

# Spectral Study of Chloro(tetrahydrofuran)titanium(III) Complexes

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In the course of slow oxidation, the blue solution of  $\text{TiCl}_3 \cdot 3\text{THF}$  in tetrahydrofuran turns from violet to yellow-brown and orange-red as a consequence of the formation of mixed oxidation-state  $\text{Ti(III,IV)}$  compounds.

On the basis of absorption and diffuse reflectance spectra in ultraviolet and visible regions, as well as absorption spectra in infrared region, it can be assumed that  $\text{TiCl}_3 \cdot 2\text{THF}$  and  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  have trigonal-bipyramidal configuration. The molecule of benzene in the complex  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  is not a component of the coordination sphere of  $\text{Ti(III)}$  atom. The compound  $\text{TiCl}_3 \cdot \text{THF}$  is a coordination polymer.

*Pregaglia* [1] reports formation of a violet solution containing  $\text{TiCl}_3 \cdot 3\text{THF}$  which is formed during the preparation of this substance from titanium(III) chloride and tetrahydrofuran. On the other hand, *Clark* [2] observed formation of a deep red solution which had a reduced magnetic moment and about a twofold molecular weight. With regard to these properties and taking into account the different absorption spectrum, when compared with the diffuse reflectance spectrum of bluish-green crystals of  $\text{TiCl}_3 \cdot 3\text{THF}$ , *Clark* believes that there are dimers in solution. A different observation was made by *Schläfer* [3]. According to him the solution of  $\text{TiCl}_3 \cdot 3\text{THF}$  in tetrahydrofuran has blue colour, whereas the red solution is formed by dissolving crystals of this substance in methanol or ethanol.

These contradictions as well as the lack of data on tetrahydrofuran titanium(III) complexes led us to investigate the properties of this group of substances in more detail.

## Experimental

The methods of the preparation of complexes as well as the methods of purification of solvents and of nitrogen have been given in the paper [4].

The absorption spectra of solutions were recorded on a CF-4 spectrophotometer (Optica Milano). The diffuse reflectance spectra were measured either by means of a Model CF-4 spectrophotometer (Optica Milano), equipped with a reflectance attachment, modified to make it suitable for measurements in inert atmosphere [5], or on a Model Cary 14 spectrophotometer by using the standard camera Model 1411, while the samples were prepared in a glove box. The measurements in ultraviolet region were made with the samples diluted with lithium fluoride (1 : 10) against  $\text{LiF}$  as standard, the samples used for the measurements in visible region were not diluted (reference substance,  $\text{MgCO}_3$ ).

The infrared spectra of the samples were determined as Nujol mulls either between KBr plates on a Perkin—Elmer spectrophotometer Model 221, or between polyethylene discs of up to 1 mm in thickness on a Perkin—Elmer Model 225 spectrophotometer. The experimental technique for sample preparation described in [6] was employed. The spectra were compared with those of the free ligands.

### Results and Discussion

It has been found that, in agreement with [3], but in contradiction to [2], a blue solution is formed in inert atmosphere by dissolving the crystals of  $\text{TiCl}_3 \cdot 3\text{THF}$  in tetrahydrofuran from which moisture and peroxides had been thoroughly removed. The absorption spectrum of this blue solution (Fig. 1, curve 2) is similar to the diffuse reflectance spectrum of the light blue powdered crystals  $\text{TiCl}_3 \cdot 3\text{THF}$  (Fig. 3, dashed curve). (The disparity may be due to the solvation.) It seems probable that the absorbing species in solution and in solid state have similar coordination of chromophores and hence the complex in solution is also considered to be  $[\text{TiCl}_3(\text{THF})_3]$ .

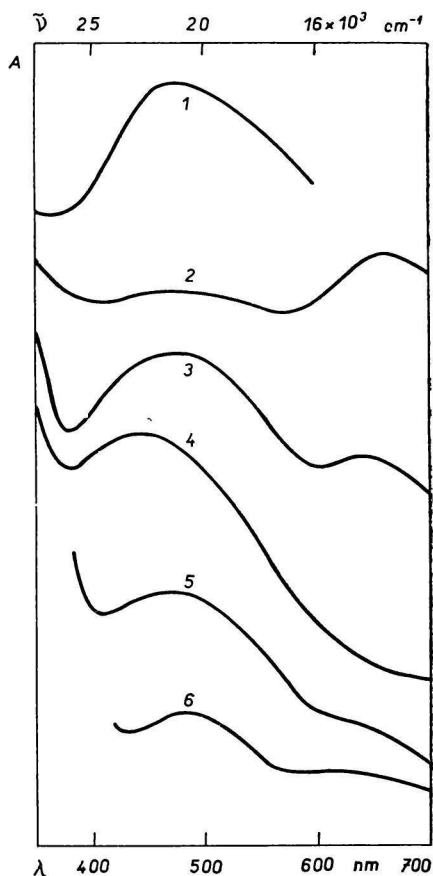


Fig. 1. Absorption spectra of chloro(tetrahydrofuran)titanium complexes in solution

