Synthesis and thermogravimetric investigation of mixed ligand chlorotitanium(III) complexes containing tetrahydrofuran and acetonitrile

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The mixed ligand chlorotitanium(III) complexes containing tetrahydrofuran (C_4H_8O) and acetonitrile (CH_3CN) were prepared using $TiCl_3(C_4H_8O)_2$, $TiCl_3(C_4H_8O)$, and $TiCl_3(CH_3CN)$ as the parent compounds. The synthesized complexes were studied thermogravimetrically and the mechanism of their thermal decomposition was discussed on the basis of gas chromatography, infrared and electronic spectral data.

Синтезированы смешанно-лигандные комплексы трихлорида титана с тетрагидрофураном и ацетонитрилом. В качестве исходных веществ использованы соединения состава $TiCl_3(C_4H_8O)_2$, $TiCl_3(C_4H_8O)$ и $TiCl_3(CH_3CN)$. Процесс термического разложения полученных комплексов исследован термогравиметрическим и газохроматографическим методом. На основе изучения инфракрасных и электронных спектров сделано заключение о механизме термического разложения исследованных соединений.

According to [1—10], by the reaction between $TiCl_3$ and molecular ligands in an inert atmosphere the compounds of composition $TiCl_3L_3$ (L = tetrahydrofuran, acetonitrile, acrylonitrile, propionitrile, benzonitrile) are formed. From among this group of Ti(III) compounds only the structure of trichlorotris(tetrahydrofuran)-titanium(III) was solved [11, 12]. As it was described in [4, 10, 11], in the course of their thermal decomposition the molecular ligands are released and the compounds with lowered coordination number of titanium(III) or coordination polymers are formed. In the present paper we report research into the reactions of complexes of the type $TiCl_3L_2$ and $TiCl_3L$ with molecular ligands L′. As we found it is possible to prepare the mixed ligand complexes of composition $TiCl_3L_2L'$ and $TiCl_3LL'_2$ by an addition reaction. The synthesis of the complexes $TiCl_3(C_4H_8O)_2(CH_3CN)$, $TiCl_3(CH_3CN)(C_2H_3CN)_2$, and $TiCl_3(C_4H_8O)_2(C_2H_3CN)$ by a substitution reaction was described in [9, 13].

Experimental

The studied chlorotitanium(III) compounds were prepared on a direct way by the reaction of $TiCl_3(C_4H_8O)_2$ and $TiCl_3(C_4H_8O)$ with acetonitrile and $TiCl_3(CH_3CN)$ with tetrahydrofuran in the stoichiometric ratio under dry nitrogen. The medium of noncoordinating solvent was used. The experimental technique was reported in [10]. In all three mentioned cases the rate of reaction was slow and the colour change from light green or grey to light blue was observed. The prepared products were washed out by hexane and dried in nitrogen. The parent complexes $TiCl_3(C_4H_8O)_2$, $TiCl_3(C_4H_8O)$, and $TiCl_3(CH_3CN)$ were prepared by thermal decomposition of $TiCl_3(C_4H_8O)_3$ or $TiCl_3(CH_3CN)_3$ as was previously reported [4, 10]. In accordance with our experimental results published in [14], the medium of noncoordinating solvent, in the present work hexane, was chosen to slow down the reaction rate so that the addition type of reaction would be favoured. Since the prepared complexes are insoluble in hexane, they give quantitative yields without subsequent evaporation of and precipitation from the solution. The prepared light blue coloured powdered compounds were of following composition (the order of molecular ligands is in agreement with the way of preparation):

$TiCl_3(C_4H_8O)_2(CH_3CN)$ (calculated: 14.12% Ti, 31.34% Cl; found: 13.77% Ti^{III}, 14.06% Ti^{IV}, 31.10% Cl).

$TiCl_3(CH_3CN)(C_4H_8O)_2$ (calculated: 14.12% Ti, 31.34% Cl; found: 13.71% Ti^{III}, 13.81% Ti^{IV}, 30.67% Cl).

$TiCl_3(C_4H_8O)(CH_3CN)_2$ (calculated: 15.53% Ti, 34.49% Cl; found: 15.33% Ti^{III}, 16.06% Ti^{IV}, 34.61% Cl).

