

Synthesis and properties of tetraethylammonium bromo-trichloro-bis(tetrahydrofuran)titanate(III)

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Trichloro-bis(tetrahydrofuran)titanium(III) reacts with tetraethylammonium bromide in chloroform solution to form tetraethylammonium bromo-trichloro-bis(tetrahydrofuran)titanate(III). The complex was characterized by e.s.r. and electronic spectral data and studied by thermogravimetric technique in an inert atmosphere.

При реакции трихлоро-бис(тетрагидрофуран)титана(III) с бромидом тетраэтиламмония в растворе хлороформа образуется тетраэтиламмониевая соль бром-трихлоро-бис(тетрагидрофуран)титаната(III). Комплекс был охарактеризован на основании ЭПР, электронных спектров и термогравиметрического анализа в инертной атмосфере.

Solid anionic titanium(III) complexes have been receiving only moderate attention. *Hoff et al.* [1] synthesized chlorotitanium(III) complexes of the composition $(C_2H_5)_4N[TiCl_4 \cdot 2L]$ ($L =$ tetrahydrofuran, dioxane, acetonitrile). *Adnitt et al.* [2] reported the synthesis of a series of bromo-aquatitanium(III) complexes of the general type $M_2TiBr_5(H_2O)_n$ ($M = Cs, Rb, pyH; n = 1, 3$ or 5). Till now no titanium(III) complex that would contain two kinds of anionic ligands in its coordination sphere has been reported. For this reason we concentrated on preparation of the complex $(C_2H_5)_4N[TiBrCl_3(C_4H_8O)_2]$ by reaction of $TiCl_3(C_4H_8O)_2$ with $(C_2H_5)_4NBr$ and on investigation of its properties.

Experimental

Starting materials and their preparation

Since titanium(III) compounds oxidize in the air, the whole experimental work was done under an atmosphere of pure nitrogen by a technique reported in [3]. $TiCl_3(C_4H_8O)_2$ was prepared by thermal decomposition of the complex $TiCl_3(C_4H_8O)_3$ at $100^\circ C$ [4]. $(C_2H_5)_4NBr$ (Lachema, Brno, reagent grade) was dried under vacuum at $150^\circ C$. Saturated solutions of

the above substances in chloroform, which had been dried and redistilled under nitrogen, were prepared. The saturated solution of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$ in CHCl_3 ($c = 394.5 \text{ mg Cl}^-/\text{g}$) was of a rich green colour, that of $(\text{C}_2\text{H}_5)_4\text{NBr}$ in CHCl_3 ($c = 89.3 \text{ mg Br}^-/\text{g}$) was yellow.

By reaction of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$ with threefold molar excess of $(\text{C}_2\text{H}_5)_4\text{NBr}$ in chloroform solution a brick-red powdered complex $(\text{C}_2\text{H}_5)_4\text{N}[\text{TiBrCl}_3(\text{C}_4\text{H}_8\text{O})_2]$ was formed. This reaction product is thermochromic. At -195°C it is yellow, at -78°C it becomes pale orange. In distinction to the starting complex $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$ it does not oxidize as readily in the air.

The analytical methods were similar to those we reported in [3]. Chlorides and bromides were determined in one procedure by Volhard's argentometric method. Their ratio was determined by potentiometric titration in aqueous solution of the sample on a pure regenerated silver electrode.

For $(\text{C}_2\text{H}_5)_4\text{N}[\text{TiBrCl}_3(\text{C}_4\text{H}_8\text{O})_2]$ (508.63) calculated: 9.42% Ti, 15.71% Br, 20.91% Cl; found: 9.76% Ti, 15.33% Br, 20.40% Cl.

The X band e.s.r. spectra were recorded at room temperature and at 77 K by means of a Varian-4 spectrometer. With a Perkin-Elmer 450 spectrometer the electronic spectra in Nujol mulls were recorded in the region $10\text{--}25 \times 10^3 \text{ cm}^{-1}$. Thermogravimetric experiments were performed using helical spring balance described in [5]. For chromatographic measurements the apparatus Chromatograf Chrom 4 (Laboratorní přístroje, Prague) was used. The infrared spectra were obtained by use of a Perkin-Elmer 221 apparatus in the region $600\text{--}5000 \text{ cm}^{-1}$. The solid samples were mullied with Nujol and enclosed in NaCl plates. Technique reported in [8] was used for sample preparation.

Results and discussion

The coordinatively unsaturated complex $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$ reacts with $(\text{C}_2\text{H}_5)_4\text{NBr}$ by an addition mechanism and a new class of distorted octahedrally coordinated complex with three kinds of ligands in the coordination sphere arises. Thermogravimetric analysis indicates that the complex is stable at relatively elevated temperature (up to 170°C) (Fig. 1). At temperatures between $170\text{--}250^\circ\text{C}$ both coordinated molecules of THF are eliminated, which has been confirmed by gas

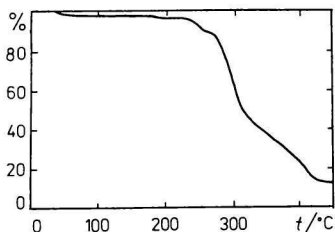


Fig. 1. Thermogravimetric curve of the complex $[\text{TiBrCl}_3(\text{C}_4\text{H}_8\text{O})_2]$.

