

Synthesis and thermogravimetric investigation of the complexes of general formula $\text{TiCl}_3\text{L}_n\text{L}'_m$ ($n + m = 3$)

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The trichlorotitanium(III) complexes of the composition $\text{TiCl}_3\text{L}_n\text{L}'_m$, where $n + m = 3$; L: tetrahydrofuran, $n = 1$ or 2 ; L: acetonitrile, $n = 1$; L': pyridine, aliphatic alcohol (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol), $m = 1$ or 2 , were prepared. Electronic spectra and magnetic susceptibility measurement data indicate that the title complexes are monomeric with distorted tetragonal bipyramidal coordination of the central Ti(III) atom. Studying their thermal behaviour in the temperature range 20—400°C the formation of two types of intermediates was observed in dependence on the neutral ligand (L') present. When L' is pyridine, the molecular ligands of lower donor numbers ($\text{C}_4\text{H}_8\text{O}$, CH_3CN) are released and when aliphatic alcohols are present then alcoholysis and simultaneous escape of HCl, alcohol, and molecular ligand take place.

Only a few works are known that deal with the synthesis and properties of Ti(III) compounds containing simultaneously various kinds of molecular ligands [1, 2]. One of the possible ways for preparation of complexes $\text{TiCl}_3\text{L}_2\text{L}'$ is the substitution method applied by Hoff and Brubaker [1]. These authors used tetrahydrofuran, acetonitrile, 2-propanol, and dioxane as molecular ligands. The complexes in question were prepared by heating the parent substances, $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_3$ and $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O}_2)_2$, dissolved in tetrahydrofuran or dioxane in excess of the substituting ligand.

In contrast to this method we made an attempt to prepare such mixed-ligand complexes in addition way [3, 4]. As parent substances the compounds $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$ (I), $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})$ (II), and $\text{TiCl}_3(\text{CH}_3\text{CN})$ (III) were used. By the reaction of I and II with acetonitrile the substances $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_n(\text{CH}_3\text{CN})_{3-n}$ ($n = 1$ or 2) were prepared [3] and the addition ability of III to react with aliphatic alcohols was confirmed and published in [4]. As it was reported in [5] the coordinatively unsaturated complex I is capable to react also with the basic centres of inorganic carriers (MgO) under formation of a surface complex in which the coordination number of Ti(III) is 6.

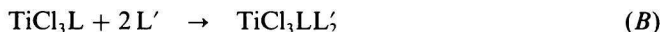
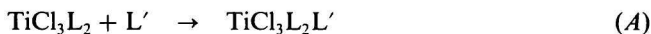
The aim of the present paper was to study the thermal stability of the title trichlorotitanium(III) complexes in more detail with special emphasis on the character of intermediates formed. To examine this aspect two types of complexes were chosen:

i) the mixed proton-free molecular ligand—chlorotitanium(III) complexes, in order to study the thermal decomposition beginning with the cleavage of the coordinative bond;

ii) the mixed alcohol—proton-free molecular ligand—chlorotitanium(III) complexes with the aim to investigate the thermal decomposition of proton-containing (alcohol) ligands. The structure and thermal stability relations of both types of initial complexes were described in our earlier communications [6, 7].

Experimental

The group of investigated mixed-ligand chlorotitanium(III) complexes, $\text{TiCl}_3\text{L}_n\text{L}'_m$, was prepared by addition reaction according to the following reaction scheme



where L is tetrahydrofuran (A), (B), acetonitrile (B) and L' is pyridine, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol.

The used parent complexes, monomeric $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$, polymeric $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})$, and $\text{TiCl}_3(\text{CH}_3\text{CN})$ were prepared by thermal decomposition of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_3$ and $\text{TiCl}_3(\text{CH}_3\text{CN})_3$ in dynamic nitrogen atmosphere [8—10].

