

# Spectral and Magnetochemical Investigation of Titanium(III) Chloro Alkoxy Complexes with Aliphatic Alcohols

M. ZIKMUND, E. ŠTEPNIČKOVÁ and M. KOHÚTOVÁ

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,  
Bratislava 9*

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On the basis of magnetic measurements, absorption, diffusion-reflectance, and infrared spectra of the complexes  $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$ ,  $\text{TiCl}_3 \cdot 5\text{CH}_3\text{OH}$ , and products of their thermal decomposition, the conclusions are drawn about the stereochemistries of these compounds in solid state and in tetrahydrofuran solution as well. Both above mentioned complexes possess structures *trans*- $[\text{TiCl}_2(\text{CH}_3\text{OH})_4]\text{Cl}$  and  $[\text{TiCl}(\text{CH}_3\text{OH})_5]\text{Cl}_2$ , while the products of their thermal decomposition are coordination polymers in which methoxide bridges occur.

In the preceding paper [1], it has been demonstrated by thermogravimetric method that the thermal decomposition of  $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$  yields the products of approximative composition  $\text{TiCl}_{2.3}(\text{OCH}_3)_{0.7} \cdot 1.5\text{CH}_3\text{OH}$  (pink red powder formed at about 100°C) and  $\text{TiCl}_{1.9}(\text{OCH}_3)_{1.1}$  (brown powder formed at about 200°C) as well as a black pyrophoric powdered product containing titanium(II) chloro methoxide and arising at about 300°C. The thermal decomposition of  $\text{TiCl}_3 \cdot 5\text{CH}_3\text{OH}$  proceeds in an analogous way while the fifth molecule of methanol is released first of all (at about 60°C). The composition of decomposition products varies in a small range according to the conditions of preparation.

*Giggenbach* and *Brubaker* [2] have prepared pink powder of the composition  $\text{TiCl}_{2.28}(\text{OCH}_3)_{0.74}(\text{CH}_3\text{OH})_2$  and red-brown powder of the composition  $\text{TiCl}_{2.30}(\text{OCH}_3)_{0.62}(\text{CH}_3\text{OH})_2$  by heating the  $\text{TiCl}_3(\text{CH}_3\text{OH})_5$  and  $\text{TiCl}_3(\text{CH}_3\text{OH})_4$  respectively *in vacuo* at about 100°C. These workers found that in both cases polymeric, diamagnetic, six-coordinate species may be present. If the two original compounds are heated to 200°C other solids are formed with the approximate composition  $\text{TiCl}_{1.5}(\text{OCH}_3)_{1.5}$ . The solutions have the same spectrum as the yellow solid compound  $\text{TiCl}_{1.5}(\text{OCH}_3)_{1.5}(\text{CH}_3\text{OH})_2$  which was formed from a solution of titanium(III) chloride and alkali methoxides in methanol [2]. The final product is described as  $\text{Ti}(\text{OCH}_3)_3$  [4]. The compounds of similar composition and colour may also be obtained by the reaction of titanium(III) methoxide in methanol with titanium(III) chloride in methanol [5], the products being  $\text{TiCl}_2(\text{OCH}_3) \cdot 2\text{CH}_3\text{OH}$  (red solid) and  $\text{TiCl}(\text{OCH}_3)_2 \cdot \text{CH}_3\text{OH}$  (dark brown solid). The diffusion reflectance spectra and the temperature independent magnetic moment of  $\text{TiCl}_2(\text{OCH}_3) \cdot 2\text{CH}_3\text{OH}$  suggest tetrahedral coordination of the titanium(III) atom [5]. The tetrahedral coordination of Ti(III) is also assumed on the basis of absorption spectra in the paper [2].

With respect to the shortage of available data and some contradictions in literature we have investigated the properties of this group of substances in more detail.

