

# Magnetochemical investigation of trichloro(aliphatic alcohol)titanium(III) complexes

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The magnetic properties of trichloro(aliphatic alcohol)titanium(III) complexes in the temperature range 77—300 K were studied. The prepared complexes of composition  $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$ ,  $\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$ ,  $\text{TiCl}_3 \cdot 3n\text{-C}_3\text{H}_7\text{OH}$ ,  $\text{TiCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$ ,  $\text{TiCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$ , and  $\text{TiCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$  exhibited effective magnetic moments at room temperature in the range 1.79—1.86 B.M. The experimentally obtained results were interpreted using Figgis' method. On the basis of found data and interpretation of diffuse reflectance spectra the structure of magnetically noninteracting structural units, which are considered to have tetragonally distorted octahedral symmetry, was proposed in these complexes.

Изучались магнитные свойства хлорокомплексов Ti(III) с алифатическими спиртами в качестве лигандов в области температур 77—300 К. Исследуемые комплексы имели состав  $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$ ,  $\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$ ,  $\text{TiCl}_3 \cdot 3n\text{-C}_3\text{H}_7\text{OH}$ ,  $\text{TiCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$ ,  $\text{TiCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$ ,  $\text{TiCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$  и обладали при лабораторной температуре эффективным магнитным моментом 1,79—1,86 В.М. Результаты были интерпретированы по методу, разработанному Б. Н. Фиггисом. На основании численных данных и расшифровки диффузионных спектров отражения была подтверждена мономерная структура комплексов, с невзаимодействующими структурными единицами с конфигурацией тетрагонально искаженного октаэдра.

From among the trichloro(aliphatic alcohol)titanium(III) complexes only the crystal structure of  $\text{TiCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$  is reported to have been determined [1]. According to the authors the crystal structure consists of  $[\text{TiCl}_2(\text{HOCH}(\text{CH}_3)_2)_4]^+$  cations and  $\text{Cl}^-$  anions. The atoms of the inner coordination sphere (2Cl + 4O) are arranged in the form of a distorted octahedron around the central atom, two chlorine atoms are in *cis* configuration and they form together with two oxygen atoms an approximatively planar arrangement of  $\text{TiCl}_2\text{O}_2$ . Other papers [2—10] on

chemistry of chloro(alcohol)titanium(III) complexes describe their properties obtained on the basis of indirect methods (magnetochemical and optical). In principle the existence of such distorted octahedral arrangement in other complexes in this group was not excluded, on the contrary, the experimental data seem to confirm this assumption. The absorptions of polychromatic light in solution of  $\text{TiCl}_3$  in absolute methanol as well as in ethanol are reported in [2, 3]. According to the authors' findings the presence of species  $[\text{Ti}(\text{CH}_3\text{OH})_6]^{3+}$  and  $[\text{Ti}(\text{C}_2\text{H}_5\text{OH})_6]^{3+}$ , respectively, was established. In other two papers [4, 5] the authors described the synthesis, magnetic and optical properties of  $\text{TiX}_3 \cdot 4\text{alc}$  type complexes, where  $\text{X} = \text{Cl}, \text{Br}$ , alc = isopropyl alcohol, isobutyl alcohol, cyclohexyl alcohol. The magnetochemical investigation of chlorotitanium(III) complexes with methyl alcohol of composition  $\text{TiCl}_3(\text{CH}_3\text{OH})_3$ ,  $\text{TiCl}_3(\text{CH}_3\text{OH})_4$ , and  $\text{TiCl}_3(\text{CH}_3\text{OH})_5$  was published in [6, 7], with propyl alcohol of composition  $\text{TiCl}_3 \cdot 4n\text{-C}_3\text{H}_7\text{OH}$  in [9]. The observed values of effective magnetic moments at room temperature were close to spin-only value and according to temperature dependence of the latter the octahedral coordination of central atom was proposed.

The aim of this work is to describe from the magnetochemical point of view the properties of trichlorotitanium(III) complexes with aliphatic alcohols ( $\text{C}_n\text{H}_{2n+1}\text{OH}$ ,  $n = 1-4$ ) and so to complete the data and suggestions outlined in our previous papers [8, 11].