The complexes $\text{TiCl}_3\text{L}_n\text{L}'_m$ ($n + m = 3$) were prepared by mixing solid TiCl_3L_n with ligand L' in the stoichiometric ratio. The ligand L' was dissolved in an excess of indifferent noncoordinating liquid medium (hexane) in which neither the parent nor the prepared complexes are soluble. To avoid the substitution reaction with ligand L' the coordinatively unsaturated parent complex TiCl_3L_n must be very finely divided to hinder the local oversaturation of added diluted ligand L' on the solid surface. The reaction proceeds several days. In all cases the yields of reaction products $\text{TiCl}_3\text{L}_n\text{L}'_m$ were practically quantitative. The experiments were performed in two-necked glass ampoules in an atmosphere of dry oxygen-free nitrogen at room temperature. All solvents and ligands were purified to eliminate traces of oxygen and moisture using the common techniques for air-sensitive organometallic compounds.

In order to determine the thermal properties all prepared complexes were investigated by means of thermogravimetric analysis in dynamic nitrogen atmosphere in the temperature range 20—400°C. The apparatus for thermogravimetric study was described elsewhere [3]. The heating rate was 2.5°C min⁻¹ and sample mass was 50—70 mg.

Some typical thermogravimetric curves are shown in Figs. 5—8. The reaction intermediates were prepared at chosen temperature in nitrogen atmosphere by a procedure described in [10].

The reaction products were characterized on the basis of their infrared spectra, diffuse reflectance spectra, and values of effective magnetic moment at room temperature. The release of individual molecular ligands during thermolysis was identified by means of gas

chromatography. Ti(III) was determined cerimetrically, Cl by the Volhard method. Table 1 presents the analytical data.

Table 1

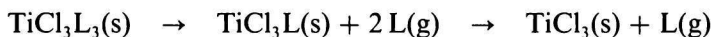
Analytical characterization of studied mixed-ligand chlorotitanium(III) complexes

Compound	Titanium(III)		Chlorine	
	w(calc.)/%	w(found)/%	w(calc.)/%	w(found)/%
$TiCl_3(C_4H_8O)_2(C_5H_5N)$	12.69	12.84	28.18	29.49
$TiCl_3(C_4H_8O)_2(CH_3OH)$	14.52	14.85	32.23	34.03
$TiCl_3(C_4H_8O)_2(C_2H_5OH)$	13.92	14.48	30.92	32.82
$TiCl_3(C_4H_8O)_2(C_3H_7OH)$	13.38	13.57	29.71	30.45
$TiCl_3(C_4H_8O)_2(2-C_3H_7OH)$	13.38	13.57	29.71	30.44
$TiCl_3(C_4H_8O)_2(C_4H_9OH)$	12.88	13.03	28.59	28.51
$TiCl_3(C_4H_8O)_2(2-C_4H_9OH)$	12.88	12.61	28.59	29.71
$TiCl_3(C_4H_8O)(C_5H_5N)_2$	12.45	12.37	27.66	29.97
$TiCl_3(C_4H_8O)(CH_3OH)_2$	16.52	15.75	36.67	37.40
$TiCl_3(C_4H_8O)(C_2H_5OH)_2$	15.02	15.12	33.44	34.64
$TiCl_3(C_4H_8O)(C_3H_7OH)_2$	13.84	13.90	30.74	31.05
$TiCl_3(C_4H_8O)(2-C_3H_7OH)_2$	13.84	13.72	30.74	30.66
$TiCl_3(C_4H_8O)(C_4H_9OH)_2$	12.81	12.79	28.44	28.46
$TiCl_3(C_4H_8O)(2-C_4H_9OH)_2$	12.81	12.62	28.44	28.25
$TiCl_3(CH_3CN)(C_5H_5N)_2$	13.56	13.89	30.13	30.54
$TiCl_3(C_4H_8O)(C_5H_5N)$	15.70	15.46	34.87	35.03
$TiCl_3(C_5H_5N)_2$	15.33	15.58	34.04	35.59

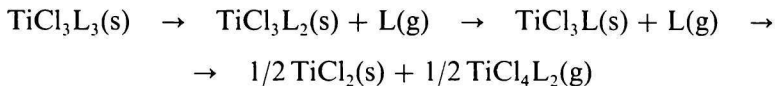
The diffuse reflectance spectra were recorded with a Specord M-40 spectrophotometer (Zeiss, Jena) in the range $\lambda = 450-850$ nm. MgO was used as a reference substance, transmittance T is presented in arbitrary units. The infrared spectra from the region of $\tilde{\nu} = 600-5000$ cm^{-1} were registered on a Perkin-Elmer 221 spectrophotometer between NaCl plates. The samples were milled with nujol. The values of the effective magnetic moment at room temperature were determined on an apparatus of our own construction based on the Gouy principle.

