

Thermogravimetric analysis of the titanium(III) complexes containing coordinated aliphatic alcohols and structural aspects of their decomposition reactions

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Dedicated to Professor R. Domanský on his 60th birthday

The thermal decomposition reactions of complexes of titanium(III) chloride with aliphatic alcohols were studied by thermogravimetric method in an inert atmosphere. On the basis of crystal structure of *cis*-[TiCl₂(2-C₃H₇OH)₄]Cl a structural view of the decomposition mechanism is given.

Термогравиметрическим методом изучено термическое разложение в инертной атмосфере комплексов трехвалентного титана с алифатическими спиртами. По данным рентгеноструктурного анализа комплекса *cis*-[TiCl₂(2-C₃H₇OH)₄]Cl предложено объяснение образования промежуточных алкоксохлоридов титана(III) переменного состава.

The preparation and characterization of complexes of titanium(III) chloride with a large series of alcohols (methanol [2, 6—10, 12, 13, 21, 24], ethanol [1, 2, 6—8, 10, 17, 21, 24], propanols [2—11, 14, 17, 21, 23, 24, 29], butanols [3—5, 17, 21, 24], cyclohexanol [3—5]) have received much attention in the last few years. It was found that in the solid state these complexes can be expressed by formulas TiCl₃·3L (L = C₂H₅OH, 1-C₃H₇OH, 1-C₄H₉OH, 2-C₄H₉OH) or TiCl₃·4L (L = CH₃OH, C₂H₅OH, 2-C₃H₇OH, 2-C₄H₉OH, C₆H₁₁OH) although the complexes TiCl₃·5CH₃OH [12] and TiCl₃·6CH₃OH [10] have also been reported. The crystal structure was established only for TiCl₃·4(2-C₃H₇OH) [23]. In a recent work [24], detailed measurements of the magnetic moments of the solid complexes have been carried out in order to complete the data found previously [21, 22].

Although the physical properties of the chloro(alcohol)titanium(III) complexes were investigated intensively in recent years, there has been little done as regards their chemical behaviour, especially their thermal decomposition reactions. Prior to our work [21] on thermogravimetric investigation of a series of chloro(alcohol)tita-

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nium(III) complexes in nitrogen atmosphere and under reduced pressure, only one report on thermal decomposition of $\text{TiCl}_3 \cdot 5\text{CH}_3\text{OH}$ and $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$ *in vacuo* has appeared in the literature [12]. In the present study we have reinvestigated the previous thermogravimetric measurements of some of these systems. The decomposition results are combined with the information on crystal structure of $\text{TiCl}_3 \cdot 4(2\text{-C}_3\text{H}_7\text{OH})$ [23] and on the magnetochemical behaviour of chloroalkoxotitanium(III) intermediates [25] in an attempt to outline the course of the thermal decomposition in terms of structural aspects.

Experimental

All experiments were carried out under purified nitrogen as it is described in [28]. The investigated compounds were prepared by the method reported previously [21]. Their analytical data are listed in paper [24]. Thermogravimetric measurements were performed under two different experimental conditions: in dynamic atmosphere of nitrogen (1 l h^{-1}) and under reduced pressure (10–15 Pa) using a quartz spiral recording thermobalance described earlier [21]. The intermediate decomposition products were prepared by heating the starting materials at selected temperatures according to the respective thermoanalytical curves in special glass tube as it is described in [26]. Chemical analyses of intermediates are collected in paper [25]. The chemical composition of the intermediates was found to vary in small extent according to the experimental conditions of preparation, although in every case $\text{Ti(III)} : (\text{Cl} + \text{OR}) = 1 : 3$.

The diffuse reflectance spectra were recorded on VEB Zeiss Spekol spectrophotometer which is equipped with the reflectance attachment Model RD/0. A special all-glass vessel for obtaining spectra in an inert atmosphere was described recently [28]. The infrared spectra of the samples were determined as mineral oil and hexachlorobutadiene mulls between NaCl plates on a Perkin—Elmer spectrophotometer Model 221. The experimental technique for sample preparation described in [27] was employed.