### Experimental

The complexes were synthesized by reaction of  $\alpha\text{-TiCl}_3$  with corresponding alcohol (methyl alcohol, ethyl alcohol,  $n$ - and isopropyl alcohol,  $n$ - and isobutyl alcohol) in noncoordinating solvent and in atmosphere of dry nitrogen since all compounds of titanium(III) are extremely sensitive towards moisture and oxygen [11]. The prepared powdered complexes, light blue coloured, were of the following composition:

$\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$  (calculated: 16.96% Ti, 37.66% Cl; found: 17.05%  $\text{Ti}^{\text{III}}$ , 17.23%  $\text{Ti}^{\text{IV}}$ , 37.64% Cl).

$\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$  (calculated: 14.95% Ti, 31.42% Cl; found: 15.08%  $\text{Ti}^{\text{III}}$ , 14.98%  $\text{Ti}^{\text{IV}}$ , 31.13% Cl).

$\text{TiCl}_3 \cdot 3n\text{-C}_3\text{H}_7\text{OH}$  (calculated: 14.32% Ti, 31.79% Cl; found: 14.36%  $\text{Ti}^{\text{III}}$ , 14.61%  $\text{Ti}^{\text{IV}}$ , 31.87% Cl).

$\text{TiCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$  (calculated: 12.14% Ti, 26.95% Cl; found: 12.42%  $\text{Ti}^{\text{III}}$ , 12.45%  $\text{Ti}^{\text{IV}}$ , 26.94% Cl).

$\text{TiCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$  (calculated: 12.72% Ti, 28.24% Cl; found: 12.81%  $\text{Ti}^{\text{III}}$ , 12.66%  $\text{Ti}^{\text{IV}}$ , 27.93% Cl).

$\text{TiCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$  (calculated: 12.72% Ti, 28.24% Cl; found: 12.83%  $\text{Ti}^{\text{III}}$ , 12.79%  $\text{Ti}^{\text{IV}}$ , 27.77% Cl).

## Analysis

Ti(III) was determined cerimetrically using ferroin as an indicator, Ti(IV) gravimetrically as  $\text{TiO}_2$  after the sample had been oxidized with  $\text{HNO}_3$ , filtered off and ignited,  $\text{Cl}^-$  was determined by the Volhard method.

Table 1

Magnetic susceptibilities and effective magnetic moments  
of the studied trichloro(aliphatic alcohol)titanium(III) complexes

$\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$											
T/K	107	153	177	196	223	237	256	276	295		
$\chi_M' \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	4254	3084	2724	2470	2215	2101	1966	1853	1739		
$\mu_{\text{eff}}/\text{B.M.}$	1.71	1.74	1.75	1.76	1.78	1.78	1.79	1.81	1.81		
$\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$											
T/K	92	126	154	185	215	245	273	300			
$\chi_M' \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	4411	3399	2884	2480	2180	1974	1808	1719			
$\mu_{\text{eff}}/\text{B.M.}$	1.61	1.66	1.68	1.71	1.73	1.76	1.78	1.81			
$\text{TiCl}_3 \cdot 3n\text{-C}_3\text{H}_7\text{OH}$											
T/K	80	108	131	154	175	194	215	234	252	272	295
$\chi_M' \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	5060	3959	3379	2946	2648	2442	2248	2098	1976	1862	1740
$\mu_{\text{eff}}/\text{B.M.}$	1.61	1.65	1.68	1.71	1.72	1.74	1.76	1.77	1.79	1.80	1.81
$\text{TiCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$											
T/K	77	134	174	201	223	246	273	293			
$\chi_M' \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	4845	3169	2584	2297	2128	2044	1835	1731			
$\mu_{\text{eff}}/\text{B.M.}$	1.55	1.65	1.70	1.72	1.74	1.79	1.78	1.80			
$\text{TiCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$											
T/K	80	103	130	154	181	208	237	266	295		
$\chi_M' \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	5037	4106	3467	2927	2554	2260	2067	1863	1702		
$\mu_{\text{eff}}/\text{B.M.}$	1.61	1.64	1.70	1.69	1.72	1.73	1.77	1.78	1.79		
$\text{TiCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$											
T/K	77	116	135	174	184	201	228	273	293		
$\chi_M' \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	5440	3797	3324	2711	2635	2360	2209	1897	1840		
$\mu_{\text{eff}}/\text{B.M.}$	1.63	1.68	1.68	1.74	1.76	1.74	1.79	1.82	1.86		

