

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

M. ZIKMUND, A. VALENT, K. HRNČIAROVÁ and M. KOHÚTOVÁ

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,  
Bratislava 9*

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The thermogravimetric analysis showed the decomposition of  $\text{TiCl}_3 \cdot 3\text{THF}$  into  $\text{TiCl}_3 \cdot 2\text{THF}$  (at about  $100^\circ\text{C}$ ) and  $\text{TiCl}_3 \cdot \text{THF}$  (at temperatures above  $150^\circ\text{C}$ ) in nitrogen or argon atmosphere. At about  $250^\circ\text{C}$  disproportionation into  $\text{TiCl}_2$  and  $\text{TiCl}_4 \cdot 2\text{THF}$  takes place. The complexes  $\text{TiCl}_3 \cdot 3\text{THF}$  and  $\text{TiCl}_3 \cdot 2\text{THF}$  react with benzene under formation of  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  which, in the same way as  $\text{TiCl}_3 \cdot 3\text{THF}$ , is thermally decomposed while benzene is released in the first stage of the decomposition. The complexes  $\text{TiCl}_3 \cdot 3\text{THF}$ ,  $\text{TiCl}_3 \cdot 2\text{THF}$  and  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  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  $\text{TiCl}_3 \cdot \text{THF}$  (1.14 B. M.) together with its insolubility in benzene indicate the existence of a coordination polymer. The complexes  $\text{TiCl}_3 \cdot 2\text{THF}$  and  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  form with methanol vapour a brown-violet chloromethoxy derivative.

*Pregaglia et al.* [1] prepared the green complex  $\text{TiCl}_3 \cdot 2\text{THF}$  by thermal decomposition of the complex  $\text{TiCl}_3 \cdot 3\text{THF}$  either at  $80^\circ\text{C}$  in nitrogen atmosphere or at  $75^\circ\text{C}$  and 1 Torr pressure. Upon further temperature increase he did not observe the formation of any other modification; at  $180^\circ\text{C}$  decomposition of the compound took place. On the other hand, *Kern* [2] prepared by thermal decomposition of the complex  $\text{TiCl}_3 \cdot 3\text{THF}$  in the temperature range  $25-100^\circ\text{C}$  and at the pressure of 1 Torr the compound  $\text{TiCl}_3 \cdot \text{THF}$  which disproportionated into  $\text{TiCl}_2$  and  $\text{TiCl}_4 \cdot 2\text{THF}$  in the temperature range  $150-200^\circ\text{C}$ . These contradictions, as regards the products of thermal decomposition of the complex  $\text{TiCl}_3 \cdot 3\text{THF}$ , 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 ( $\alpha$ -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  $\text{CaH}_2$  with a final distillation from potassium and benzophenone immediately before use.

### *Preparation of complexes*

#### *Trichlorotris(tetrahydrofuran)titanium(III)*

Complex  $\text{TiCl}_3 \cdot 3\text{THF}$  [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  $\text{TiCl}_3 \cdot 3\text{THF}$  was precipitated from the supersaturated 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  $\text{TiCl}_4$  which, as a consequence of insufficient purification of  $\text{TiCl}_3$  [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  $\text{TiCl}_3 \cdot 3\text{THF}$ . It is, therefore, useful to filtrate and remove the precipitated  $\text{TiCl}_3 \cdot 3\text{THF}$  immediately after the reaction is completed. The complex  $\text{TiCl}_3 \cdot 3\text{THF}$  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  $\text{TiCl}_3 \cdot 2\text{THF}$  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  $\text{TiCl}_3 \cdot 3\text{THF}$  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  $\text{TiCl}_3 \cdot 3\text{THF}$  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  $\text{TiCl}_3 \cdot 3\text{THF}$  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  $\text{TiCl}_3 \cdot 3\text{THF}$  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  $\text{TiCl}_3 \cdot 3\text{THF}$  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  $\text{TiCl}_3 \cdot 2\text{THF}$  was prepared by heating the complex  $\text{TiCl}_3 \cdot 3\text{THF}$  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  $\text{TiCl}_3 \cdot 3\text{THF}$  in hexane or heptane (about 10 g in 500 ml). The reaction may be accelerated by raising the temperature [1].

