

# Synthesis and thermal investigation of solid mixed-ligand chlorotitanium(III) complexes containing acetonitrile and aliphatic alcohols

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*Dedicated to Professor Dr. Ing. J. Klikorka, DrSc.,  
in honour of his 65th birthday*

The mixed-ligand chlorotitanium(III) complexes containing acetonitrile and aliphatic alcohols were prepared by the reaction of solid  $\text{TiCl}_3(\text{CH}_3\text{CN})$  with aliphatic alcohols ( $\text{C}_n\text{H}_{2n+1}\text{OH}$ ,  $n = 1-4$ ) in stoichiometric ratio and in medium of noncoordinating solvent. Their thermal properties were investigated in the temperature range  $20^\circ\text{C}-400^\circ\text{C}$ . It has been found that in the course of thermal treating the alcoholysis of corresponding alcohol takes place and the intermediates involving alkoxo groups are formed.

Посредством реакции твердого  $\text{TiCl}_3(\text{CH}_3\text{CN})$  с алифатическими спиртами ( $\text{C}_n\text{H}_{2n+1}\text{OH}$ ,  $n = 1-4$ ) в стехиометрическом соотношении, растворенными в избытке некоординирующего растворителя, были получены твердые комплексы трихлорида титана содержащие одновременно ацетонитрил и соответствующий алифатический спирт. Изучен ход их термического разложения в интервале температур  $20^\circ\text{C}-400^\circ\text{C}$ . Образующиеся продукты содержат алкоксидные группы, что означает, что в процессе их термического разложения происходит алкоголиз соответствующего алифатического спирта, находящегося в исходном соединении.

Studying the thermal properties of solid chlorotitanium(III) complex  $\text{TiCl}_3-(\text{CH}_3\text{CN})_3$  it has been found that in the nitrogen atmosphere at  $150^\circ\text{C}$  [1] and in vacuum at  $100^\circ\text{C}$  [2, 3] the acetonitrile is stepwise released and the polymeric product of composition  $\text{TiCl}_3(\text{CH}_3\text{CN})$  is formed. The predicted higher reactivity of this compound, first of all in addition reactions with other molecular ligands, was confirmed in its reaction with tetrahydrofuran ( $\text{C}_4\text{H}_8\text{O}$ ) [4], as well as with pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) [5]. On the other hand, in contrast with the results in [1-3], by the thermal treating of chlorotitanium(III) complexes containing aliphatic alcohols the escape of  $\text{HCl}$  and corresponding alcohol was observed and the polymeric species of nonstoichiometric ratio of components involving alkoxo groups were found to be formed [6-8]. As it was previously reported [9] the mechanism of thermal

decomposition depends on the composition and stereochemistry of the coordination sphere of the chlorotitanium(III) complexes, on the arrangement of the species in the crystal structure, as well as on the chemical properties of the components of the individual complex. From this point of view we found it interesting to study the group of chlorotitanium(III) complexes containing simultaneously the molecule of acetonitrile and aliphatic alcohol since each of these ligands affects the course of thermal decomposition in quite a different manner.

## Experimental

The studied mixed-ligand chlorotitanium(III) complexes were synthesized by the reaction of solid  $\text{TiCl}_3(\text{CH}_3\text{CN})$  with corresponding aliphatic alcohol (ROH) in the stoichiometric ratio  $\text{TiCl}_3(\text{CH}_3\text{CN}) : \text{ROH} = 1 : 2$  under nitrogen atmosphere and in medium of hexane. According to the results of chemical analysis (Table 1) the prepared light-blue coloured powdered compounds were of composition  $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{ROH})_2$ , ROH = methyl alcohol, ethyl alcohol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol. Ti(III) was determined by titration with cerium(IV) sulfate under nitrogen atmosphere, using ferroin as indicator. The total titanium content was determined gravimetrically as  $\text{TiO}_2$ . The content of chloride ions was determined by the Volhard method. The infrared spectra were recorded by means of Nujol mulls in sodium chloride plates on the Perkin—Elmer 221 spectrophotometer in the range  $\tilde{\nu} = 600\text{—}5000\text{ cm}^{-1}$ . Diffuse reflectance spectra were measured in the range  $\tilde{\nu} = 25\,000\text{—}12\,500\text{ cm}^{-1}$  using the Spekol (Zeiss, Jena) spectrophotometer. MgO was used as a standard. The magnetic susceptibility measurements were performed by means of the Gouy method at room temperature on the apparatus of our own construction. The thermal properties of investigated compounds were studied in the temperature range  $20\text{ }^\circ\text{C—}400\text{ }^\circ\text{C}$ . An equipment of our own construction based on the principle of a spring balance was used [4]. The heating rate was  $2.5\text{ }^\circ\text{C min}^{-1}$  and the sample mass 20—40 mg.