Results and discussion

In our previous communication [9] we reported that the thermal decomposition process of $TiCl_3(CH_3CN)_3$ occurs in two distinct stages ($L = CH_3CN$)

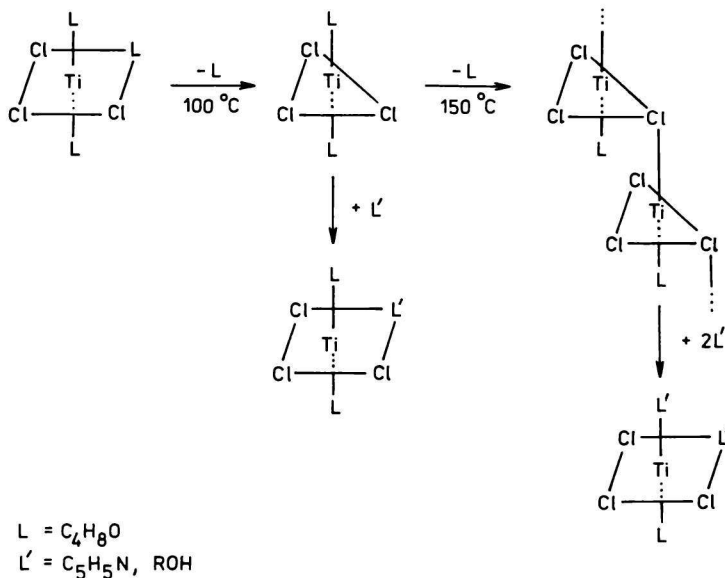


In contrast to this the thermal decomposition of $TiCl_3(C_4H_8O)_3$ takes place by the following sequence of reactions [6] ($L = C_4H_8O$)



The intermediate decomposition products TiCl_3L_2 and TiCl_3L were characterized by means of the temperature dependence of the effective magnetic moment (μ_{eff}) and the electronic spectral data [6, 9]. On the basis of these results the monomeric arrangement and trigonal bipyramidal coordination of Ti(III) atom in the complex $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$ were proposed. On the other hand, the magnetic properties of TiCl_3L were typical of polymeric arrangement with antiferromagnetic interaction between Ti(III) atoms, the five-coordination of Ti(III) atom was suggested on the basis of the shapes of their electronic spectra (Fig. 2, curve 2; Fig. 3, curve 1; Fig. 4, curve 1).

The proposed reaction mechanism of the thermal decomposition of TiCl_3L_3 ($\text{L} = \text{C}_4\text{H}_8\text{O}$) and the formation of mixed-ligand complexes $\text{TiCl}_3\text{L}_2\text{L}'$ and $\text{TiCl}_3\text{LL}'_2$ ($\text{L}' = \text{C}_5\text{H}_5\text{N}$, aliphatic alcohol) is shown in Scheme 1.



Scheme 1

The course of the reaction $\text{TiCl}_3\text{L}_2 + \text{L}'$ indicates that an addition of molecular ligand L' to unoccupied coordination site in the parent complex takes place. In the reactions $\text{TiCl}_3\text{L} + 2\text{L}'$, apart from addition, also the depolymerization processes are assumed to occur.

The reaction products $\text{TiCl}_3\text{L}_2\text{L}'$ and $\text{TiCl}_3\text{LL}'_2$ form light blue ($\text{L}' =$ aliphatic alcohol) or light green ($\text{L}' =$ pyridine) powders. Figs. 1—4 show the reflectance

