Potassium yttrium hexaniobium octadecachloride, KYNb$_6$Cl$_{18}$

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The structure of potassium yttrium hexaniobium octadecachloride is built of anionic $[\text{Nb}_6\text{Cl}_{12}^i\text{Cl}_6^a]^{4-}$ cluster units (where 'i' and 'a' denote inner and outer ligands, respectively), linked together by K$^+$ and Y^{3+} cations. The K$^+$ cations occupy half of the tetrahedral vacancies in the face-centered cubic lattice of cluster units, and are coordinated by 12 chloride ligands. The Y atom is located in an octahedral site and is bonded to six outer chloride ligands.

Comment

A large number of metal-rich niobium chlorides with $[\text{Nb}_6\text{Cl}_{18}]^{n-}$-type cluster units have been crystallized previously using a variety of metal cations, for instance, the two series ARENb$_6$Cl$_{18}$ (where A is an alkali and RE is a rare earth element; Ihmaïne *et al.*, 1987, 1988, 1989) and ATiNb$_6$Cl$_{18}$ (where A is an alkali or group 13 element; Nagele *et al.*, 2000), and the recently prepared cluster compounds Cs$_2$PbNb$_6$Cl$_{18}$ (Gulo *et al.*, 2001) and K$_2$SrNb$_6$Cl$_{18}$ (Duraisamy & Lachgar, 2002), which contain Pb^{2+} and Sr^{2+}, respectively. For the series ARENb$_6$Cl$_{18}$, the crystal structures of the compounds with RE = Gd^{3+} (Ihmaïne *et al.*, 1987) and Lu^{3+} (Ihmaïne *et al.*, 1988, 1989) have been reported, while compounds with other rare-earth metal cations are still unknown.

In the present paper, we report the crystal structure of potassium yttrium hexaniobium octadecachloride, KYNb$_6$Cl$_{18}$, which crystallizes in trigonal space group $R\bar{3}$. The structure is based on discrete anionic cluster units, *viz.* $[\text{Nb}_6\text{Cl}_{12}^i\text{Cl}_6^a]^{4-}$ (where 'i' and 'a' denote inner and outer ligands, respectively). The anionic cluster unit consists of an Nb$_6$ octahedron in which all edges are bridged by chloride ligands, and six other ligands are in apical positions (Fig. 1). The intra-cluster bond lengths, Nb—Nb = 2.9143 (6)–2.9182 (6), Nb—Cl^i = 2.4476 (10)–2.4556 (10) and Nb—Cl^a = 2.6497 (10) Å, are typical for $[\text{Nb}_6\text{Cl}_{18}]^{4-}$ clusters. The Nb—Nb bond length indicates that the VEC (valence electrons per cluster) is 16. The three-dimensional structure of the title compound is based on the cluster units interlinked by K$^+$ and Y^{3+} cations (Fig. 2). The cluster layers are arranged according
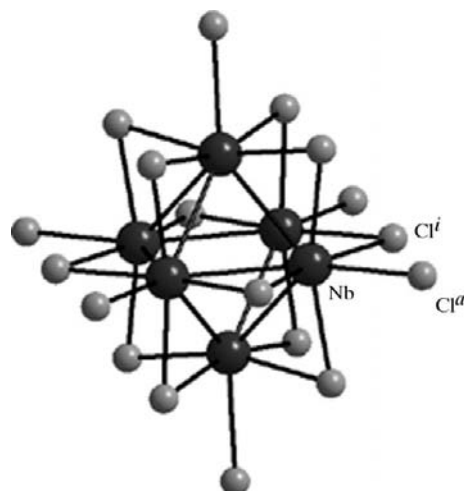

Figure 1
The chloride cluster anion, $[\text{Nb}_6\text{Cl}_{12}^i\text{Cl}_6^a]^{4-}$, present in KYNb$_6Cl_{18}$. The superscripts '$i$' and '$a$' denote inner and outer ligands, respectively.

