# Synthesis, Spectroscopic Properties, and Crystal Structure of the Oxonium Acid $[H(OEt_2)_2]^+[Ti_2Cl_9]^-$

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Z. Naturforsch. **58b,** 745 – 750 (2003); received April 9, 2003

The oxonium acid $[H(OEt_2)_2]^+[Ti_2Cl_9]^-$ (**1**) was obtained by the reaction of $TiCl_4$ with $Et_2O$ in *n*-pentane and subsequent partial hydrolysis. Suitable single crystals of **1** were obtained by sublimation at 5 °C ($[H(OEt_2)_2]^+[Ti_2Cl_9]^-$, $P2_12_12_1$ (no. 19), $Z = 4$, $a = 1101.08(8)$, $b = 1328.4(2)$, $c = 1525.0(2)$ pm, $T = 193(2)$ K, 4489 independent reflections, 197 parameters, $R1 = 0.049$). The cation is made up from two independent $Et_2O$ molecules and one disordered proton on two split positions. Both ether molecules exhibit a W form, and their molecular planes include an angle of 74.1(7)°. Thus a distorted tetrahedron is formed by the four methyl carbon atoms of the two ether molecules. The distance O···O amounts to 237.7(1) pm. The proton of the cation was characterized both by $^1$H NMR ($CDCl_3$, $T$ = 23 °C: $\delta = 11.7$ ppm, $w_{1/2}$ = 100 Hz) and IR spectroscopy (3120 cm$^{-1}$, $\nu$ vbr). The $[Ti_2Cl_9]^-$ ion consists of two face sharing octahedra. $^{47}$Ti and $^{49}$Ti NMR spectra were recorded in solution ($CH_2Cl_2$, $T = 23$ °C: $\delta\,^{49}$Ti = 137 ppm, $w_{1/2}$ = 175 Hz; $\delta\,^{47}$Ti = −124 ppm, $w_{1/2} = 250$ Hz). The absence of a signal for $TiCl_4$ at $\delta\,^{49}$Ti = 0 ppm indicates the stability of the dinuclear anion in solution.

*Key words:* Oxonium Ion, $^1$H NMR, $^{47,49}$Ti NMR, Hydrogen Bonding