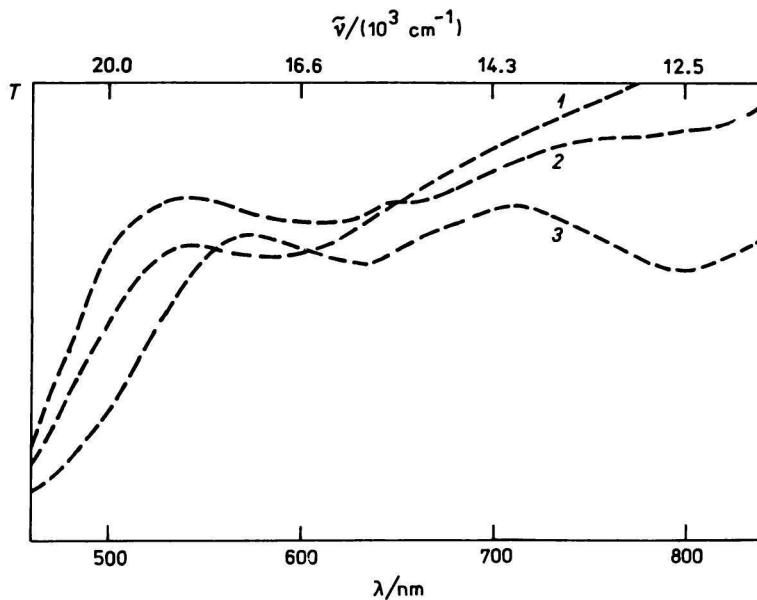


Fig. 1. Diffuse reflectance spectra of $TiCl_3(C_4H_8O)(C_5H_5N)_2$ (1), $TiCl_3(C_4H_8O)_2(C_5H_5N)$ (2), and $TiCl_3(C_4H_8O)(C_5H_5N)$ (3).

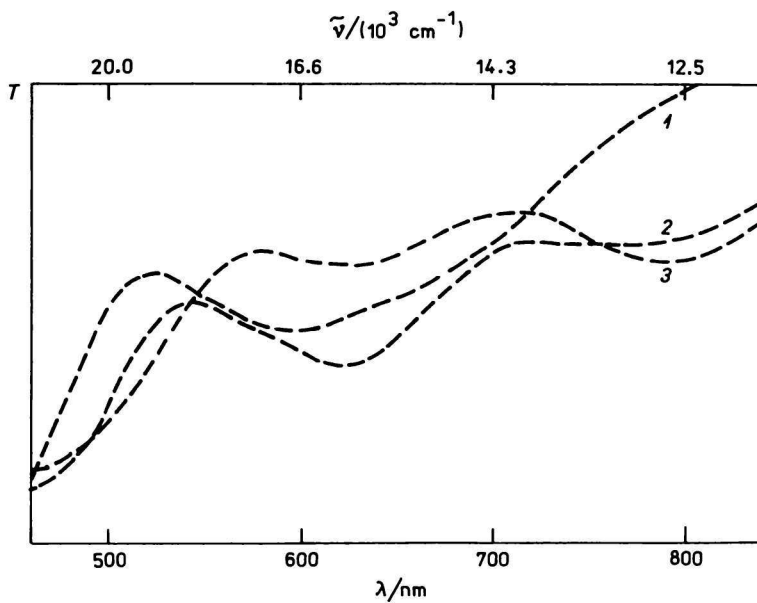


Fig. 2. Diffuse reflectance spectra of $TiCl_3(CH_3CN)(C_5H_5N)_2$ (1), $TiCl_3(CH_3CN)$ (2), and $TiCl_3(C_5H_5N)_2$ (3).