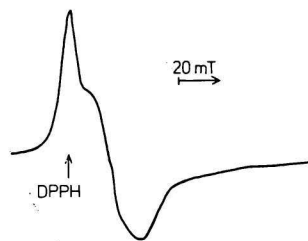


Fig. 2. ESR spectrum of the complex $(\text{C}_2\text{H}_5)_4\text{N}[\text{TiBrCl}_3(\text{C}_4\text{H}_8\text{O})_2]$.

chromatography data. Between 220—270°C releasing of $(C_2H_5)_4NCl$ from the complex in the form of a white sublimate takes place. From the thermogravimetric curves it was not possible to determine the percentual value of the residue left after decomposition, since at temperatures between 270—320°C, destruction and frothing of the sample took place.

The complex $(C_2H_5)_4N[TiBrCl_3(C_4H_8O)_2]$ shows an e.s.r. spectrum the intensity of which is strongly temperature dependent. At laboratory temperature it is rather broadened, which indicates a small energetical separation of the excited levels from the ground level. At 77 K the spectrum is rhombic, $g_1 = 1.81$, $g_2 = 1.86$, $g_3 = 1.94$, $\bar{g} = 1.87$ (Fig. 2). These are values similar to those reported for the complex $(C_2H_5)_4N[TiCl_4(C_4H_8O)_2]$ [1], which indicates that the symmetry of the coordination polyhedron is similar in both complexes. In the shortwave region of the electronic spectrum there is a descending shoulder of a broad intensive band related to the charge transfer transitions halide (π) \rightarrow Ti. This band, in comparison to those of the complex $TiCl_3(C_4H_8O)_3$ and $TiCl_3(C_4H_8O)_2$, is much broader [6] and it is also shifted toward the region of lower energies (Fig. 3). This phenomenon can be explained as a consequence of Br^- entering the coordination sphere of the complex $TiCl_3(C_4H_8O)_2$. In the complex $(C_2H_5)_4N[TiBrCl_3(C_4H_8O)_2]$ there is a maximum at $13.4 \times 10^3 \text{ cm}^{-1}$ assigned to $d-d$ transitions. By Gaussian analysis

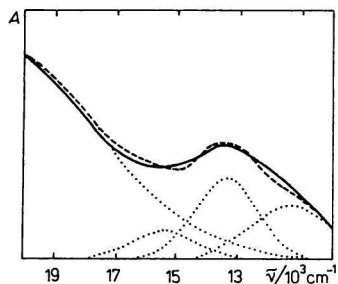
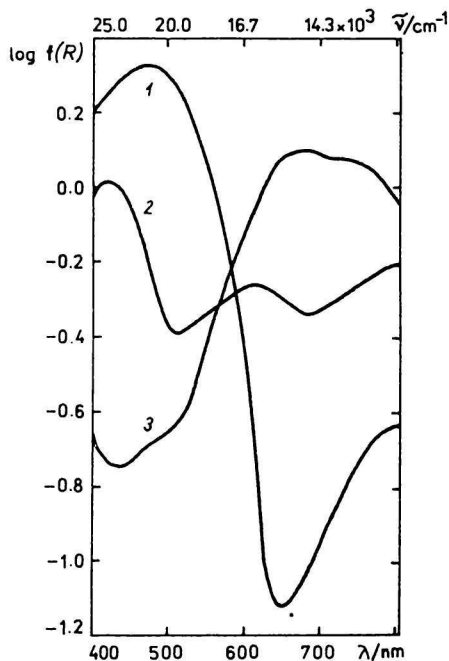


Fig. 4. Electronic spectrum of the complex $(C_2H_5)_4N[TiBrCl_3(C_4H_8O)_2]$.

· · · Individual curves; - - - summation curve; ——— experimental curve.

Fig. 3. Diffuse reflectance spectra of the complexes:

1. $(C_2H_5)_4N[TiBrCl_3(C_4H_8O)_2]$;
2. $TiCl_3(C_4H_8O)_2$; 3. $TiCl_3(C_4H_8O)_3$.

[7] on both sides of this band shoulders at 11.25×10^3 and $15.45 \times 10^3 \text{ cm}^{-1}$ can be discerned (Fig. 4). The bands at 13.4×10^3 and $11.25 \times 10^3 \text{ cm}^{-1}$ can be assigned to the electron transitions $T_{2g} \rightarrow E_g$ in the distorted octahedral coordination of $[\text{TiBrCl}_3(\text{C}_4\text{H}_8\text{O})_2]^-$. Shifts of the locations of the bands of $d-d$ transitions toward energy region that is lower in comparison to that of the complex $(\text{C}_2\text{H}_5)_4\text{N}[\text{TiCl}_4(\text{C}_4\text{H}_8\text{O})_2]$ is a proof for the presence of the ion Br^- in the coordination sphere of the complex.

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