New Compounds in the Ta$_6$ Bromide Chemistry: M_2RETa$_6$Br$_{18}$, MRETa$_6$Br$_{18}$, RETa$_6$Br$_{18}$ (M = monovalent cation, RE = rare earth)—Crystal Structure of CsErTa$_6$Br$_{18}$

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The new compounds M_2RETa$_6$Br$_{18}$ (M = K, Rb, Cs; RE = Eu, Yb), MRETa$_6$Br$_{18}$ (M = K, Rb, Cs; RE = La to Lu and Y), and RETa$_6$Br$_{18}$ (RE = Nd to Tm) have been isolated. All these compounds are isotypic with KLuNb$_6$Cl$_{18}$, space group $R\bar{3}$, except the series CsRETa$_6$Br$_{18}$, which is isotypic with CsLuNb$_6$Cl$_{18}$, space group $P\bar{3}1c$. They exhibit 16 or 15 e^-/Ta$_6$ depending on the monovalent cation stoichiometry and the rare earth oxidation state, in opposition to the corresponding niobium bromide chemistry for which only compounds with 16 e^-/Nb$_6$ had been obtained. The structure of CsErTa$_6$Br$_{18}$ has been determined by X-ray diffraction on a single crystal: $P\bar{3}1c$ (Z = 2) with a = 9.661(1) Å and c = 18.037(3) Å, R = 0.048 and R_w = 0.062 for 620 symmetry-independent reflections. A comparison with the isotypic CsEr-Nb$_6$Br$_{18}$ allows discussion of the Me–Me intracluster distances, which mainly influence the stability of the various oxidation states of the Nb$_6$ or Ta$_6$ cluster in bromide chemistry. © 1995 Academic Press, Inc.

INTRODUCTION

Only a few crystal structures are fully described in the literature for ternary niobium or tantalum halides based on edge-capped Me_6X_{18} units. For instance, K$_4$Nb$_6$Cl$_{18}$ (1) and Ba$_2$Nb$_6$Cl$_{18}$ (2) were characterized many years ago, and In$_2$Li$_2$Nb$_6$Cl$_{18}$ (3) was described very recently. In recent years we have found two new structure types, KLuNb$_6$Cl$_{18}$ and CsLuNb$_6$Cl$_{18}$—labeled ($R\bar{3}$) and ($P\bar{3}1c$), respectively, in this paper—in the niobium and tantalum cluster halide chemistry, with monovalent cations and rare earth as counter cations (4, 5). These two structure types have been also encountered in the centered zirconium cluster halide chemistry, for instance K$_2$Zr$_7$Cl$_{18}$H ($R\bar{3}$) (6) and CsLaZr$_6$Cl$_{18}$Fe ($P\bar{3}1c$) (7). The more general formula of our cluster halides is $M_xREMe_6X_{18}$ (M = monovalent cation, RE = rare earth, Me = Nb or Ta, X = Cl or Br) (8). The value of x can be 0, 1, or 2 in ($R\bar{3}$), corresponding to the M site being empty, half full, or full, respectively, and x = 1 in ($P\bar{3}1c$), corresponding to the M site being full. In the latter structure type, we have never found any example of the M site being partially occupied. All these structures are fully described in (4, 5) for niobium chlorides and in (9) for niobium bromides.

In all these $M_xREMe_6X_{18}$ compounds, the number of valence electrons per cluster (VEC) can be 16 or 15, depending on the stoichiometry and charge of the counter cations. In the synthesis conditions utilized, we have never obtained compounds with a VEC = 14. Indeed, this VEC corresponds to the less stable Me_6 cluster oxidation state in the niobium and tantalum halide chemistry, which can be only stabilized under mild conditions (8). In these niobium or tantalum chlorides, compounds with VEC = 15 or 16 are easily obtained and the same feature was also observed in the isotypic tantalum bromides; however, in the similar niobium bromides, no compound with a VEC = 15 has been isolated, even though, at first sight, all structural and chemical considerations could allow this VEC.

In this paper, we present in detail the chemistry of the tantalum bromides M_xRETa$_6$Br$_{18}$ and the structural determination of CsErTa$_6$Br$_{18}$, in order to compare them with the corresponding niobium bromides and to determine if chemical or structural features could influence the stability of compounds with VEC = 16 or 15.

