

# Magnetochemical, electronic spectral, and crystal chemical characterization of thermal decomposition of trichlorotris(tetrahydrofuran)titanium(III)

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*Dedicated to Professor J. Gažo, Corresponding Member of the  
Czechoslovak Academy of Sciences, on his 50th birthday*

The magnetic properties of complex  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$  (*I*) as well as the products of its thermal decomposition  $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}$  (*II*) and  $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}$  (*III*) in the temperature range 77—300 K were studied using the Gouy method. The obtained magnetochemical data in the cases (*I*) and (*II*) are consistent with their assumed monomeric structure which, for the complex (*I*) was confirmed by crystal structure determination. In the case (*III*) the formation of polymeric species was confirmed. Cryomagnetic data are completed by the data of diffuse reflectance spectra and finally a scheme for thermal decomposition of  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$  is proposed.

Методом Гуи изучены магнитные свойства комплекса  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$  (*I*) и продуктов его термического разложения  $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}$  (*II*) и  $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}$  (*III*) в интервале температур 77—300 К. Полученные магнитные данные для (*I*) и (*II*) находятся в согласии с предложенной мономерной структурой, которая для комплекса (*I*) была подтверждена рентгеноструктурным исследованием. В случае (*III*) подтверждено образование полимерной структуры. Криомагнитные данные дополнены диффузионными спектрами отражения и в заключение предлагается схема термического разложения  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$ .

Studying the thermal properties of the light-blue coloured trichlorotris(tetrahydrofuran)titanium(III) complex [1], the formation of the green complex  $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}$  at about 100°C and of the grey compound  $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}$  at about 150°C was observed. According to [2] in the course of thermal decomposition the whole molecules of tetrahydrofuran are successively released and first formation of complex with lower coordination number and then formation of coordination polymer is assumed. From among the trichloro(tetrahydrofuran)titanium(III) complexes only the crystal structure of  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$  was reported [3] and in accordance with [13] the *mer*-coordination of central Ti(III) ion was determined.

The magnetic properties of the investigated complexes were studied also by other authors [4—8], but no conclusions were drawn as to the relation between the course of thermal decomposition and the structure.

### Experimental

The complex  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$  was prepared by reaction of  $\alpha\text{-TiCl}_3$  with tetrahydrofuran in the atmosphere of pure nitrogen, the compounds  $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}$  and  $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}$  by thermal decomposition of the above complex by a method reported in [1].

Magnetic measurements were carried out in the temperature range 77—300 K by the Gouy method as it is described in [9]. The results of magnetic measurements are presented in Table 1. Diffuse reflectance spectra were recorded on the spectrophotometer SPEKOL equipped with additional amplifier SPEKOL ZV (Zeiss, Jena) in the range 25 000—12 500  $\text{cm}^{-1}$  and the  $\text{MgO}$  was used as a reference substance.

Table 1

Magnetic susceptibilities and effective magnetic moments of investigated titanium(III) compounds

| $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$ |      |      |      |      |      |      |      |      |      |      |      |
|---|------|------|------|------|------|------|------|------|------|------|------|
| $T/\text{K}$  | 77   | 120  | 149  | 189  | 201  | 216  | 244  | 269  | 293  |      |      |
| $\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$ | 5368 | 3569 | 2985 | 2449 | 2342 | 2252 | 2015 | 1895 | 1765 |      |      |
| $\mu_{\text{eff}}/\text{B.M.}$                      | 1.62 | 1.66 | 1.69 | 1.72 | 1.74 | 1.76 | 1.77 | 1.81 | 1.82 |      |      |
| $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}$ |      |      |      |      |      |      |      |      |      |      |      |
| $T/\text{K}$  | 103  | 142  | 177  | 193  | 213  | 234  | 257  | 276  | 285  | 296  |      |
| $\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$ | 4144 | 3041 | 2475 | 2291 | 2138 | 1935 | 1793 | 1677 | 1628 | 1579 |      |
| $\mu_{\text{eff}}/\text{B.M.}$                      | 1.65 | 1.66 | 1.68 | 1.68 | 1.71 | 1.70 | 1.72 | 1.72 | 1.72 | 1.73 |      |
| $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}$  |      |      |      |      |      |      |      |      |      |      |      |
| $T/\text{K}$  | 80   | 102  | 126  | 139  | 160  | 181  | 199  | 223  | 250  | 275  | 295  |
| $\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$ | 419  | 546  | 608  | 614  | 622  | 639  | 656  | 668  | 685  | 693  | 691  |
| $\mu_{\text{eff}}/\text{B.M.}$                      | 0.46 | 0.60 | 0.70 | 0.74 | 0.80 | 0.86 | 0.91 | 0.98 | 1.05 | 1.10 | 1.14 |