Results and discussion

The mechanism of thermal decomposition of alcoholate complexes of titanium(III) chloride differs markedly from that of complexes containing other neutral ligands, such as dioxan [26] or acetonitrile [28]. Since the structures of the solid reactants, decomposition intermediates, and final products of thermal decomposition of crystalline compounds are closely related, it is important to know the crystal structure of starting alcoholate titanium(III) complex for elucidation of the course and reaction mechanism of its thermal decomposition in an inert atmosphere. From among the titanium(III) alcoholate complexes only the crystal structure of *cis*-dichlorotetrakis(2-propanol)titanium(III) chloride, *cis*- $[\text{TiCl}_2(\text{HOCH}(\text{CH}_3)_2)_4]\text{Cl}$ is known [23]. The structure of this compound, formally

formulated as $\text{TiCl}_3 \cdot 4$ isopropyl alcohol, was previously investigated by spectroscopic methods [4, 11]. A comparison of the absorption spectra from a single crystal with the energy-splitting diagram in tetrahedral (T_d) and octahedral (O_h) coordination made it possible to predict octahedral coordination of Ti(III). The ionic complex $[\text{TiCl}_2(\text{HOCH}(\text{CH}_3)_2)_4]^+ \text{Cl}^-$ was suggested to have a *trans*-configuration [11].

This assumption is in contrast with the results of X-ray diffraction analysis [23] of $\text{TiCl}_3 \cdot 4$ isopropyl alcohol, according to which the $[\text{TiCl}_2(\text{HOCH}(\text{CH}_3)_2)_4]^+$ cation has the *cis*-configuration with C_2 symmetry. The atoms in the inner coordination sphere (2 Cl + 4 O) are arranged in a form of a distorted octahedron around the central Ti(III) atom. Two chlorine atoms at distances Ti—Cl 232 pm, are in a *cis*-position. They form together with the two oxygen atoms an approximately planar arrangement TiCl_2O_2 , the distances Ti—O being 210 pm. The deviation from the ideal planar coordination can be expressed by the angle of twist of the two lines passing through the Cl...Cl and Cl...O atoms which is 5° . A pair of the *trans*-oriented oxygen atoms are at distances Ti—O 209 pm, the bond angle O—Ti—O being $171.1 \pm 0.2^\circ$. The steric effects and the ligand—ligand repulsions

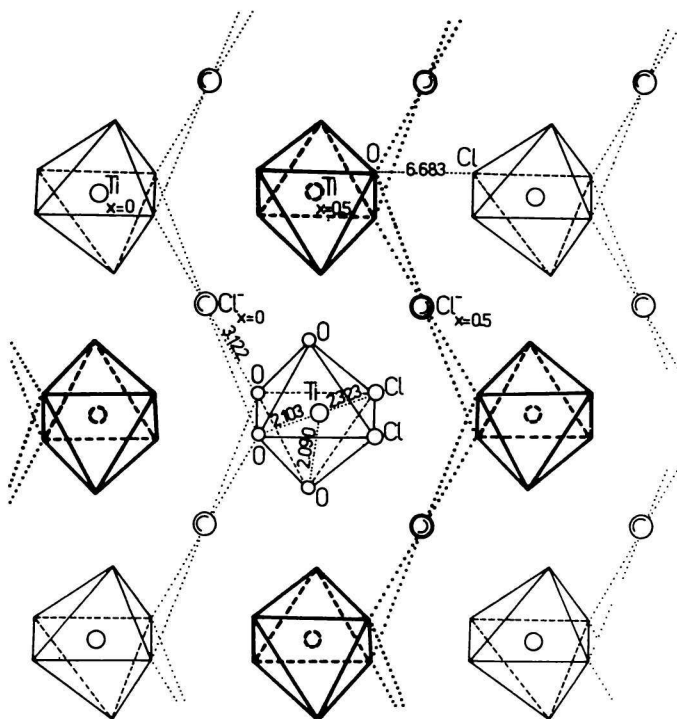


Fig. 1. Packing of *cis*- $[\text{TiCl}_2(2\text{-C}_3\text{H}_7\text{OH})_4]^+$ and Cl^- ions in the crystal structure of *cis*-dichlorotetrakis(2-propanol)titanium(III) chloride (view along (100) direction).

in the Ti(III) coordination sphere raise the bond angle Cl—Ti—Cl to $96.8 \pm 0.1^\circ$ and those of Cl—Ti—O to 91.3 and 93.9° . This arrangement indicates that the positive charge of the complex cation is localized mainly on 2-propanol groups and the cation itself is highly polarized (Fig. 1).