EXPERIMENTAL

Crystallochemistry of M_2RETa$_6$Br$_{18}$, MRETa$_6$Br$_{18}$, RETa$_6$Br$_{18}$

The compounds of the three series M_2RETa$_6$Br$_{18}$, MRETa$_6$Br$_{18}$, and RETa$_6$Br$_{18}$ were prepared by solid state chemistry, from stoichiometric amounts of MBr (Prolabo, purity 99.5%), TaBr$_5$ (Alfa, purity 99.9%), tantalum powder (Alfa, purity $m3N$, $t2N6$), and REBr$_3$ synthesized from rare earth oxides according to the procedure described in (10). The mixture, handled under dry atmosphere, was pressed into the form of pellets and heated in an evacuated, sealed silica tube for 24 hr, at temperatures ranging from 600 to 700°C, depending on the nature of the rare earth. Single crystals of these compounds, of

sufficient size and quality for structural determination, were very difficult to obtain, much more difficult than in the corresponding niobium chemistry. We have tried several techniques of crystal growth without success. Ultimately, a crystal of CsErTa$_6$Br$_{18}$ with sufficiently good characteristics for structural determination was obtained directly during a two-week synthesis, using molybdenum foil as reducing agent. Under these conditions of synthesis, the molybdenum foil is slightly attacked and volatile secondary phases are observed, but no molybdenum was detected in the CsErTa$_6$Br$_{18}$ crystals at the sensitivity level of EDS microprobe analysis.

The unit-cell parameters were determined from the X-ray powder patterns, using Si as internal standard, recorded with an INEL CPS 120 diffractometer, fitted with a curved position sensitive detector (Cu$K\alpha1$ radiation). They were refined by a least-square fit.

Data Collection for Structural Determination of CsErTa$_6$Br$_{18}$

The intensity data of CsErTa$_6$Br$_{18}$ were recorded at room temperature with a NONIUS CAD-4 diffractometer. The unit-cell parameters were determined by least-square refinement of 18 reflections. The experimental details of the data collection are given on Table 1. Additional materials, anisotropic thermal parameters, and the observed and calculated structure factors, can be obtained on request from the authors.

The treatment of the data collection and the refinements were performed with MOLEN programs from Enraf-Nonius (13), using a MICROVAX computer. The measured intensities have been corrected for the Lorentz and polarization effects.

RESULTS .

In the compounds described below, the rare earth is always trivalent. However, for europium and ytterbium, some special features appear, since, as it is well known, these two rare earths can exhibit two oxidation states. Indeed, the charge of the rare earth is influenced by the proportion of the monovalent cation in the starting mixture, in order to favor the formation of the most stable 16 e^-/Ta$_6$ cluster compounds. Moreover, for these two rare earths, the special case where ($R\bar{3}$) and ($P\bar{3}1c$) structures coexist in the synthesized product will be discussed at the end of Section (b).

(a) RETa$_6$Br$_{18}$

This series belonging to the ($R\bar{3}$) structure type in which the M site is empty, has been only obtained for RE = Y and Nd to Tm, with unit-cell parameters ranging from a = 9.751(1) Å, c = 26.729(3) Å for NdTa$_6$Br$_{18}$ to a =

TABLE 1
Crystal Data and Experimental Parameters for the Intensity Data Collection

I. Crystal data

Formula: CsErTa$_6$Br$_{18}$	M = 2824
Crystal system: trigonal	space group: $P\bar{3}1c$ (no. 163)
a = 9.661(1) Å, c = 18.037(3) Å	V = 1457.8(3) Å^3
Unit-cell refined from 18 reflections (5 < θ < 18°)	
ρ_{cal} = 6.43 g·cm^{-3}	Z = 2
Crystal size: 0.09 × 0.09 × 0.09 mm^3	
Linear absorption factor: 50.72 mm^{-1}	

II. Data collections

Temperature: 295 K	Wavelength: Mo$K\alpha$ radiation
Diffractometer: Enraf-Nonius CAD-4	Scan mode: ω-2θ
Monochromator: graphite	Scan width: 1.0 + 0.35 tgθ
$-13 < h < 0$; $0 < k < 13$; $0 < l < 25$	θ_{max} = 30°
3 standard reflections	
3150 measured reflections	
989 independent reflections (with $I > \sigma(I)$),	
R_{int} = 0.067	

