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# The EPR Spectra of some Chlorotitanium(III) Complexes Containing Aliphatic Alcohols

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*The complexes* $TiCl_3(C_2H_5OH)_4$ *(I),* $TiCl_3(1\text{-}C_3H_7OH)_3$ *(II),* $TiCl_3(1\text{-}C_4H_9OH)_3$ *(III) and* $TiCl_3(2\text{-}C_4H_9OH)_3$ *(IV) provide no observable EPR signals at room temperature. At 77 K (I) and (III) show axial EPR spectra with* $g_\parallel$ *greater than* $g_\perp$*, while the spectra of (II) and (IV) are single absorption lines. The character of the EPR spectra is more consistent with a facial than with a meridional configuration of Cl ligands in a coordination polyhedron.*

## Introduction

In a recent report from our laboratory the preparation of the complexes of titanium(III) chloride with aliphatic alcohols ($C_nH_{2n+1}OH$, n = 1–4) was described and their characterization was attempted [1]. Their susceptibility and electronic spectral data were interpreted in terms of an axial ligand field and spin–orbit coupling. Until now, the EPR spectra were reported only for the complexes with methanol, $[TiCl_{6-x}(CH_3OH)_x]^{(3-x)-}$ and 2-propanol, $[TiCl_2(2\text{-}C_3H_7OH)_4]Cl$ [2, 3]. In the present paper the studies on the EPR spectra of the chlorotitanium(III) complexes containing ethanol, 1-propanol, 1-butanol and 2-butanol $TiCl_3(C_2H_5OH)_4$, $TiCl_3(1\text{-}C_3H_7OH)_3$, $TiCl_3(1\text{-}C_4H_9OH)_3$ and $TiCl_3(2\text{-}C_4H_9OH)_3$ are described.

## Experimental

The complexes $TiCl_3(C_2H_5OH)_4$, $TiCl_3(1\text{-}C_3H_7OH)_3$, $TiCl_3(1\text{-}C_4H_9OH)_3$ and $TiCl_3(2\text{-}C_4H_9OH)_3$ were prepared as described previously [1] by the reaction of $\alpha$-$TiCl_3$ with the corresponding alcohol in a non-coordinating solvent. Since the complexes were extremely sensitive towards oxygen and water, all reactions and manipulations were carried out in an atmosphere of dry nitrogen.

The EPR spectra of polycrystalline solids were recorded on a Varian E-4 spectrometer in X band ($\nu \sim 9.1$ GHz) employing 100 kHz modulation at 295 and 77 K. DPPH was used as a standard for the evaluation of g factors.

## Results and Discussion

The complexes under investigation provide no observable EPR spectra at room temperature because of the short spin–lattice relaxation time. At 77 K, $TiCl_3(C_2H_5OH)_4$ and $TiCl_3(1\text{-}C_4H_9OH)_3$ show axial EPR spectra with $g_\parallel > g_\perp$, while the spectra of $TiCl_3(1\text{-}C_3H_7OH)_3$ and $TiCl_3(2\text{-}C_4H_9OH)_3$ are single absorption lines even at this temperature (Fig. 1, Table I).

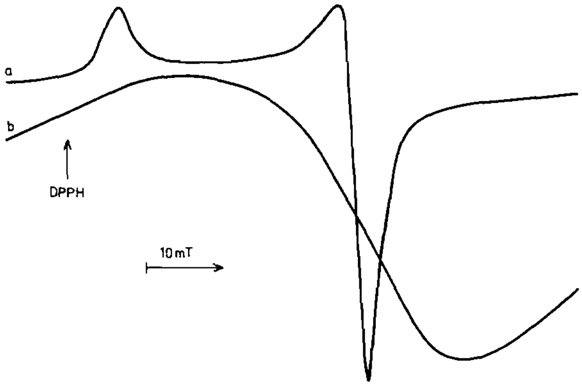

Fig. 1. The EPR spectra of a) $TiCl_3(1\text{-}C_4H_9OH)_3$, b) $TiCl_3(2\text{-}C_4H_9OH)_3$.

TABLE I. The EPR Spectra of Chlorotitanium(III) Complexes Containing Aliphatic Alcohols.

| Complex | $g_\perp$ | $g_o$ | $g_\parallel$ | $\bar{g}$ | $\Delta H/mT^a$ |
|---|---|---|---|---|---|
| $TiCl_3(C_2H_5OH)_4$ | 1.795 | | 1.962 | 1.852 | |
| $TiCl_3(1\text{-}C_3H_7OH)_3$ | | 1.820 | | | 31 |
| $TiCl_3(1\text{-}C_4H_9OH)_3$ | 1.789 | | 1.959 | 1.847 | |
| $TiCl_3(2\text{-}C_4H_9OH)_3$ | | 1.802 | | | 36 |

[a] Peak to peak line width of single line spectra.

