An Original Series in the Tantalum Cluster Oxohalide Chemistry with Isolated $(Ta_6Br_{15}O_3)^{5-}$ Units: Crystal Structure of $Cs_2LaTa_6Br_{15}O_3$

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A new ternary oxobromide series, $M_2RETa_6Br_{15}O_3$ (M = monovalent cation, RE = rare earth) based on $(Ta_6Br_{15}O_3)^{5-}$ units, for which the valency electron count (VEC) is 14, has been isolated by solid state chemistry. The crystal structure of $Cs_2LaTa_6Br_{15}O_3$, which crystallizes in the $P\bar{3}1c$ space group ($a = 9.512(2)$ Å and $c = 17.935(3)$ Å), has been refined from single crystal X-ray diffraction data. This structure is strongly related to the structure of $CsErTa_6Br_{18}$ with a shift of the units along the c axis, which allows the building of new cationic sites. The developed formula of this compound is $M_2RE[(Ta_6Br_6^iO_3^i)Br_6^a]$. The lanthanum is located in an original environment formed by three O^i and six Br^a belonging to three adjacent units, and the cesium is 12-coordinated in a complex site formed by six Br^i and six Br^a belonging to six adjacent units. Short distances between rare earths and Ta_6 clusters are encountered. © 1995 Academic Press, Inc.

I. INTRODUCTION

In previous works on the synthesis and characterization of Nb_6 and Ta_6 cluster halides with rare earths as countercations we have obtained many compounds $M_xREMe_6X_{18}$ (M = monovalent 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 divalent rare earth)) which exhibit two structure types: $KLuNb_6Cl_{18}$ (trigonal, $R\bar{3}$) (1) and $CsLuNb_6Cl_{18}$ (trigonal, $P\bar{3}1c$) (2), depending on the nature of the countercations. In order to decrease the separation between the rare earth and the Me_6 cluster to favor their interaction, we have introduced the oxygen around the Me_6 cluster and obtained the first series of cluster oxohalides: $ScNb_6Cl_{13}O_3$ (3) and $RETa_6Br_{13}O_3$ (4) with 14 e^-/Me_6. In these compounds the units are connected via halogen bridges to form an original stacking in helices, which leads to short rare earth–Me_6 cluster distances.

These novel Nb_6 and Ta_6 cluster oxohalides, synthesized

by the techniques of solid state chemistry, open the way to a new class of materials. Indeed, the modification of the oxygen/halogen ratio around the Me_6 cluster in the Me_6L_{18} units (L = halogen, oxygen), when the same VEC is maintained could lead to the possibility of unit condensation via L^{a-a}, L^{i-a} and L^{i-i} ligands, as was obtained in the series of molybdenum cluster chalcohalides (5). Another possibility when increasing the oxygen/halogen ratio is to increase the charge of the Me_6L_{18} unit and so to increase the number of countercations around the octahedral cluster with the formation of original structure types. Indeed, up to now the maximum value of n for the $(Me_6L_{18})^{n-}$ unit was 4, leading to a maximum of 4 monovalent countercations, for instance in $K_4Nb_6Cl_{18}$ (6). Another alternative is to change the VEC by oxygen/halogen substitution but, up to now, we have not had sufficient examples of cluster oxohalides to discuss efficiently the value of the VEC in these compounds. However, it must be recalled that for the oxoniobates based on Nb_6 clusters, the 14-electron species seems much preferred, in agreement with the calculation (7). Experimentally, Nb_6 clusters with VEC = 13 to 15 have been isolated, for instance in KNb_8O_{14}, $SrNb_8O_{14}$, and $LaNb_8O_{14}$ (8) and in $Rb_4Al_2Nb_{35}O_{70}$ (9).

We present here the synthesis and the crystallochemistry of the second series obtained in our Me_6 cluster oxohalides investigation, $M_2RETa_6Br_{15}O_3$, based on $(Ta_6Br_{15}O_3)^{5-}$ units. The structure type of this new series has been refined by X-ray diffraction data obtained from a $Cs_2LaTa_6Br_{15}O_3$ single crystal.