III. Structure determination

Lorentz and polarization correction	
Refinement on F	
620 independent reflections (with $I > 3\sigma(I)$)	and 10 bad reflections eliminated
Refined parameters: 42	
Unweighted agreement factor R = 0.048	
Weighted agreement factor R_w = 0.062	$w = 4F_0^2/[\sigma^2(F_0^2) + (0.07F_0^2)^2]$
S = 0.957	$(\Delta/\sigma)_{max}$ < 0.004
$\Delta\rho_{max}$ = 2.2(7)e Å^{-3}	
Extinction correction (11)	Extinction coefficient: 3.7(6) × 10^{-8}
Atomic scattering factors from International Tables for X-Ray Crystallography (12)	

9.704(2) Å, c = 26.426(7) Å for TmTa$_6$Br$_{18}$. The unit-cell volume variation versus the ionic radius of the trivalent rare earth is displayed in Fig. 1. A good correlation can be observed, as expected. It must be noticed that the compound with RE = Lu is not obtained in these conditions of synthesis, even though it exists in the chloride chemistry. Indeed, this rare earth is probably too small to bind together the large Ta$_6$Br$_{18}$ units, and steric effects have to be taken into account.

Up to now, we have not obtained RETa$_6$Br$_{18}$ compounds with RE = Yb or Eu.

(b) MRETa$_6$Br$_{18}$

With M = Na, we have obtained only one compound of the ($R\bar{3}$) structure type in which the M site is half-
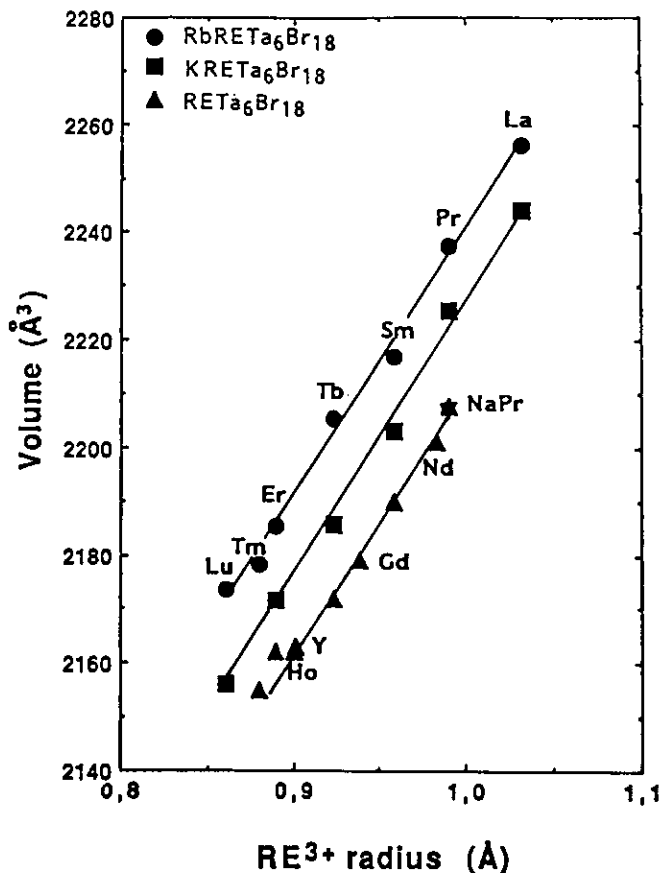
FIG. 1. Variation of the hexagonal unit-cell volume versus the ionic radius of the trivalent rare earth for the $MRETa_6Br_{18}$ ($M = K$, Rb) and $RETa_6Br_{18}$ compounds.

occupied: $NaPrTa_6Br_{18}$ with $a = 9.755(4)$ Å and $c = 26.788(1)$ Å. In Fig. 1, one can see that the unit-cell volume of this bromide falls exactly at the expected value for "$PrTa_6Br_{18}$" if the latter should exist. In fact, in ternary compounds, the structure is maintained by the rare earth. The size of the rare earth influences the size of the empty M site. When the latter is too large, for instance with rare earths such as Pr, the structure cannot be stabilized. In this case, it is necessary to fill the M site. $NaPrTa_6Br_{18}$ constitutes the limit for which a good compromise exists between the size of the rare earth and the size of the M site which can be filled by a small cation such as Na. With $RE = Ce$ or La, the M site is too large for Na, and the structure must be distorted to accept K in this site.

