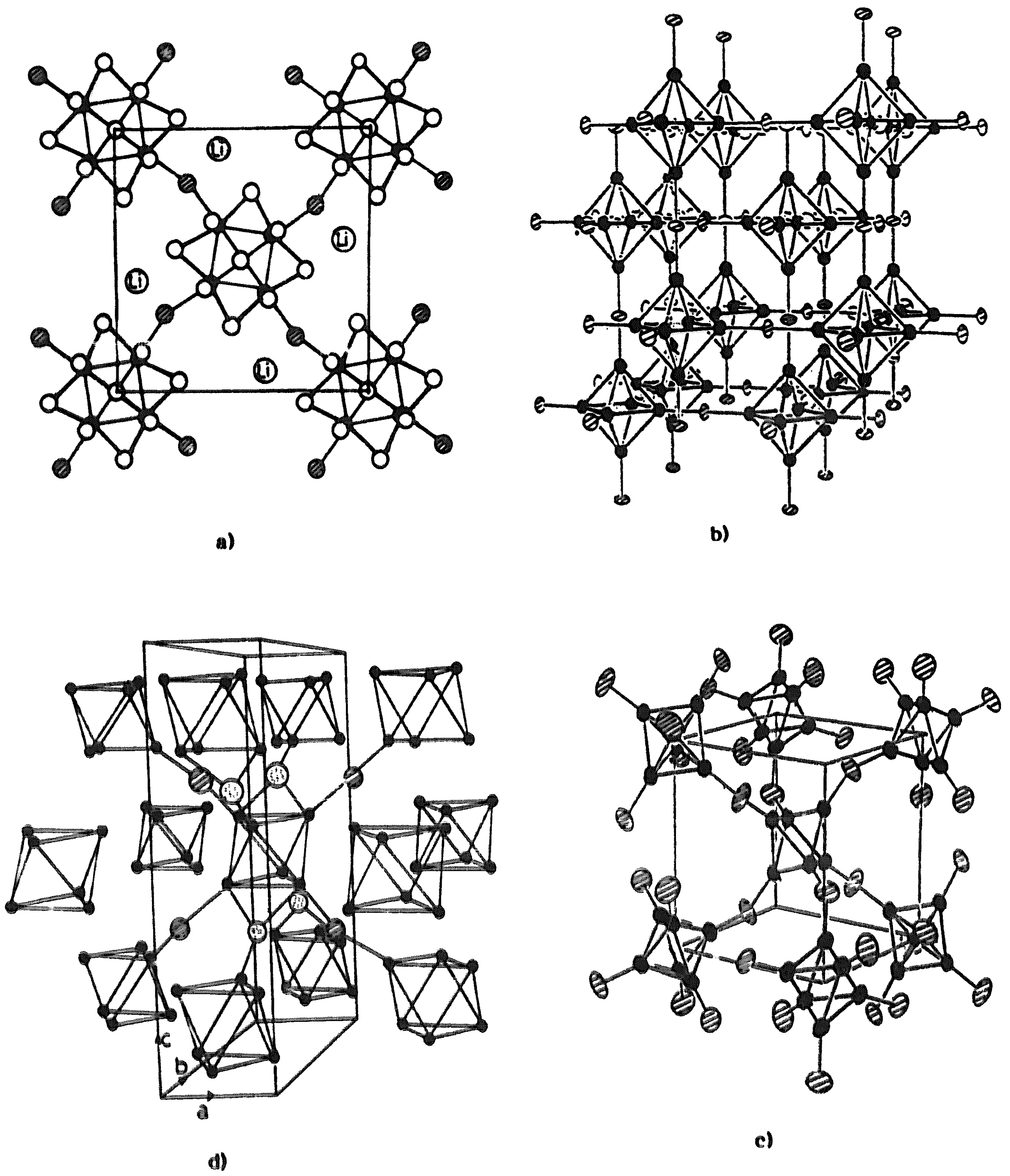


Fig. 12. Increasing condensation of the Nb_6L_{18} units in Nb_6 halides. Examples of: (a) $n = 16$, $Li_2Nb_6Cl_{16}$ ($Li_2Nb_6Cl^i_{12}Cl^a_2Cl^{a-a}_{4/2}$); (b) $n = 15$, Nb_6F_{15} ($Nb_6F^i_{12}F^{a-a}_{6/2}$); (c) $n = 15$, Ta_6Cl_{15} ($Ta_6Cl^i_{12}Cl^{a-a}_{6/2}$); and (d) $n = 14$, Nb_6Cl_{14} ($Nb_6Cl^i_{10}Cl^{i-a}_{2/2}Cl^{a-i}_{2/2}Cl^a_4$).

