

## Structure of a New Quaternary Niobium Chloride with Nb<sub>6</sub> Clusters: CsLuNb<sub>6</sub>Cl<sub>18</sub>

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**Abstract.** Caesium lutetium hexaniobium octadecachloride,  $M_r = 1503.46$ , hexagonal,  $P\bar{3}1c$ ,  $a = 9.1882$  (7),  $c = 17.1681$  (3) Å,  $V = 1255.2$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 3.978$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 97.866$  cm<sup>-1</sup>,  $F(000) = 1356$ ,  $R = 0.022$  ( $wR = 0.027$ ) for 1131 independent reflections. The structure is built up from  $([\text{Nb}_6\text{Cl}_{12}]\text{Cl}_6)^{4-}$  units, linked together by Lu atoms lying in a slightly distorted chlorine octahedron. The Cs atoms are surrounded by twelve Cl atoms also belonging to six adjacent  $(\text{Nb}_6\text{Cl}_{18})$  units.

**Introduction.** This work is part of a larger research project on new ternary and quaternary chlorides with general formulae  $\text{REMe}_6\text{Cl}_{18}$  and  $M\text{REMe}_6\text{Cl}_{18}$  respectively ( $M =$  monovalent cation; RE = rare earth; Me = Nb or Ta) (Ihmaïne, Perrin & Sergent, 1986, 1987; Perrin, Ihmaïne & Sergent, 1988). They have been synthesized from high-temperature solid-state reactions and the structures of  $\text{LuNb}_6\text{Cl}_{18}$  and  $\text{KLuNb}_6\text{Cl}_{18}$  have been reported (Ihmaïne, Perrin, Peña & Sergent, 1988). Ternary chlorides  $\text{REMe}_6\text{Cl}_{18}$  and quaternary chlorides  $M\text{REMe}_6\text{Cl}_{18}$  exhibit  $(\text{Me}_6\text{Cl}_{18})^{3-}$  and  $(\text{Me}_6\text{Cl}_{18})^{4-}$  units respectively. They form an isostructural series except when  $M = \text{Cs}$ . We present here the structure of  $\text{CsLuNb}_6\text{Cl}_{18}$ .

**Experimental.**  $\text{CsLuNb}_6\text{Cl}_{18}$  was synthesized from  $\text{CsCl}$  (Prolabo),  $\text{LuCl}_3$  obtained from  $\text{Lu}_2\text{O}_3$  as previously reported (Meyer & Ax, 1982),  $\text{NbCl}_5$  (Ventron: 99.998%) and Nb (Ventron: *m2N8*) in stoichiometric proportions. The mixture handled under an inert atmosphere was pressed into a pellet and heated at 1073 K for 24 h in an evacuated sealed silica tube, with some pieces of Nb foil (Ventron: 0.025 mm thick, *m2N8*). Black single crystals were obtained directly when the mixture was heated for three days at 1123 K.

A single crystal  $0.12 \times 0.12 \times 0.12$  mm was chosen. Weissenberg and precession photographs gave evidence for a hexagonal cell. The diffracted intensities were recorded at ambient temperature on an Enraf–Nonius CAD-4 four-circle diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation. The unit-cell dimensions were calculated by least-squares refinement on setting angles of 25 reflections with  $2 < \theta < 16^\circ$ . Systematic

absences in diffractometer data of reflections such as  $hhl$ ,  $l = 2n + 1$ , are consistent with space group  $P\bar{3}1c$ .

All reflections within a sphere defined by  $2\theta \leq 60^\circ$  were examined by an  $\omega$ -scan mode ( $1.20 + 0.35 \tan\theta$ ). 3291 intensities were measured ( $-12 < h < 12$ ,  $0 < k < 12$ ,  $0 < l < 24$ ). After averaging, 1223 independent reflections were kept. 1131 reflections with  $I > \sigma(I)$  were used. For the calculations, computer programs from Enraf–Nonius *SDP* described by Frenz (1978) were used on a PDP11/60 computer; no absorption correction was applied. 3 standard reflections, no intensity variation.

The structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). *MULTAN* solution gave all atoms: one Nb atom and three Cl atoms in general position 12(*i*), one Lu atom in position 2(*d*) and one Cs atom in position 2(*c*).

The full-matrix least-squares refinement on  $F$  with isotropic and anisotropic thermal parameters resulted in converged values of  $R = 0.0217$  and  $wR = 0.0270$  where  $1/w = \frac{1}{4}[\sigma^2(I) + (0.03I)^2]/I$  (Stout & Jensen, 1968). The scattering factors and  $f'$ ,  $f''$  are taken from *International Tables for X-ray Crystallography* (1974). A final difference Fourier synthesis was flat to  $\pm 1.0 \text{ e } \text{Å}^{-3}$ . Max.  $\Delta/\sigma < 0.01$ . The final atomic parameters are reported in Table 1. The interatomic distances and angles are summarized in Table 2. A refinement in  $P\bar{3}1c$  gives evidence for strong correlations.\*

**Discussion.** The  $\text{CsLuNb}_6\text{Cl}_{18}$  structure is based on the presence of  $([\text{Nb}_6\text{Cl}_{12}]^{2+}\text{Cl}_6)^{4-}$  units (Fig. 1). The unit cell of this structure is displayed in Fig. 2. The  $(\text{Nb}_6\text{Cl}_{18})$  units are centred at 0,0,0 and  $0,0,\frac{1}{2}$  positions; the Lu and the Cs atoms are located on the threefold axes at  $\frac{2}{3}, \frac{1}{3}, \frac{1}{4}$  and  $\frac{2}{3}, \frac{1}{3}, \frac{3}{4}$  respectively.

1. *The  $([\text{Nb}_6\text{Cl}_{12}]\text{Cl}_6)$  unit.* The average Nb–Nb intracluster distance in  $\text{CsLuNb}_6\text{Cl}_{18}$  agrees well with

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51628 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters and equivalent isotropic B values ( $\text{\AA}^2$ ) with their e.s.d.'s

		x	y	z	$B_{\text{eq}}^*$
Nb(1)	12(i)	0.20040 (3)	0.04130 (3)	0.06913 (2)	0.588 (5)
Cl(1)	12(i)	0.08822 (9)	0.63571 (9)	0.83765 (5)	1.21 (1)
Cl(2)	12(i)	0.57734 (9)	0.71931 (9)	0.00136 (5)	1.07 (1)
Cl(3)	12(i)	0.76373 (9)	0.95263 (9)	0.16187 (5)	1.12 (1)
Lu	2(d)				0.706 (4)
Cs	2(c)				4.79 (2)

$$* B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in  $\text{CsLuNb}_6\text{Cl}_{18}$ 

<b>Nb<sub>6</sub> cluster</b>			
Nb—Nb <sup>iii</sup>	2.910 (1)	Nb <sup>iii</sup> —Nb—Nb <sup>iv</sup>	59.93 (1)
Nb—Nb <sup>ii</sup>	2.917 (1)	Nb <sup>iii</sup> —Nb—Nb <sup>v</sup>	60.14 (1)