### Experimental

The complexes  $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$  and  $\text{TiCl}_3 \cdot 5\text{CH}_3\text{OH}$  were prepared by the method given in the paper [1]. The products of their thermal decomposition were prepared by heating powdered initial complexes in nitrogen atmosphere under stirring at 100, 200 and 300°C, respectively according to the thermogram presented in paper [1]. The yellow-brown  $\text{TiCl}_{1.3}(\text{OCH}_3)_{1.7} \cdot 3.5\text{CH}_3\text{OH}$  was obtained by the reaction of the pink powdered complex  $\text{TiCl}_{2.4}(\text{OCH}_3)_{0.6} \cdot 2\text{CH}_3\text{OH}$  with methanol vapour under stirring at about 40°C.

The synthesized products were analysed according to the procedures given in the paper [1].

Magnetic susceptibilities were obtained by the Gouy method as previously described [6]. The method of measurement of absorption and diffuse reflectance spectra in visible and ultraviolet region is given in the papers [7, 8]. The method of measurement of infrared spectra is supplied in the papers [7–9].

### Results and Discussion

The diffuse reflectance spectra of the complexes  $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$  and  $\text{TiCl}_3 \cdot 5\text{CH}_3\text{OH}$  (Fig 1, curves 1 and 5) are typical of deformed octahedral  $d^1$  complexes. The transitions for  $\text{TiCl}_3 \cdot 5\text{CH}_3\text{OH}$  are at 17,200 and 15,600  $\text{cm}^{-1}$  in good agreement with [3]. The octahedral structure of both complexes is also confirmed by the value of magnetic moment (1.79 B. M.) for  $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$  (see also [2]) which is close to the spin-only value. The absorption band in infrared spectrum of  $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$  at 978  $\text{cm}^{-1}$  corresponding to Ti—O—C stretching mode of coordinated methanol indicates that all four molecules are coordinated in an equivalent (planar) manner.

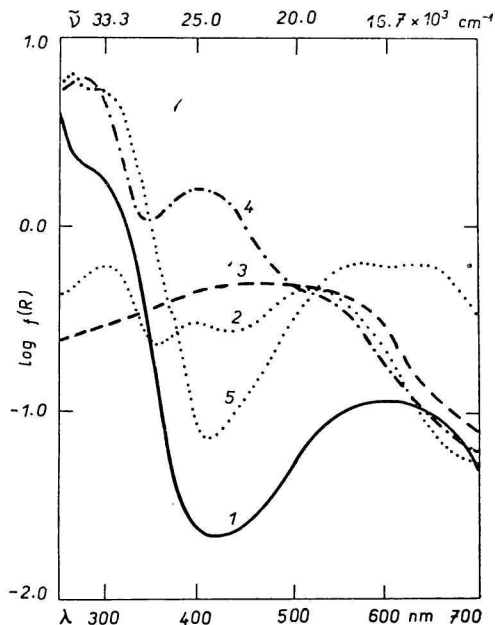


Fig. 1. Diffusion reflectance spectra of titanium(III) chloro and chloro methoxy complexes.

On contrary, the splitting of this absorption band in the infrared spectrum of  $\text{TiCl}_3 \cdot 5\text{CH}_3\text{OH}$  (see Table 1) is corroboration for the presence of methanol ligands in different bonding situations. The course of thermic decomposition of  $\text{TiCl}_3 \cdot 5\text{CH}_3\text{OH}$  is in agreement with the assumed different coordination of methanol molecules in this complex [1]. Since all methanol molecules in both complexes are coordinated (the C—O stretch in pure methanol occurs at  $1025\text{ cm}^{-1}$ ), the structures of the complexes may be formulated as  $[\text{TiCl}_2(\text{CH}_3\text{OH})_4]\text{Cl}$  and  $[\text{TiCl}(\text{CH}_3\text{OH})_5]\text{Cl}_2$  (see also [3]).

Table 1

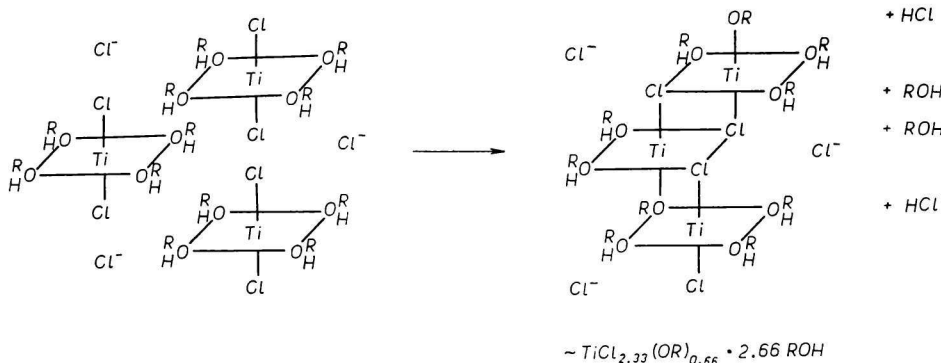
Infrared spectra of titanium(III) chloro and chloro methoxy complexes

