Synthese, Kristallstruktur und spektroskopische Charakterisierung von Bis(dimethylammonium)hexachlorotitanat $[Me_2NH_2]_2[TiCl_6]$

Synthesis, Crystal Structure, and Spectroscopic Characterization of Bis(dimethylammonium) Hexachlorotitanate $[Me_2NH_2]_2[TiCl_6]$

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By the reaction of $(Me_3SiNH)_2SiClNMe_2$ with $TiCl_4$ the by-product $[Me_2NH_2]_2[TiCl_6]$ was obtained in form of crystals suitable for single-crystal XRD (*Pnnm*, $Z = 2$, $a = 722.01(3)$, $b = 1428.36(5)$, $c = 703.31(3)$ pm, $T = 200$ K, 901 independent reflections, 57 variables, $R1 = 0.0636$). The product was also synthesized in higher yield by the stoichiometric reaction of two equivalents of $[Me_2NH_2]Cl$ with $TiCl_4$ in $CHCl_3$ at room temperature as a yellow crystalline powder. Bis(dimethylammonium) hexachlorotitanate is built up from $[TiCl_6]^{2-}$ anions forming elongated octahedra and $[Me_2NH_2]^+$ ions. The $[TiCl_6]^{2-}$ ions are connected by the $[Me_2NH_2]^+$ ions through N–H···Cl hydrogen bridges forming an arrangement which resembles that of an expanded rutile structure type. The elongation of the $[TiCl_6]^{2-}$ octahedra was also verified by IR and Raman spectroscopy, confirming a local symmetry reduction from O_h to D_{4h}. The solubility of $[Me_2NH_2]_2[TiCl_6]$ in $MeNO_2$ and MeCN was determined by means of ^{14}N-NMR to be about 0.1 mol% and 0.3 mol%, respectively.

Key words: Hexachlorotitanate, Rutile Structure Type, Solubility, Hydrogen Bonds