**([Nb<sub>6</sub>Cl<sub>12</sub>]<sub>2</sub>Cl<sub>6</sub>) unit**

Nb—Cl(1)	2.667 (1)	Cl(1)—Nb—Cl(2 <sup>iii</sup> )	83.36 (2)
Nb—Cl(2 <sup>iv</sup> )	2.445 (1)	Cl(1)—Nb—Cl(2 <sup>iv</sup> )	81.96 (2)
Nb—Cl(2 <sup>iii</sup> )	2.446 (1)	Cl(1)—Nb—Cl(3 <sup>iv</sup> )	80.03 (2)
Nb—Cl(3)	2.438 (1)	Cl(1)—Nb—Cl(3)	80.95 (2)
Nb—Cl(3 <sup>iv</sup> )	2.452 (1)	Cl(2 <sup>iii</sup> )—Cl(2)—Cl(3 <sup>v</sup> )	89.76 (3)
Cl(2)—Cl(1 <sup>ii</sup> )	3.356 (1)	Cl(2 <sup>iv</sup> )—Cl(2)—Cl(3)	89.02 (3)
Cl(2)—Cl(1 <sup>v</sup> )	3.404 (1)		
Cl(2)—Cl(3)	3.384 (1)		
Cl(2)—Cl(3 <sup>v</sup> )	3.429 (1)		
Cl(2)—Cl(2 <sup>iii</sup> )	3.423 (1)		
Cl(3)—Cl(1 <sup>ii</sup> )	3.296 (1)		
Cl(3)—Cl(1)	3.318 (1)		
Cl(3)—Cl(3 <sup>ii</sup> )	3.446 (1)		

**Caesium environment**

Cs—Cl(1 <sup>ii</sup> )	3.772 (1)
Cs—Cl(3 <sup>iv</sup> )	3.800 (1)

**Lutetium environment**

Lu—Cl(1)	2.603 (1)	Cl(1 <sup>viii</sup> )—Lu—Cl(1)	89.93 (2)
		Cl(1 <sup>ix</sup> )—Lu—Cl(1 <sup>vii</sup> )	82.95 (3)

**Other distances (<6 \AA)**

Nb—Lu	4.868 (1)
Nb—Cs <sup>iv</sup>	5.214 (1)
Lu—Cs <sup>iv</sup>	5.305 (1)

Symmetry operations: (i)  $-x, -y, -z$ ; (ii)  $-y, x-y, z$ ; (iii)  $y, y-z, -z$ ; (iv)  $y-x, -x, z$ ; (v)  $x-y, x, -z$ ; (vi)  $1-y, 1-(x-y), z$ ; (vii)  $x, x-y, \frac{1}{2}-z$ ; (viii)  $1-y, x-y, z$ ; (ix)  $1-(y-x), -x, z$ .

the 2.91 \AA average distance in  $\text{K}_4\text{Nb}_6\text{Cl}_{18}$  (Simon, von Schnering & Schäfer, 1968), and 2.92 \AA in  $\text{KGd-Nb}_6\text{Cl}_{18}$  (Ihmaine *et al.*, 1987) and  $\text{KLuNb}_6\text{Cl}_{18}$  (Ihmaine *et al.*, 1988), all of them exhibiting  $(\text{Nb}_6\text{Cl}_{18})^{4-}$  units. In contrast, these Nb—Nb distances are larger for  $(\text{Nb}_6\text{Cl}_{18})^{3-}$  units; indeed the change in the oxidation state of the Nb<sub>6</sub> cluster (15 e<sup>-</sup>/Nb<sub>6</sub> in  $\text{LuNb}_6\text{Cl}_{18}$  to 16 e<sup>-</sup>/Nb<sub>6</sub> in  $\text{CsLuNb}_6\text{Cl}_{18}$  for instance) causes a significant decrease in the Nb—Nb bond strength: 2.96 \AA in  $\text{LuNb}_6\text{Cl}_{18}$  to 2.92 \AA in  $\text{CsLuNb}_6\text{Cl}_{18}$ .

Twelve Cl(2) and Cl(3) atoms bridging edges of the metal octahedron build the  $[\text{Nb}_6\text{Cl}_{12}]$  unit with average Nb—Cl distances of 2.44 \AA (2.45 \AA in  $\text{KLuNb}_6\text{Cl}_{18}$ ).