The Cl^- ions occupy the positions at symmetry centres. Each of them is in contact with four oxygen atoms from the two complex cations at distances $\text{Cl}^- \dots \text{O}$ 304 ($2 \times$) and 312 pm ($2 \times$), respectively. The 2-propanol molecules are oriented in such a way that their OH groups may create hydrogen bridges of the type $\text{O}—\text{H} \dots \text{Cl}^-$. It means that the Cl^- anions are in contact with the positively charged part of the complex cation $[\text{TiCl}_2(\text{HOCH}(\text{CH}_3)_2)_4]^+$. The two chlorine atoms from the coordination sphere around Ti(III) atom increase their distances from the Cl^- anions due to the *cis*-orientation. *trans*-Orientation of two chlorine atoms from the

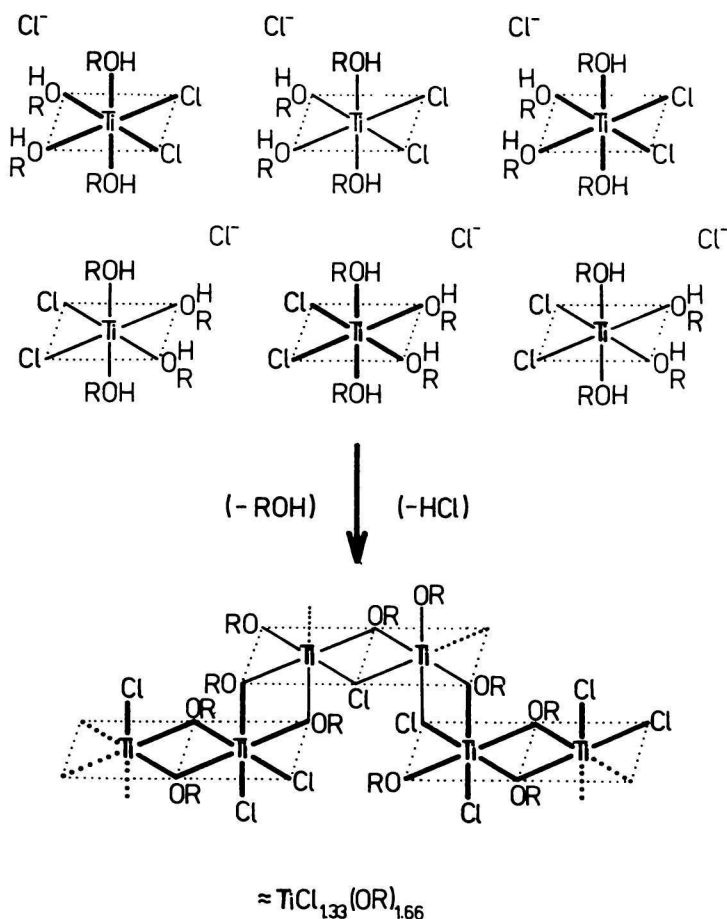


Fig. 2. The formation and probable structure of the intermediate $\text{TiCl}_{1.40}(\text{2-OC}_3\text{H}_7)_{1.60}$.

$[\text{TiCl}_2(\text{HOCH}(\text{CH}_3)_2)_4]^+$ cation would bring these atoms into closer contact with Cl^- anions.