II. EXPERIMENTAL

1. Synthesis of the $M_2RETa_6Br_{15}O_3$ Oxohalides

Reaction of powdered Ta (Alfa, purity m3N, t2N6), Ta_2O_5 (Ventron, purity 99.5%), RE_2O_3, and MCl (Prolabo, purity 99.5%) in stoichiometric proportions leads to $M_2RETa_6Br_{15}O_3$. The mixture is handled under a dry atmo-

TABLE 1
Unit-Cell Parameters of the $M_2RETa_6Br_{15}O_3$ Oxohalides

M	K	Rb	Cs
$M_2LaTa_6Br_{15}O_3$	$a = 9.463(3)$ Å	$a = 9.467(1)$ Å	$a = 9.512(2)$ Å
	$c = 17.669(4)$ Å	$c = 17.715(3)$ Å	$c = 17.935(3)$ Å
	$V = 1370$ Å^3	$V = 1379$ Å^3	$V = 1406$ Å^3
$M_2CeTa_6Br_{15}O_3$		$a = 9.458(2)$ Å	$a = 9.496(2)$ Å
		$c = 17.714(4)$ Å	$c = 17.929(3)$ Å
		$V = 1372$ Å^3	$V = 1400$ Å^3

sphere and pressed in the form of a pellet; then it is heated for 24 hr at 700°C with some pieces of tantalum foil in an evacuated silica tube. The phases are obtained without a noticeable quantity of secondary phases detectable in the X-ray powder patterns; they can be indexed in the trigonal system. The unit cell parameters versus rare earth and alkali element countercations are summarized in Table 1. They have been refined by a least-squares fit, from X-ray powder patterns using Si as internal standard, recorded with an INEL CPS 120 diffractometer ($CuK\alpha_1$ radiation).

The reaction is prolonged for 1 week to obtain Cs_2LaTa_6 $Br_{15}O_3$ single crystals of good quality suitable for structural determination.

2. Crystal Data and Structural Determination of $Cs_2LaTa_6Br_{15}O_3$

Intensity data were recorded at room temperature with a Nonius CAD-4 four-circle diffractometer. The unit-cell parameters were determined by a least-squares refinement of 25 reflections. Conditions limiting the possible reflections in diffractometer data are hhl, $l = 2n$. The experimental conditions for data collection are summarized in Table 2.

Intensity data treatment and refinement calculations were performed using the MOLEN programs from Enraf–Nonius (13) on a Digital Micro VAX 3100. The measured intensities have been corrected for Lorentz and polarization effects. Empirical absorption correction was applied. The structure was solved in the $P\bar{3}1c$ space group by direct methods using MULTAN 11/82 (14) and difference Fourier synthesis. The atomic positional parameters are reported in Table 3; the interatomic distances and angles are given in Table 4. Additional materials, anisotropic thermal parameters, and observed and calculated structure factors can be obtained upon request to the authors.

III. RESULTS

In this section, comparisons will be made between $Cs_2LaTa_6Br_{15}O_3$ and $CsErTa_6Br_{18}$ (15), for which the unit

TABLE 2
Crystal Data and Experimental Parameters for the Intensity Data Collection

I. Crystal data

Formula: $Cs_2LaTa_6Br_{15}O_3$	$M = 2737$ g/mole
Crystal system: trigonal	Space group: $P\bar{3}1c$, No. 163
$a = 9.512(2)$ Å, $c = 17.935(3)$ Å	$V = 1405.6(3)$ Å^3
Unit cell refined from 25 reflections ($8° < \theta < 14°$)	
$\rho_{cal} = 6.47$ g·cm^{-3}	$Z = 2$
Crystal size: $0.11 \times 0.11 \times 0.16$ mm^3	
Linear absorption factor: 48.157 mm^{-1}	

II. Data collections

Temperature: 295 K	Wavelength: Mo$K\alpha$ radiation
Diffractometer: Enraf–Nonius CAD-4	Scan mode: $\omega - 2\theta$
Monochromator: graphite	Scan width: $1.20 + 0.35 \tan\theta$
$-13 < h < 0$; $0 < k < 13$; $0 < l < 25$	$\theta_{max} = 30°$
3 standard reflections	
3053 measured reflections	
1210 independent reflections (with $I > \sigma(I)$)	$R_{int} = 0.018$