The direct dissolution of anhydrous titanium(III) chloride in tetrahydrofuran results in the formation of a solution the colour of which varies from violet to brown-violet in agreement with [2]. We have found that the titanium(IV) chloride sorbed on the initial solid titanium(III) chloride is responsible for this violet colour. The absorption spectrum of brown-violet solution containing tetrahydrofuran titanium(III) chloro complex which has been prepared from thoroughly purified tetrahydrofuran and from non-purified titanium(III) chloride containing titanium(IV) chloride (Fig. 1, curve 3), is similar to the homonuclear intervalence-transfer absorption spectrum [7–10] of the aqueous solution of dimeric species  $\text{Ti(III)} \cdot \text{Ti(IV)Cl}_x$  in hydrochloric acid [8], this being indicative of the existence of an analogous absorbing species in the solution.

Very similar is the absorption spectrum of the violet solution which was formed in a slow partial air oxidation of the blue solution of  $\text{TiCl}_3 \cdot 3\text{THF}$  in tetrahydrofuran. Further oxidation of this violet solution produces a yellow-brown (Fig. 1, curve 4), orange-red and subsequently colourless solution. Analogous orange-red solution forms by dissolving  $\text{TiCl}_3 \cdot 3\text{THF}$  in non-purified tetrahydrofuran. The absorption spectrum of the orange-red solution (Fig. 1, curve 5) is similar to that of the deep-red solution which has been characterised by Clark [2] as a solution of  $\text{TiCl}_3 \cdot 3\text{THF}$  in tetrahydrofuran (Fig. 1, curve 6). It is suggested that this red solution contains an oxidation product of  $\text{TiCl}_3 \cdot 3\text{THF}$ . This conclusion agrees with the finding of Clark [2] that the solution has a reduced magnetic moment and contains a dimer which has been found among intervalence-transfer  $\text{Ti(III,IV)}$  complexes by Jørgensen, too [8].

By addition of water, the blue solution of  $\text{TiCl}_3 \cdot 3\text{THF}$  in tetrahydrofuran will be converted to a violet aquo complex (Fig. 1, curve 1).

The complex  $\text{TiCl}_3 \cdot 3\text{THF}$  is subject not only to substitution reactions (*e.g.* aquation) but also to elimination reactions. Thus, in a medium of hydrocarbons, one tetrahydrofuran molecule is being lost under formation of the green complex  $\text{TiCl}_3 \cdot 2\text{THF}$  [4]. In contrast to the statements of Pregaglia [1] and Kern [11] this complex dissolves in aromatic solvents, *e.g.* in benzene [4]. The absorption spectrum of the brown-green solution of  $\text{TiCl}_3 \cdot 2\text{THF}$  in benzene (Fig. 2, curve 1) differs in ultraviolet region from that of the green solution formed by dissolving  $\text{TiCl}_3 \cdot 3\text{THF}$  in benzene (Fig. 2, curve 2) which may be caused by the presence of tetrahydrofuran in solution

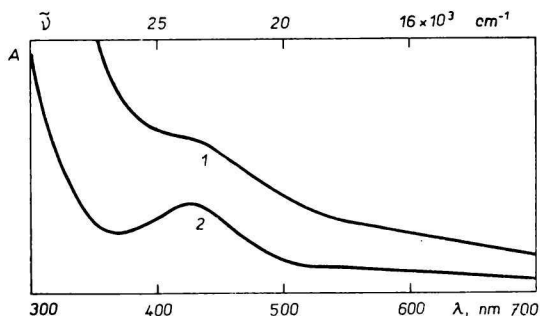


Fig. 2. Absorption spectra of  $\text{TiCl}_3 \cdot 2\text{THF}$  and  $\text{TiCl}_3 \cdot 3\text{THF}$  in benzene solution.