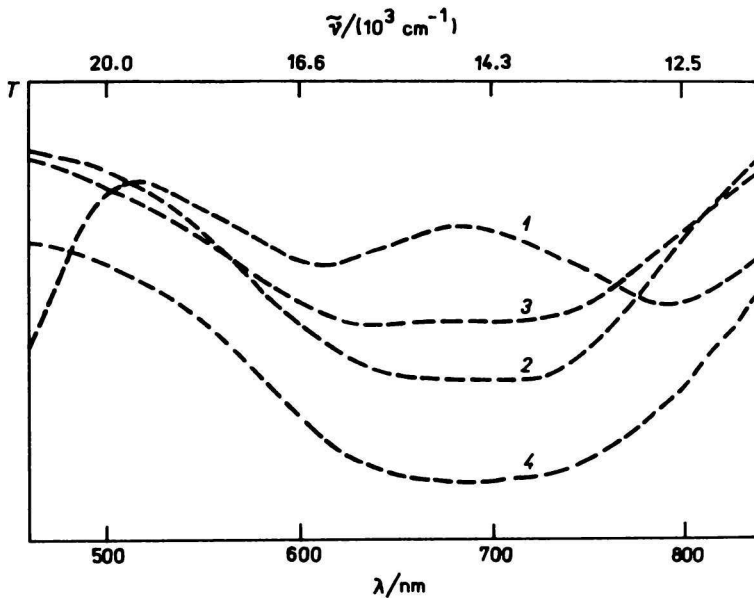


Fig. 3. Diffuse reflectance spectra of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$ (1), $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{OH})$ (2), $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(2\text{-C}_3\text{H}_7\text{OH})$ (3), and $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{C}_4\text{H}_9\text{OH})$ (4).

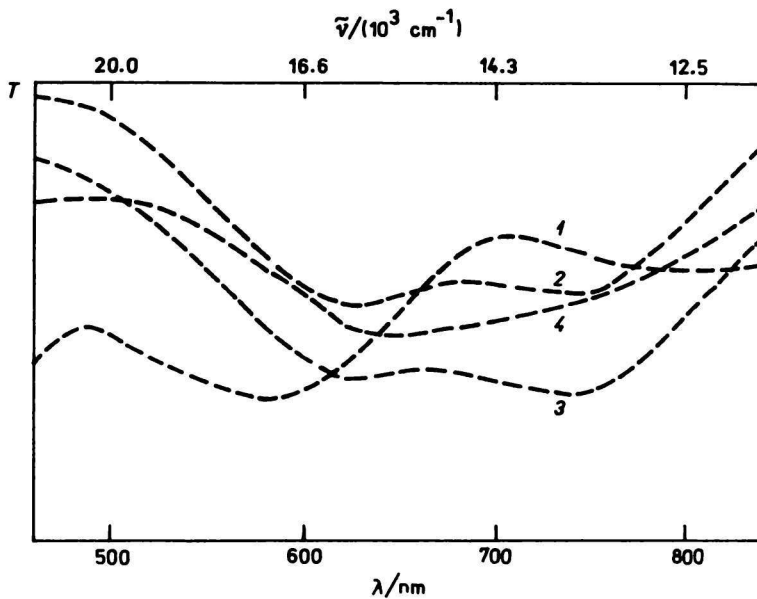


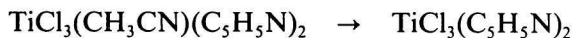
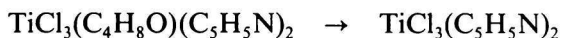
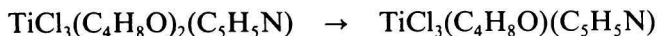
Fig. 4. Diffuse reflectance spectra of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})$ (1), $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{C}_2\text{H}_5\text{OH})_2$ (2), $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{C}_3\text{H}_7\text{OH})_2$ (3), and $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(2\text{-C}_4\text{H}_9\text{OH})_2$ (4).

tance spectra of the mixed-ligand reaction products $TiCl_3L_2L'$ and $TiCl_3LL'_2$ compared with those of the parent coordinatively unsaturated compounds $TiCl_3L_2$ and $TiCl_3L$. With regard to the character of the diffuse reflectance spectra of the complexes of the composition $TiCl_3L_2L'$ and $TiCl_3LL'_2$ (Fig. 1, curves 1, 2; Fig. 2, curve 1; Fig. 3, curves 2, 3, 4; Fig. 4, curves 2, 3, 4) a distorted tetragonal bipyramidal coordination can be assumed. The experimentally obtained values of effective magnetic moment at room temperature ($\mu_{\text{eff}} = 1.74\text{--}1.86 \mu_B$) corroborate the proposed monomeric structure.

The thermal behaviour of the investigated trichlorotitanium(III) complexes in the temperature range 20—400°C is affected by several factors: the strength of the metal—ligand bond, the donor number and chemical properties of the ligand (its protic and aprotic character), and finally the stereochemistry of the complex. The decomposition temperature of the complexes is a measure of their thermal stability. It should be pointed out that only thermogravimetric data recorded under completely identical conditions can be compared. The temperature of decomposition depends, besides chemical composition and structure of the substance to be tested, also on the experimental conditions, *e.g.* rate of heating, the flow rate of the inert atmosphere, the mass of the sample, the shape of the sample holder, *etc.*

In the case of trichlorotitanium(III) complexes containing cyclic ethers or nitriles, the liberation of molecular ligands under formation of either coordinatively unsaturated monomers, or condensed polymers, was observed [8—11].