*Compound  $\text{TiCl}_3 \cdot \text{THF}$*

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

*Trichlorobis(tetrahydrofuran)titanium(III)-benzene*

The green complex  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  may be prepared by suspending complex  $\text{TiCl}_3 \cdot 3\text{THF}$  in benzene. The blue crystals of  $\text{TiCl}_3 \cdot 3\text{THF}$  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  $\text{TiCl}_3 \cdot 2\text{THF}$  under stirring in benzene. The powdered substance, non-dissolved in saturated brown-green benzene solution had, after drying with nitrogen stream, the composition  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$ . 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  $\text{TiCl}_3 \cdot 2\text{THF}$  or  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  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  $\text{TiCl}_3 \cdot 3\text{THF}$  reacts but slowly whereas the compound  $\text{TiCl}_3 \cdot \text{THF}$  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  $\text{TiO}_2$ . The composition of  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  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 content any ferromagnetic admixtures.  $\text{HgCo}(\text{SCN})_4$  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  $\text{CuK}\alpha$  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  $\text{TiCl}_3 \cdot 3\text{THF}$  in nitrogen atmosphere proceeds in three steps (Fig. 1, curve 1). At about 100°C, the green complex  $\text{TiCl}_3 \cdot 2\text{THF}$  arises, at the temperature above 150°C, the grey compound  $\text{TiCl}_3 \cdot \text{THF}$  comes into existence, while the disproportionation into the black  $\text{TiCl}_2$  and yellow sublimate  $\text{TiCl}_4 \cdot 2\text{THF}$  sets in at about 250°C. The decomposition proceeds analogously under reduced pressure (1 Torr) (Fig. 1, curve 2), but the pure compounds

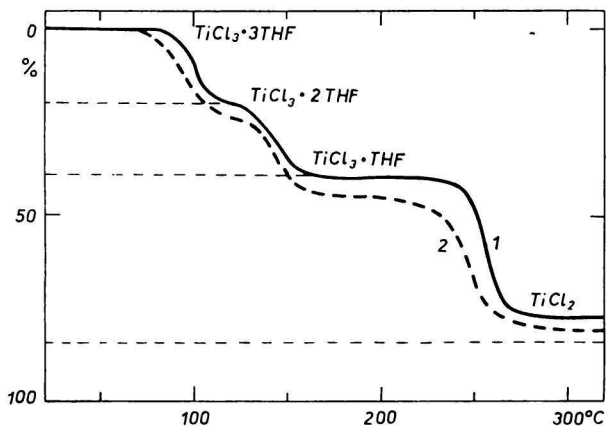


Fig. 1. Thermogravimetry of  $\text{TiCl}_3 \cdot 3\text{THF}$ .  
1. in nitrogen atmosphere; 2. in vacuum.

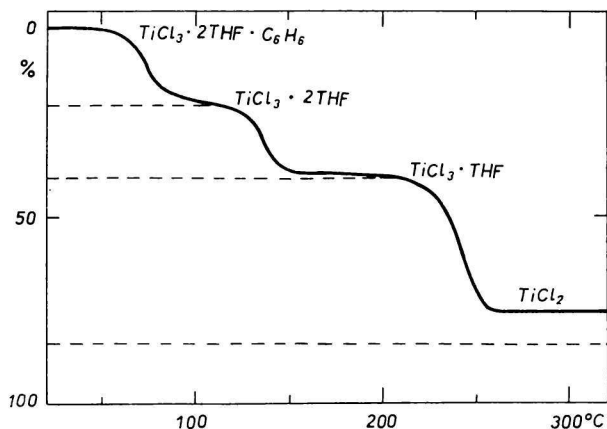


Fig. 2. Thermogravimetry of  $TiCl_3 \cdot 2THF \cdot C_6H_6$  in nitrogen atmosphere.

$TiCl_3 \cdot 2THF$  and  $TiCl_3 \cdot THF$  are more difficult to isolate. On the other hand, the purity of  $TiCl_2$  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  $TiCl_3 \cdot THF$  and the preparation decomposed already at  $180^\circ C$ , nor with the paper of *Kern* [2] who did not report any formation of the compound  $TiCl_3 \cdot 2THF$  while the product  $TiCl_3 \cdot THF$  was formed within the temperature interval between 20 and  $100^\circ C$  and the disproportionation took place in the temperature range of  $150-200^\circ C$ .