This  $[\text{Nb}_6\text{Cl}_{12}]$  structural unit is surrounded by six Cl(1) atoms in apical positions: each Nb atom of the

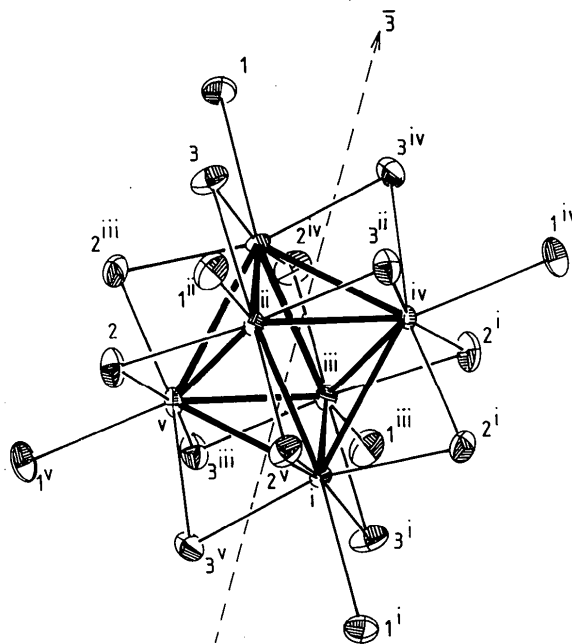


Fig. 1. The  $([\text{Nb}_6\text{Cl}_{12}]\text{Cl}_6)$  unit. The atomic indices correspond to the symmetry code listed in Table 2.

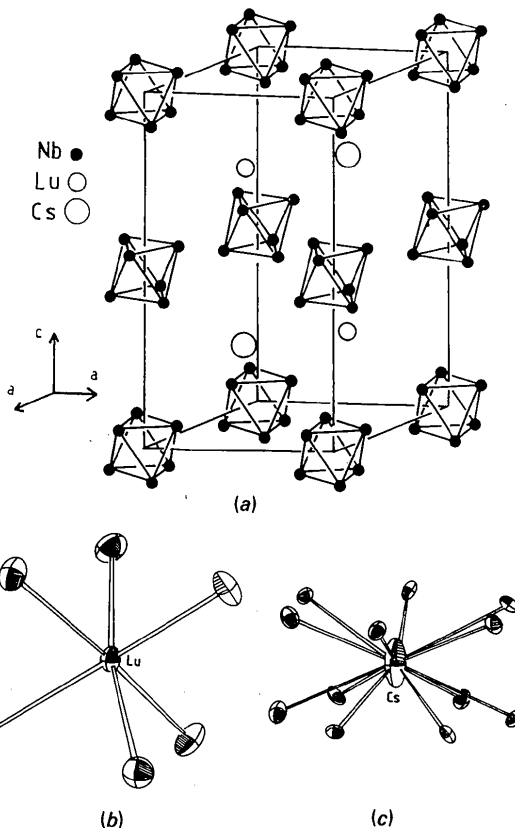


Fig. 2. (a) Unit cell of the  $\text{CsLuNb}_6\text{Cl}_{18}$  structure. The Cl atoms are omitted for clarity. (b) Lutetium coordination polyhedron in  $\text{CsLuNb}_6\text{Cl}_{18}$ . (c) Caesium coordination polyhedron in  $\text{CsLuNb}_6\text{Cl}_{18}$ .

Nb<sub>6</sub> cluster is bonded to one Cl(1) atom with Nb—Cl(1) distance of 2.667 (1) Å [2.654 (1) Å in KLuNb<sub>6</sub>Cl<sub>18</sub>].

2. *Lutetium environment.* The Lu atom is surrounded by six Cl(1) atoms belonging to six different units, forming a distorted octahedron, with Lu—Cl(1) distance of 2.603 (1) Å [KLuNb<sub>6</sub>Cl<sub>18</sub>: Lu—Cl(1) = 2.596 (1) Å]. This environment represented in Fig. 2(b) is closely similar to that in KLuNb<sub>6</sub>Cl<sub>18</sub>, the main difference being that in CsLuNb<sub>6</sub>Cl<sub>18</sub> this chlorine octahedron is less regular owing to the absence of an inversion centre at the Lu atom. The values of the Cl(1)—Lu—Cl(1) angles are 89.93 (2) and 82.95 (2)° [cf. 90.33 (3)° in KLuNb<sub>6</sub>Cl<sub>18</sub>].