Magnetic measurements were carried out partly on the apparatus at the Institute of Physical Chemistry of the Goethe University in Frankfurt/Main (GFR) based on the Gouy method and working continually in the temperature range 77—300 K [12], partly on the apparatus at the Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava (also based on the Gouy method and working continually in the temperature range 100—300 K) that was modified after [13]. As a standard  $\text{HgCo}(\text{SCN})_4$  was used [14] and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  served for temperature calibration [15]. Corrections for diamagnetism were made according to [16—18]. The experimentally obtained magnetic data of the studied chlorotitanium(III) complexes with aliphatic alcohols are presented in Table 1. The Weiss' constants were calculated according to the relation

$$\chi'_M = \frac{C}{T - \Theta}$$

numerically using the least square method. The effective magnetic moment was calculated using the equation [19]

$$\mu_{\text{eff}} = D(\chi'_M T)^{1/2}$$

$$D = 800 \text{ m}^{-3/2} \text{ K}^{-1/2} \text{ mol}^{1/2}.$$

The diffuse reflectance spectra were registered on the spectrophotometer SPEKOL which was equipped with additional amplifier SPEKOL ZV (Zeiss, Jena), in the range 25 000—12 500  $\text{cm}^{-1}$ , and MgO was used as a reference.

## Discussion

Assuming, as the first approximation, the octahedral symmetry in the titanium(III) complexes, the  $d$ -electron of Ti(III) is mostly influenced by the ligand field created by octahedrally arranged point charges or ligand dipoles. In this way the free ion ground term,  ${}^2D$ , with an orbital degeneracy of 5 is split into a lower orbital triplet  ${}^2T_{2g}$  and an upper orbital doublet  ${}^2E_g$  (Fig. 1) [20]. From the magnetochemical point of view the ground triplet state is interesting the degenera-

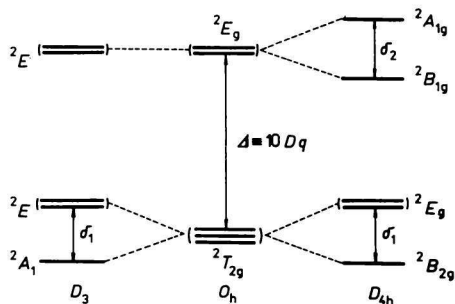


Fig. 1. Splitting diagram of the  ${}^2D$  term in an octahedral field ( $O_h$ ) as well as in fields of tetragonally ( $D_{4h}$ ) and trigonally ( $D_3$ ) compressed octahedron.

cy of which can be lifted by a ligand field component of axial symmetry as well as by spin-orbit coupling. In accordance with the ligand field theory and on the basis of theoretical calculations the complexes of titanium(III) being of perfect octahedral symmetry should exhibit at room temperature the effective magnetic moment 1.86 B.M. [21]. But the majority of complexes exhibit values approaching the spin-only value, *i.e.* 1.73 B.M., consequently it can be concluded that this symmetry is lowered, as it is also evident from the analysis of their optical spectra [20].

The Figgis' method of curve fitting worked out for estimation of magnetic properties of ions with formal cubic field orbital triplet ground state, perturbed simultaneously by the effect of an axial ligand field distortion and spin-orbit coupling, was used for the interpretation of the obtained magnetic data of the investigated group of chlorotitanium(III) complexes [22]. The effective magnetic moment arising from the  ${}^2T_2$  term of transition metal complex ion, the degeneracy of which has been lifted by a ligand field component of axial symmetry and by spin-orbit coupling, is presented in graphical form as a function of temperature ( $kT/\lambda'$ )

$$\mu_{\text{eff}} = \left| f\left(\frac{kT}{\lambda'}\right) \right|_{v,K}$$

where  $k$  = Boltzmann's constant,  $K$  = Stevens' delocalization factor,  $v = \delta_1/\lambda'$ ,  $\delta_1$  = separation between the levels of  ${}^2T_{2g}$  created by the axial ligand field component,  $\lambda'$  = spin-orbit coupling constant.