The absorption spectrum of dissolved  $\text{TiCl}_3 \cdot 2\text{THF}$  is qualitatively similar to the diffuse reflectance spectrum of  $\text{TiCl}_3 \cdot 2\text{THF}$  (Fig. 3, full curve). The absorption bands in the diffuse reflectance spectrum found at 12,000 and 16,000  $\text{cm}^{-1}$  can be assigned to the transitions  ${}^2E'' \rightarrow {}^2E'$  ( $\nu_1$ ) and  ${}^2E'' \rightarrow {}^2A'_1$  ( $\nu_2$ ) characteristic of five-coordinate *trans*-trigonal-bipyramidal complexes of  $D_{3h}$  symmetry. This spectrum

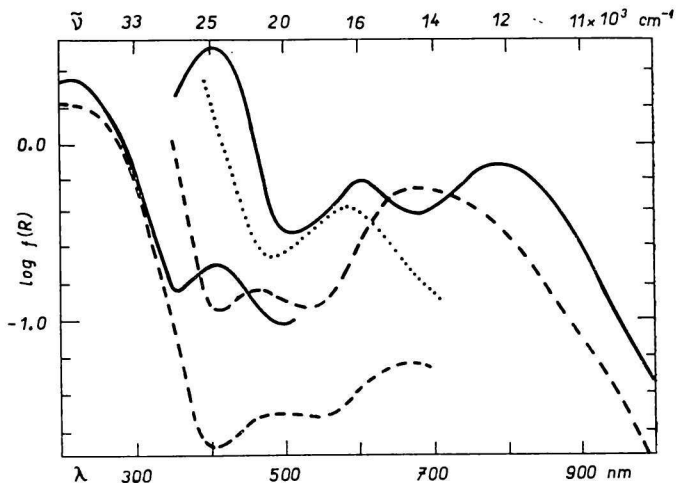


Fig. 3. Diffuse reflectance spectra of  $\text{TiCl}_3 \cdot 3\text{THF}$ ,  $\text{TiCl}_3 \cdot 2\text{THF}$ , and  $\text{TiCl}_3 \cdot \text{THF}$ .

is markedly different from those of pseudo-octahedral titanium(III) complexes of the type  $\text{MX}_3 \cdot 3\text{L}$  characterised by a single absorption band in the visible region, or from those of square-pyramidal  $d^1$  complexes of the type  $\text{TiX}_3 \cdot 2\text{L}$ , characterised by three transitions, *viz.*  $B_2 \rightarrow E$  ( $\nu_1$ ),  $B_2 \rightarrow A_1$  ( $\nu_2$ ), and  $B_2 \rightarrow B_1$  ( $\nu_3$ ) [12, 17].

It is remarkable that the diffuse reflectance spectrum of  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  is identical with that of  $\text{TiCl}_3 \cdot 2\text{THF}$ . We found that this complex has a five-coordinate

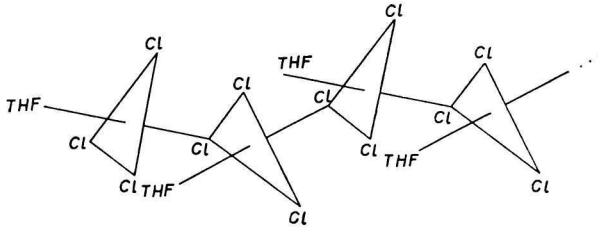


Fig. 4. Far infrared spectra of  $\text{TiCl}_3 \cdot 3\text{THF}$ ,  $\text{TiCl}_3 \cdot 2\text{THF}$ ,  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$ , and  $\text{TiCl}_3 \cdot \text{THF}$ .

trigonal-bipyramidal structure, the benzene molecule being not a component of coordination sphere of the Ti(III) atom, but only a component of crystal structure between polyhedrons  $[\text{TiCl}_3(\text{THF})_2]$  (cf. [4]). It is therefore possible to characterise this crystal solvate by the formula *trans*- $[\text{TiCl}_3(\text{THF})_2] \cdot \text{C}_6\text{H}_6$ .

