Synthesis, Thermogravimetric and Magnetochemical Investigation of Chloro(tetrahydrofuran)titanium(III) Complexes

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The thermogravimetric analysis showed the decomposition of TiCl$_3$·3THF into TiCl$_3$·2THF (at about 100°C) and TiCl$_3$·THF (at temperatures above 150°C) in nitrogen or argon atmosphere. At about 250°C disproportionation into TiCl$_2$ and TiCl$_4$·2THF takes place. The complexes TiCl$_3$·3THF and TiCl$_3$·2THF react with benzene under formation of TiCl$_3$·2THF·C$_6$H$_6$ which, in the same way as TiCl$_3$·3THF, is thermally decomposed while benzene is released in the first stage of the decomposition. The complexes TiCl$_3$·3THF, TiCl$_3$·2THF and TiCl$_3$·2THF·C$_6$H$_6$ dissolve in benzene and other aromatic solvents, which, together with magnetic moments near the expecting spin-only value, are indicative of the monomer structure of these complexes. On the other hand, the anomalous low value of magnetic moment of the compound TiCl$_3$·THF (1.14 B. M.) together with its insolubility in benzene indicate the existence of a coordination polymer. The complexes TiCl$_3$·2THF and TiCl$_3$·2THF·C$_6$H$_6$ form with methanol vapour a brown-violet chloromethoxy derivative.

Pregaglia et al. [1] prepared the green complex TiCl$_3$·2THF by thermal decomposition of the complex TiCl$_3$·3THF either at 80°C in nitrogen atmosphere or at 75°C and 1 Torr pressure. Upon further temperature increase he did not observe the formation of any other modification; at 180°C decomposition of the compound took place. On the other hand, Kern [2] prepared by thermal decomposition of the complex TiCl$_3$·3THF in the temperature range 25—100°C and at the pressure of 1 Torr the compound TiCl$_3$·THF which disproportionated into TiCl$_2$ and TiCl$_4$·2THF in the temperature range 150—200°C. These contradictions, as regards the products of thermal decomposition of the complex TiCl$_3$·3THF, induced us to submit the decomposition process to thermogravimetric investigation in the course of which the decomposition products were isolated and some of their chemical and physical properties examined.

Experimental

Reagents

Because of pronounced tendency of titanium(III) compounds to oxidize and to hydrate, the complexes must be prepared and stored out of contact with the atmosphere. All operations were carried under dry nitrogen. This was done in all-glass equipments connected to a nitrogen manifold under head of about 10 Torr pressure above atmospheric. Nitrogen was deoxygenated by passage through a heated activated copper column and dehydrated by passage through the columns filled with the molecular sieve type 4A (commercial mark Nalsit 4), as well as through freezing traps cooled with liquid nitrogen.
Titanium(III) chloride (α-modification), supplied by Research Institute of Macromolecular Chemistry in Brno, was first purified from the sorbed titanium(IV) chloride by repeated decantation with anhydrous hexane wherein 1% of methanol has been added, followed by repeated washing with anhydrous hexane alone and finally by drying in a stream of nitrogen and evacuation.

Hexane, heptane and tetrahydrofuran, which were of reagent grade, were purified and dried by appropriate methods [3, 4]. All solvents used were dried rigorously by repeated distillation under nitrogen from CaH₂ with a final distillation from potassium and benzophenone immediately before use.

Preparation of complexes

*Trichlorotris(tetrahydrofuran)titanium(III)*

Complex TiCl₃·3THF [1, 2, 11] was prepared by direct reaction of anhydrous titanium(III) chloride with anhydrous tetrahydrofuran (about 10 g in 250 ml). The reaction took place in a sealed 500 ml flask to prevent the access of the air atmosphere. The reaction mixture was stirred perpetually with a magnetic stirrer. In the course of the reaction the light blue powdered complex TiCl₃·3THF was precipitated from the super-saturated solution. The colour of the solution over the precipitate changed from light violet to dark violet or brown-violet [1] according to the amount of TiCl₄ which, as a consequence of unsufficient purification of TiCl₃ [6], got into the reaction system. After a certain time, a grey-violet flaky precipitate of intervalence tetrahydrofuran-Ti(III,IV) compound was formed, which, after sedimentation, formed a discrete layer over the precipitated light-blue complex TiCl₃·3THF. It is, therefore, useful to filtrate and remove the precipitated TiCl₃·3THF immediately after the reaction is completed. The complex TiCl₃·3THF was dried on a sintered glass by means of a stream of dry nitrogen. Subsequent washing with hexane effectuated a slow decomposition and formation of the green complex TiCl₃·2THF in accordance with [1].