With $M = K$ and Rb, we have synthesized a lot of compounds of the ($R\bar{3}$) structure type with the M site half-occupied, for $RE = La$ to Lu and trivalent Eu or Yb. We have refined the unit-cell constants of the compounds reported in Fig. 1. Their unit-cell parameters range from $a = 9.823(2)$ Å, $c = 26.998(5)$ Å for $RbLaTa_6Br_{18}$ to $a = 9.721(2)$ Å, $c = 26.556(4)$ Å for $RbLuTa_6Br_{18}$, and from

$a = 9.792(2)$ Å, $c = 27.019(3)$ Å for $KLaTa_6Br_{18}$ to $a = 9.693(3)$ Å, $c = 26.947(4)$ Å for $KLuTa_6Br_{18}$. The hexagonal unit-cell volumes of these two series are displayed in Fig. 1. The two evolutions correlate well with the variation of the ionic radius of the trivalent rare earth and of the monovalent cation.

Note that for europium and ytterbium, when $M = K$, Rb, the X-ray patterns give evidence that a mixture of the two ($R\bar{3}$) phases, $M_2RETa_6Br_{18}$ (M site fully occupied) and $MRETa_6Br_{18}$, is always obtained, even if the conditions of synthesis or the stoichiometry of the starting mixture are changed. In these compounds the rare earth would be divalent or trivalent, respectively. The same results are obtained with $M = Tl$.

When $M = Cs$, the compounds exhibit the ($P\bar{3}1c$) structure type with the monovalent site always fully occupied. They are obtained with all the trivalent rare earths (La to Lu including the trivalent Eu or Yb), with the unit-cell constants ranging between $a = 9.760(2)$ Å, $c = 18.206(7)$ Å for $CsLaTa_6Br_{18}$ and $a = 9.658(2)$ Å and $c = 18.028(3)$ Å for $CsLuTa_6Br_{18}$. Their unit-cell volume variation is represented on Fig. 2 with the evolution of the corre-
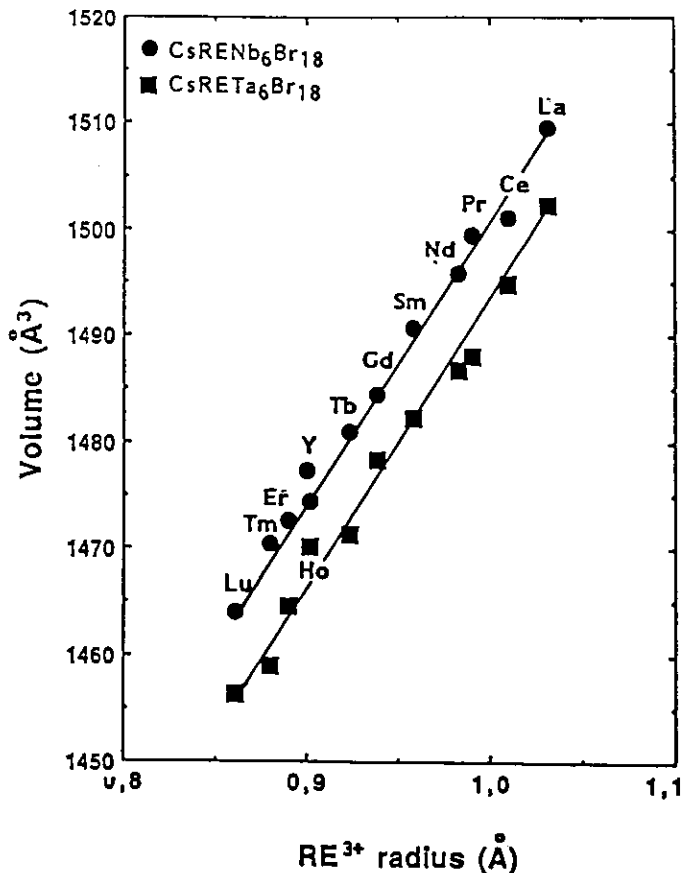

FIG. 2. Variation of the unit-cell volume versus the ionic radius of the trivalent rare earth for $CsRETa_6Br_{18}$.

sponding $CsRENb_6Br_{18}$ for comparison. One can notice that the volume of the tantalum compounds is systematically smaller than the corresponding niobium ones. For the latter compounds the unit-cell parameters range from $a = 9.778(2)$ Å, $c = 18.230(6)$ Å for $CsLaNb_6Br_{18}$ to $a = 9.675(2)$ Å, $c = 18.057(5)$ Å for $CsLuNb_6Br_{18}$.