### Results and discussion

The magnetochemical data of the complex  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$  measured in the temperature range 77—300 K ( $\mu_{\text{eff}}(293 \text{ K}) = 1.82 \text{ B.M.}$ ,  $\Theta = -37 \text{ K}$ ) are in agreement with the monomeric structure and distorted octahedral coordination of the central atom, as these were determined by X-ray analysis [3]. The diffuse

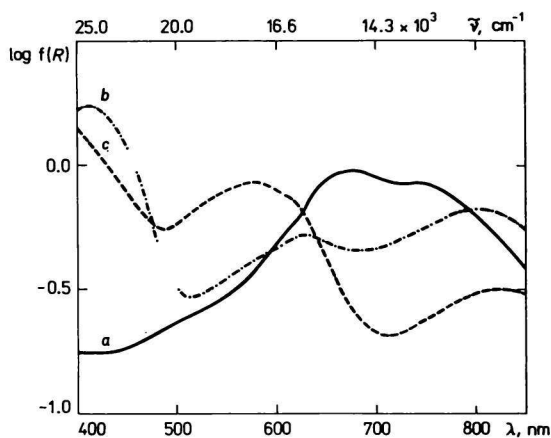


Fig. 1. Diffuse reflectance spectra of  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$  (a),  $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}$  (b), and  $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}$  (c).

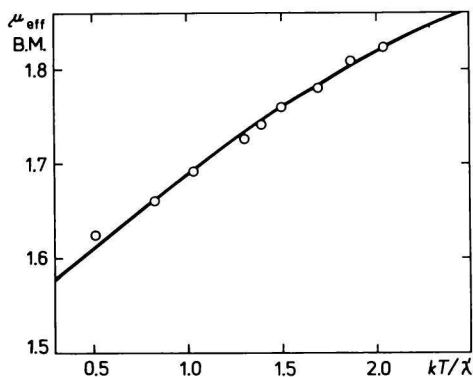


Fig. 2. Plot of  $\mu_{\text{eff}}$  vs.  $kT/\lambda'$  for  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$ .  
 ○○ Experimental points;  
 — theoretical curve ( $k = 0.8$ ,  $\nu = 5$ ,  
 $\lambda' = 100 \text{ cm}^{-1}$ ).

reflectance spectrum (Fig. 1a) showing a broad asymmetric band with maxima located at  $14\,900$  and  $13\,500 \text{ cm}^{-1}$  is also typical of this coordination. Using the Figgis' method [10] (Fig. 2) the value of the delocalization factor  $k = 0.8$ , spin-orbit coupling constant  $\lambda' = 100 \text{ cm}^{-1}$ , and the separation between the levels of  ${}^2T_{2g}$  created by an axial ligand field component,  $\delta_1 = 500 \text{ cm}^{-1}$ , were determined. These values are in fairly good agreement with the results published in [6]. The separation between the levels arising from the excited state  ${}^2E_g$  found on the basis of diffuse reflectance spectrum  $\delta_2$ , is  $1400 \text{ cm}^{-1}$ .

On the basis of magnetochemical values (Table 1) the complex  $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}$  ( $\mu_{\text{eff}}(296 \text{ K}) = 1.73 \text{ B.M.}$ ,  $\Theta = -21 \text{ K}$ ) also could be taken for a mono-

