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Recent investigations on the $(Me_6L_{18})^{n-}$ unit based halides and oxyhalides (Me = Nb, Ta and L = Cl, Br, O) with rare earths as countercations: electronic and steric effects

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Abstract

In this paper are reviewed a number of recently obtained $(Me_6L_{18})^{n-}$ based halides and oxyhalides with rare earths as countercations: $M_xREMe_6X_{18}$ ($KLuNb_6Cl_{18}$ type, $R\bar{3}$, and $CsLuNb_6Cl_{18}$ type, $P\bar{3}1c$) and $REMe_6X_{13}O_3$ ($ScNb_6Cl_{13}O_3$ type, $I4_122$). Their crystal structure data, obtained from isotypic compounds with judiciously chosen M–RE–Me–X combinations, have allowed us to discuss rigorously the most important structural features appearing commonly in the Me_6 cluster chemistry: the systematic evolution of the Me–Me intracluster and the Me–ligand distances, depending on both electronic and steric effects. The influence of countercation size on the $(Me_6L_{18})^{n-}$ stacking is also considered. All these results form the basis of a consistent understanding of the $(Me_6L_{18})^{n-}$ based chemistry, when substitutions are performed on the various elements constituting these compounds.

Keywords: Halides; Oxyhalides; Electronic effects

1. Introduction

The low-valency niobium and tantalum halides have been investigated for a long time, and lead to compounds based on the units $(Me_6L_{18})^{n-}$ (Me = Nb or Ta), in which the Me_6 aggregate builds an octahedral cluster with metal–metal bonding. In these units the Me_6 cluster is edge-capped by 12 L^i ligands; six additional L^a ligands lie in apical position (Fig. 1(a)). These 18 ligands can be shared with two Me_6 clusters as shown in Fig. 1b in accordance with Shäfer's [1] notation. In the special case of niobium iodides, for instance in Nb_6I_{11} [2] or Nb_6I_9S [3], the Nb_6 cluster exhibits a different environment, being face-capped, as is usually observed in molybdenum [4], tungsten and rhenium [5] cluster chemistry based on $(Me_6L_{14})^{n-}$ units (Fig. 1(c)). In the latter $(Me_6L_{14})^{n-}$ based compounds the d-electron concentration (VEC: valency electron concentration) is high (19–24), 24 being the optimal VEC corresponding to completely filled energy levels of metal–metal bonding orbitals. In contrast, for $(Me_6L_{18})^{n-}$ based halides the VEC can be 16, 15 or 14 when $n = 4$, 3 or 2 respectively. A specially interesting value of the VEC is 15, since a magnetic cluster with one unpaired electron is then expected [6], leading to potentially unusual physical properties when both a magnetic cluster and a magnetic rare earth are combined in the same compound [7,10].

Such $(Me_6L_{18})^{n-}$ units are also encountered in zirconium chemistry, for which the cluster is necessarily stabilized by an interstitial element like H, B, C, Fe, Co [8], and more recently in rare-earth chemistry where the rare-earth clusters are also centered by interstitial atoms [9]. Even if the size of the cluster centered by these elements is significantly larger than those with niobium or tantalum, some structure types isotypic with those of niobium and tantalum have been encountered [9,11,12]. In this paper we focus on the case of niobium and tantalum halides and oxyhalides with rare earths as countercations, concerning our recent results for $M_xREMe_6X_{18}$ (M = monovalent

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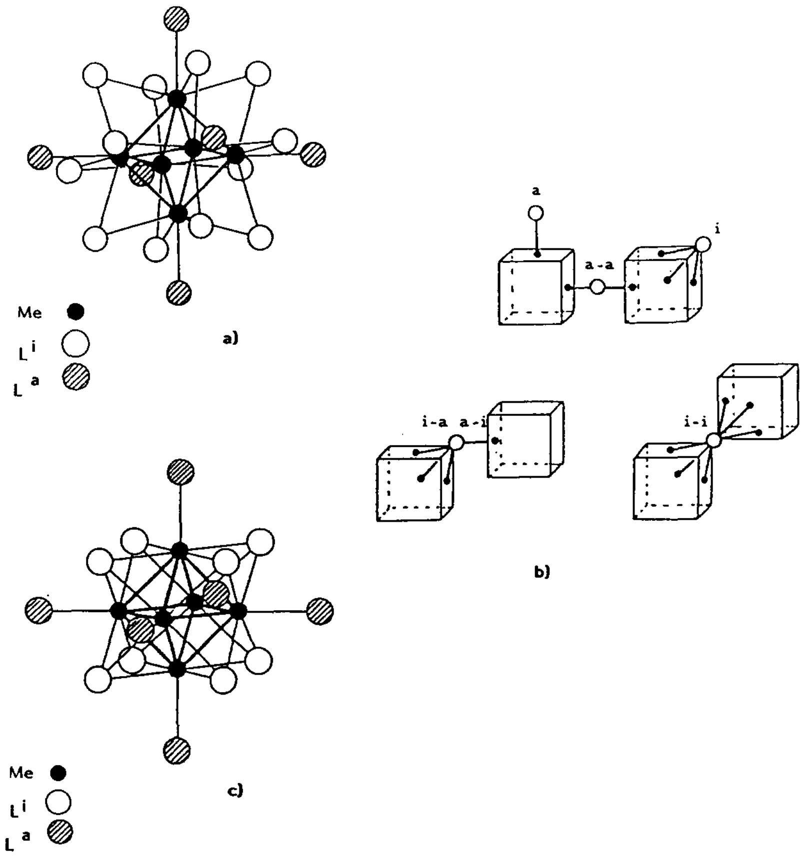

Fig. 1. (a) the $(Me_6L^i_{12})L^a_6$ unit; (b) schematic representation of the various types of ligand; (c) the $(Me_6L^i_8)L^a_6$ unit.

cation, RE = rare earth, Me = Nb or Ta, X = Cl or Br, $x = 0$ (VEC = 15), $x = 1$ (VEC = 16) and $x = 2$ (VEC = 16 with a divalent rare earth), and $REMe_6X_{13}O_3$ (RE = rare earth, Me = Nb or Ta, X = Cl, Br and VEC = 14) with some selected comparisons with zirconium or rare-earth cluster compounds. In this chemistry, a number of isotypic structures enable us to discuss efficiently the electronic and steric effects on the $(Me_6L_{18})^{n-}$ stacking and on the metal–metal intracluster bonding, due to various countercations, metal or ligand substitutions.