Experimentally obtained values of effective magnetic moments of the studied

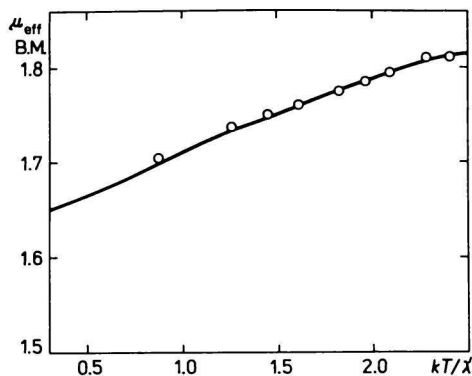


Fig. 2. Plot of  $\mu_{\text{eff}}$  vs.  $kT/\lambda'$  for  $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$ .  
 ○○○ Experimental points;  
 — theoretical curve ( $k = 0.8$ ,  $v = 9$ ,  
 $\lambda' = 85 \text{ cm}^{-1}$ ).

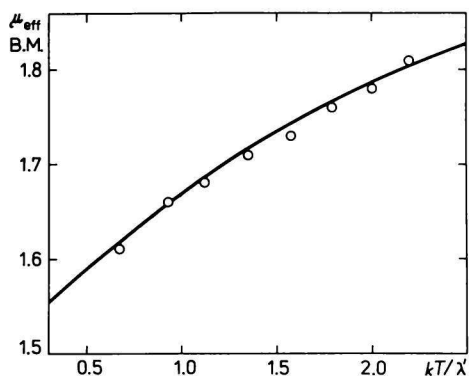


Fig. 3. Plot of  $\mu_{\text{eff}}$  vs.  $kT/\lambda'$  for  $\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$ .  
 ○○○ Experimental points;  
 — theoretical curve ( $k = 0.7$ ,  $v = 4$ ,  
 $\lambda' = 95 \text{ cm}^{-1}$ ).

trichloro(aliphatic alcohol)titanium(III) complexes in the temperature range 77—300 K compared with theoretical curves are presented in Figs. 2—7, the other quantities found by this method are listed in Table 2.

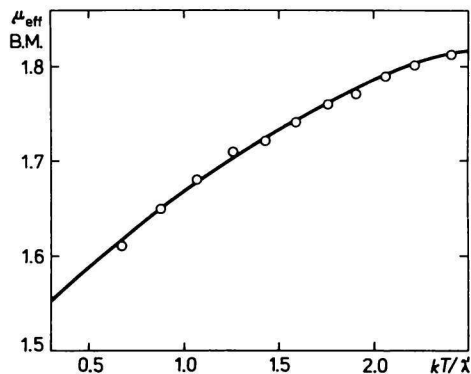


Fig. 4. Plot of  $\mu_{\text{eff}}$  vs.  $kT/\lambda'$  for  $\text{TiCl}_3 \cdot 3n\text{-C}_3\text{H}_7\text{OH}$ .  
 ○○○ Experimental points;  
 — theoretical curve ( $k = 0.7$ ,  $\nu = 4$ ,  
 $\lambda' = 85 \text{ cm}^{-1}$ ).

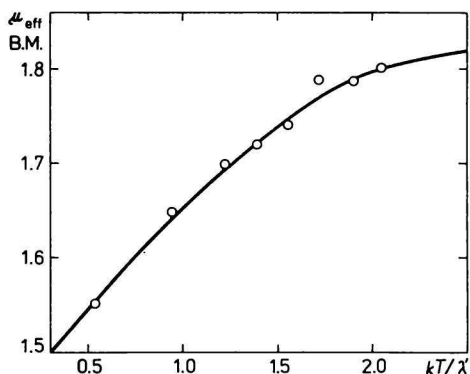


Fig. 5. Plot of  $\mu_{\text{eff}}$  vs.  $kT/\lambda'$  for  $\text{TiCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$ .  
 ○○○ Experimental points;  
 — theoretical curve ( $k = 0.7$ ,  $\nu = 3$ ,  
 $\lambda' = 100 \text{ cm}^{-1}$ ).