The composition and stereochemistry of the coordination sphere of the titanium(III) alcoholate complex, the arrangement of the species in the crystal structure, as well as the chemical properties of the components of the individual complex determine the mechanism of its thermal decomposition reaction. In accord with our findings described in the previous publications [21, 22], when the alcoholate complexes of titanium(III) chloride are heated in an inert atmosphere, three processes occur simultaneously. First, the complexes undergo thermal decomposition with the loss of coordinated alcohol molecules which results in the formation of coordinatively unsaturated species. Second, a part of the liberated alcohol molecules reacts with the coordinated chloride atoms in the crystal structure of the alcoholate complex to form coordinated alkoxide groups and liberated hydrogen chloride. Third, the coordinatively unsaturated species polymerize immediately to polynuclear chloroalkoxotitanium(III) macromolecules of the variable composition containing alkoxide and/or chloride bridges. The formation and probable structure of the brown intermediate $\text{TiCl}_{1.40}(\text{2-OC}_3\text{H}_7)_{1.60}$ may be diagrammatically expressed by Fig. 2.

Since the titanium(III) alkoxides and chloroalkoxides, described in [15, 17—19], are formed in solutions under different reaction conditions, we assumed that their structure also differs from the thermally produced titanium(III) chloroalkoxo polymers.

Based upon the analogy in the composition of the compounds of the type $\text{TiCl}_3 \cdot 3\text{L}$ ($\text{L} = \text{C}_2\text{H}_5\text{OH}$, $2\text{-C}_3\text{H}_7\text{OH}$, $1\text{-C}_4\text{H}_9\text{OH}$, $2\text{-C}_4\text{H}_9\text{OH}$) and upon similarity of the thermal decomposition curves of these complexes, presented in this work (Figs. 4, 5, 7), it might be concluded that the structures of the above-mentioned complexes are not significantly different.

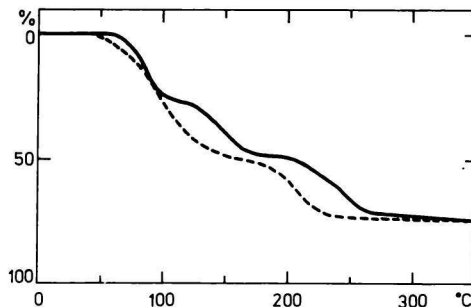


Fig. 3. Thermogravimetric curve of $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$ in nitrogen atmosphere (—) and under reduced pressure (---).

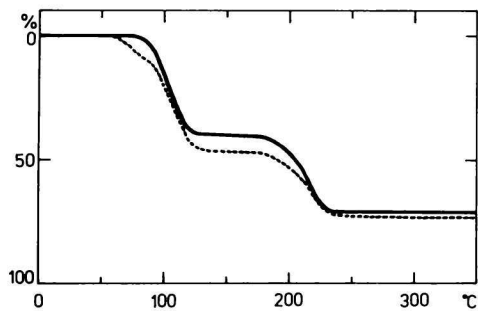


Fig. 4. Thermogravimetric curve of $\text{TiCl}_3 \cdot 3\text{C}_2\text{H}_5\text{OH}$ (—) and $\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$ (----) in nitrogen atmosphere.

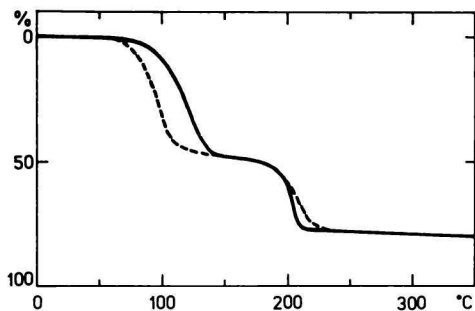


Fig. 5. Thermogravimetric curve of $\text{TiCl}_3 \cdot 3(1\text{-C}_3\text{H}_7\text{OH})$ in nitrogen atmosphere (—) and under reduced pressure (----).

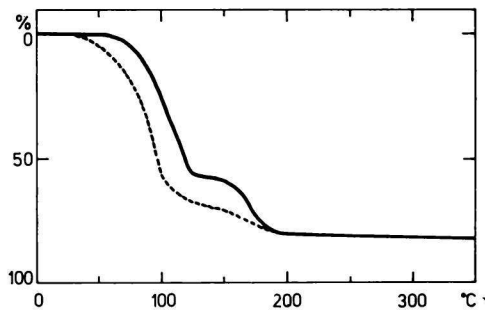


Fig. 6. Thermogravimetric curve of $\text{TiCl}_3 \cdot 4(2\text{-C}_3\text{H}_7\text{OH})$ in nitrogen atmosphere (—) and under reduced pressure (----).