2. Preparation and characterization

All the compounds reported in this paper have been prepared by solid-state reactions at temperatures ranging between 600 °C and 850 °C. A mixture of stoichiometric amounts of halides, oxides and metallic element is weighed according to the formula of the planned compound; it is then pressed in the form of a pellet and heated in a sealed silica tube. It must be pointed out that all these compounds exhibit Me_6 clusters, corresponding to a low oxidation state of the metal. Therefore it is necessary to retain reducing conditions during the synthesis by introducing some pieces of Nb or Ta foil together with the pellet in the silica tube. The same result would of course be obtained with an excess of metallic powder, but the advantage of the metal foil is that it can be easily removed after the reaction and therefore the contamination of the powdered compound by the metallic element can be avoided.

Usually the compounds are obtained with a good degree of purity. However, as discussed below, in some cases a coexistence of two varieties of the same compound is systematically obtained. For instance, for the composition $RbLaNb_6Cl_{18}$ two different structure types can be obtained simultaneously, their ratio in the mixture depending on the temperature of the synthesis. Usually, the reaction time does not change the results significantly, and typically 24 h of reaction are sufficient. Another example of the competition between the formation of two different structure types is given by $Cs_xRETa_6Br_{18}$: their existence depends on both the stoichiometry of the starting composition ($x = 1$ or 2; RE = Yb^{3+}, Eu^{3+} when $x = 1$ and Yb^{2+}, Eu^{2+} when $x = 2$) and the temperature of reaction. Thus thermodynamic or kinetic factors have to be taken into account during the synthesis.

Single crystals with a suitable size for structural determination by X-ray diffraction have been obtained directly during the syntheses in most cases. If not, the reaction time is increased up to 1 week. In the case of niobium chemistry the crystals are usually well formed and of a high quality, in contrast to the case of tantalum chemistry for which they appear to be very difficult to grow. However, in the latter case, good crystals can be obtained if some pieces of niobium foil are used instead of tantalum, but in these conditions mixed ($Ta_{6-x}Nb_x$) clusters are formed, as shown by electron microprobe analysis.

3. Description of structures

We briefly review the three new structure types that we have obtained in the Me_6 cluster chemistry with rare earth as countercations, labelled with their space group notation, $R\bar{3}$, $P\bar{3}1c$ and $I4_122$ in the following discussion. The structure types existing for the various M, RE, Me, X and O combinations are summarized in Tables 1, 2 and 3.

3.1. $KLuNb_6Cl_{18}$ structure type ($R\bar{3}$) [10]

In these $M_xREMe_6X_{18}$ compounds (trigonal system with rhombohedral unit-cell, space group $R\bar{3}$), the units are arranged in an approximately close packed cubic stacking, giving ...ABCA... succession of planes of Me_6X_{18} units (Fig. 2). The corresponding classical octahedral sites formed by the Me_6X_{18} units are fully occupied by the rare earth, and the tetrahedral ones, which can be either empty, half-filled or full-filled when $x = 0$, 1 or 2 respectively, are occupied by the M^+ countercation. The rare earth is six-coordinate in an almost perfect octahedral site formed by six X^a ligands belonging to six adjacent units; the M atom

Table 1

Ternary and quaternary compounds obtained in niobium and tantalum chloride chemistry in relation to the nature of the rare earth[a]

RE^{3+}	La	Ce	Pr	Nd→Gd	Tb	Dy→Er	Tm	Yb	Lu	Sc
$REMe_6Cl_{18}$						$R\bar{3}$	$R\bar{3}$		$R\bar{3}$	
$NaREMe_6Cl_{18}$			$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$				
$KREMe_6Cl_{18}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$
$RbREMe_6Cl_{18}$	$R\bar{3}$ $P\bar{3}1c$	$R\bar{3}$ $P\bar{3}1c$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$
$CsREMe_6Cl_{18}$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$
$REMe_6Cl_{13}O_3$										$I4_122$

[a] All the combinations of this table have been tested. The obtained compounds are labelled with the space group notation of their structure type.

Table 2

Ternary and quaternary compounds obtained in niobium and tantalum bromide chemistry in relation to the nature of the rare earth

RE^{3+}	La	Ce	Pr	Nd	Sm	Eu^{3+}	Gd→Er	Tm	Yb^{3+}	Lu	Sc
$RETa_6Br_{18}$[a]				$R\bar{3}$	$R\bar{3}$		$R\bar{3}$	$R\bar{3}$			
$NaRETa_6Br_{18}$[a]			$R\bar{3}$								
$KRETa_6Br_{18}$[a]	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	
$RbRETa_6Br_{18}$[a]	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	
$CsRETa_6Br_{18}$[a]	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	
$RETa_6Br_{13}O_3$[a]					$I4_122$		$I4_122$	$I4_122$		$I4_122$	
$CsRENb_6Br_{18}$[b]	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	$P\bar{3}1c$	

[a] All these combinations have been tested. The obtained compounds are labelled with the space group notation of their structure type.

[b] The other combinations have been tested as for tantalum bromides, but they have given no compounds.

Table 3

Quaternary compounds obtained with europium and ytterbium in niobium and tantalum bromide and in niobium chloride chemistry[a]

	$M_2REMe_6X_{18}$ Eu^{2+}	$MREMe_6X_{18}$ Eu^{3+}		$M_2REMe_6X_{18}$ Yb^{2+}	$MREMe_6X_{18}$ Yb^{3+}	
Nb–Br	$R\bar{3}$ M = Tl, Rb, Cs			$R\bar{3}$ M = Tl, Rb, Cs		
Ta–Br	$R\bar{3}$ M = K, Tl, Rb, Cs	$R\bar{3}$ M = K, Tl, Rb	$P\bar{3}1c$ M = Cs	$R\bar{3}$ M = Tl, Rb, Cs	$R\bar{3}$ M = K, Tl, Rb	$P\bar{3}1c$ M = Cs
Nb–Cl	$R\bar{3}$ M = K, Cs				$R\bar{3}$ M = K	$P\bar{3}1c$ M = Cs

[a] All the combinations of this table have been tested in niobium and tantalum chemistry. The obtained compounds are labelled with the space group notation of their structure type. For the niobium chloride chemistry the only combinations corresponding to the compounds mentioned in this table have been only tested. No tantalum chloride compounds have been tested.