close to the halides. In fact, three oxygens around the cluster are not sufficient enough to strongly reduce the size of the units and to induce actual interactions between the clusters. Moreover, up to now, it has not been possible to substitute more than three oxygens on the units. Therefore, a large gap exists between these oxyhalides and the next step formed by the niobium oxides. These Nb_6 based oxides constitute a very different class of compounds because an important anionic charge surrounds the cluster and, in a same compound, coexist frequently octahedral clusters, triangles, isolated element and sometimes condensed clusters [38].

5. The Zr_6 clusters: an example of interstitial octahedral cluster

Zirconium has only four valence electrons and an

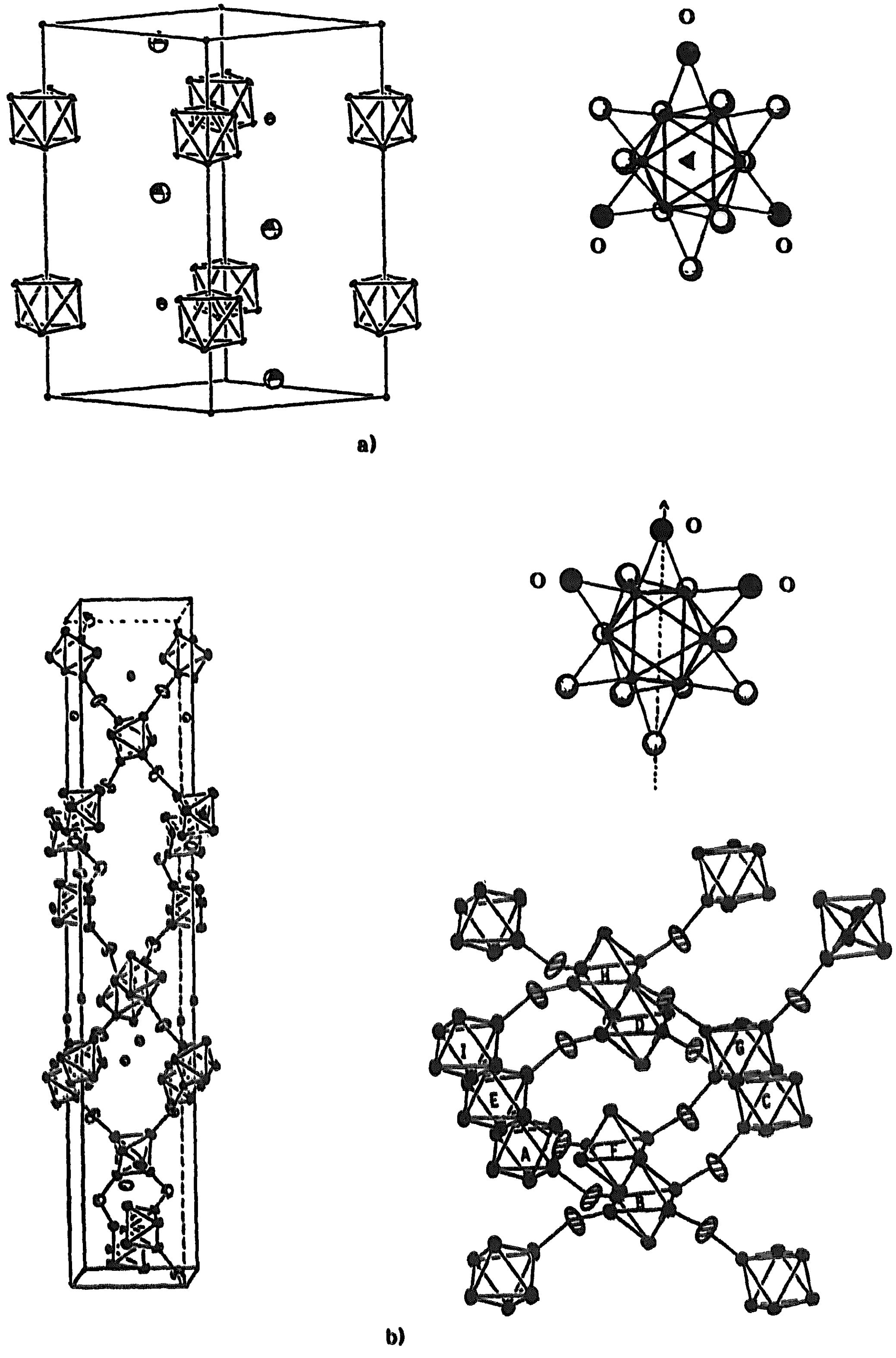


Fig. 13. (a) Unit-cell and $Nb_6Cl^i_9O^i_3$ core representations for $M_2RENb_6Cl_{15}O_3$ ($M_2RENb_6Cl^i_9O^i_3Cl^a_6$) ($n = 18$). (b) unit-cell, $Nb_6Cl^i_9O^i_3$ core and helix of units representations for $RENb_6Cl_{13}O_3$ ($RENb_6Cl^i_9O^i_3Cl^a_2Cl^{a-a}_{4/2}$) ($n = 16$). Only Cl^{a-a} atoms are represented.

interstitial element (Z) is necessary on the center of the zirconium octahedral cluster in order to stabilize it [39]. Such a situation is also encountered for octahedral clusters of electron-poor elements like rare earths. This interstitial element participates in the metal–metal bonding states and increases the number of electrons involved in the metal–metal bonds. A large variety of elements can be inserted like Be to N, Al to P, K, Cr to Ni and Ge. The crystallochemistry of these $Zr_6(Z)$ based compounds is very rich and a great

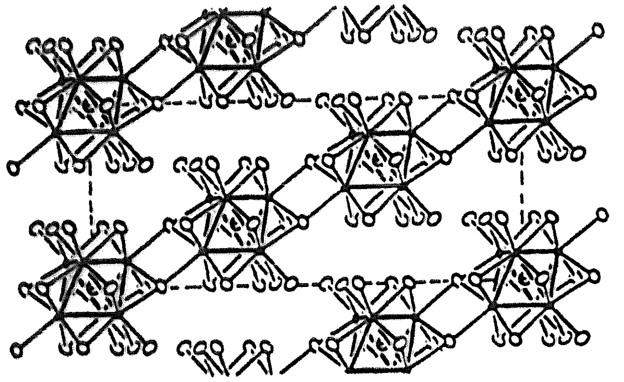


Fig. 14. A [100] section of rhombohedral $Zr_6X_{12}Be$ ($Zr_6X^i_6X^{i-a}_{6/2}X^{a-i}_{6/2}$) ($n = 12$) according to Corbett [41].