Ti(IV) was determined spectrophotometrically, Ti(III) by titration with cerium(IV) sulfate (ferroin was used as an indicator), Cl^- by the Volhard method.

Thermal decomposition of the prepared complexes was studied in the temperature range 20—350°C and in dynamic nitrogen atmosphere. An equipment of our own construction, based on the principle of a spring balance, was used. In comparison with the original equipment [15] the present apparatus possessed an improved sensitivity and an automatic recording of measured data. The thermogravimetric apparatus (Fig. 1) is made of glass. Three parts can be discerned: Part *A* contains a mechanical device (*2*) with the aid of which vertical shifting of the sample holder (*10*) is feassible. In part *B* a quartz spring (*4*) is placed. In the part *C*, which is heated from outside by an electric furnace (*20*), the investigated sample is placed. With the present apparatus it is possible to work at reduced pressure and in a static or dynamic inert or controlled atmosphere. The tube *D* serves for insertion of the sample into the apparatus under an inert atmosphere. The required amount of the sample is introduced in such a way that the lifting device (*2*) lifts the sample holder (*10*) to a position in which the shovel (*13*) can be placed underneath sample holder (*10*) which is then moved, with the aid of the shovel (*13*) and placed under the opening (*14*) through which the sample is introduced into the apparatus. Then the sample holder (*10*) is returned to its original position. The change of the sample weight in the course of thermal decomposition is registered by an optoelectronic system [16] and it is recorded, together with the programmed temperature changes with a line recorder. In our thermogravimetric experiment we used the heating rate of 4°C min^{-1} and the sample weight was between 50—70 mg.

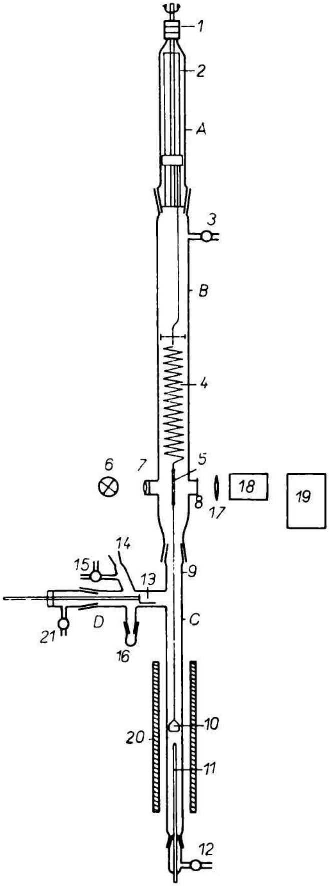


Fig. 1. Scheme of thermogravimetric apparatus.
1. Packing;
2. mechanical lifting device;
3. gas inlet;
4. quartz spring;
5. aluminium screen;
6. lamp;
7. set of lenses;
8. glass window;
9. platinum chain;
10. sample holder;
11. thermocouple;
12. gas inlet;
13. shovel;
14. opening through which the sample is filled in;
15. gas outlet or connecting of vacuum;
16. opening for removing the sample;
17. lens;
18. set of flat mirrors;
19. electric recorder adapted to beam follower;
20. electric furnace;
21. gas inlet.

On the basis of thermogravimetric data the intermediates were prepared by the procedure described in [17]. The process of releasing of individual ligands was estimated using chromatograph CHROM-4 (Laboratorní přístroje, Prague), column length 2500 mm, packing Rysorb BLK with polyethylene glycol adipate, temperature 92°C, carrier gas argon. The diffuse reflectance spectra from 25 000—12 500 cm^{-1} were registered on a SPEKOL spectrophotometer equipped with additional amplifier SPEKOL ZV (Zeiss, Jena), MgO was used as a reference. For obtaining spectra in an inert atmosphere a special all-glass vessel was used [10]. The infrared spectra were recorded from 600—5000 cm^{-1} using the Nujol technique, on a Perkin—Elmer 221 spectrophotometer between NaCl plates. The method of sample preparation is described in [18]. The values of effective magnetic moments were determined at room temperature by the Gouy method on an apparatus of our own construction.