Complex or ligand	$\text{CH}_3\text{OH}$		Shift		$\text{OCH}_3$	
$\text{CH}_3\text{OH}$	1109 m		1025 vs	0		
$\text{TiCl}_3 \cdot 5\text{CH}_3\text{OH}$	1110 m	1010 s	980 vs	45		
$\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$	1110 m		978 vs	47		
$\text{TiCl}_{1.3}(\text{OCH}_3)_{1.7} \cdot 3.5\text{CH}_3\text{OH}$	1120 m	1010 s	980 vs	45	1070 vs	1045 sh
$\text{TiCl}_{2.15}(\text{OCH}_3)_{0.85} \cdot 1.8\text{CH}_3\text{OH}$	1105 m		980 vs	45	1068 m	1047 s
$\text{TiCl}_{1.7}(\text{OCH}_3)_{1.3}$					1064 sh	1047 vs
$\text{Ti}(\text{OCH}_3)_3$					1087 s	

The pink  $\text{TiCl}_{2.4}(\text{OCH}_3)_{0.6} \cdot 2\text{CH}_3\text{OH}$  possesses a reduced magnetic moment (0.63 B. M. at  $293^\circ\text{K}$  falling to 0.28 B. M. at  $77^\circ\text{K}$ ). The reduction of magnetic moment illustrated in Table 2 is similar to that observed in other polymeric chlorides and alkoxides and is due to antiferromagnetism probably arising by superexchange through bridging chlorine and/or methoxide groups.

The evidence for the existence of methoxide groups in this structure is supplied by the infrared absorption bands at  $1047\text{ cm}^{-1}$  corresponding probably to the Ti—O—C stretching mode of the terminal coordinated methoxide group and at  $1068\text{ cm}^{-1}$  corresponding probably to the stretching vibration  $\nu(\text{C—O})$  of the methoxide bridge.

The formation and structure of the pink compound may be expressed by the following scheme



The diffuse reflectance spectrum (Fig. 1, curve 2) indicated that a deformed octahedral coordination with three types of chromophores in coordination sphere is conserved in this polymer. Our findings are thus not in agreement with the finding in the paper [2], *i.e.* that the complex is diamagnetic, as well as with the finding in the paper [3], that the complex of similar composition and colour has a temperature independent magnetic moment of 1.0 B. M. and a tetrahedral configuration of coordination sphere as well.

Table 2

Magnetic susceptibilities ( $\chi'_M \cdot 10^6$ ) and magnetic moments ( $\mu_{eff}$ , B. M.) of titanium(III) chloro and chloro methoxy complexes

Complex	293°K		273°K		201°K		77°K	
$\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$	1365	1.79	1378	1.74	1811	1.71	4036	1.58
$\text{TiCl}_{1.3}(\text{OCH}_3)_{1.7} \cdot 3.5\text{CH}_3\text{OH}$	703	1.29	713	1.30	1024	1.29	2316	1.20
$\text{TiCl}_{2.4}(\text{OCH}_3)_{0.6} \cdot 2\text{CH}_3\text{OH}$	170	0.63	142	0.56	164	0.52	127	0.28
$\text{TiCl}_{1.7}(\text{OCH}_3)_{1.3}$	96	0.47	74	0.40	107	0.42	33	0.14