III. Structure determination

Lorentz and polarization corrections	
Absorption correction empirical: (DIFABS (10))	$T_{min} = 0.70$, $T_{max} = 1.43$
Refinement on F	
1140 independent reflections with $I > 2\sigma(I)$ and 5 bad reflections eliminated	
Refined parameters: 44	
Unweighted agreement factor $R = 0.029$	
Weighted agreement factor $R_w = 0.034$	$\omega = 4 F_0^2/[\sigma^2(F_0^2) + (0.04 F_0^2)^2]$
$S = 1.007$	$(\Delta/\sigma)_{max} < 0.03$
$\Delta\rho_{max} = 2.0(5)$ e Å^{-3}	$\Delta\rho_{min} = -2.4(5)$ e Å^{-3}
Extinction correction (11)	Extinction coefficient: $4.4(3) \times 10^{-8}$
Atomic scattering factor from Internal Tables for X-Ray Crystallography (12)	

stackings are directly connected, and with $LuTa_6Br_{13}O_3$ (4), for which the units and the VEC are similar.

The structure of $Cs_2LaTa_6Br_{15}O_3$ is strongly connected to the structure of $CsErTa_6Br_{18}$ ($CsLuNb_6Cl_{18}$ type, $P\bar{3}1c$), which we have previously determined (15). Their comparison is represented in Fig. 1. This oxohalide crystallizes also in the trigonal system with the $P\bar{3}1c$ space group, but these two structures are not isotypic.

In both $Cs_2LaTa_6Br_{15}O_3$ and $CsErTa_6Br_{18}$ structures, the $(Me_6L_{18})^{n-}$ units are located on the ternary axes of the trigonal unit cell, with the Ta and Br^a atoms and one Br^i atom occupying general $12i$ positions. The x and y

TABLE 3
Positional Parameters, Isotropic Equivalent B, and Their Estimated Standard Deviations for $Cs_2LaTa_6Br_{15}O_3$

Atom	Position	x	y	z	B (Å^2)
Ta	12 i	0.82680(3)	0.01643(3)	0.68546(2)	0.143(5)
La	2 c	$\frac{2}{3}$	$\frac{1}{3}$	0.750	0.36(1)
Cs	4 f	$\frac{2}{3}$	$\frac{1}{3}$	0.04781(6)	1.60(1)
Br3	12 i	0.22312(9)	0.01908(9)	0.08534(5)	0.52(1)
Br1	12 i	0.6038(1)	0.0742(1)	0.61657(5)	0.86(2)
Br2	6 h	0.42833	0.21417(7)	0.250	0.61(2)
O	6 h	0.1812(5)	0.3624	0.250	0.5(2)

Note. The isotropic equivalent displacement parameter is defined as: $(\frac{4}{3})$ $[a^2B(1, 1) + b^2B(2, 2) + c^2B(3, 3) + ab(\cos \gamma)B(1, 2) + ac(\cos \beta)B(1, 3) + bc(\cos \alpha)B(2, 3)]$.

positional parameters of these atoms are very close to each other in the two structures, but a shift of the units along the c axis gives units centered at $0\ 0\ \frac{1}{4}$ and $0\ 0\ \frac{3}{4}$ (32 point symmetry) in $Cs_2LaTa_6Br_{15}O_3$ instead of $0\ 0\ 0$ and $0\ 0\ \frac{1}{2}$ ($\bar{3}$ point symmetry) in $CsErTa_6Br_{18}$. The last general 12i position occupied by a Br^i atom in $CsErTa_6Br_{18}$ is now split into two special 6h positions in $Cs_2LaTa_6Br_{15}O_3$, one of them being occupied by the oxygen and the other by the bromine. In the $AA'A$ stacking represented in Fig. 1, the units of the A' layer are rotated about 13° around the ternary axis with respect to the units of the A layer; the corresponding rotation was about 20° for $CsErTa_6Br_{18}$.

The new situation of the units in the structure of $Cs_2La Ta_6Br_{15}O_3$, as compared to $CsErTa_6Br_{18}$, leads to new positions for the cationic sites, 4f for the cesium and 2c for the lanthanum instead of 2c and 2d for the cesium and erbium, respectively, in $CsErTa_6Br_{18}$, allowing two cesium per formula in this new oxohalide.

1. The $Ta_6Br_9^iO_3^i)Br_6^a$ Unit

The $(Ta_6Br_9^iO_3^i)Br_6^a$ unit represented in Fig. 2 exhibits $D3$ symmetry. Nine bromine and three oxygen atoms, which are ordered, lie in inner positions and six bromine atoms are located in apical positions. The difference between the size of the oxygen and the bromine, both bound to the Ta_6 cluster, induces great distortions in the cluster. Indeed, the Ta–Ta intracluster distances range from 2.753(1) to 3.033(1) Å.