Results and discussion

Since the most frequent coordination number of Ti(III) in its complexes is supposed to be 6, the mixed ligand chloro complexes were prepared using the coordinative unsaturated (pentacoordinated) chlorotitanium(III) complexes as the parent compounds. Thus by addition reaction of $TiCl_3(C_4H_8O)_2$, $TiCl_3(C_4H_8O)$ with acetonitrile and $TiCl_3(CH_3CN)$ with tetrahydrofuran the mixed ligand complexes of composition $TiCl_3(C_4H_8O)_2(CH_3CN)$, $TiCl_3(C_4H_8O)(CH_3CN)_2$, and $TiCl_3(CH_3CN)(C_4H_8O)_2$ were synthesized. The registered diffuse reflectance spectra of these compounds (Fig. 2) exhibit a bright asymmetric band in the range typical of octahedral coordination. This fact could be taken for indirect evidence of an addition reaction. The infrared spectral data were used to confirm the chemical composition of prepared complexes. On the basis of these data (Table 1) the presence of coordinated acetonitrile (band located at 2300 cm^{-1}) and of tetrahydrofuran (two bands in the range 800—1000 cm^{-1}) in these complexes can be assumed. Figs. 3—5 show the course of thermal decomposition of the studied complexes. The isolated intermediates were also estimated by means of infrared spectral data listed in Table 1. The presence of individual ligands in the products of thermal decomposition is in agreement with the composition of gas escaping in the course of their thermal treating, found by chromatographic analysis.

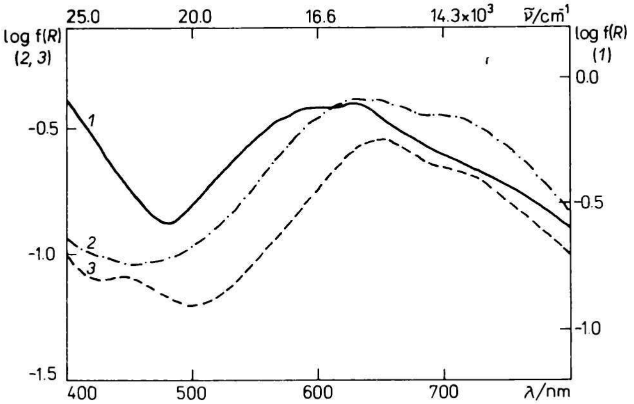


Fig. 2. Diffuse reflectance spectra of:
——— $TiCl_3(C_4H_8O)(CH_3CN)_2$; — · — · — $TiCl_3(C_4H_8O)_2(CH_3CN)$;
– – – – $TiCl_3(CH_3CN)(C_4H_8O)_2$.

In the case of complex $TiCl_3(C_4H_8O)_2(CH_3CN)$, synthesized by the reaction $TiCl_3(C_4H_8O) + CH_3CN$, the molecule of acetonitrile occupies a *trans* position to

Table 1

Infrared spectral data of investigated chlorotitanium(III) compounds [cm^{-1}]

Ligand/compound	$\tilde{\nu}(\text{COC})$		$\tilde{\nu}(\text{C}\equiv\text{N})$
	$\tilde{\nu}_1$	$\tilde{\nu}_2$	
C_4H_8O	909	1069 [19]	
CH_3CN			2253 [10]
$TiCl_3(C_4H_8O)_2$	850	1007 [19]	
$TiCl_3(C_4H_8O)$	827	987 [19]	
$TiCl_3(CH_3CN)$			2325 [10]
$TiCl_3(C_4H_8O)_2(CH_3CN)$ (*1*)	840	1000	2300
(*1*) therm. decomp. at 100°C	840	990	2250
(*1*) therm. decomp. at 130°C	824	980	
$TiCl_3(CH_3CN)(C_4H_8O)_2$ (*2*)	843	1000	2300
(*2*) therm. decomp. at 100°C	843	1000	2300
(*2*) therm decomp. at 130°C	824	980	
$TiCl_3(C_4H_8O)(CH_3CN)_2$ (*3*)	846	1000	2300
(*3*) therm. decomp. at 130°C	827	985	2300

chlorine [11]; in the course of thermal decomposition (Fig. 3) in the first step the molecule of tetrahydrofuran is released. The thermogravimetric curve, chromatographic and infrared spectral data indicate the presence of both molecular ligands. The molecule of acetonitrile is released in the second step within which the formation of polymeric $TiCl_3(C_4H_8O)$ [11, 19] was observed. As it is evident from Fig. 4, the complex of the same composition, prepared by the reaction

