Synthesis and Crystal Structures of $ATi[Nb_6Cl_{18}]$ Compounds (A = K, Rb, Cs, In, Tl)

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New quaternary niobium cluster chlorides corresponding to the general formula $ATi[Nb_6Cl_{18}]$ (A = K, Rb, Cs, In, Tl) have been synthesized in sealed quartz tubes at 720 °C, starting from stoichiometric amounts of $NbCl_5$, niobium metal, $TiCl_3$, and ACl (A = K, Rb, Cs), or In or Tl metals. The structures of $RbTi[Nb_6Cl_{18}]$ and $CsTi[Nb_6Cl_{18}]$ were determined using single-crystal X-ray diffraction. $RbTi[Nb_6Cl_{18}]$ crystallizes in the rhombohedral crystal system, space group $R\bar{3}$ (no. 148), $Z = 3$, with lattice parameters: $a = 9.163(4)$, $c = 25.014(14)$ Å (hexagonal setting). The structure refinement converged to $R_1 = 0.044$ and $wR_2 = 0.058$ for all data. In this structure, discrete $[Nb_6Cl_{18}]^{4-}$ cluster units are linked by Rb^+ and Ti^{3+} cations, located in a 12-coordinated anticubeoctahedral and octahedral chloride coordination environment, respectively. In contrast, $CsTi[Nb_6Cl_{18}]$ crystallizes in the trigonal crystal system, space group $P\bar{3}1c$ (no. 163), $Z = 2$. The lattice parameters were determined to be $a = 9.1075(6)$, $c = 17.0017(8)$ Å. The structure refinement gives the reliability factors $R_1 = 0.029$ and $wR_2 = 0.063$ for all data. The structure is built up of discrete octahedral $[Nb_6Cl_{18}]^{4-}$ cluster units, linked by Cs^+ and Ti^{3+} cations which are located in a distorted hexagonal antiprismatic and octahedral chloride coordination environment, respectively. The structures of the compounds $ATi[Nb_6Cl_{18}]$ (A = K, In, Tl) were found to be isotypic with $RbTi[Nb_6Cl_{18}]$, and their unit cell parameters were refined using X-ray powder diffraction analysis.