to a face-centered cubic stacking along the c axis. The K$^+$ ions occupy tetrahedral vacancies between the units and are coordinated to 12 chloride ligands, with K—Cl distances in the range 3.4520 (11)–3.5292 (10) Å. The Y^{3+} ions are located in octahedral sites between the units and are bonded to six chloride ligands from six different units in a regular octahedral geometry, with Y—Cl distances of 2.6414 (10) Å. Only half of the tetrahedral sites are occupied by K$^+$ in the title compound, in contrast to the situation in both Cs$_2$PbNb$_6$Cl$_{18}$ (Gulo *et al.*, 2001) and K$_2$SrNb$_6$Cl$_{18}$ (Duraisamy & Lachgar, 2002) where the alkali metal site is fully occupied.
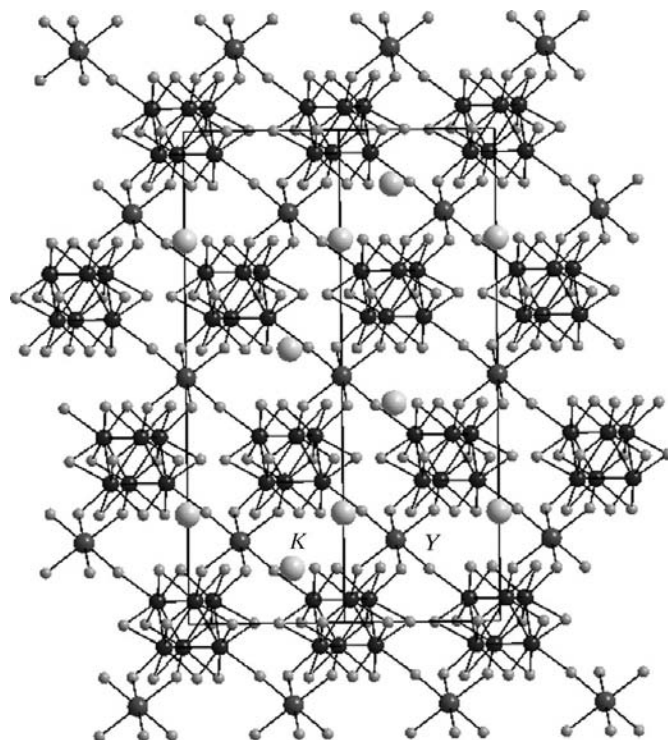

Figure 2
Projection of the crystal structure of KYNb$_6$Cl$_{18}$ in the [110] direction.

inorganic compounds

Experimental

The title compound, $KYNb_6Cl_{18}$, was initially obtained as shiny black cuboctahedral crystals from a reaction proposed to yield an oxychloride compound of the composition $K_2Y_2Nb_6Cl_{14}O_5$. The compound was prepared quantitatively from a stoichiometric mixture containing $NbCl_5$ (Alfa, 99.8%), Nb powder (Alfa 99.8%), YCl_3 (Alfa 99.9%), and KCl (Alfa, 99.99%). The mixture was handled under an argon atmosphere and the reaction was performed in a sealed quartz tube at 1023 K over a period of 4 d. The heating and cooling ramps were 20 and 10 K h^{-1}, respectively.

Crystal data

$KYNb_6Cl_{18}$
$M_r = 1323.57$
Trigonal, $R\overline{3}$
$a = 9.2527 (6)$ Å
$c = 25.410 (2)$ Å
$V = 1884.0 (2)$ Å^3
$Z = 3$
$D_x = 3.500$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 38 reflections
$\theta = 2.7–12.5°$
$\mu = 7.00$ mm^{-1}
$T = 293 (2)$ K
Truncated cuboctahedron, black
$0.20 \times 0.17 \times 0.15$ mm

Data collection

Bruker $P4$ diffractometer
ω scans
Absorption correction: empirical via ψ scan (North et al., 1968)
$T_{min} = 0.709$, $T_{max} = 0.965$
1803 measured reflections
1342 independent reflections
1045 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$
$\theta_{max} = 31.0°$
$h = -1 \rightarrow 13$
$k = -13 \rightarrow 1$
$l = -1 \rightarrow 36$
3 standard reflections
every 297 reflections
intensity decay: none

Table 1
Selected geometric parameters (Å, °).

Nb—Cl3	2.4476 (10)	Nb—Nb^{ii}	2.9182 (6)
Nb—Cl2	2.4556 (10)	Cl1—Y	2.6414 (10)
Nb—Cl1	2.6497 (10)	Cl1—K	3.4520 (11)
Nb—Nb^{i}	2.9143 (6)	Cl2—K	3.5292 (10)
Nb^{i}—Nb—Nb^{iii}	60.090 (15)	Nb—Cl3—Nb^{iii}	73.03 (3)

Symmetry codes: (i) $y, -x + y, -z$; (ii) $-y, x - y, z$; (iii) $x - y, x, -z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.050$
$S = 1.03$
1342 reflections
42 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0137P)^2 + 0.4236P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.90$ e Å^{-3}

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: SHELXTL (Bruker, 1999); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1007). Services for accessing these data are described at the back of the journal.

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