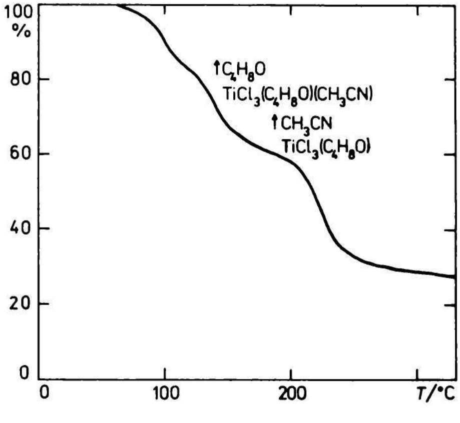


Fig. 3. Thermogravimetric curve of $TiCl_3(C_4H_8O)_2(CH_3CN)$.

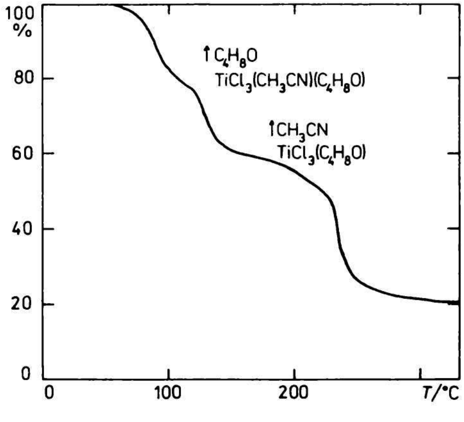


Fig. 4. Thermogravimetric curve of $TiCl_3(CH_3CN)(C_4H_8O)_2$.

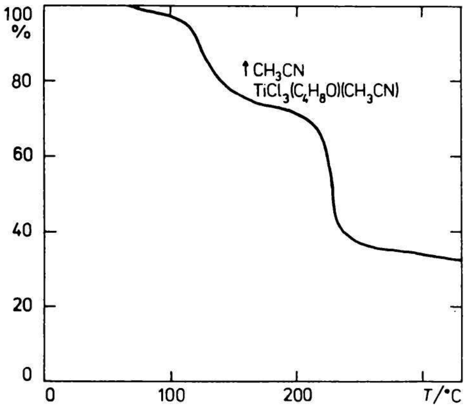


Fig. 5. Thermogravimetric curve of $\mathrm{TiCl_3(C_4H_8O)(CH_3CN)_2}$.

$\mathrm{TiCl_3(CH_3CN) + 2\,C_4H_8O}$ decomposes in a similar way. In the course of thermal decomposition of $\mathrm{TiCl_3(C_4H_8O)(CH_3CN)_2}$ (Fig. 5) the molecule of acetonitrile is released in the first step and the formation of compound involving both molecular ligands was observed. In this case this compound could be prepared also on laboratory scale and the found analytical data correspond to composition $\mathrm{TiCl_3(C_4H_8O)(CH_3CN)}$. The observed thermal decompositions may be represented by the following schemes:

$$1.\ \mathrm{TiCl_3(C_4H_8O)_2(CH_3CN)} \xrightarrow{100\,^\circ\mathrm{C}} \mathrm{TiCl_3(C_4H_8O)(CH_3CN)} \xrightarrow{140\,^\circ\mathrm{C}}$$

$$\xrightarrow{140\,^\circ\mathrm{C}} \mathrm{TiCl_3(C_4H_8O)} \xrightarrow{200\,^\circ\mathrm{C}} 1/2\mathrm{TiCl_2} + 1/2\,\mathrm{TiCl_4(C_4H_8O)_2}\uparrow$$