Analysis of thermograms of complexes $TiCl_3(C_4H_8O)_2(C_5H_5N)$, $TiCl_3(C_4H_8O)(C_5H_5N)_2$, and $TiCl_3(CH_3CN)(C_5H_5N)_2$ (Fig. 5, curves 3, 2, 1) indicates the existence of three steps in the decomposition. The following scheme represents the first step of decomposition



The release of corresponding molecular ligands (C_4H_8O , CH_3CN) was estimated using gas chromatography, the results were compared with infrared spectral data of intermediates prepared on laboratory scale. The elimination of both the mentioned molecular ligands was observed in general above 150°C and in this temperature range the products $TiCl_3(C_4H_8O)(C_5H_5N)$ and $TiCl_3(C_5H_5N)_2$ were prepared. These first-stage decomposition products were well-defined solid brown yellowish substances. They were isolated and characterized. The found values of the effective magnetic moment ($\mu_{\text{eff}} = 1.74\text{--}1.83 \mu_B$) are typical of monomeric structure and the character of their diffuse reflectance

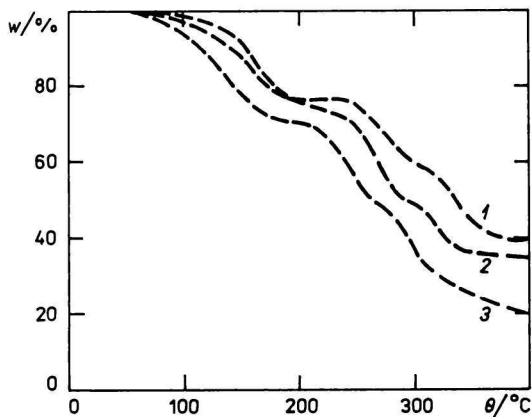


Fig. 5. Thermogravimetric curves of $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_5\text{H}_5\text{N})_2$ (1), $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{C}_5\text{H}_5\text{N})_2$ (2), and $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{C}_5\text{H}_5\text{N})$ (3).

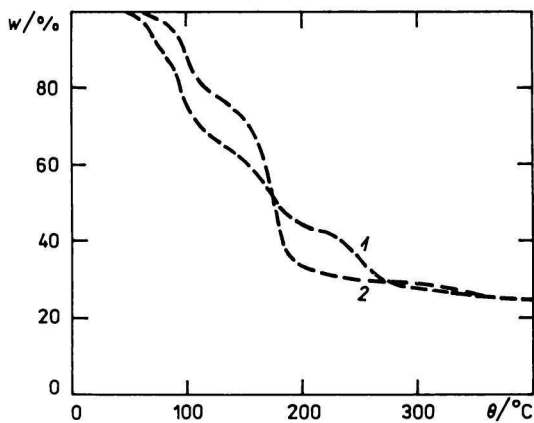


Fig. 6. Thermogravimetric curves of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{OH})_2$ (1) and $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{OH})$ (2).

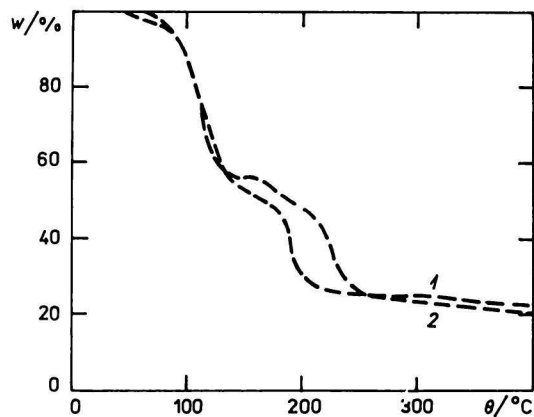
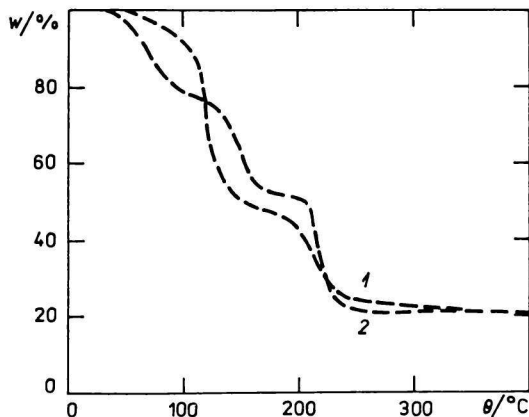