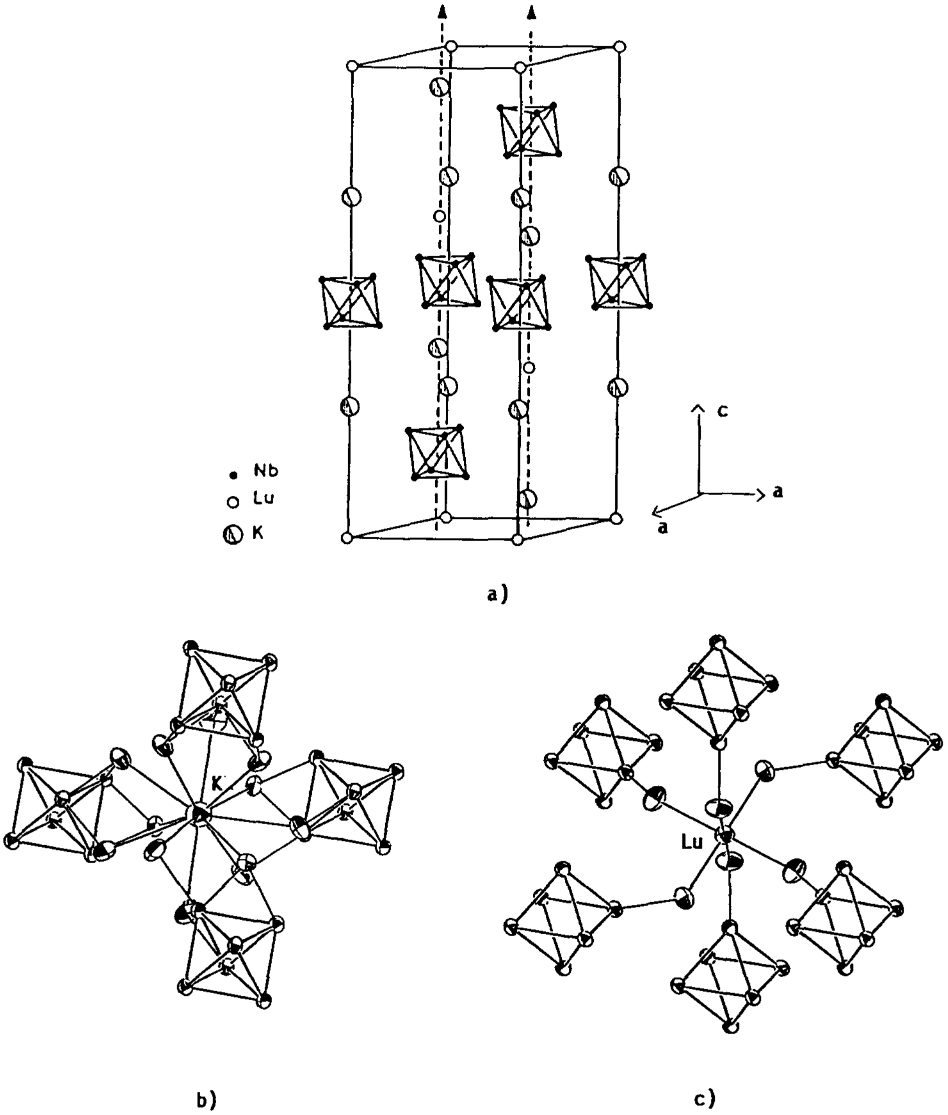

Fig. 2. Structure of $KLuNb_6Cl_{18}$: (a) representation of the hexagonal unit cell (chlorine atoms are omitted for clarity); (b) potassium environment; (c) lutetium environment.

located on the ternary axis is 12-coordinate by eight X^i and four X^a ligands belonging to four adjacent units. The structural formula is then $M_xRE(Me_6X^i_{12})X^a_6$.

This structure type had been previously encountered in zirconium chemistry for $K_2ZrZr_6Cl_{18}H$ [11] and subsequently reported for $M_2M'Zr_6Cl_{18}Z$ and $MM'Zr_6Cl_{18}Z$ (M = K–Cs; M′ = Ca, Ba, La; Z = B, C, Mn, Fe) [12], and also in the rare-earth octahedral cluster compound $Cs_2LuLu_6Cl_{18}C$ [9]. In all these compounds the Me_6 cluster is centred by an interstitial atom, which stabilizes the cluster by providing the cluster with additional electrons and strong Me–Z bonding.

3.2. $CsLuNb_6Cl_{18}$ structure type ($P\bar{3}1c$) [14]

In the $CsREMe_6X_{18}$ compounds (trigonal, space group $P\bar{3}1c$) a . . . AA′A . . . stacking of Me_6X_{18} units is observed, in which the units of the A′ plane are tilted by about 20° with respect to the units of the A plane (Fig. 3). This rotation leads to a more compact stacking for this structure type than for the $R\bar{3}$ one. The cationic sites are formed by a pseudo-prismatic arrangement of units. The RE atom is six-coordinate in a slightly distorted octahedron formed by six X^a ligands belonging to six adjacent units, and the Cs atoms is 12-coordinate by six X^a and six X^i belonging also to six adjacent units. All these cationic sites are fully occupied. The developed formula is then $CsRE(Me_6X^i_{12})X^a_6$.

In zirconium chemistry, several compounds with this structure type have very recently been isolated: $CsLaZr_6Cl_{18}Z$ (Z = C or Fe) and $RbLaZr_6Cl_{18}Fe$ with interstitial atom in the Zr_6 cluster [12], but to our knowledge, no similar rare-earth cluster compound has been synthesized up to now.

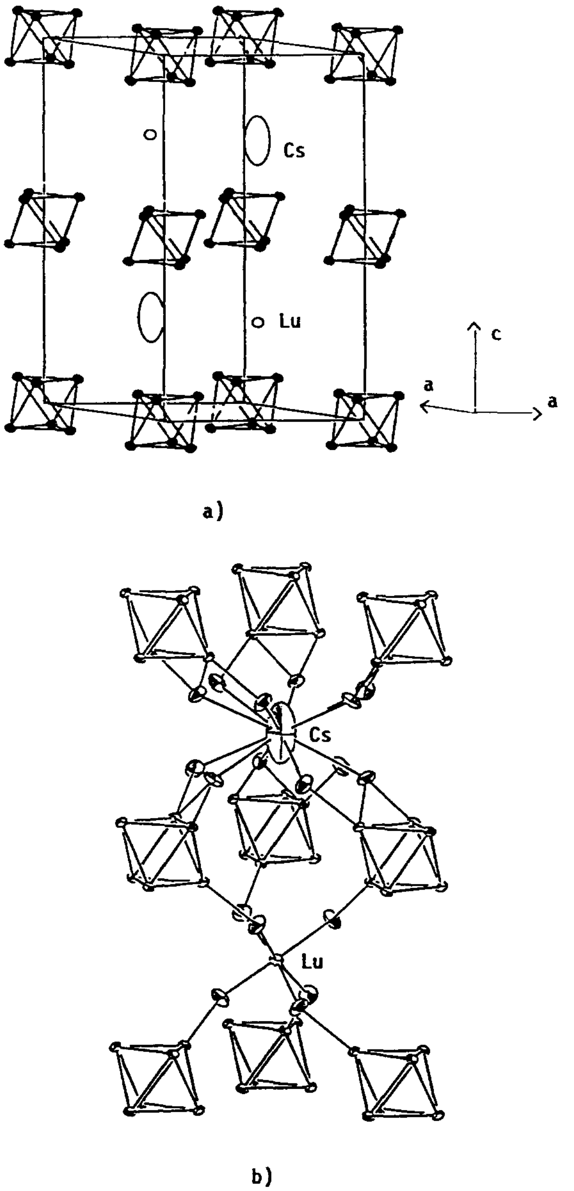

Fig. 3. Structure of CsLuNb$_6$Cl$_{18}$: (a) representation of the unit cell (chlorine atoms are omitted for clarity); (b) cesium and lutetium environment.