Note that for europium and ytterbium, two compounds can be obtained: $CsRETa_6Br_{18}$ ($P\bar{3}1c$) as detailed above, and $Cs_2RETa_6Br_{18}$ ($R\bar{3}$) in which the monovalent site is fully occupied. The synthesis 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 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 ($P\bar{3}1c$) compound being preferentially formed at lower temperatures. An increase in the reaction time does not change the ratio of ($R\bar{3}$)/($P\bar{3}1c$) phases in the final product.

The coexistence of the two ($R\bar{3}$) and ($P\bar{3}1c$) phases had also been observed for $RbRENb_6Cl_{18}$ (RE = La, Ce): the ($R\bar{3}$) phase is formed at low temperatures, while the proportion of ($P\bar{3}1c$) increases at higher temperatures, but in that case the stoichiometry and charge of the counter cations were exactly the same for the two structures. A similar observation was also made by J. Zhang and J. D. Corbett (7) in the zirconium chemistry with $CsLaZr_6$ Cl_8(Fe) which can exhibit the ($R\bar{3}$) or ($P\bar{3}1c$) phase, depending on the temperature of synthesis, ($R\bar{3}$) being more stable at lower temperatures. The coexistence of ($R\bar{3}$) and ($P\bar{3}1c$) phases observed for the tantalum bromides is difficult to compare with the similar coexistence in $RbRENb_6Cl_{18}$ or $CsLaZr_6Cl_{18}$(Fe) compounds. Indeed, the rare earth has not the same oxidation state in these two $CsRETa_6Br_{18}$ and $Cs_2RETa_6Br_{18}$ phases. Moreover, as we have previously discussed (9), it is not possible to obtain an ($R\bar{3}$) phase with only one Cs in the formula with divalent europium or ytterbium. So, other factors could influence the stability of these two ($R\bar{3}$) and ($P\bar{3}1c$) tantalum bromides when comparing to $RbRENb_6Cl_{18}$ and $CsLaZr_6Cl_{18}$(Fe), but, nevertheless, we can assume that for Eu and Yb the trivalent oxidation state is difficult to stabilize.

Due to the complexity of the X-ray patterns obtained for europium and ytterbium quaternary compounds, it has been difficult to determine the unit-cell parameters of all these compounds with sufficient accuracy, with the exception of $Cs_2YbTa_6Br_{18}$ and $Cs_2EuTa_6Br_{18}$, for which $a = 9.836(4)$ Å, $c = 27.11(2)$ Å and $a = 9.920(2)$ Å, $c = 27.36(1)$ Å, respectively. For the latter tantalum compounds, the unit-cell volume is smaller than for the corre-

TABLE 2

Positional Parameters and Their Estimated Standard Deviations for $CsErTa_6Br_{18}$

Atom	x	y	z	B (Å²)
Ta	0.8481(1)	0.0372(1)	0.56535(7)	1.22(2)
Br1	0.6338(3)	0.0825(3)	0.6610(2)	1.98(6)
Br2	0.7212(3)	0.1440(3)	0.0010(2)	1.79(6)
Br3	0.2346(3)	0.0446(3)	0.1618(2)	1.75(6)
Cs	2/3	1/3	1/4	7.6(3)
Er	2/3	1/3	3/4	1.55(4)

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

sponding niobium ones (9), as observed for the ($P\bar{3}1c$) structure type.