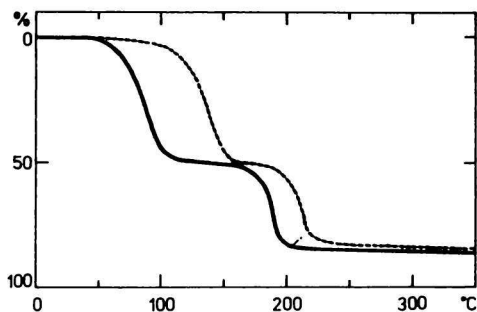


Fig. 7. Thermogravimetric curve of $\text{TiCl}_3 \cdot 3(1\text{-C}_4\text{H}_9\text{OH})$ (—) and $\text{TiCl}_3 \cdot 3(2\text{-C}_4\text{H}_9\text{OH})$ (---) in nitrogen atmosphere.

On the other hand, the course of the thermogravimetric curves of the complexes $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$ (Fig. 3) and $\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$ (Fig. 4), as well as their diffuse reflectance spectra, described in the paper [24], differ substantially from each other and from those of $\text{TiCl}_3 \cdot 4(2\text{-C}_3\text{H}_7\text{OH})$ (Fig. 6). In the blue complex $\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$ one molecule of ethanol is only loosely bound and under 100°C this compound completely transforms to the blue $\text{TiCl}_3 \cdot 3\text{C}_2\text{H}_5\text{OH}$. Examination of the thermogravimetric curve of the blue complex $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$ (Fig. 3) indicates three steps in which the decomposition under nitrogen atmosphere proceeds. The first mass loss corresponds to the formation of the pink intermediate $\text{TiCl}_{2.70}(\text{OCH}_3)_{0.30}(\text{CH}_3\text{OH})_{2.90}$. The second mass loss leads to the brown intermediate $\text{TiCl}_{1.74}(\text{OCH}_3)_{1.26}$. The black solid residue formed in the third step of thermal decomposition contains predominantly titanium(II) chloride-methoxide. In the first two steps both methanol and hydrogen chloride are simultaneously evolved. In the third step, as it was found by gas chromatographic analysis, both methane and carbon dioxide are produced [21]. The mechanism of this third stage of decomposition has not yet been elucidated.

The blue complex $\text{TiCl}_3 \cdot 4(2\text{-C}_3\text{H}_7\text{OH})$ decomposes completely only in two steps (Fig. 6). The first step associated with the simultaneous liberation of both 2-propanol and hydrogen chloride, corresponds to the formation of brown intermediate $\text{TiCl}_{1.40}(2\text{-OC}_3\text{H}_7)_{1.60}$ (see also Fig. 2). Since, according to crystal structure analysis, the complex $\text{TiCl}_3 \cdot 4(2\text{-C}_3\text{H}_7\text{OH})$ has *cis*-octahedral stereochemistry, *cis*- $[\text{TiCl}_2(\text{HOCH}(\text{CH}_3)_2)_4]\text{Cl}$, and, according to magnetic, spectral and conductivity measurements, the complex $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$, has the structure $[\text{TiCl}_2(\text{CH}_3\text{OH})_4]\text{Cl}$, it seems very probable that the latter compound has the *trans*-configuration.

For a more detailed structural research the individual intermediate products of thermal decomposition of complexes of titanium(III) chloride with alcohols have been synthesized by technique described in the paper [26]. Comparing the course

of the thermal decomposition of the starting complexes in nitrogen atmosphere and under reduced pressure (Figs. 3—8) we may see that generally the preparation procedure under reduced pressure cannot be regarded as suitable as it is rather difficult to isolate substance of a defined composition.