## Results and discussion

According to the results of chemical analysis and infrared spectral data (Table 1) the prepared light-blue coloured complexes were of composition  $\text{TiCl}_3(\text{CH}_3\text{CN})\text{-(ROH)}_2$  and contained simultaneously both the molecular ligands. On the basis of the found values of effective magnetic moment ( $1.76\text{—}1.80\text{ }\mu_{\text{B}}$ ) it could be assumed that in the course of reaction the depolymerization process of  $\text{TiCl}_3\text{-(CH}_3\text{CN)}$  occurs, the coordination sphere becomes complete and the monomeric compounds with coordination number 6 are formed. The obtained diffuse reflectance spectra of complexes under study (Figs. 1—3) show the bright asymmetric band typical for distorted octahedral symmetry [10]. The thermal properties of the prepared compounds were studied thermogravimetrically in the temperature range  $20\text{ }^\circ\text{C—}400\text{ }^\circ\text{C}$  (Figs. 4—6). It has been found that the decomposition proceeds in two steps. As it can be seen from the shapes of thermogravimetric curves these steps become more marked with increasing *n* (*n* = number of carbon atoms in

Table 1

Results of chemical analysis, magnetic susceptibility measurements at room temperature, and infrared spectral data of the investigated chlorotitanium(III) complexes

Compound	$M_r$	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			$\mu_B$	$\tilde{\nu}/\text{cm}^{-1}$	
		Ti(III)	Ti(IV)	Cl		$\nu(\text{C—O})$	$\nu(\text{C}\equiv\text{N})$
$\text{TiCl}_3(\text{CH}_3\text{CN})(\text{CH}_3\text{OH})_2$	259.38	18.47		41.00	1.76	990	2270
		18.77	18.66	40.68			
$\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_2\text{H}_5\text{OH})_2$	287.44	16.66		37.00	1.79	1020	2273
		16.76	16.60	36.69			
$\text{TiCl}_3(\text{CH}_3\text{CN})(n\text{-C}_3\text{H}_7\text{OH})_2$	315.49	15.18		33.71	1.78	975	2325
		15.08	15.44	32.65			
$\text{TiCl}_3(\text{CH}_3\text{CN})(i\text{-C}_3\text{H}_7\text{OH})_2$	315.49	15.18		33.71	1.8—2.0 <sup>a</sup>	1087	2273
		15.39	14.74	34.04			
$\text{TiCl}_3(\text{CH}_3\text{CN})(n\text{-C}_4\text{H}_9\text{OH})_2$	343.54	13.94		30.96	1.79	926	2273
		13.52	13.78	29.72			
$\text{TiCl}_3(\text{CH}_3\text{CN})(i\text{-C}_4\text{H}_9\text{OH})_2$	343.54	13.94		30.96	1.80	982	2300
		13.68	13.77	29.94			

a) The value  $\mu_B$  could not be reliably determined.

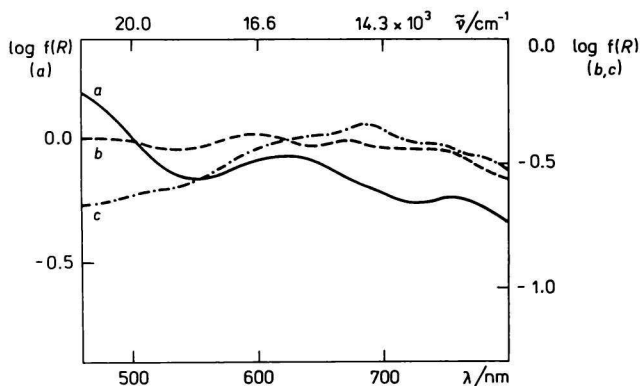


Fig. 1. Diffuse reflectance spectra.

—  $\text{TiCl}_3(\text{CH}_3\text{CN})$ ; — —  $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{CH}_3\text{OH})_2$ ; — · —  $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_2\text{H}_5\text{OH})_2$ .

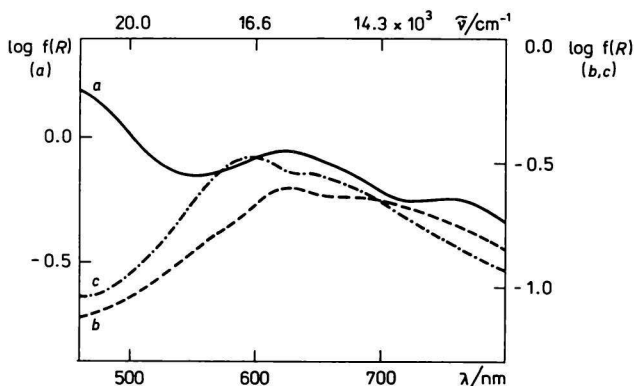


Fig. 2. Diffuse reflectance spectra.

—  $\text{TiCl}_3(\text{CH}_3\text{CN})$ ; — —  $\text{TiCl}_3(\text{CH}_3\text{CN})(n\text{-C}_3\text{H}_7\text{OH})_2$ ; — · —  $\text{TiCl}_3(\text{CH}_3\text{CN})(i\text{-C}_3\text{H}_7\text{OH})_2$ .