The product thus obtained may be contaminated by the insoluble grey-violet intervalence tetrahydrofuran-Ti(III,IV) compound and for this reason it is useful to dissolve it in an excess of hot tetrahydrofuran. By slow cooling well developed needle-like crystals are formed, whereas a very pure powdered substance is obtained by precipitation with hexane (approximate ratio 1:1). Precipitation with hexane or heptane may also be used for preparation of the light blue complex TiCl₃·3THF from the violet solution which is formed by direct reaction of titanium(III) chloride with tetrahydrofuran.

The use of heptane as a precipitating agent has an advantage over hexane, in that tetrahydrofuran (having rather lower boiling point) may be removed by distillation from the solution formed. Consequently, the precipitation of TiCl₃·3THF may be performed with a relatively small amount of heptane added to an excess tetrahydrofuran solution because the solution is being constantly enriched by heptane in the course of the distillation, while TiCl₃·3THF is continuously separated from the solution.

The rate of the direct reaction of titanium(III) chloride with tetrahydrofuran largely depends on temperature (the reaction proceeded in a sealed flask for about 24 hours at 20°C), on granularity or on size of the surface area of initial titanium(III) chloride, on the excess of tetrahydrofuran in reaction system since the complex TiCl₃·3THF is relatively little soluble in tetrahydrofuran at room temperature and forms a protective layer on titanium(III) chloride which has not reacted yet, etc. With regard to the above said it is advantageous to use for the preparation of TiCl₃·3THF a laboratory rotatory
spherical reactor [5] which is usually applied to the synthesis and grinding of substances in controlled atmosphere since the surface of original solid titanium(III) chloride is incessantly restored owing to intensive stirring and grinding of the reaction system.

Trichlorobis(tetrahydrofuran)titanium(III)

The green complex TiCl$_3$ • 2THF was prepared by heating the complex TiCl$_3$ • 3THF in a stream of nitrogen at 100—105°C under frequent stirring in a glass flask (250 ml) dipped in an oil bath. A complex of the same composition may be prepared by approximately two hours' mixing of the suspension of TiCl$_3$ • 3THF in hexane or heptane (about 10 g in 500 ml). The reaction may be accelerated by raising the temperature [1].

Compound TiCl$_3$ • THF

The grey compound TiCl$_3$ • THF can be prepared by heating TiCl$_3$ • 3THF or TiCl$_3$ • 2THF in a stream of nitrogen at 200°C in an equipment analogous to that used for the preparation of the complex TiCl$_3$ • 2THF.

Trichlorobis(tetrahydrofuran)titanium(III) • benzene

The green complex TiCl$_3$ • 2THF • C$_6$H$_5$ may be prepared by suspending complex TiCl$_3$ • 3THF in benzene. The blue crystals of TiCl$_3$ • 3THF turn green immediately upon contact with benzene and dissolve under formation of a green solution. The green crystals which did not still pass into saturated solution were separated by filtration in nitrogen atmosphere and dried on sintered glass with a stream of a nitrogen. The green powdered substance of equal composition can also be prepared by suspending TiCl$_3$ • 2THF under stirring in benzene. The powdered substance, non-dissolved in saturated brown-green benzene solution had, after drying with nitrogen stream, the composition TiCl$_3$ • 2THF • C$_6$H$_5$. The bound benzene may be gradually removed from the substance by washing with hexane, with nitrogen stream or by heating. The crystal solvates containing toluene or chlorobenzene are difficult to isolate since the relatively low volatility of solvents requires protracted drying in the course of which the bound toluene or chlorobenzene escapes too.

Chloromethoxy(tetrahydrofuran)titanium(III) derivative

Powdered complex compounds TiCl$_3$ • 2THF or TiCl$_3$ • 2THF • C$_6$H$_5$ react quickly with methanol vapour under elimination of hydrogen chloride (methanolysis). In this reaction the brown-violet titanium(III) chloromethoxide derivative forms. Under these conditions, the complex TiCl$_3$ • 3THF reacts but slowly whereas the compound TiCl$_3$ • THF does not react in an observable way.

Chemical analysis

The content of titanium(III) and chlorine in complexes was determined by the methods given in paper [7]. The total content of titanium was determined by repeated evaporation of sample with nitric acid in a porcelain crucible and by annealing the content to form TiO$_2$. The composition of TiCl$_3$ • 2THF • C$_6$H$_5$ was corroborated by thermogravimetry and by gas chromatography.
Thermogravimetry

All synthesized complexes were also analyzed by thermogravimetric method in an equipment described in the paper [7]. The course of thermal decomposition in nitrogen atmosphere was the same as in argon atmosphere.

Magnetic measurements

Magnetic susceptibility was measured between 293 and 77°K by the Gouy method. The complexes were sealed from the air. The measurements were made at two different field strengths between 2000 and 3000 Oe. The substances investigated did not contain any ferromagnetic admixtures. HgCo(SCN)₄ was used as a standard [8]. The average values for each temperature and field strength were corrected for the diamagnetism of the glass tube. The molar susceptibilities were corrected for the diamagnetism of the atoms using Pascal's constants [9] or experimental values for the diamagnetic ligands.