The magnetic susceptibility [25], and further the diffuse reflectance spectra (Figs. 9—14) and infrared spectra of the individual intermediate products were measured. In the infrared spectrum of $\text{TiCl}_{2.7}(\text{OCH}_3)_{0.3}(\text{CH}_3\text{OH})_{2.9}$ the band at 3125 cm^{-1} is undoubtedly connected with the O—H stretching frequency of the coordinated methanol. The C—O stretching frequency of the methoxy group is observed at 1010 cm^{-1} . The band at 1110 cm^{-1} is believed to be methyl rocking

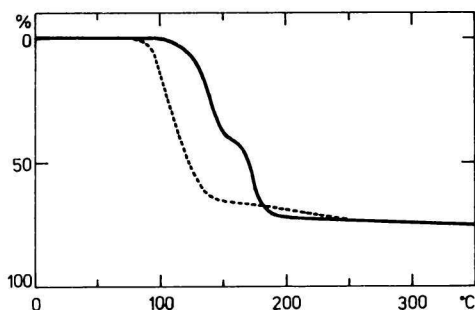


Fig. 8. Thermogravimetric curve of $\text{TiCl}_3 \cdot 3\text{cyclopentanol}$ (—) and $\text{TiCl}_3 \cdot 3\text{benzylalcohol}$ (---).

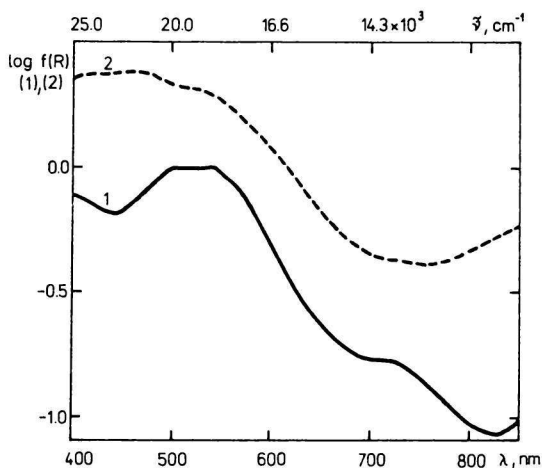


Fig. 9. Diffuse reflectance spectra of $\text{TiCl}_{2.70}(\text{OCH}_3)_{0.30}(\text{CH}_3\text{OH})_{2.90}$ (pink) (—) and $\text{TiCl}_{1.74}(\text{OCH}_3)_{1.26}$ (brown) (---).

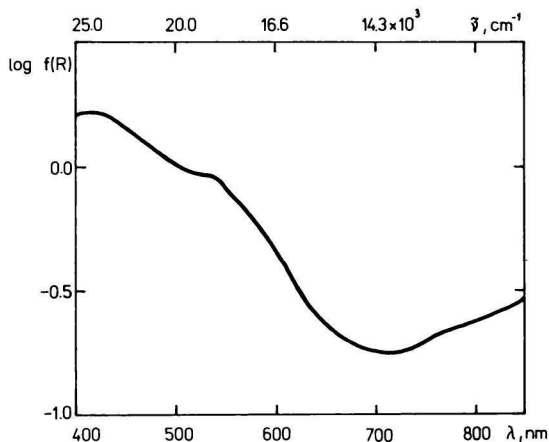


Fig. 10. Diffuse reflectance spectrum of $\text{TiCl}_{1.86}(\text{OC}_2\text{H}_5)_{1.14}(\text{C}_2\text{H}_5\text{OH})_{0.35}$.

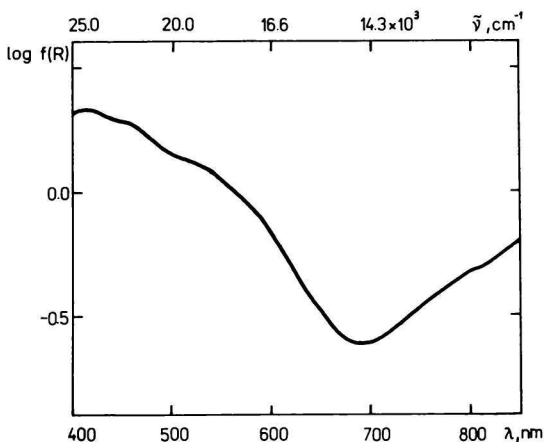


Fig. 11. Diffuse reflectance spectrum of $\text{TiCl}_{1.60}(1\text{-OC}_3\text{H}_7)_{1.40}$.

mode. In the i.r. spectra of the brown titanium(III) chloro-alkoxides no O—H stretch in the $3100\text{--}3200\text{ cm}^{-1}$ was observable. The bands at 1055 , 1050 , 1070 , and 1070 cm^{-1} can be assigned to the C—O stretching frequencies of the methoxy, ethoxy, propoxy, and butoxy groups, respectively. In the absence of detailed structural information, it is not possible to differentiate those Ti—O modes which involve terminal alkoxide groups from those which involve bridging alkoxide groups.