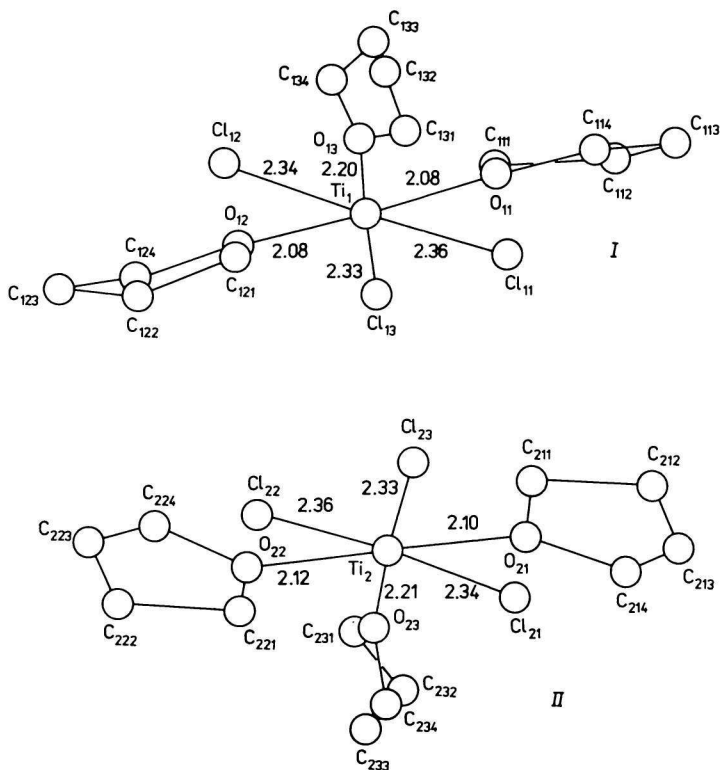


Fig. 3. Two independent molecules *I* and *II* of the complex  $[\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_3]$ .

mer, but the character of its diffuse reflectance spectrum indicates the trigonal bipyramidal coordination of the central ion. The recorded spectrum (Fig. 1*b*) exhibits two well separated bands at  $16\,000$  and  $12\,000\text{ cm}^{-1}$ , typical of this coordination [11]. The trigonal bipyramidal coordination with two molecules of tetrahydrofuran in axial positions can also be proposed on the basis of the solved crystal structure of the parent complex  $[\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_3]$ .

As it is evident from Fig. 3, the *O*-donor tetrahydrofuran atoms are placed in meridional positions of the coordination polyhedra. While the atomic distances Ti—Cl are approximately the same for all atoms in the two independent molecules, the distances Ti(1)—O(13) and Ti(2)—O(23) are significantly longer than the distances Ti(1)—O(11), Ti(1)—O(12) and Ti(2)—O(21), Ti(2)—O(22), respectively, this being apparently caused by the *trans* effect of atoms Cl(13) and Cl(23). Moreover, the respective tetrahydrofuran rings point towards the free space in the crystal structure (Fig. 4). Consequently in this position the possibility of thermal cleavage of tetrahydrofuran molecule is most probable.