A $(Ta_6Br_9^iO_3^i)Br_2^aBr_{4/2}^{a-a}$ unit, which also exhibits three oxygen ligands in inner positions, has been observed in the other oxohalide $LuTa_6Br_{13}O_3$ (4), but with the lower $C2$ symmetry, with one oxygen lying on the binary axis. For the latter compound the Ta_6 cluster is also greatly deformed, with the Ta–Ta distances ranging from 2.780(4) to 3.009(4) Å. The other $Ta–Br^i$, $Ta–Br^a$, and $Ta–O^i$ distances are very close to the corresponding distances in these two structures.

TABLE 4
Interatomic Distances (Å) and Angles (°) for $Cs_2LaTa_6Br_{15}O_3$

Ta_6 cluster				
Ta–Ta	2.998(1)	6×	Ta–Ta–Ta	92.43(1)
Ta–Ta	2.753(1)	3×	Ta–Ta–Ta	87.10(1)
Ta–Ta	3.033(1)	3×	Ta–Ta–Ta	60
Ta–Ta	4.156(1)		Ta–Ta–Ta	62.19(1)
			Ta–Ta–Ta	63.49(1)
			Ta–Ta–Ta	54.33(1)
$(Ta_6Br_9O_3)Br_6$ unit				
Ta–Br3	2.615(1)	6×	Ta–O–Ta	88.10(2)
Ta–Br2	2.591(1)	3×	Ta–Br3–Ta	69.91(3)
Ta–Br1	2.738(1)	6×	Ta–Br2–Ta	71.63(1)
Ta–O	1.980(2)	3×		
Shortest other distances in the unit				
O–O	4.342(1)			
Br2–Br2	3.401(1)			
Br1–Br1	3.858(1)			
Lanthanum environment				
La–O	2.507(1)	3×	Br1–La–Br1	120.75(1)
La–Br1	3.269(1)	6×	Br1–La–Br1	98.45(1)
Br1–Br1	3.858(1)	6×	Br1–La–Br1	161.77(1)
O–O	4.342(1)	3×	Br1–La–Br1	72.32
			Br1–La–O	120
			O–La–O	120
			Br1–Br1–Br1	60
			O–O–O	60
Cesium environment				
Cs–Br1	3.695(1)	3×		
Cs–Br1	3.632(1)	3×		
Cs–Br3	3.818(1)	3×		
Cs–Br2	4.124(1)	3×		
Br1–Br1	5.918(1)			
Shortest other distances				
La–Ta	4.164(1)			
Cs–Ta	4.856(1)			
Ta–Ta	6.488(1)			
La–La	9.513(1)			
Cs–La	5.341(1)			
Cs–Cs	5.574(1)			