Fig. 7. Thermogravimetric curves of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(2\text{-C}_3\text{H}_7\text{OH})$ (1) and $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(2\text{-C}_3\text{H}_7\text{OH})_2$ (2).

Fig. 8. Thermogravimetric curves of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{C}_4\text{H}_9\text{OH})$ (1) and $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{C}_4\text{H}_9\text{OH})_2$ (2).



spectra (Fig. 1, curve 3; Fig. 2, curve 3) indicates distorted five-coordination of the central Ti(III) atom.

In contrast to this, for the intermediate product $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})$, prepared by thermal decomposition of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})_2$ [3], the polymeric arrangement of the species ($\mu_{\text{eff}}(293 \text{ K}) = 1.42 \mu_{\text{B}}$) and unchanged tetragonal bipyramidal six-coordination of Ti(III) atom was confirmed [12].

In the second process further molecular ligand is liberated at temperatures between 200—250°C and a continuing gradual mass loss at temperatures up to 400°C suggests the formation of either TiCl_3 (Fig. 5, curves 1, 2) or TiCl_2 (Fig. 5, curve 3) as the final decomposition products.

The observed sequence of the thermal decomposition might be explained by an increase of thermal stability with the increasing donor numbers of the ligands (CH_3CN 14.1; $\text{C}_4\text{H}_8\text{O}$ 20.0; $\text{C}_5\text{H}_5\text{N}$ 33.1). According to [13] the donor number is a molecular property which expresses the total amount of interaction with an acceptor molecule, including contribution by both the dipole—dipole or dipole—ion interactions and the bonding effect caused by the availability of the lone electron pair.

In contrast to the thermal behaviour of trichlorotitanium(III) complexes with proton-free molecular ligands, chlorotitanium(III) complexes with proton-containing ligands (aliphatic alcohols) of the general formula $\text{TiCl}_3\text{L}_2(\text{ROH})$ and $\text{TiCl}_3\text{L}(\text{ROH})_2$ decompose in a rather different way. When these complexes are heated in an inert atmosphere four processes occur practically simultaneously in the first stage of the thermal decomposition (in the temperature range *ca.* 30—100°C): *a*) loss of the proton-free molecular ligand, L; *b*) partial loss of the alcoholic ligand, ROH; *c*) alcoholysis of the complex under the evolution of HCl, and *d*) polymerization of the reaction intermediate to nonstoichiometric polynuclear species, $\text{TiCl}_{3-x}(\text{OR})_x$, containing alkoxy groups. These processes are overlapping, therefore the alcoholysis cannot be separated from the loss of

ligands (Figs. 6—8). Thus it is difficult to get a clear picture of the thermal stability of the mixed-ligand chlorotitanium(III) complexes containing C_1 to C_4 aliphatic alcohols in dependence on the length and stereochemistry of the hydrocarbon chain. Further heating above $\approx 100^\circ\text{C}$ leads to a one- or two-step gradual mass loss continuing to $\approx 200^\circ\text{C}$ as the intermediate $\text{TiCl}_{3-x}(\text{OR})_x$ decomposes, leaving grey-black final product of disproportionation.

The composition and properties of solid intermediates in the first stage of thermal decomposition of $\text{TiCl}_3\text{L}_2(\text{ROH})$ and $\text{TiCl}_3\text{L}(\text{ROH})_2$ are supposed to be analogous with those in the group of chloroalkoxotitanium(III) compounds formed in the course of thermal decomposition of trichloro(aliphatic alcohol)titanium(III) complexes [7].

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