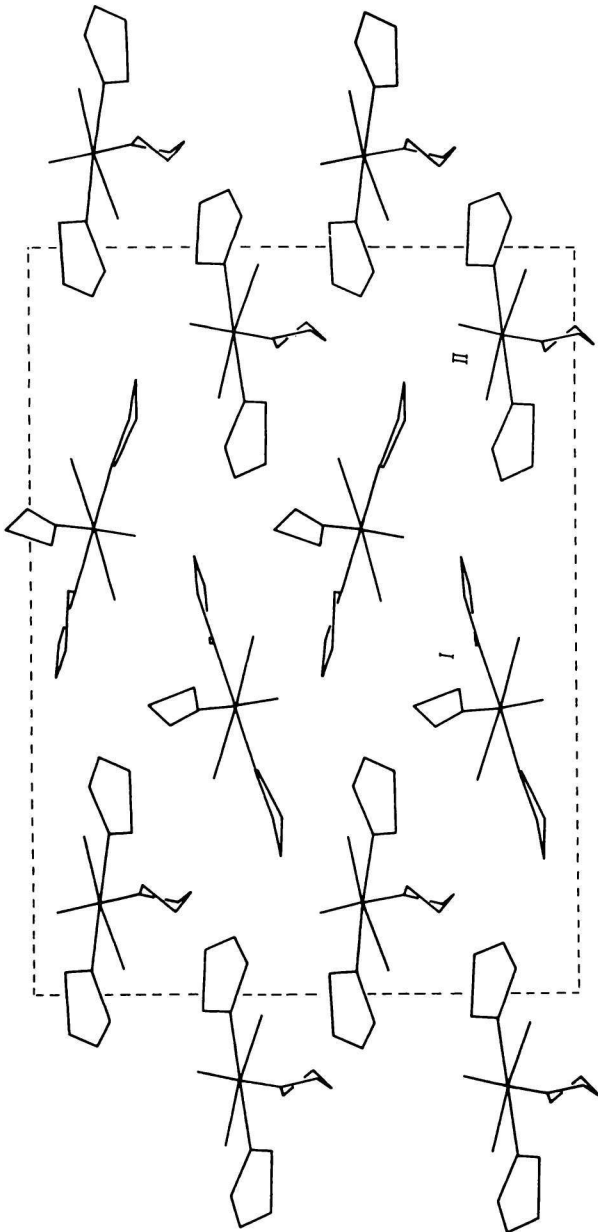


Fig. 4. Packing of the molecules in the crystal structure of  $[\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_3]$ .

The markedly lowered value of the effective magnetic moment at room temperature suggests the formation of polynuclear species in the case of compound  $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}$  ( $\mu_{\text{eff}} = 1.14$  B.M.) formed in the second step of thermal decomposition of  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$ . According to our findings no oxidation of Ti(III) to Ti(IV) took place as the determined amount of Ti(III) within experimental errors agreed with the theoretically predicted values. The assumed formation of polymeric structure was confirmed by the possibility to explain the obtained magnetic data in the temperature range 100–300 K using the Ising model [12], which describes interactions between an infinite linear chain of neighbouring paramagnetic atoms, in the form

$$\mu_{\text{eff}} = \frac{g}{2} \left[ \frac{e^{4K} + 2 + K^{-1} e^{2K} - K^{-1} e^{-2K} + 5}{e^{2K} + e^{-2K} + 2} \right]^{1/2}$$

where  $K = J k^{-1} T^{-1}$ .

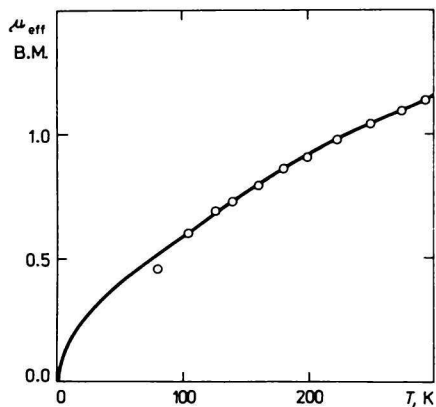


Fig. 5. Plot of  $\mu_{\text{eff}}$  vs.  $T$  for  $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}$ .

○○○ Experimental points;  
 ——— theoretical curve  
 ( $g = 1.90$ ,  $J = -185 \text{ cm}^{-1}$ ).

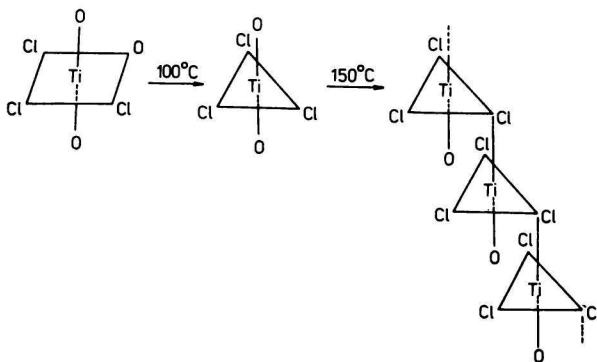


Fig. 6. The assumed scheme of thermal decomposition of the complex  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$ . (O represents the molecule  $\text{C}_4\text{H}_8\text{O}$ .)

The experimentally obtained values of effective magnetic moments in the studied temperature range fit in with the theoretical curve computed for  $g = 1.90$  and  $J = -185 \text{ cm}^{-1}$  ( $-36.8 \times 10^{22} \text{ J}$ ) (Fig. 5). The value of  $g$  factor was verified by e.s.r. measurements and the obtained value was consistent with that reported in [8].

On the basis of obtained experimental data the assumed course of thermal decomposition of  $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}$  was confirmed [1, 2]. As it is shown in Fig. 6, in the first step the coordination number is lowered and the change of octahedral to trigonal bipyramidal coordination of central atom takes place. In the second step the polymeric structure is formed and the existence of interaction *via* chloride bridges can be proposed. The trigonal bipyramidal coordination is assumed to remain intact as it is evident from the diffuse reflectance spectra of these compounds (Fig. 1b and 1c).

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