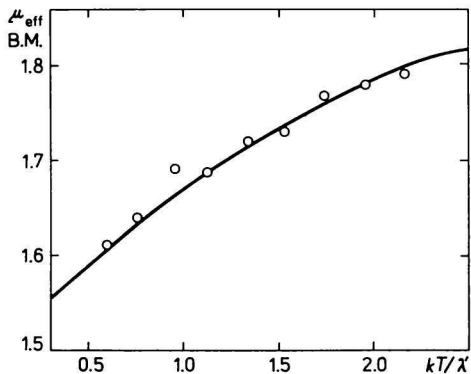


Fig. 6. Plot of  $\mu_{\text{eff}}$  vs.  $kT/\lambda'$  for  $\text{TiCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$ .  
 ○○○ Experimental points;  
 — theoretical curve ( $k = 0.7$ ,  $\nu = 4$ ,  
 $\lambda' = 95 \text{ cm}^{-1}$ ).

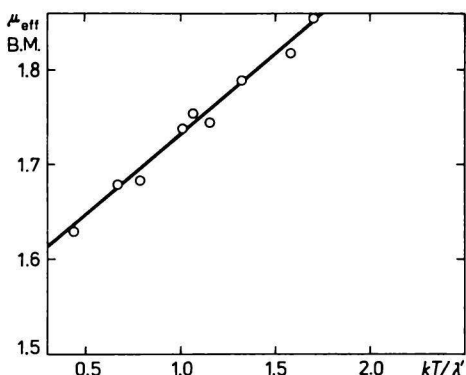


Fig. 7. Plot of  $\mu_{\text{eff}}$  vs.  $kT/\lambda'$  for  $\text{TiCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$ .  
 ○○○ Experimental points;  
 — theoretical curve ( $k = 1$ ,  $\nu = 7$ ,  
 $\lambda' = 120 \text{ cm}^{-1}$ ).

Table 2

Values of parameters obtained on the basis of the Figgis' method

Complex	$\mu_{\text{eff}}/\text{B.M.}$	$-\Theta/\text{K}$	$\lambda'/\text{cm}^{-1}$	$k$	$\nu$	$\delta_1/\text{cm}$
$\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$	1.81 (295 K)	21.5	85	0.8	9	765
$\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$	1.81 (300 K)	46	95	0.7	4	380
$\text{TiCl}_3 \cdot 3n\text{-C}_3\text{H}_7\text{OH}$	1.81 (295 K)	40	85	0.7	4	340
$\text{TiCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$	1.80 (293 K)	45	100	0.7	3	300
$\text{TiCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$	1.79 (295 K)	34	95	0.7	4	380
$\text{TiCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$	1.86 (293 K)	42	120	1	7	840

To complete the found magnetic data the diffuse reflectance spectra of the investigated complexes were recorded. The obtained spectra (Figs. 8—10) are typical of tetragonally distorted octahedral titanium(III) complexes showing a broad asymmetric band with either rather well separated peaks or a shoulder. Considering the scheme of terms (Fig. 1) in the case of tetragonally compressed octahedron (on the basis of magnetic measurements  $\delta_1 > 0$ ) these observed maxima can be assigned to  $d-d$  transition

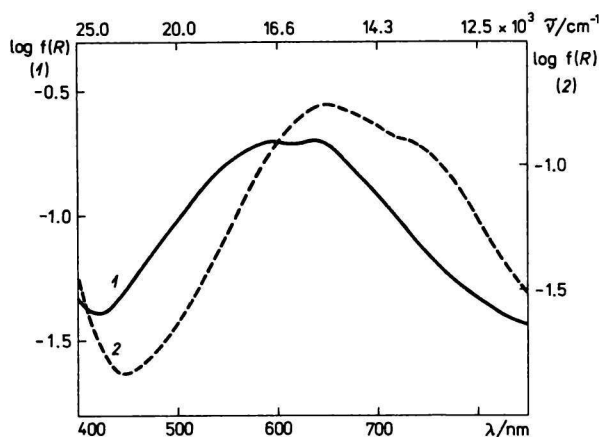
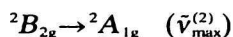
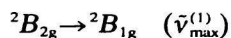


Fig. 8. Diffuse reflectance spectra of  $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$  (1) and  $\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$  (2).