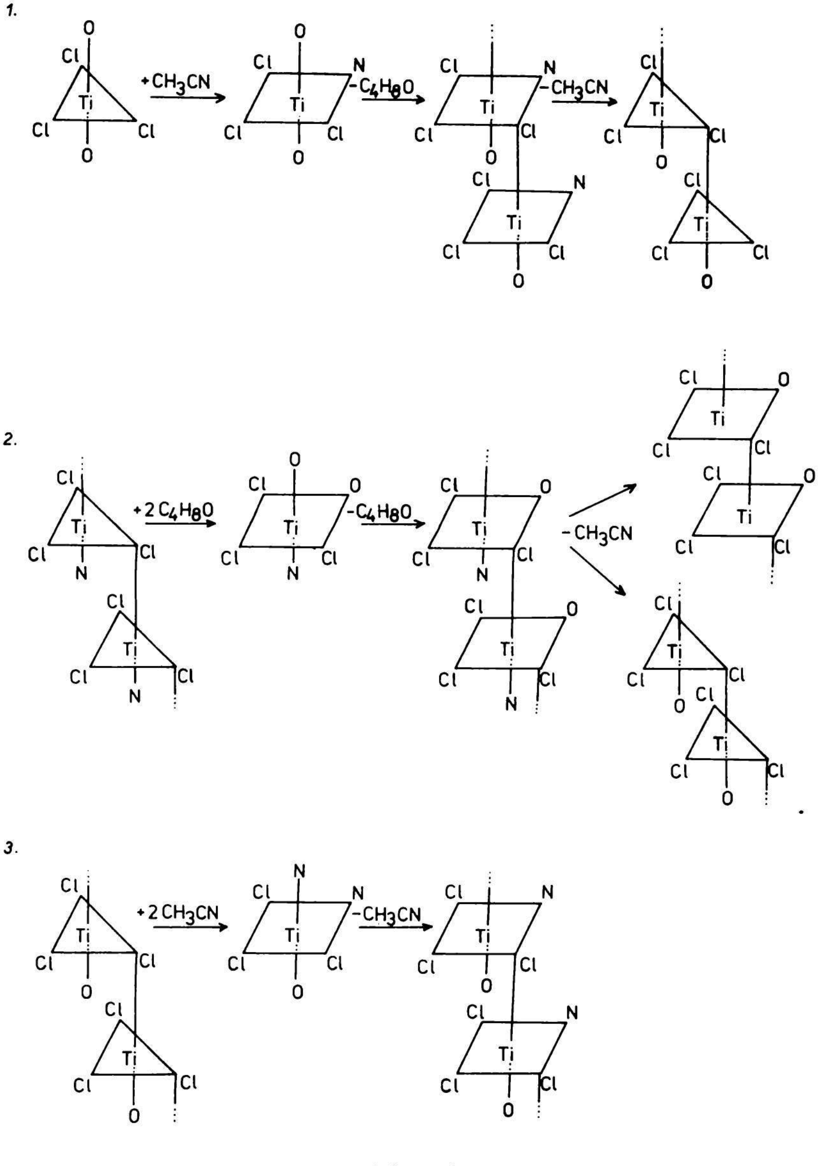
$$2.\ \mathrm{TiCl_3(CH_3CN)(C_4H_8O)_2} \xrightarrow{100\,^\circ\mathrm{C}} \mathrm{TiCl_3(C_4H_8O)(CH_3CN)} \xrightarrow{130\,^\circ\mathrm{C}}$$

$$\xrightarrow{130\,^\circ\mathrm{C}} \mathrm{TiCl_3(C_4H_8O)} \xrightarrow{200\,^\circ\mathrm{C}} 1/2\mathrm{TiCl_2} + 1/2\mathrm{TiCl_4(C_4H_8O)_2}\uparrow$$

$$3.\ \mathrm{TiCl_3(C_4H_8O)(CH_3CN)_2} \xrightarrow{130\,^\circ\mathrm{C}} \mathrm{TiCl_3(C_4H_8O)(CH_3CN)} \xrightarrow{200\,^\circ\mathrm{C}}$$

$$\xrightarrow{200\,^\circ\mathrm{C}} 1/2\mathrm{TiCl_2} + 1/2\mathrm{TiCl_4(C_4H_8O)_2}\uparrow$$

The course of thermal decomposition, the mechanism of formation, and the properties of compounds thus formed can be understood on the basis of crystal structure data on $\mathrm{TiCl_3(C_4H_8O)_3}$ [12]. According to our results the atom Ti is octahedrally coordinated with $\mathrm{Cl^-}$ atoms arranged in meridional positions and all Ti—Cl distances are equal. The other three sites are occupied by the O-donor atoms from tetrahydrofuran, the bonds Ti—O in *trans* position with regard to Cl



Scheme 1

Proposed mechanism of formation and thermal decomposition of investigated mixed ligand chlorotitanium(III) complexes are longer, and in this site the possibility of thermal splitting off is most probable.