3.3. *ScNb$_6$Cl$_{13}$O$_3$ structure type (I4$_1$22) [15]*

The structure of this REMe$_6$X$_{13}$O$_3$ series is tetragonal, space group I4$_1$22 (Fig. 4). The Me$_6$L$_{18}$ units, in which the three oxygen atoms occupy the inner position, are linked together by four X^{a-a} ligands to form pseudo-helices of units, the axes of which are orthogonal to each other. Two additional X^a ligands are in apical positions. The RE atom is five-coordinate by two X^a and three O^i belonging to three adjacent units. The developed formula can be written RE(Me$_6$X$^i_9$O$^i_3$)X$^a_2$X$^{a-a}_{4/2}$.

This structure type, never encountered up to now, is very original in cluster chemistry, since it constitutes the first example of an oxyhalide cluster compound, in which the Me$_6$ cluster is very distorted, owing to the presence of the small oxygen among the halogen atoms. Another surprising feature of this structure type is the five-coordination of the rare earth, usually six-coordinate in M$_x$REMe$_6$X$_{18}$ or in more complex sites in the rare earth oxides or in ternary cluster oxydes [29].

4. Discussion about structural data

In the three series discussed in this paper, we have obtained a lot of isotypic compounds. The appropriate choice of various combinations of M, RE, Me and X for structural determination gives us an unprecedented opportunity to discuss rigorously, from strictly isotypic compounds, the most important structural features appearing commonly in Me$_6$ cluster chemistry: the systematic evolution of both the metal–metal bonding and the metal–ligand bonding and also the influence of the countercation size on the Me$_6$L$_{18}$ stacking. The relevant structural results obtained from all the compounds the structures of which we have refined are summarized in Table 4.

4.1. Evolution of intra-unit distances

4.1.1. Influence of VEC on Me–Me intracluster distances. When comparing the structures of KLuNb$_6$Cl$_{18}$ (VEC = 16) and LuNb$_6$Cl$_{18}$ (VEC = 15), which differ only by the occupancy of the M site, the variation of the interatomic distances in these two compounds is mainly due to the change in the oxidation state of the Nb$_6$ cluster [10]. A significant increase of 0.04 Å for the Nb–Nb intracluster distances and a simultaneous decrease of 0.02 and 0.03 Å for Nb–Cl^i and Nb–Cl^a distances respectively are observed when going from 16 to 15 e$^-$/Nb$_6$.

A molecular orbital calculation has shown that there are 24 d orbitals available for Nb–Nb bonding within the octahedral cluster in the Me$_6$X$_{18}$ units: 8 bonding and 16 antibonding orbitals [21,22]. For the compounds with 16 e$^-$/Nb$_6$, the eight bonding orbitals are filled; the compounds with 15 e$^-$/Nb$_6$ correspond to the removal of one electron from the highest a$_{2u}$ (in O$_h$ approximation) bonding orbital, thus weakening the Nb–Nb intracluster bonds, and, as a consequence, the Nb–Nb intracluster distance increases. Simultaneously, the Nb–Cl bonds are significantly shorter in LuNb$_6$Cl$_{18}$ than in KLuNb$_6$Cl$_{18}$ as a result of the different formal oxidation state of each niobium atom in these two compounds: 2.50+ and 2.33+ respectively, increasing the coulombian attraction in the former one.