3. *Caesium environment.* The Cs coordination polyhedron is represented in Fig. 2(c). The Cs atom is bonded to twelve Cl atoms belonging to six different units: six Cl(1) at a distance of 3.772 (1) Å and six Cl(3) at a distance of 3.800 (1) Å. The Cs-atom site is then approximately a flattened hexagonal antiprism. In KLuNb<sub>6</sub>Cl<sub>18</sub> the K atom is also surrounded by twelve Cl atoms but they belong only to four neighbouring units and the site so created is less regular (Ihmaïne *et al.*, 1988).

When comparing the structures of CsLuNb<sub>6</sub>Cl<sub>18</sub> presented in this paper and the previously reported KLuNb<sub>6</sub>Cl<sub>18</sub> structure, a close similarity appears between the (Nb<sub>6</sub>Cl<sub>18</sub>)<sup>4-</sup> units, which exhibit in these two compounds  $\bar{3}$  symmetry and comparable Nb—Nb and Nb—Cl distances. The actual difference is in the stacking of the (Nb<sub>6</sub>Cl<sub>18</sub>)<sup>4-</sup> units: an approximately close-packed cubic arrangement ...*ABCA*... in KLuNb<sub>6</sub>Cl<sub>18</sub> and an ...*AAA*... stacking type in CsLuNb<sub>6</sub>Cl<sub>18</sub>. This packing leaves a larger and more regular site for the Cs atom compared to the K-atom site in KLuNb<sub>6</sub>Cl<sub>18</sub>, while the Lu-atom site is approximately

the same size in the two structures, but appears somewhat less regular in CsLuNb<sub>6</sub>Cl<sub>18</sub>. Obviously the structural modification when Na, K or Rb monovalent cations are replaced by Cs is related to the necessity of formation of a site large enough to accommodate the Cs ion.

Another difference is the multiplicity of the monovalent cation sites. Owing to the chemical formula, the K-atom site in KLuNb<sub>6</sub>Cl<sub>18</sub> is half-occupied (it is vacant in the ternary compound LuNb<sub>6</sub>Cl<sub>18</sub>) while in CsLuNb<sub>6</sub>Cl<sub>18</sub> the Cs-atom site is fully occupied.

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## The Structure of 1,1,1,2,2,3,3,3-Nonacarbonyl-1,2;1,3-( $\mu_2$ -dihydrido)-1,3- $\sigma$ ;2- $\pi$ -[ $\mu_3$ - $\eta^2$ -methyl(phenyl)vinylidene]-triangulo-triruthenium

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**Abstract.** [Ru<sub>3</sub>H<sub>2</sub>(CO)<sub>9</sub>{ $\mu_3$ - $\eta^2$ -CC(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>}], *M*, = 673.47, triclinic, *P* $\bar{1}$ , *a* = 9.040 (4), *b* = 10.067 (4), *c* = 12.315 (5) Å,  $\alpha$  = 102.15 (3),  $\beta$  = 108.17 (3),  $\gamma$  = 92.43 (3)°, *V* = 1033.9 (7) Å<sup>3</sup>, *Z* = 2, *D*<sub>x</sub> = 2.163 Mg m<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71073 Å,  $\mu$  = 2.17 mm<sup>-1</sup>, *F*(000) = 644, *T* = 298 K, *R* = 0.023 for

3404 measured reflections. The molecular structure consists of a triangle of ruthenium atoms, the two longest edges [Ru(1)—Ru(2) = 2.840 (1), Ru(1)—Ru(3) = 2.821 (1) Å] bridged by hydrides; the triangle is capped by an alkenylidene ligand which is formally  $\sigma$ -bonded to Ru(1) and Ru(3) [Ru(1)—C(10) =