(c) Structure of $CsErTa_6Br_{18}$

The structure of $CsErTa_6Br_{18}$ has been solved by isotypy with $CsErNb_6Br_{18}$ (9). The atomic positions are reported in Table 2. This structure is based on a pseudo-prismatic stacking of Ta_6Br_{18} units with $\bar{3}$ symmetry (Fig. 3), each unit being centered at the origin of the trigonal unit cell. The Cs and Er cations are located in $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$ and in $\frac{2}{3}$, $\frac{1}{3}$, $\frac{3}{4}$, respectively, in pseudo-prismatic environments of Ta_6Br_{18} units. They are bound to bromine atoms forming sites of $D3d$ symmetry, a distorted octahedron in the case of Er and a complex site of 12 bromine atoms in the case of Cs (Fig. 4). The large value and anisotropy of the Cs thermal factor is related to the great size and anisotropy of its bromine site, as already observed for the corresponding $CsErNb_6Br_{18}$ (9). Indeed, Cs is located between two Br_6 rings which arrange large openings above and
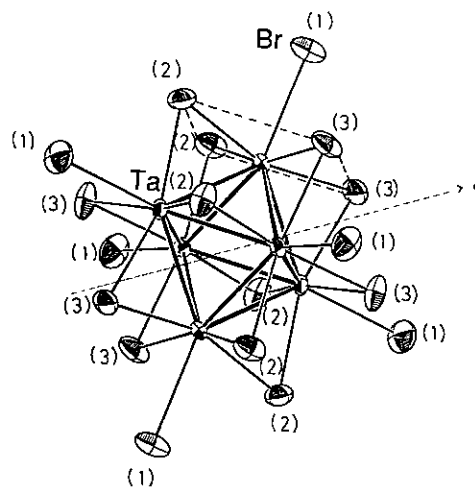

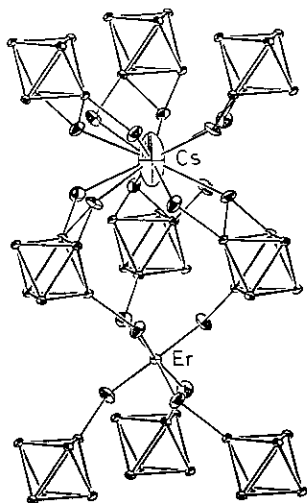FIG. 3. The Ta_6Br_{18} unit (97% probability ellipsoids).

FIG. 4. Caesium and erbium environments. For clarity, only the Br atoms coordinated to Cs and Er are represented (97% probability ellipsoids).

tance is greatly influenced by the oxidation state of the cluster (VEC = 16 or 15) and by the nature of the Me element (Ta or Nb):

—When the VEC decreases from 16 to 15, this corresponds to removal of one electron from the bonding a_{2u} orbital which weakens the Me–Me bonding, and the Me–Me distances increase (8, and references therein). This feature was clearly observed in the isotypic chlorides KLuNb$_6$Cl$_{18}$ (VEC = 16) and LuNb$_6$Cl$_{18}$ (VEC = 15) for which the Nb–Nb intracluster distance increases from 2.916(1) to 2.956(1) Å (14). So, for the compounds with VEC = 15, the Me$_6$ cluster is less stable than for VEC = 16 and the corresponding compounds are difficult to obtain; indeed, only a few of them are known.

—When comparing Nb$_6$ clusters to Ta$_6$ clusters, we can observe that in the latter the Me–Me distances are smaller than in Nb$_6$ clusters. Indeed in this work we have found, for instance in the case of CsREMe$_6$Br$_{18}$, that the volumes

below it. A similar large and anisotropic thermal factor has been also observed for the isotypic CsLaZr$_6$Cl$_{18}$Fe (7). This structure type was previously fully described and illustrated in (5, 9).

The interatomic distances are reported in Table 3 with the CsErNb$_6$Br$_{18}$ ones for comparison. When comparing these distances, we can observe that all the distances in the Me$_6$X$_{18}$ units are very similar within one standard deviation, with the exception of the Me–Me distances which are significantly shorter in the tantalum bromide than in the niobium one.

DISCUSSION

As we have described above, a great number of ternary (x = 0, VEC = 15) and quaternary (x = 1 or 2, VEC = 16) M_xRENb$_6$Cl$_{18}$ and M_xRETa$_6$Cl$_{18}$ chlorides had been previously obtained. In bromide chemistry, similar ternary and quaternary compounds are obtained with tantalum, but in the case of niobium bromides the chemistry is less developed. Indeed, the series CsRENb$_6$Br$_{18}$($P\bar{3}1c$) with VEC = 16 is obtained for all the trivalent rare earths except Eu and Yb, while in the ($R\bar{3}$) family only the M_2RENb$_6$Br$_{18}$ compounds (RE = divalent rare earth and VEC = 16) in which the M site is fully occupied have been isolated. Moreover, no ternary bromides RENb$_6$Br$_{18}$ (VEC = 15) have been obtained and, to our knowledge, no Nb$_6$ bromides with VEC = 15 are reported in the literature. We can postulate that an Nb$_6$ cluster with 15 valence electrons is difficult to stabilize in bromine systems, perhaps due to structural factors.