4.1.2. Influence of X size on Me–Me intracluster distances (matrix effect). This effect is exemplified in

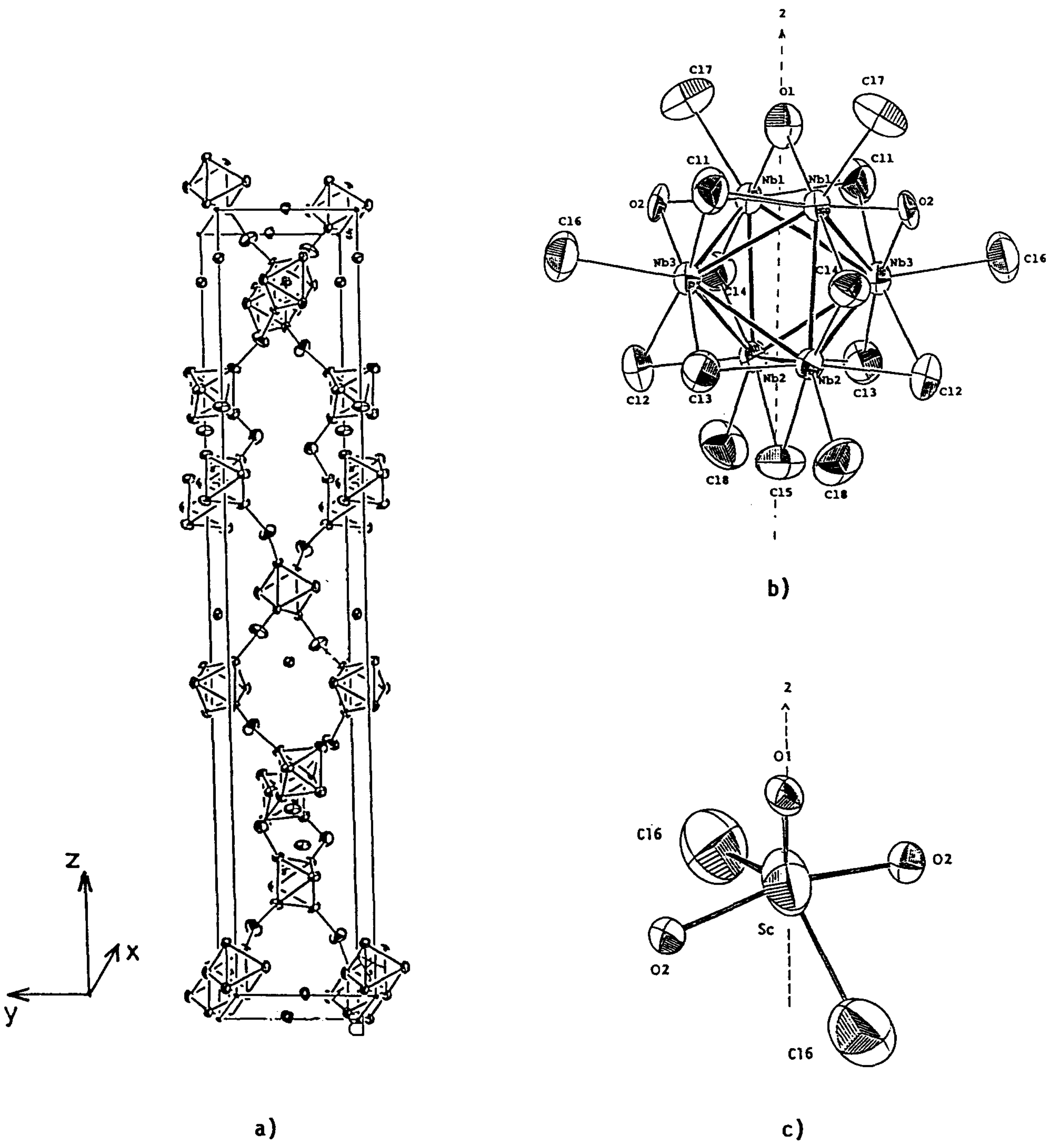

Fig. 4. Structure of ScNb$_6$Cl$_{13}$O$_3$: (a) representation of the unit cell (for more clarity some chlorine and oxygen atoms are not represented; the isolated atoms are scandium); (b) (Nb$_6$Cl$^i_9$O$^i_3$)Cl$^a_2$Cl$^{a-a}_{4/2}$ unit; (c) the scandium environment.

the two halides CsLuNb$_6$Cl$_{18}$ and CsErNb$_6$Br$_{18}$. The main difference between these two compounds is the size of the halogen, the size of the two rare earths being quite similar. This matrix effect was extensively discussed several years ago, mainly by Corbett in the field of cluster chemistry [23]. In the Me$_6$ cluster the metal–metal distances depend strongly on the X–X van der Waals contact distances between the X ligands bonded to the cluster. When the X ligand size increases the X–X distances increase and simultaneously the Me–Me intracluster distances are increased. When considering CsLuNb$_6$Cl$_{18}$ and CsErNb$_6$Br$_{18}$ the Me–Me intracluster distances increase by 0.04 Å when going from chloride to bromide. The ability of the cluster to be distorted by this matrix effect can constitute a measure of the strength of the metal–

Table 4
Structural data concerning all the niobium and tantalum cluster compounds for which we have refined the structure[a]

		Ref	Space group, Z, unit cell constants	VEC	Me–Me intracluster	Me–X^i	Me–X^a	RE–X^a	M–X	Me–RE shortest	Me_6–Me_6 centre to centre
$CsErTa_6Br_{18}$	Ta → Nb: size of the Me_6 cluster	17	P$\bar{3}$1c; $Z = 2$ $a = 9.661(1)$ Å $c = 18.037(3)$ Å	16	2.898(2)	2.587(3)	2.892(3)	2.789(3)	3.972(3)	5.231(1)	9.018(3)
$CsErNb_6Br_{18}$	Br → Cl matrix effect Influence of the RE charge on Me–Br distance	18	P$\bar{3}$1c; $Z = 2$ $a = 9.692(2)$ Å $c = 18.110(5)$ Å	16	2.954(1)	2.587(1)	2.885(2)	2.791(1)	3.984(1)	5.219(1)	9.055(5)
$CsLuNb_6Cl_{18}$		14	P$\bar{3}$1c; $Z = 2$ $a = 9.1882(7)$ Å $c = 17.1681(3)$ Å	16	2.913(1)	2.445(1)	2.667(1)	2.603(1)	3.786(1)	4.868(1)	8.584(3)
$Cs_2EuNb_6Br_{18}$		18	R$\bar{3}$; $Z = 3$ (hex) $a = 9.934(2)$ Å $c = 27.452(4)$ Å	16	2.970(1)	2.595(1)	2.804(1)	3.022(1)	3.749(1)	5.348(1)	9.934(2)
$KGdNb_6Cl_{18}$	Influence of the RE size on the stacking	19	R$\bar{3}$; $Z = 3$ (hex) $a = 9.272$ Å $c = 25.513$ Å	16	2.917(1)	2.455(1)	2.648(1)	2.679(1)	3.489(1)	4.883(1)	9.272
$KLuNb_6Cl_{18}$	Influence of the VEC on the Me–Me intracluster distances	10	R$\bar{3}$; $Z = 3$ (hex) $a = 9.228$ Å $c = 25.287$ Å	16	2.916(1)	2.452(1)	2.654(1)	2.596(1)	3.474(2)	4.832(1)	9.228
$LuNb_6Cl_{18}$		10	R$\bar{3}$; $Z = 3$ (hex) $a = 9.217$ Å $c = 25.213$ Å	15	2.956(1)	2.431(2)	2.623(2)	2.589(2)		4.793(1)	9.217
$ScNb_6Cl_{13}O_3$	Nb → Ta and Cl → Br simultaneously: influence on the cluster size	15	$I4_122$; $Z = 8$ $a = 9.086(2)$ Å $c = 52.40(2)$ Å	14	2.943(1) 2.805(1) to 3.007(1)	Me–X^i = 2.451(3) Me–O^i = 1.991(6)	Me–X^a = 2.590(3) Me–X^{a-a} = 2.600(2)	RE–X^a = 2.476(3) RE–O = 2.004(7)		3.391(1)	7.99
$LuTa_6Br_{13}O_3$		20	$I4_122$; $Z = 8$ $a = 9.383(1)$ Å $c = 54.60(1)$ Å	14	2.936(4) 2.780(4) to 3.009(4)	Me–X^i = 2.591(8) Me–O^i = 2.00(4)	Me–X^a = 2.743(7) Me–X^{a-a} = 2.772(5)	RE–X^a = 2.727(8) RE–O = 2.11(4)		3.585(1)	8.32

[a] All the distances are averaged and given in Å.

metal bonding [1]. In these isotypic Me_6 cluster compounds, when going from chloride to bromide the Me–Me intracluster elongation due to the matrix effect is comparable to the removal of one electron from the a_{2u} highest bonding orbital (VEC = 16 to VEC = 15: see above), indicating the ability of this Me–Me bonding to be similarly modified by these two different effects.

A similar variation had been also observed in two other isotypic ternary halides previously reported in the literature: $K_4Nb_6Cl_{18}$ [24] and $K_4Nb_6Br_{18}$ [25] for which the Nb–Nb intracluster distances are 2.915 Å and 2.971 Å respectively.