number of compounds are isotypic with the Nb_6 and Ta_6 ones. Condensation of these $Zr_6(Z)L_{18}$ units by apical–apical ligands appears in a lot of compounds, but only few examples of condensation are known which involve inner ligands. Indeed, the important steric effect of the eighteen ligands makes difficult such a condensation and usually the molecular character is retained for these compounds.

A particular zirconium compound is specially interesting in the frame of this review: $Zr_6X_{12}(Z)$ in which the units are condensed in the three directions by six inner-apical ligands (Fig. 14) [40], exactly as in Chevrel phases. In fact this compound is the analogue of Chevrel phases based on Me_6L_{18} units, instead of Me_6L_{14}. But due to the important steric effect of the ligands, the Zr-X^{a-i} distances are large — like Nb–Cl^{i-a} distances in Nb_6Cl_{14} described above — and the clusters cannot get closer. Then in this compound the molecular character is retained in contrast to the situation observed in Chevrel phases.

6. Concluding remarks

Although the Me_6L_{14} and Me_6L_{18} units look very similar, their condensation acts very differently due to the strong influence of the steric effect of the ligand shell. Beyond the condensation of the units, a further step will involve the clusters by themselves. For instance, the Me_6L_{14} units can be condensed in one direction of the space giving the one-dimensional $Mo_6I_8Se_2$ reported above. A further condensation in the same direction gives infinite molybdenum clusters condensed by they faces like in $Tl_2Mo_6Se_6$ [42]. A large varieties of such condensations of cluster are well known giving a great number of materials which constitute another important field of cluster chemistry [43].

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