2. The Lanthanum Environment

The lanthanum site represented in Fig. 3 is built by three $(Ta_6Br_9O_3)Br_6$ units, each of them giving one inner oxygen and two apical bromines to build a 9-coordination of $D3$ symmetry. One triangle of bromine lies above and one lies below a triangle of oxygen, the center of the latter being occupied by the lanthanum. The Br1–Br1 distance of 3.858(1) Å in each triangle of bromine is short and corresponds to the ionic radius sum of two Br^- ions (Br^- radius = 1.96 Å). The length of this distance indicates that it should not be possible to insert a smaller rare earth in this site, because it seems not to be possible to bring these
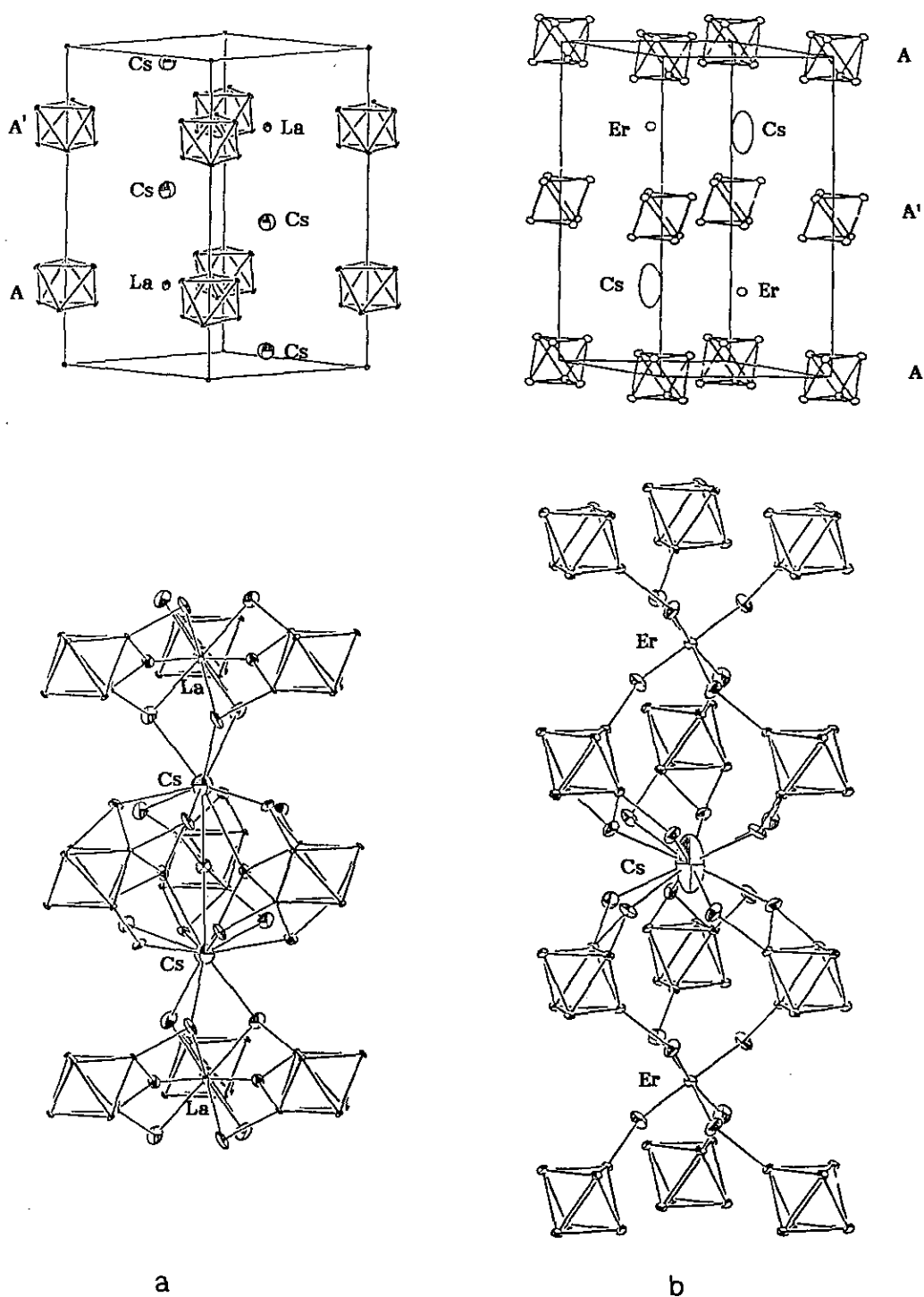
a

b

FIG. 1.   Structures of $Cs_2LaTa_6Br_{15}O_3$ (a) and $CsErTa_6Br_{18}$ (b) for comparison. (a) top: unit cell of $Cs_2LaTa_6Br_{15}O_3$ (for clarity the Br and O atoms are not represented), bottom: Cs and La environment (only the Br and O atoms involved in the coordination spheres are represented); (b) top: unit cell of $CsErTa_6Br_{18}$ (for clarity the Br atoms are not represented), bottom: Cs and Er environment (only the Br atoms involved in the coordination spheres are represented).
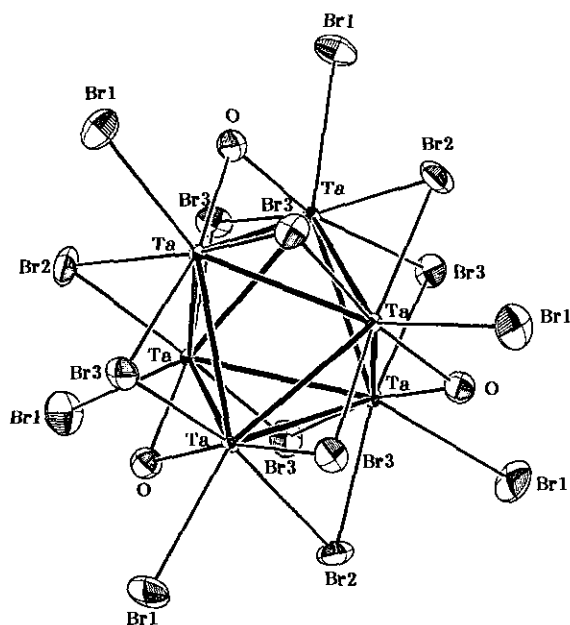
FIG. 2. The $(Ta_6Br_9^iO_3^i)Br_6^a$ unit.