The diffuse reflectance spectra of the pink intermediate $\text{TiCl}_{2.70}(\text{OCH}_3)_{0.30}\text{-(CH}_3\text{OH)}_{2.90}$ indicate that the distortion octahedral configuration was maintained

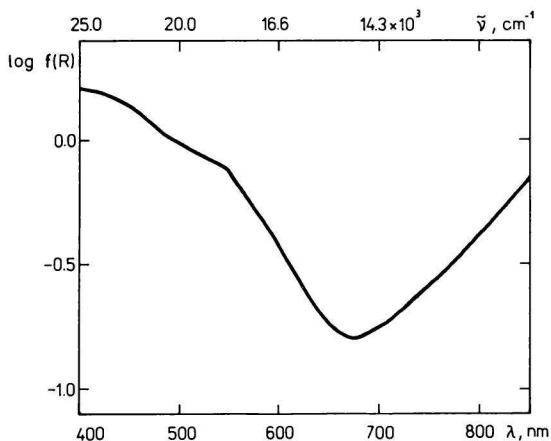


Fig. 12. Diffuse reflectance spectrum of $\text{TiCl}_{1.40}(\text{2-OC}_3\text{H}_7)_{1.60}$.

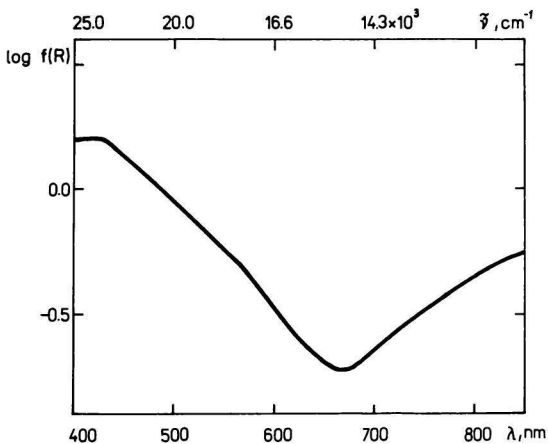


Fig. 13. Diffuse reflectance spectrum of $\text{TiCl}_{1.55}(\text{1-OC}_4\text{H}_9)_{1.45}$.

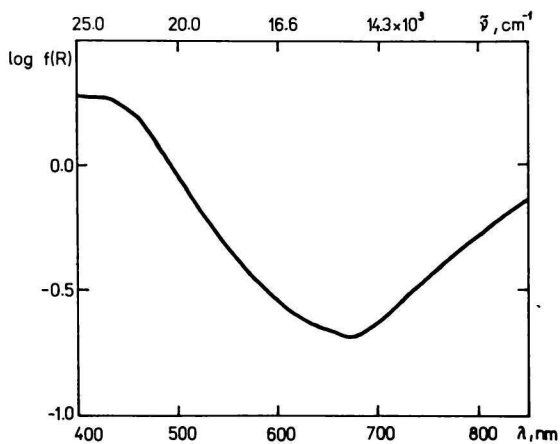


Fig. 14. Diffuse reflectance spectrum of $\text{TiCl}_{1.70}(\text{2-OC}_4\text{H}_9)_{1.30}$.

also after first stage of methanolysis had been finished. The evaluation of the diffuse reflectance spectrum of the brown intermediate $\text{TiCl}_{1.74}(\text{OCH}_3)_{1.26}$ formed during the second stage of thermal decomposition of the complex $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$ is rather difficult since the charge-transfer band overlaps into the visible part of the spectrum. Similar difficulties are encountered on evaluation of the other brown-coloured intermediate products which have been formed in the course of the first stage of the thermal decomposition of the respective alcohol complexes of titanium(III) chloride.

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