4.1.3. Dependence of Me_6 cluster size on the nature of the transition element. The two compounds $CsErTa_6Br_{18}$ and $CsErNb_6Br_{18}$ only differ from one another by the nature of the element constituting the Me_6 cluster: niobium or tantalum. One can see that the Ta_6 cluster is significantly smaller than the Nb_6 one. This is consistent with the fact that the unit-cell volumes of $MRETa_6X_{18}$ compounds are systematically smaller than the volume of the isotypic $MRENb_6X_{18}$ ones [17]. This difference between these two Me_6 cluster sizes can be due to relativistic effects, from which the Ta element is more contracted than the Nb one, and then leads to shorter Ta–Ta bonds. This observation could explain the existence of the Ta_6L_{18} unit in tantalum cluster iodides, for instance in Ta_6I_{14} [26] and, in contrast, the absence of the corresponding Nb_6L_{18} units in niobium cluster iodides (only Nb_6L_{14} units have been encountered in Nb_6I_{11} [2] and related compounds). Indeed, when the halogen size increases the Me–Me intracluster distance increases simultaneously (matrix effect). Moreover, the Nb_6 clusters are larger than the Ta_6 ones as discussed in this section. Then, in the "Nb_6I_{18}" unit the Nb_6 cluster would be too large to be stabilized.

4.1.4. Influence of RE charge on intra-unit distances. In the two compounds $CsErNb_6Br_{18}$ and $Cs_2EuNb_6Br_{18}$ with VEC = 16, the rare earth is trivalent or divalent respectively, which influences the intra-unit distances. Indeed, the Nb–Nb intracluster distances are slightly larger in $Cs_2EuNb_6Br_{18}$ than in $CsErNb_6Br_{18}$ and, moreover, the Nb–Br^a distance is significantly smaller in $Cs_2EuNb_6Br_{18}$ (2.804 Å) than in $CsErNb_6Br_{18}$ (2.885 Å), the other Nb–Br^i distances being very close to each other in the two structures. This difference can be related to electrostatic effects due to the divalent oxidation state of the rare earth in $Cs_2EuNb_6Br_{18}$. The Br^a atom bonded to europium is less attracted by this divalent rare earth than by the trivalent one in $CsErNb_6Br_{18}$, and it pushes out the other bromines forming the Br^i_4 pseudo square, leading to a larger Br^i_{12} volume. The other distances can be discussed in terms of a steric effect: it is easy for the Nb_6 cluster to expand in its bromine environment and to approach the Br^a atom, shortening significantly the Nb–Br^a distance and increasing slightly the Nb–Nb one. In summary, the Nb_6Br_{18} unit is smaller when the RE countercation is divalent than when it is trivalent, the more important effect appearing on the Nb–Br^a distance.

4.2. Evolution of Me_6L_{18} stacking

The two compounds $KLuNb_6Cl_{18}$ and $KGdNb_6Cl_{18}$ only vary in the size of the rare earth. From Table 1, one can see that the intra-unit distances are the same within the standard deviations, which means that the size of the rare earth does not influence the geometry of the unit. In fact, the most important variation concerns the RE–Cl distances in relation to the ionic radius of the rare earth, and then the stacking of the units. As a consequence the Me–RE distance is shorter for Lu than for Gd. The rare earth size also slightly influences the M site size, which is larger in $KGdNb_6Cl_{18}$ than in $KLuNb_6Cl_{18}$. For a large rare earth the M site will be too large for small M cations like Na, giving a simple explanation for the fact that the corresponding phases have not been obtained.

5. Existence of cluster compounds in the M–RE–Me–L system, as a consequence of electronic and steric effects

5.1. $M_xREMe_6X_{18}$ halides

All the structural considerations discussed above can explain the existence of the various phases – stability of the Me_6 cluster and/or stability of the unit stacking – depending on steric and electronic effects, due to the charge and the size of the M and RE countercations and to the nature of the Me element and of the halogen. Moreover, it must be pointed out that there is a competition between the M and the RE sites for the stability of the unit stacking.

The compounds obtained with Eu and Yb lead to special cases, since these two rare earths can present either the divalent or the trivalent oxidation state. When they are divalent the compounds exhibit the $R\bar{3}$ structure type and the formula is $M_2REMe_6X_{18}$, which corresponds to a VEC of 16. Indeed, the radius of the divalent rare earth is large and it is necessary to completely fill the M site in order to stabilize the compound; moreover, this formula corresponds to the most stable oxidation state of the Me_6 cluster.

5.1.1. Influence of rare-earth size on stacking in ternary $REMe_6X_{18}$ compounds. The ternary $REMe_6X_{18}$ compounds for which the VEC = 15 exist for Me = Nb or Ta, X = Cl and for Me = Ta, X = Br. They have not been encountered in niobium bromide chemistry. Indeed, as we have discussed above, the Me–Me intracluster distance tends to increase when: (a) the VEC = 15, (b) the metal is niobium compared with tantalum; and (c) the ligand is bromine (matrix effect). Thus all three factors may contribute to the lesser stability of the niobium bromide clusters with VEC = 15.

All these ternary $REMe_6X_{18}$ compounds exhibit the $R\bar{3}$ structure type and do not exist with the $P\bar{3}1c$ structure type. Indeed, even if this $R\bar{3}$ structure is less compact, the empty M sites are smaller owing to the different Me_6X_{18} unit stacking. In all these compounds, the cohesion of the structure is provided by the rare earth, the size of which also influences the size of the empty M site. This is the reason why such $REMe_6X_{18}$ compounds exist only with small rare earths, which induce the smallest M sites: RE = Dy to Lu for Me = Ta or Nb and X = Cl, RE = Nd to Tm for Me = Ta and X = Br. In the latter case the steric effect due to the bromine needs a rare-earth ion large enough to separate the units sufficiently, but not too large, because in that case the volume of empty M sites would be great. When the vacant M site is too large the structure cannot be formed and it is necessary to fill it. For instance, in the tantalum bromide series, "$PrTa_6Br_{18}$" cannot be obtained. If it did exist, it should exhibit exactly the unit cell volume of $NaPrTa_6Br_{18}$, as shown from the extrapolation of the unit cell volume variation of the $RETa_6Br_{18}$ series that we have reported previously [17]. The latter $NaPrTa_6Br_{18}$ compound constitutes the limit of a good compromise between the size of the rare earth and the size of the M site that can be filled by a small cation such as Na. Then, with Pr, we can obtain the quaternary compound with the smallest M cation. Indeed, when RE = Ce or La, the M site becomes too large and the quaternary phases cannot be obtained with Na. A similar observation is made with tantalum or niobium chlorides (see Table 1), but in these cases several compounds with RE = Er to Pr are obtained with Na, since the M site becomes sufficiently large.