According to our results published previously [4, 11] at about 100°C one molecule of tetrahydrofuran is released and pentacoordinated monomeric compound $TiCl_3(C_4H_8O)_2$ is formed. In this case the molecule of acetonitrile is placed in *trans* position to chlorine. At about 150°C the polymeric compound $TiCl_3(C_4H_8O)$ is formed and here in the reaction with acetonitrile 1Ti : :2CH_3CN besides addition also depolymerization process is believed to take place. The thermal decomposition of chlorotitanium(III) complex with acetonitrile, $TiCl_3(CH_3CN)_3$, is nearly the same, only no formation of compound with two acetonitrile molecules was observed, the polymeric compound $TiCl_3(CH_3CN)$ is directly formed [10]. Then in the reaction with tetrahydrofuran also both, the addition and depolymerization processes, are assumed to take place and on this way the coordination sphere becomes complete and monomeric compound with coordination number of Ti(III) 6 is formed. The proposed mechanism of formation and thermal decomposition of prepared mixed ligand chlorotitanium(III) complexes with tetrahydrofuran and acetonitrile are shown in Scheme 1.

The found values of effective magnetic moments of the investigated compounds determined at room temperature are listed in Table 2. These values for $TiCl_3(C_4H_8O)_2(CH_3CN)$, $TiCl_3(CH_3CN)(C_4H_8O)_2$, $TiCl_3(C_4H_8O)(CH_3CN)_2$ are indicative of monomeric structure and suggest the depolymerization process in the course of their synthesis. These data are in good agreement with the theoretical values typical of distorted octahedral coordination of central d^1 ion. Simultaneously they also reflect the lowering of symmetry due to more heterogeneous coordination sphere ($TiCl_3(C_4H_8O)_3$ $\mu_{eff}(293\ K) = 1.82$ B.M. [11], $TiCl_3(CH_3CN)_3$ $\mu_{eff}(293\ K) = 1.84$ B.M. [10]).

The markedly lowered value of effective magnetic moment of compound $TiCl_3(C_4H_8O)(CH_3CN)$ indicates the existence of antiferromagnetic interaction between the paramagnetic centres and hence the polymeric structure in this

Table 2

Magnetic susceptibilities and effective magnetic moments at room temperature of the studied chlorotitanium(III) compounds

Compound	$\chi'_M \cdot 10^{11}/m^3\ mol^{-1}$	μ_{eff}/B.M.
$TiCl_3(C_4H_8O)_2(CH_3CN)$	1653	1.76
$TiCl_3(CH_3CN)(C_4H_8O)_2$	1692	1.78
$TiCl_3(C_4H_8O)(CH_3CN)_2$	1589	1.73
$TiCl_3(C_4H_8O)(CH_3CN)$	1068	1.42

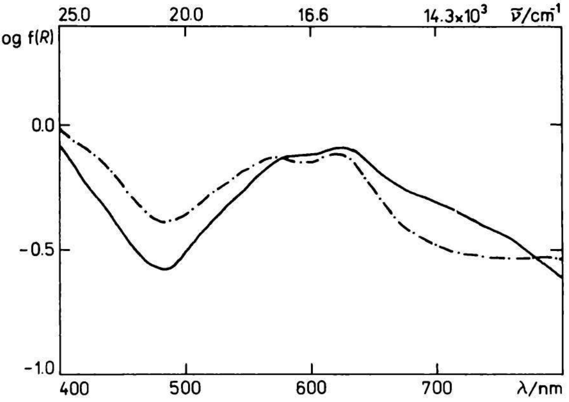


Fig. 6. Diffuse reflectance spectra of:
——— $TiCl_3(C_4H_8O)(CH_3CN)_2$; – · – · – $TiCl_3(C_4H_8O)(CH_3CN)$.

compound can be postulated. The insolubility of this compound in chloroform corroborates this assumption and as it is evident from diffuse reflectance spectra (Fig. 6), the octahedral coordination of central ion remains intact (Scheme 1).

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