The assumption that this complex possesses a configuration of deformed octahedron is also supported by the diffuse reflectance spectrum of the yellow-brown  $\text{TiCl}_{1.3}(\text{OCH}_3)_{1.7} \cdot 3.5\text{CH}_3\text{OH}$  which is produced by the addition of methanol molecules to the above mentioned pink complex. This spectrum has an analogous course (Fig. 1, curve 4) to that of the pink complex with the main difference that the intensity of the absorption band at  $25,000 \text{ cm}^{-1}$  is increased which is probably due to the increase in the number of coordinated methanol molecules in the coordination sphere. Since the methanol molecules have been able to coordinate by breaking down the bridge-bonds among the titanium(III) atoms, the number of chlorine or alkoxide bridges taking part in super-exchange is less than in the case of the pink complex. This is responsible for the increase of the magnetic moment (to 1.29 B. M.). Since it is, however, smaller than the spin-only value, it may be assumed that it is also a coordination polymer with chlorine and/or methoxide bridges. The evidence for terminal methoxide groups and methoxide bridges is supplied by the infrared absorption bands at  $1045$  and  $1070 \text{ cm}^{-1}$  respectively corresponding to the stretching vibration  $\nu(\text{C}-\text{O})$  of coordinated alkoxide groups. The evidence that all methanol molecules are coordinated in two different bonding situations is supplied by the absorption bands at  $980 \text{ cm}^{-1}$  and  $1010 \text{ cm}^{-1}$  which corresponds to the stretching vibration  $\nu(\text{C}-\text{O})$  of coordinated methanol molecule.

Diffuse reflectance spectrum of the brown product  $\text{TiCl}_{1.7}(\text{OCH}_3)_{1.3}$  shows a broad absorption band (Fig. 1, curve 3). The reduced magnetic moment (0.47 B. M. at  $293^\circ\text{K}$  falling to 0.14 B. M. at  $77^\circ\text{K}$ ) gives evidence of a coordination polymer. The existence of alkoxide bridge which effect the super-exchange is confirmed by absorption bands at  $1047$  and  $1064 \text{ cm}^{-1}$  which correspond to the coordinated terminal and bridged alkoxide groups, respectively. The absorption band at  $1087 \text{ cm}^{-1}$  in the infrared spectrum of titanium(III) methoxide  $\text{Ti}(\text{OCH}_3)_3$  [10] corresponds to the bridged methoxide group.

All above mentioned compounds dissolve in methanol or tetrahydrofuran. The absorption spectra of the compound  $\text{TiCl}_3 \cdot 4\text{CH}_3\text{OH}$  in these both solvents are clearly different (Fig. 2, curves 1 and 2) what indicated a different coordination of Ti(III) in these donor solvents. On the other hand, the absorption spectra of the complexes  $\text{TiCl}_{1.3}(\text{OCH}_3)_{1.7} \cdot 3.5\text{CH}_3\text{OH}$  (Fig. 2, curve 3),  $\text{TiCl}_{2.4}(\text{OCH}_3)_{0.6} \cdot 2\text{CH}_3\text{OH}$

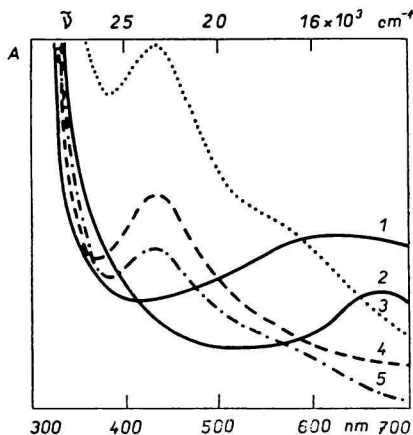


Fig. 2. Absorption spectra of chloro and chloro alkoxy complexes in tetrahydrofuran solution.

(Fig. 2, curve 4). and  $\text{TiCl}_{1.7}(\text{OCH}_3)_{1.3}$  (Fig. 2, curve 5) in tetrahydrofuran are analogous not only to each other but also to the diffuse reflectance spectrum of the solid compound  $\text{TiCl}_{1.3}(\text{OCH}_3)_{1.7} \cdot 3.5\text{CH}_3\text{OH}$  (Fig. 1, curve 4) except that for the peak of the solid at  $25,000\text{ cm}^{-1}$  which has moved to a somewhat lower wave number in solution. This indicated a similar coordination of chromophores under these conditions in both tetrahydrofuran solution and solid state.

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