Stability of the Me$_6$ Cluster in Bromides with VEC = 15

First we intend to discuss the stability of the Me$_6$ cluster in relation to the Me–Me intracluster distance. This dis-

TABLE 3

Interatomic Distances (Å) and Angles (°) for CsErTa$_6$Br$_{18}$ (This Work) and CsErNb$_6$Br$_{18}$ (6)

	CsErTa$_6$Br$_{18}$	CsErNb$_6$Br$_{18}$
Me$_6$ cluster		
Me–Me	2.893(2)	2.950(1)
Me–Me	2.903(2)	2.958(1)
Me–Me–Me	60.24(6)	60.19(3)
Me–Me–Me	59.88(6)	59.90(3)
(Me$_6$Br$_{12}$)Br$_6$ unit		
Me–Br1	2.892(3)	2.885(2)
Me–Br2	2.585(3)	2.587(1)
Me–Br2	2.590(3)	2.589(1)
Me–Br3	2.594(3)	2.595(1)
Me–Br3	2.578(3)	2.576(1)
Br2–Br3	3.567(4)	3.578(1)
Br2–Br3	3.592(5)	3.603(1)
Br3–Br3	3.611(6)	3.615(2)
Br2–Br2	3.597(3)	3.606(1)
Br2–Br2	3.709(3)	3.722(1)
Caesium environment		
Cs–Br1	3.934(3)	3.940(1)
Cs–Br3	4.011(3)	4.029(1)
Erbium environment		
Er–Br1	2.789(3)	2.791(1)
Br1–Er–Br1	90.20(9)	90.25(3)
Br1–Er–Br1	168.68(9)	168.11(3)
Br1–Er–Br1	98.33(9)	98.74(3)
Br1–Er–Br1	82.39(9)	81.99(3)
Other distances		
Er–Cs	5.577	5.595
Er–Cs	9.661	9.692
Cs–Cs	9.661	9.692
Me–Er	5.231(1)	5.219(1)
Me–Cs	5.553(1)	5.550(1)

of the tantalum compounds are systematically smaller than the corresponding niobium ones. Moreover, when comparing the two structures CsErNb$_6$Br$_{18}$ and CsEr Ta$_6$Br$_{18}$, the only difference is for the *Me–Me* intracluster distance, which is smaller in the case of tantalum (2.898(2) Å) than for niobium (2.954(1) Å), all the other distances being very similar. This feature may be due to relativistic effects appearing when going from 4d to 5d elements. Several other families of isotypic compounds are known in niobium and tantalum cluster chemistry, but no sufficiently complete or precise data are available for useful comparison. To our knowledge, no systematic structural determination has been previously reported on isotypic Ta$_6$ and Nb$_6$ compounds for which the *Me*$_6$ clusters are in exactly the same environment (identical counter cation and identical ligand) and then differ only by the nature of the element (Nb or Ta).

—In all these isotypic series, $M_xREMe_6X_{18}$, the nature of the halogen influences the size of the *Me*$_6$ cluster (matrix effect). For instance, we had previously shown that the *Me–Me* intracluster distance is larger in bromides than in chlorides, when comparing the two isotypic structures CsErNb$_6$Br$_{18}$ and CsLuNb$_6$Cl$_{18}$ (Nb–Nb = 2.954(1) and 2.914(1) Å, respectively).

To summarize, a large *Me–Me* intracluster distance is favored, when VEC = 15, when the metal is niobium, and when the ligand is bromine. Thus, all three factors may contribute to the lower stability of the niobium bromide clusters with VEC = 15.

Stability of the Stacking in Bromides with VEC = 16

Another feature to be discussed is the stacking of the Me_6X_{18} units in the bromide clusters with VEC = 16, this stacking being greatly influenced by the size of the units, which is obviously larger with bromine than with chlorine. We have shown that the Me_6Br$_{18}$ units are smaller with tantalum than with niobium. Moreover, we had previously shown in the niobium bromides that the smaller unit is obtained with a divalent rare earth when comparing, for instance, the structures of CsErNb$_6$Br$_{18}$($P\overline{3}1c$) and Cs$_2$EuNb$_6$Br$_{18}$ ($R\overline{3}$) (9).