bromine ions closer. Effectively, during the synthesis, we have not succeeded in obtaining compounds with small rare earths.

This original rare earth environment, which is non-centrosymmetric, is encountered for the first time in the cluster halide chemistry. In the $M_xREMe_6X_{18}$ compounds the rare earth lies in a more or less strongly distorted octahedron formed by six apical halogen atoms belonging to six adjacent units (16), while in the $REMe_6X_{13}O_3$ it is five-coordinated by three inner oxygen and two apical halogen atoms in a site of $C2$ symmetry (3). Usually, in the oxoniobates the rare earth environment is more complex, for instance, 12-coordinated in $LaNb_8O_{14}$ (8).

This situation of the rare earth in the structure leads to shorter RE–Ta distances than in the corresponding halide: for instance, RE–Ta = 4.164(1) and 5.231(1) Å in Cs_2La $Ta_6Br_{15}O_3$ and $CsErTa_6Br_{18}$, respectively, but this distance is longer than in $LuTa_6Br_{13}O_3$ (RE–Ta = 3.585(1) Å), even taking into account the ionic radius of the rare earth considered in these three compounds.

3. The Cesium Environment

Similarly as for $CsErTa_6Br_{18}$, the cesium atom surrounded by six adjacent units is 12-coordinated by bromine atoms, but the building of this site is different in the two structures. Indeed, in order to form the cesium site, each of three units gives two Br^i and one Br^a and each of the three other units gives only one Br^a (Fig. 4), while in $CsErTa_6Br_{18}$ each of the six units gave one Br^i and one Br^a. This bromine environment is smaller and more isotropic in
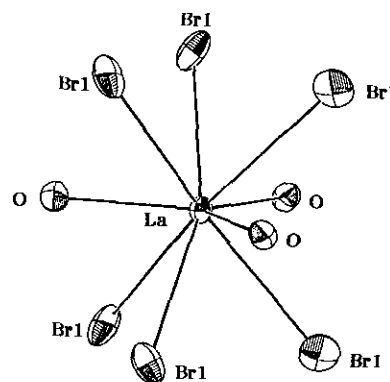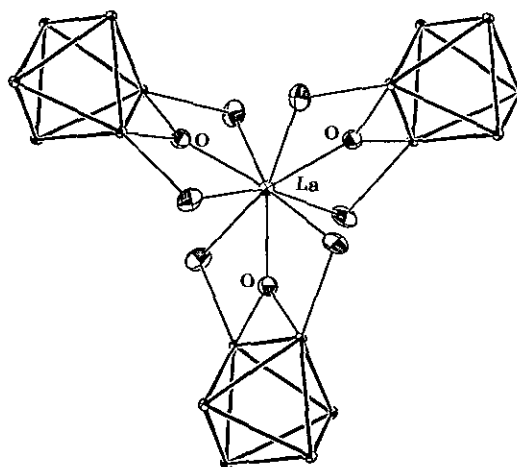

FIG. 3. The lanthanum environment.

$Cs_2LaTa_6Br_{15}O_3$ than in $CsErTa_6Br_{18}$, as evidenced by the shorter Cs–Br distances (averaged Cs–Br distances: 3.817 and 3.972 Å in $Cs_2LaTa_6Br_{15}O_3$ and $CsErTa_6Br_{18}$, respectively) and by the value and the shape of the Cs thermal factor. This latter value was especially high (7.60 Å^2) and anisotropic for $CsErTa_6Br_{18}$, due to the large opening of the bromine environment above and below the cesium (see Fig. 1b).