5.1.2. Influence of M cation size on the existence of quaternary $MREMe_6X_{18}$ compounds. The cohesion of the units stacking in the quaternary $MREMe_6X_{18}$ compounds mainly depends on the M cation when its radius is sufficiently large (K, Rb, Cs), and is less sensitive to the rare earth size.

When M = K, Rb the $MREMe_6X_{18}$ phases exist with the $R\bar{3}$ structure type, which is less compact than the $P\bar{3}1c$ one, but in which the M site is smaller. In that case, with a small halogen ligand like chlorine, $MRENb_6Cl_{18}$ and $MRETa_6Cl_{18}$ can exist with all the rare earths. But with bromine the situation is different, since the steric effect of this halogen, which creates large cationic sites in the structure is important. With the small Ta_6 cluster this steric effect is not sufficient to destabilize the $MRETa_6Br_{18}$ compounds, which can be obtained for all rare earths, even for europium and ytterbium in their divalent and trivalent oxidation states. But with niobium this steric effect of bromine acts in addition to the large size of the Nb_6 cluster when compared with that of Ta_6, and the $MRENb_6Br_{18}$ compounds are more difficult to form than the tantalum ones. Then, in that case it is necessary to use a large rare earth, such as divalent europium or ytterbium, and to fill the monovalent site completely with two M cations per formula, the VEC = 16 being maintained in these $M_2RE^{II}Nb_6Br_{18}$ compounds. Moreover, it must be remembered that the divalent state of the rare earth leads to a smaller unit, as discussed above.

When M = Cs, the $MREMe_6X_{18}$ phases exist with M = Nb or Ta, X = Cl or Br, RE = all the rare earths except Eu and Yb, and exhibit in contrast the $P\bar{3}1c$ structure type. The M sites are larger than in the $R\bar{3}$ structure type and so can accept a large M cation such as cesium.

5.1.3. Coexistence of $P\bar{3}1c$ and $R\bar{3}$ structure types. In some cases, the coexistence of $P\bar{3}1c$ and $R\bar{3}$ structure types during the synthesis has been observed with or without a change of stoichiometry for the two corresponding compounds.

For instance, in tantalum bromide chemistry two different compounds can be obtained for europium and ytterbium: $CsRETa_6Br_{18}$ ($P\bar{3}1c$) as detailed above, and $Cs_2RETa_6Br_{18}$ ($R\bar{3}$) in which the monovalent site is fully occupied. The preferential formation of any of these two compounds depends on the stoichiometry of the starting mixture. For the composition $Cs_2RETa_6Br_{18}$ heated in the 600–700 °C range, the pure $R\bar{3}$ phase is obtained. For the composition $CsRETa_6Br_{18}$ heated in the same temperature range, the X-ray pattern of the final product is complex, but both the two phases $Cs_2RETa_6Br_{18}$ ($R\bar{3}$) and $CsRETa_6Br_{18}$($P\bar{3}1c$) are clearly observed. The proportion of the two phases in the final mixture depends on the synthesis conditions: the $P\bar{3}1c$ phase is preferentially formed at lower temperature.

On the other hand, the coexistence of the two $R\bar{3}$ and $P\bar{3}1c$ structure types has also been observed for $RbRENb_6Cl_{18}$ (RE = La, Ce): the $R\bar{3}$ structure is formed at low temperature, while the proportion of the $P\bar{3}1c$ phase increases at higher temperature. In that case, the stoichiometry and charge of the rare earth is exactly the same for the two structures. A similar observation has been also reported by Corbett [12] in zirconium chemistry with $CsLaZr_6Cl_{18}$(Fe), which can exhibit the $R\bar{3}$ or $P\bar{3}1c$ structure depending on the temperature of synthesis, $R\bar{3}$ being more stable at lower temperature.

However, comparison between the tantalum bromides and $RbRENb_6Cl_{18}$ or $CsLaZr_6Cl_{18}(Fe)$ is difficult because the rare earth does not have the same oxidation state in the two phases $Cs_2RETa_6Br_{18}$ and $CsRETa_6Br_{18}$, which induces these two different stoichiometries. Indeed, in the case of divalent europium or ytterbium it is not possible to obtain an $R\bar{3}$ phase with only one Cs in the formula, as we have previously discussed [17]. For these two rare earths, the trivalent oxidation state seems more difficult to stabilize.

5.1.4. Coexistence of two stochiometries for the same structure type ($R\bar{3}$). For europium and ytterbium, when M = K, Rb, Tl, indexing of the X-ray patterns gives evidence that a mixture of the two ($R\bar{3}$) phases, $M_2RETa_6Br_{18}$ (M site fully occupied) and $MRETa_6Br_{18}$ (M site half occupied) is always obtained, even if the condition of synthesis or the stoichiometry of the starting mixture is changed. In these compounds the rare earth would be divalent or trivalent respectively and their VEC = 16. Our attempts to prepare a solid solution between these two definite compositions have failed. This feature is consistent with the existence of discrete energy levels for these compounds.

5.2. $REMe_6X_{13}O_3$ oxyhalides

In the two oxyhalides $ScNb_6Cl_{13}O_3$ and $LuTa_6Br_{13}O_3$, the influence of the nature of the transition metal and the matrix effect appear simultaneously, as shown by the structural data reported in Table 4. Indeed, in $LuTa_6Br_{13}O_3$ the size of the Ta_6 cluster, usually smaller than the Nb_6 one, is increased by the matrix effect due to the bromine and becomes close to the Nb_6 one in $ScNb_6Cl_{13}O_3$.

These oxyhalide cluster compounds with VEC = 14 correspond to a new chemistry in which the units are close to each other owing to the substitution of smaller oxygen atoms for part of the halogens. The RE sites formed in this new stacking are small and can accept only small rare earths. In tantalum and niobium oxychlorides the scandium is the only one element that can act as countercation. In the tantalum oxybromides, the RE sites are of course larger and accept rare earths such as Nd to Lu, but not Sc. The corresponding niobium oxybromides do not exist because, as discussed above, some Nb–Nb distances would be too large to be consistent with the formation of an actual metal–metal bonding.

When writing this paper we have obtained a new family of oxyhalides, whose structure type is $Cs_2LaTa_6Br_{15}O_3$ (Fig. 5). This compound crystallizes in the trigonal system with $a = 9.512(2)$ Å, $c = 17.935(3)$ Å and the $P\bar{3}1c$ space group. Its structure, just solved, is closely related to the $CsLuNb_6Cl_{18}$ one, but a shift of the units along the *c* axis gives units now centred in 0 0 1/4 and 0 0 3/4 instead of 0 0 0 and 0 0 1/2. One 12 i position occupied by chlorine in $CsLuNb_6Cl_{18}$ is now split in two 6h positions, one of them being occupied by the oxygen. This new situation of the units in the structure arranges new cationic sites: 4f for the cesium and 2c for the lantanum. The developed formula of this compound is then $Cs_2La(Ta_6Br^i_9O^i_3)Br^a_6$. This new family with a VEC = 14 is very rich, since isotypic compounds have been obtained with various countercations, even without rare earth, which lead in some cases to compounds with VEC = 13. Detailed results will soon be published elsewhere [27]. This new series lies exactly at the boundary between the $M_xREMe_6X_{18}$ halides and the new oxyhalides presented in this paper.