Different results were also obtained in the course of the study of the solution of  $TiCl_3 \cdot 3THF$  and  $TiCl_3 \cdot 2THF$  in aromatic solvents. According to the papers [1, 2] these complexes ought to be insoluble. We found that only the compound  $TiCl_3 \cdot THF$  (the solubility of which had not been mentioned before) was insoluble, while  $TiCl_3 \cdot THF$  and  $TiCl_3 \cdot 2THF$  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  $TiCl_3 \cdot 3THF$  or  $TiCl_3 \cdot 2THF$  in benzene has the composition  $TiCl_3 \cdot 2THF \cdot C_6H_6$ . 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  $TiCl_3 \cdot 3THF$  (Fig. 2).

The powder diffraction pattern for the crystal solvate  $TiCl_3 \cdot 2THF \cdot C_6H_6$  (Fig. 3a) suggests a different structure in comparison to complex  $TiCl_3 \cdot 2THF$ , regardless whether it was prepared by thermal decomposition (Fig. 3c) or by effect of hexane (Fig. 3d) on the solid complex  $TiCl_3 \cdot 3THF$ . For comparison, an X-ray diffraction pattern of the initial complex  $TiCl_3 \cdot 3THF$  (Fig. 3b) as well as that of the decomposition product  $TiCl_3 \cdot THF$  (Fig. 3e) are presented.

According to literature, magnetic susceptibility was measured only for the complex  $TiCl_3 \cdot 3THF$  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  $293^\circ K$ ). 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.

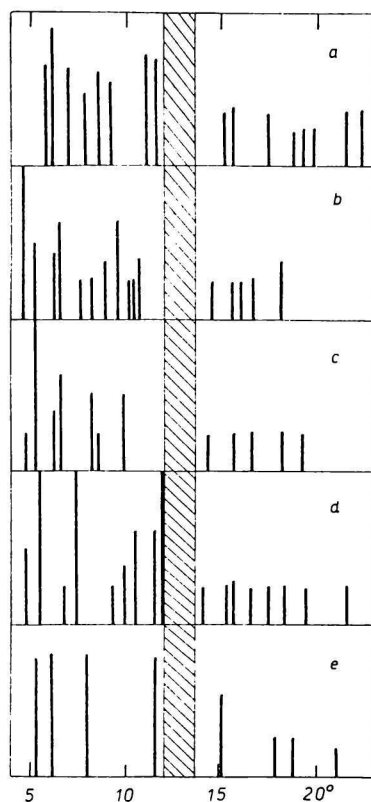


Table 1

Magnetic susceptibilities ( $\chi'_M \cdot 10^6$ ) and magnetic moments ( $\mu_{\text{eff}}$ , B. M.) of chloro(tetrahydrofuran)titanium(III) complexes

$T$ , °K	$\text{TiCl}_3 \cdot 3\text{THF}$		$\text{TiCl}_3 \cdot 2\text{THF}$		$\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$		$\text{TiCl}_3 \cdot \text{THF}$	
293	1400	1.82	1418	1.83	1376	1.80	547	1.14
273	1422	1.77	1455	1.78	1402	1.76	522	1.07
201	1874	1.74	1905	1.76	1775	1.70	475	0.88
77	4079	1.59	4463	1.66	4057	1.59	257	0.40

The magnetic measurements (Table 1) show that the compounds  $\text{TiCl}_3 \cdot 2\text{THF}$  (1.83 B. M.) and  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  (1.80 B. M.), as well as  $\text{TiCl}_3 \cdot 3\text{THF}$ , have monomeric structure. On the other hand, the magnetic moment of  $\text{TiCl}_3 \cdot \text{THF}$  (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  $\text{TiCl}_3 \cdot 3\text{THF}$ ,  $\text{TiCl}_3 \cdot 2\text{THF}$  and  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  complexes in aromatic hydrocarbons while  $\text{TiCl}_3 \cdot \text{THF}$  is insoluble.

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