X-ray diffraction measurements

The X-ray powder measurements were taken with the X-ray goniometer GON-3 (Chirana, Prague) and CuKα radiation with a nickel filter. The preparation of samples for the measurements in inert atmosphere was performed in an equipment of original construction [10].

Results and Discussion

The thermal decomposition of the complex TiCl₃ • 3THF in nitrogen atmosphere proceeds in three steps (Fig. 1, curve 1). At about 100°C, the green complex TiCl₃ • 2THF arises, at the temperature above 150°C, the grey compound TiCl₃ • THF comes into existence, while the disproportionation into the black TiCl₂ and yellow sublimate TiCl₄ • 2THF sets in at about 250°C. The decomposition proceeds analogously under reduced pressure (1 Torr) (Fig. 1, curve 2), but the pure compounds

![Fig. 1. Thermogravimetry of TiCl₃ • 3THF. 1. in nitrogen atmosphere; 2. in vacuum.](image-url)
SYNTHESIS OF CHLORO(TETRAHYDROFURAN)TITANIUM(III) COMPLEXES

TiCl₃ • 2THF and TiCl₃ • THF are more difficult to isolate. On the other hand, the purity of TiCl₂ is higher than it would be in case of the decomposition in nitrogen or argon atmosphere at laboratory pressure.

These statements agree neither with the paper of Pregaglia [1] who did not observe any formation of TiCl₃ • THF and the preparation decomposed already at 180°C, nor with the paper of Kern [2] who did not report any formation of the compound TiCl₃ • 2THF while the product TiCl₃ • THF was formed within the temperature interval between 20 and 100°C and the disproportionation took place in the temperature range of 150—200°C.

Different results were also obtained in the course of the study of the solution of TiCl₃ • 3THF and TiCl₃ • 2THF in aromatic solvents. According to the papers [1, 2] these complexes ought to be insoluble. We found that only the compound TiCl₃ • THF (the solubility of which had not been mentioned before) was insoluble, while TiCl₃ • THF and TiCl₃ • 2THF dissolved in benzene, toluene, chlorobenzene and saturated solution of naphthalene in hexane under formation of green solutions. The insoluble portion in saturated solution, which comes into existence by suspending TiCl₃ • 3THF or TiCl₃ • 2THF in benzene has the composition TiCl₃ • 2THF • C₆H₆. In the course of thermal decomposition, the benzene molecule is liberated and at the end a disproportionation sets in analogously to the thermal decomposition of complex TiCl₃ • 3THF (Fig. 2).

The powder diffraction pattern for the crystal solvate TiCl₃ • 2THF • C₆H₆ (Fig. 3a) suggests a different structure in comparison to complex TiCl₃ • 2THF, regardless whether it was prepared by thermal decomposition (Fig. 3c) or by effect of hexane (Fig. 3d) on the solid complex TiCl₃ • 3THF. For comparison, an X-ray diffraction pattern of the initial complex TiCl₃ • 3THF (Fig. 3b) as well as that of the decomposition product TiCl₃ • THF (Fig. 3e) are presented.

According to literature, magnetic susceptibility was measured only for the complex TiCl₃ • 3THF and various values are to be found, e.g. 1.80 B. M. [1], 1.73 B. M. [11] and 1.83 B. M. [12] (for 293°C). The value we have been measured is 1.82 B. M. what is close to the values according to [1] and [12].
Fig. 3. X-ray diffraction patterns of chloro(tetrahydrofuran)titanium(III) complexes.

Table 1
Magnetic susceptibilities ($\chi''_M \cdot 10^4$) and magnetic moments ($\mu_{\text{eff}}, \text{B. M.}$) of chloro(tetrahydrofuran)titanium(III) complexes

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<th>$T$, $^\circ$K</th>
<th>TiCl$_3$ · 3THF</th>
<th>TiCl$_3$ · 2THF</th>
<th>TiCl$_3$ · 2THF · C$_6$H$_6$</th>
<th>TiCl$_3$ · 2THF</th>
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The magnetic measurements (Table 1) show that the compounds TiCl$_3$ · 2THF (1.83 B. M.) and TiCl$_3$ · 2THF · C$_6$H$_6$ (1.80 B. M.), as well as TiCl$_3$ · 3THF, have monomeric structure. On the other hand, the magnetic moment of TiCl$_3$ · THF (1.14 B. M.) indicates the intramolecular antiferromagnetism due to coordination polymerization. It is proposed that this association of magnetically interacting titanium atoms is achieved through chlorine bridges which are known to provide inefficient pathways for super-exchange. This conclusion also agrees with the solubility of TiCl$_3$ · 3THF, TiCl$_3$ · 2THF and TiCl$_3$ · 2THF · C$_6$H$_6$ complexes in aromatic hydrocarbons while TiCl$_3$ · THF is insoluble.
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References


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