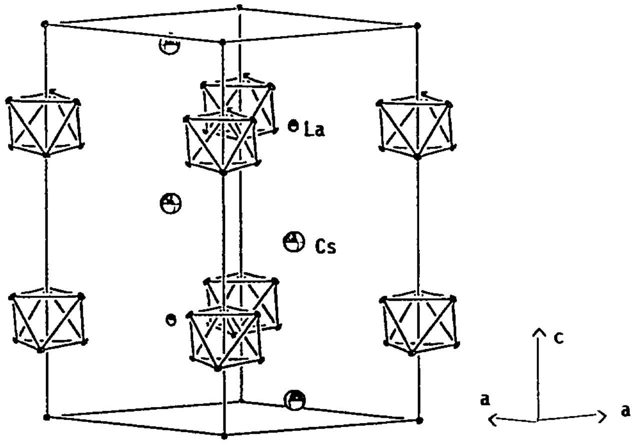

Fig. 5. Structure of $Cs_2LaTa_6Br_{15}O_3$ (bromine and oxygen atoms are omitted for clarity).

6. Conclusion

The new chemistry reported in this paper is very extended, since a lot of isotypic compounds can be obtained with various combinations of M–RE–Me–X. The structural determinations carried out from single crystals of judiciously selected combinations are of first importance in discussing the bonding in the Me_6L_{18} units depending on the various substitutions. The next step of this work will be an extended study of physical properties, especially the optical properties in relation to the non-centered structure of $REMe_6X_{13}O_3$, which could favour nonlinear effects, and magnetic properties because of the possibility of combining magnetic rare earth and/or magnetic clusters in these compounds. Up to now, the results of magnetic studies performed in recent years on the niobium and tantalum cluster chlorides gave no evidence of such interactions, but only the coexistence of the magnetism of the cluster and of the magnetism of the rare earth in the $REMe_6X_{18}$ compounds. The only compound in which we could suppose any actual interaction from the susceptibility measurements was $LuNb_6Cl_{18}$ [10]. This special behaviour could be explained by the particular closeness of the magnetic clusters in the structure. For this reason we started to reduce the distance between the clusters by introducing oxygen among the ligands and, indeed, we have succeeded in obtaining the first oxyhalide cluster compounds. In this new chemistry, situated between the well-known halide chemistry and the more recently developed oxide chemistry [28–30], both based on the Me_6L_{18} units, we hope to obtain new magnetic clusters with reduced distance between them, favouring potential magnetic interactions. Moreover, this oxyhalide cluster chemistry should be of first interest from the structural point of view, since other original structure types can be expected owing to the unprecedented dissymmetry of the cluster induced by the difference of steric effect of the oxygen and the halogen bounded to the Me_6 cluster.

References

[1] H. Schäfer and H.G. von Schnering, *Angew. Chem.*, *76* (1964) 833.
[2] A. Simon, H.G. von Schnering and H. Schäfer, *Z. Anorg. Allgem. Chem.*, *355* (1967) 295.
[3] H.J. Meyer and J.D. Corbett, *Inorg. Chem.*, *30* (1991) 963.
[4] C. Perrin and M. Sergent, *J. Less-Common Met.*, *123* (1986) 117.
[5] A. Perrin and M. Sergent, *New J. Chem.*, *12* (1988) 337.
[6] J.G. Converse and R.E. McCarley, *Inorg. Chem.*, *9* (1970) 1361.
[7] S. Ihmaïne, C. Perrin, O. Peña and M. Sergent, *Physica B*, *163* (1990) 615.
[8] R.P. Ziebarth and J.D. Corbett, *J. Am. Chem. Soc.*, *111* (1989) 3272.
[9] H.M. Artelt, T. Schleid and G. Meyer, *Z. Anorg. Allg. Chem.*, *618* (1992) 18.
[10] S. Ihmaïne, C. Perrin, O. Peña and M. Sergent, *J. Less-Common Met.*, *137* (1988) 323.
[11] H. Imoto, J.D. Corbett and A. Cisar, *Inorg. Chem.*, *20* (1981) 145.
[12] J. Zhang and J.D. Corbett, *Inorg. Chem.*, *32* (1993) 1566.
[13] H.M. Artelt, T. Schleid and G. Meyer, *Z. Anorg. Allg. Chem.*, *618* (1992) 18.
[14] S. Ihmaïne, C. Perrin and M. Sergent, *Acta Crystallogr. C45* (1989) 705.
[15] S. Cordier, C. Perrin and M. Sergent, *Eur. J. Solid State Inorg. Chem.*, *31* (1994) 1049.
[16] R.P. Ziebarth and J.D. Corbett, *J. Am. Chem. Soc.*, *111* (1989) 3272.
[17] S. Cordier, C. Perrin and M. Sergent, *J. Solid State Chem.*, in press.
[18] S. Cordier, C. Perrin and M. Sergent, *Z. Anorg. Allg. Chem.*, *619* (1993) 621.
[19] S. Ihmaïne, C. Perrin and M. Sergent, *Acta Crystallogr.*, *C43* (1987) 813.
[20] S. Cordier, C. Perrin and M. Sergent, *Croatica Chem. Acta*, in press.
[21] F.A. Cotton and T.E. Haas, *Inorg. Chem.*, *3* (1964) 10.
[22] D.J. Robbins and A.J. Thomson, *J. Chem. Soc. Dalton Trans.*, *21* (1972) 2350.
[23] J.D. Corbett, *J. Solid State Chem.*, *37* (1981) 335.
[24] A. Simon, H.G. von Schnering and H. Schäfer, *Z. Anorg. Allg. Chem.*, *361* (1968) 235.
[25] F. Ueno and A. Simon, *Acta Crystallogr.*, *C41* (1985) 308.
[26] D. Bauer, H.G. Schnering and H. Schäfer, *J. Less-Common Met.*, *8* (1965) 388.
[27] S. Cordier, C. Perrin and M. Sergent, *J. Solid State Chem.*, in press.
[28] O. Marinder, *Chem. Scr.*, *11* (1977) 97.
[29] J. Köhler, R. Tischtau and A. Simon, *J. Chem. Soc. Dalton Trans.*, *S* (1991) 829.
[30] M.J. Geselbracht and A.M. Stacy, *J. Solid State Chem.*, *110* (1994) 1.