For all the rare earths except Eu and Yb and for both niobium and tantalum, the ($P\overline{3}1c$) structure type can be obtained with Cs, which maintains the cohesion of the structure by fully occupying the large *M* site arranged between the units. Oppositely, the ($R\overline{3}$) structure type is obtained only with tantalum, for which the units are smaller and so lead to smaller *M* sites which can be filled by *K*, Rb, or Tl.

Eu and Yb can exhibit two oxidation states. So, in niobium chemistry, the +2 oxidation state is observed, leading to M_2RENb_6Br$_{18}$ for which the Nb$_6$Br$_{18}$ unit is smaller than in ($P\overline{3}1c$) with RE^{3+}, if it should exist. Oppositely, in the tantalum chemistry where the units are

smaller, the +2 and +3 oxidation states can appear for these two rare earths and even coexist in the synthesized product. So, when *M* = Cs, we observe a mixture of CsRETa$_6$Br$_{18}$ ($P\overline{3}1c$) and Cs$_2RE$Ta$_6$Br$_{18}$ ($R\overline{3}$) phases, and when *M* = *K*, Rb, or Tl, we obtain a mixture of MRETa$_6$Br$_{18}$ and M_2RETa$_6$Br$_{18}$, both with the ($R\overline{3}$) structure.

Finally, in the niobium chemistry, it is necessary to have the smaller unit and full occupancy of the *M* sites, which leads to the more compact structure. In the tantalum chemistry, the cohesion of the structure is easily obtained, even with empty *M* sites, because the Ta$_6$Br$_{18}$ units are small.

In conclusion, the chemistry of these tantalum bromides is more extended than that of the corresponding niobium bromides. Particularly interesting is the fact that the ternary compounds RETa$_6$Br$_{18}$ with VEC = 15 can be obtained, in which the Ta$_6$ cluster is magnetic with one unpaired electron (14, 15). Interesting magnetic behavior, due to the presence in the compounds of both a magnetic cluster and a magnetic rare earth, could be encountered as in chloride compounds (16). But, due to the complexity of this chemistry, it is important to obtain single crystals to perform rigorous magnetic measurements which could complete our previous works on the magnetism of the cluster in these compounds. Another important goal is to obtain single crystals in the case of europium and ytterbium to perform X-ray and magnetic studies in order to clarify the complex chemistry of the compounds formed with these two rare earths. This work is now in progress.

REFERENCES

1. A. Simon, H. G. von Schnering, and H. Schäfer, *Z. Anorg. Allg. Chem.* **361**, 235 (1968).
2. A. Broll and H. Schäfer, *J. Less-Common Met.* **22**, 367 (1970).
3. A. Lachgar, and H.-J. Meyer, *J. Solid State Chem.* **110**, 15 (1994).
4. S. Ihmaïne, C. Perrin, and M. Sergent, *Acta Crystallogr. Sect. C* **43**, 813 (1987).
5. S. Ihmaïne, C. Perrin, and M. Sergent, *Acta Crystallogr. Sect. C* **45**, 705 (1989).
6. H. Imoto, J. D. Corbett, and A. Cisar, *Inorg. Chem.* **20**, 145 (1981).
7. J. Zhang and J. D. Corbett, *Inorg. Chem.* **32**, 1566 (1993).
8. C. Perrin, S. Ihmaïne, and M. Sergent, *New J. Chem.* **12**, 321 (1988).
9. S. Cordier, C. Perrin, and M. Sergent, *Z. Anorg. Allg. Chem.* **619**, 621 (1993).
10. G. Meyer and P. Ax, *Mater. Res. Bull.* **17**, 1447 (1982).
11. G. Stout and L. H. Jensen, "X-Ray Structure Determination." McMillan, London, 1968.
12. "International Tables for X-Ray Crystallography," Vol. IV. Kynoch Press, Birmingham, UK, 1974. [Present distributor Kluwer Academic Publishers, Dordrecht]
13. C. K. Fair, "MOLEN: An Interactive Intelligent System for Crystal Structure Analysis." Enraf-Nonius, Delft, The Netherlands, 1990.
14. S. Ihmaïne, C. Perrin, O. Peña, and M. Sergent, *J. Less-Common Met.* **137**, 323 (1988).
15. J. G. Converse and R. E. Mc Carley, *Inorg. Chem.* **9**, 1361 (1970).
16. S. Ihmaïne, C. Perrin, O. Peña, and M. Sergent, *Physica B* **163**, 615 (1990).