The trigonal-bipyramidal configuration is also indicated by far infrared spectra of these complexes. In this region  $[\text{TiCl}_3(\text{THF})_2]$  (Fig. 4, dashed line) and  $[\text{TiCl}_3(\text{THF})_2] \cdot \text{C}_6\text{H}_6$  (Fig. 4, dot-and-dashed line) have practically identical spectra and each shows two intense absorption bands assigned to  $\nu(\text{Ti}-\text{Cl})$  at  $\sim 360 \text{ cm}^{-1}$  and  $\nu(\text{Ti}-\text{O})$  at  $294 \text{ cm}^{-1}$  which is in agreement with data for trigonal-bipyramidal titanium(III) halide complexes with nitrogen-containing ligands [12–14].

The far infrared spectrum (Fig. 4, dotted curve) and the diffuse reflectance spectrum (Fig. 3, dotted curve) of  $\text{TiCl}_3 \cdot \text{THF}$  are similar to those of  $\text{TiCl}_3 \cdot 2\text{THF}$  and  $\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$  indicating the trigonal-bipyramidal configuration of this compound. The reduced value of the magnetic moment (1.14 B. M.) and insolubility in aromatic solvents led us to the conclusion that  $\text{TiCl}_3 \cdot \text{THF}$  is a coordination polymer with chlorine bridges [4]. Its structure may be expressed by the formula



According to *Clark et al.* [15, 19, 21], for six-coordinate complexes the frequencies of metal–chlorine stretching modes are expected in the  $300\text{--}380 \text{ cm}^{-1}$  region, although they are higher for five- or four-coordinate complexes [19, 20]. Furthermore, they predict for  $\text{MX}_3 \cdot 3\text{L}$  [21] two and three metal–halogen stretching modes respectively for *cis* ( $C_{3v}$ ) and *trans* ( $C_{2v}$ ) configurations, respectively. *Alyea et al.* [18] have found that solid titanium(III) chloride shows three absorption bands at  $490 \text{ cm}^{-1}$  (m),  $380 \text{ cm}^{-1}$  (s), and  $290 \text{ cm}^{-1}$  (vs). In the complexes the major absorption bands occur in the range  $340\text{--}380 \text{ cm}^{-1}$  with very little absorption in the  $400\text{--}420 \text{ cm}^{-1}$  region. In the spectra of titanium(III) chloride complexes *Duckworth et al.* [22] assigned the bands between  $400$  and  $421 \text{ cm}^{-1}$  to metal–chlorine stretching modes; these spectra, however, were determined using KBr optics which would not record the absorption below  $400 \text{ cm}^{-1}$ .

In the case of  $\text{TiCl}_3 \cdot 3\text{THF}$  *Clark* [15] reports for  $\nu(\text{Ti}-\text{Cl})$  the values of  $360$  (s),  $331$  (s), and  $300$  (m)  $\text{cm}^{-1}$  and deduced a *trans* configuration for this complex. We observe a different far infrared spectrum for this compound which shows only a single strong band at  $\sim 380 \text{ cm}^{-1}$  that can be attributed to metal–chlorine stretching (Fig. 4, full curve). The latter two of these values were not observed in the spectrum measured by us.

The infrared spectra of all the investigated complexes in the range  $1200\text{--}400 \text{ cm}^{-1}$ , are in fair agreement with those found for  $\text{TiCl}_3 \cdot 3\text{THF}$  by [1, 2, 11] and for  $\text{TiCl}_3 \cdot 2\text{THF}$  by [1], and are typical of the coordinated ligands, because the symmetric ( $909 \text{ cm}^{-1}$ ) and the asymmetric ( $1069 \text{ cm}^{-1}$ ) C–O–C stretching vibrations of free tetrahydrofuran [16] are split and lowered on coordination (Table 1). This proves

Table 1

Shifts the observed  $\nu(\text{COC})$  frequencies [ $\text{cm}^{-1}$ ]

Complex or ligand	$\nu_1$	Shift	$\nu_2$	Shift
THF	909	0	1069	0
$\text{TiCl}_3 \cdot 3\text{THF}$	850	59	1008	61
$\text{TiCl}_3 \cdot 2\text{THF}$	850	59	1007	62
$\text{TiCl}_3 \cdot 2\text{THF} \cdot \text{C}_6\text{H}_6$	850	59	1007	62
$\text{TiCl}_3 \cdot \text{THF}$	827	82	987	82

that coordination to the Ti(III) atom occurs through the oxygen atom. A similar phenomenon is observed in the infrared spectra of the other tetrahydrofuran complexes of transition metal chlorides [11]. No unmodified  $\nu(\text{COC})$  bands are found in the spectra of any of these complexes, and we accordingly conclude that all the available ligand oxygen atoms are coordinated.

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