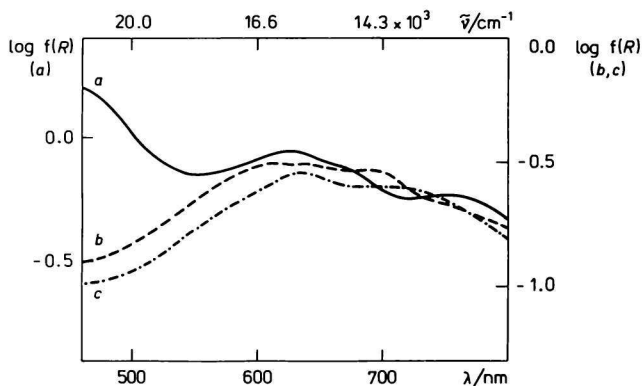


Fig. 3. Diffuse reflectance spectra.

—  $\text{TiCl}_3(\text{CH}_3\text{CN})$ ; — —  $\text{TiCl}_3(\text{CH}_3\text{CN})(n\text{-C}_4\text{H}_9\text{OH})_2$ ; — · —  $\text{TiCl}_3(\text{CH}_3\text{CN})(i\text{-C}_4\text{H}_9\text{OH})_2$ .

alcohol). The decomposition temperature raised also proportionally to  $n$ , from 100 °C to 140 °C. According to thermogravimetric curves data the products of thermal decomposition were prepared in laboratory scale. The prepared substances were light-brown or green coloured solid powder with the exception of intermediate of chlorotitanium(III) complex with methyl alcohol. In this case an undefinable liquid substance was formed by heating. The intermediates of thermal decomposition were characterized with the aid of chemical analysis, the presence of individual ligands was confirmed by infrared spectroscopy [5]. In the course of decomposition process the release of gaseous HCl, acetonitrile, and corresponding alcohol was estimated. It has been stated that the prepared solid products are of nonstoichiometric composition  $\text{TiCl}_{3-x}(\text{OR})_x$  and both molecular ligands may be present in negligible amounts.

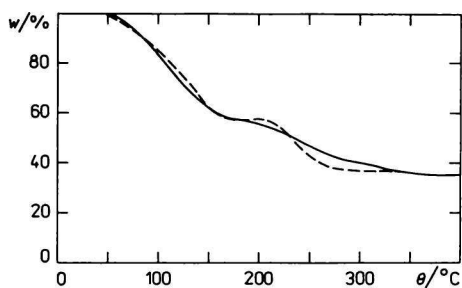


Fig. 4. Thermogravimetric curves.

—  $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{CH}_3\text{OH})_2$ ;  
 ---  $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_2\text{H}_5\text{OH})_2$ .

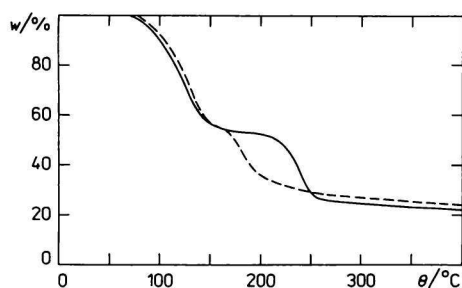
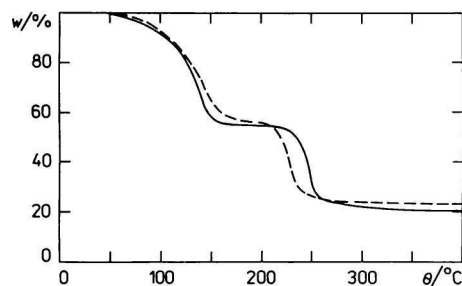


Fig. 5. Thermogravimetric curves.

—  $\text{TiCl}_3(\text{CH}_3\text{CN})(n\text{-C}_3\text{H}_7\text{OH})_2$ ;  
 ---  $\text{TiCl}_3(\text{CH}_3\text{CN})(i\text{-C}_3\text{H}_7\text{OH})_2$ .

Fig. 6. Thermogravimetric curves.

—  $\text{TiCl}_3(\text{CH}_3\text{CN})(n\text{-C}_4\text{H}_9\text{OH})_2$ ;  
 ---  $\text{TiCl}_3(\text{CH}_3\text{CN})(i\text{-C}_4\text{H}_9\text{OH})_2$ .



The mechanism of formation and thermal decomposition of the studied mixed-ligand chlorotitanium(III) complexes could be to some extent explained using the results given in paper [11]. In this study the  $C_{3v}$  symmetry for the complex  $\text{TiCl}_3(\text{CH}_3\text{CN})_3$  was suggested on the basis of EPR and UV spectral data. In analogy with this suggestion the *mer* arrangement of ligands in coordination

polyhedron could be assumed while both the added alcohol molecules are localized in nonequivalent positions. Thus by heating the reaction of coordinated chlorine atom with alcohol molecule in *cis* position under HCl escape and the formation of coordinatively unsaturated species could be considered. The subsequent mutual reactions of these units presumably result in formation of polymeric chains involving alkoxide and/or chlorine bridges. The other possibilities and modes of polymerization are connected with further successive release of acetonitrile and alcohol.

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