IV. DISCUSSION AND CONCLUSION

The presence of both oxygen and halogen ligands around the Me_6 cluster in niobium and tantalum oxohalides allows an increase in the charge of the $(Me_6L_{18})^{n-}$, when comparing to halides synthesized by solid state chemistry, for which this charge is usually 3, or 4, for instance in $Ba_2Nb_6Cl_{18}$ (17), $LuNb_6Cl_{18}$ (1), and $K_4Nb_6Cl_{18}$ (6). As a consequence, the charge and/or the number of the countercations can be increased. Indeed, in $Cs_2LaTa_6Br_{15}O_3$ we have obtained for the first time in the tantalum cluster
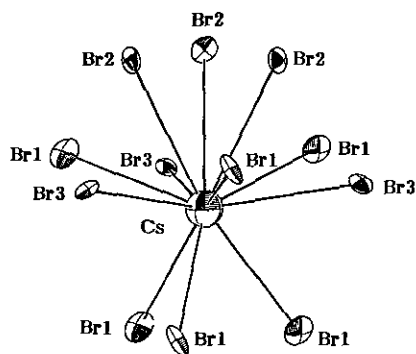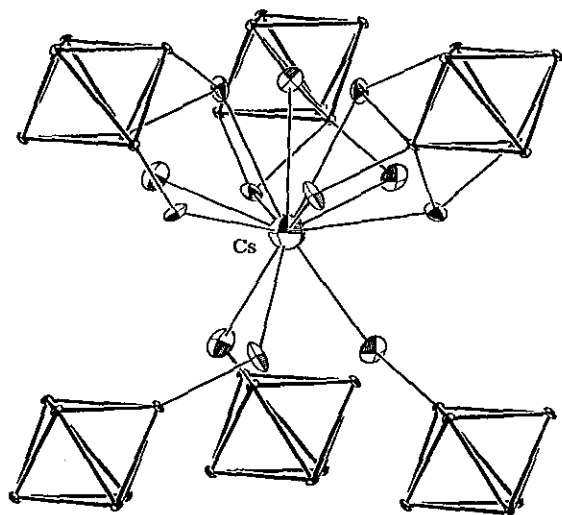
FIG. 4. The cesium environment.

halide chemistry the anionic $(Me_6L_{18})^{n-}$ unit with $n = 5$, which has led to a new structure type. Such important anionic charge was also observed in the zirconium cluster halide chemistry, for instance in $Rb_5Zr_6Cl_{18}B$ ($n = 5$) (18) or in $Li_6Zr_6Cl_{18}H$ ($n = 6$) (19). In the latter case it is the presence of an interstitial element inside the cluster which allows the control of the anionic charge of the $(Me_6L_{18})^{n-}$ unit and not a repartition of different types of ligands around the cluster as in $Cs_2LaTa_6Br_{15}O_3$.

The VEC of 14, observed in $Cs_2LaTa_6Br_{15}O_3$, has been obtained for the second time in the oxohalide chemistry, the first one being in the $REMe_6X_{13}O_3$ series. It must be noted that these Me_6 ($Me = $ Nb or Ta) oxohalides with VEC = 14 are obtained by solid state synthesis. In contrast, the Me_6 halides are usually easily obtained for VEC = 16 or 15, the compounds with VEC = 14 being synthesized

only under mild conditions mainly by solution chemistry. The VEC of 14 seems to correspond to a stable oxidation state of the Me_6 cluster in the oxohalide chemistry. Thus, the presence of the oxygen around the Me_6 cluster reduces the boundary between the cluster halides and the cluster oxides, with the latter being usually stabilized for a VEC < 16 (7).

Very recently, we have obtained a compound isotypic with $Cs_2LaTa_6Br_{15}O_3$ in which the rare earth is replaced by the barium ($a = 9.728(3)$ Å, $c = 17.804(3)$ Å, and $V = 1459(1)$ Å^3) for which the VEC should be 13. This value of the VEC is rare in the niobium cluster halide and oxohalide chemistry and it could be interesting to study the magnetic behavior of this compound in which the clusters are close to each other; this work is now in progress. To our knowledge, the only other example of a Nb_6 cluster compound with VEC = 13 is KNb_8O_{14}, which exhibits a weak temperature-independent paramagnetism (8); according to (8), additional pairing of spin between isolated clusters in this compound must be implied.

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