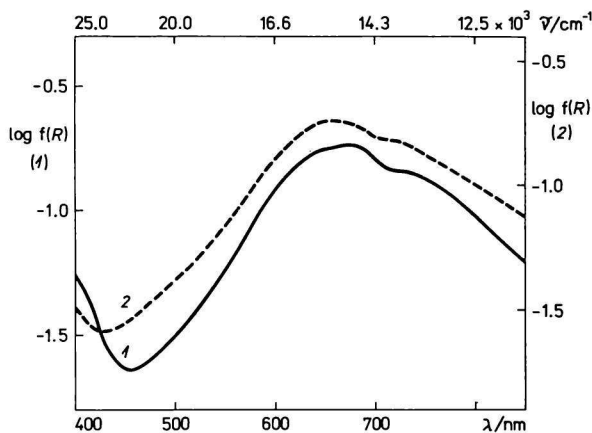


Fig. 9. Diffuse reflectance spectra of  $\text{TiCl}_3 \cdot 3n\text{-C}_3\text{H}_7\text{OH}$  (1) and  $\text{TiCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$  (2).

Then the splitting  $\delta_2$  of the excited state  ${}^2E_g$  is identical with separation of the observed maxima

$$\tilde{\nu}_{\max}^{(2)} - \tilde{\nu}_{\max}^{(1)} = \delta_2 \quad \text{with} \quad \tilde{\nu}_{\max}^{(2)} > \tilde{\nu}_{\max}^{(1)}$$

The data of the optical spectra are given in Table 3.

As it is evident from the obtained results the experimental values of effective magnetic moments at room temperature of the studied trichloro(aliphatic alcohol)titanium(III) complexes are below the theoretical value valid for perfect octahedral symmetry. Hence it can be concluded that the symmetry is lowered due to the presence of an axial ligand field component. The observed temperature dependence of magnetic moments confirmed the suggestion of their monomeric structure and according to positive value  $\delta_1$ , the symmetry of compressed octahedron can be proposed with an orbital singlet  ${}^2B_{2g}$ , resulting from the resolution of the  ${}^2T_{2g}$ , lying lower. The other quantities obtained using the Figgis'

Table 3

Data obtained from the diffuse reflectance spectra

Complex	$\tilde{\nu}_{\max}^{(2)}/\text{cm}^{-1}$	$\tilde{\nu}_{\max}^{(1)}/\text{cm}^{-1}$	$\delta_2/\text{cm}^{-1}$
$\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$	16 700	15 600	1100
$\text{TiCl}_3 \cdot 4\text{C}_2\text{H}_5\text{OH}$	15 600	13 700	1900
$\text{TiCl}_3 \cdot 3n\text{-C}_3\text{H}_7\text{OH}$	14 900	13 500	1400
$\text{TiCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$	15 150	13 700	1450
$\text{TiCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$	15 150	13 900	1250
$\text{TiCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$	15 150	14 000	1050



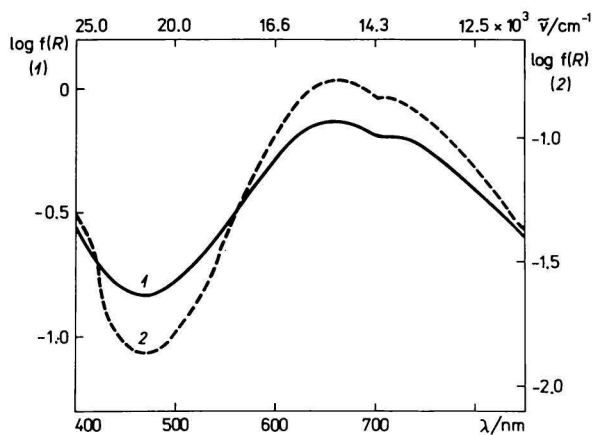


Fig. 10. Diffuse reflectance spectra of  $\text{TiCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$  (1) and  $\text{TiCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$  (2).

method refer to some  $t_{2g}$  electron delocalization, the values of spin-orbit coupling constants and Weiss' constants are consistent with values for compounds of this group.

The presence of tetragonal axial field component was confirmed by asymmetric or double structure of  $\text{Ti(III)}$  band in the recorded diffuse reflectance spectra.

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