Thermogravimetric measurements indicate [4] that in $TiCl_3(C_2H_5OH)_4$ one ethanol molecule is only loosely attached and the structure of this complex is probably $[TiCl_3(C_2H_5OH)_3]C_2H_5OH$. Consequently the composition of the inner coordination sphere of this complex as well as the complexes $TiCl_3L_3$, where L represents an aliphatic alcohol, is $[TiCl_3O_3]$.

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For complexes with the coordination sphere $[TiCl_3O_3]$ two configurations of ligands are possible: either with the meridional arrangement of Cl ligands, as was determined by X-ray structural analysis for $TiCl_3(C_4H_8O)_3$ ($C_4H_8O$ = tetrahydrofuran) [5], or with facial arrangement of Cl ligands.

Assuming the ligands are located on the Cartesian axes, the symmetry of the meridional configuration is $C_{2v}$. The order of the five energy states resulting from the splitting of the $^2D$ term is [6] : $B_1 < A_2 < B_2 < A_1' < A_1''$. For such a system it was derived that $g_{\perp}$ must be greater than $g_{\parallel}$ [6]. Since for $TiCl_3(C_2H_5OH)_4$ and $TiCl_3(1\text{-}C_4H_9OH)_3$ $g_{\parallel}$ was found to be greater than $g_{\perp}$, the $C_{2v}$ local symmetry was rejected for these complexes.

If a facial arrangement of Cl ligands is assumed, the symmetry of the coordination polyhedron becomes $C_{3v}$. For this symmetry three energy states $A_1$, $E'$ and $E''$ with the following wave functions are obtained [7]:

$$\begin{array}{ll} A_1 & |z^2> \\ E' & \left\{\begin{array}{l} \sin\omega|yz> - \cos\omega|xy> \\ \sin\omega|xz> + \cos\omega|x^2 - y^2> \end{array}\right. \\ E'' & \left\{\begin{array}{l} \cos\omega|yz> + \sin\omega|xy> \\ \cos\omega|xz> - \sin\omega|x^2 - y^2> \end{array}\right. \end{array}$$

The order of energy states is $A_1 < E' < E''$. If we assume that the mixing coefficients $\pm \sin \omega$ and $\pm \cos \omega$ are not significantly different from the values $\pm(1/3)^{1/2}$ and $\pm(2/3)^{1/2}$ for the octahedral $d^1$ system with trigonal distortion, the expressions for g factors are [8, 9]:

$$g_{\parallel} = 3\left(\frac{\delta + 1/2\lambda}{S}\right) - 1$$

$$g_{\perp} = \frac{\delta - 3/2\lambda}{S} + 1$$

Here $S = [(\delta + 1/2\lambda)^2 + 2\lambda^2]^{1/2}$, $\delta$ is the trigonal splitting parameter and $\lambda$ is the spin–orbit coupling constant ($\lambda = 154$ cm$^{-1}$ for $Ti^{3+}$). By using $\delta = 1400$ cm$^{-1}$, the values $g_{\perp} = 1.783$, $g_{\parallel} = 1.968$ are in a reasonable agreement with the experimental values of $g_{\perp}$ and $g_{\parallel}$ for $TiCl_3(C_2H_5OH)_4$ and $TiCl_3(1\text{-}C_4H_9OH)_3$. On the basis of these results it can be assumed that the complexes $TiCl_3(C_2H_5OH)_4$ and $TiCl_3(1\text{-}C_4H_9OH)_3$ probably adopt a facial configuration of Cl ligands. The values of $\delta$ are higher than those derived from the susceptibility data [1]. This probably lies in the nature of approximations involved in the models used [7, 8].

The ligand field absorption bands in the electronic spectra of the complexes under investigation are caused by the transitions from the $A_1$ state into the $E''$ state. Since in $C_{3v}$ symmetry the degeneracy of the $E''$ level cannot be removed, the presence of assymmetric bands of d–d transitions in the experimental electronic spectra [1] can be explained by the Jahn–Teller splitting of the excited state $E''$, or by some additional distortion.

The EPR spectra of $TiCl_3(1\text{-}C_3H_7OH)_3$ and $TiCl_3(2\text{-}C_4H_9OH)_3$ are not very informative. Owing to a rapid spin–lattice relaxation at 77 K, only a single line spectrum can be observed. From the similarity of the thermal decomposition curves it was concluded that the structures of $TiCl_3(C_2H_5OH)_4$, $TiCl_3(1\text{-}C_3H_7OH)_3$, $TiCl_3(1\text{-}C_4H_9OH)_3$ and $TiCl_3(2\text{-}C_4H_9OH)_3$ are not significantly different from each other [4]. Hence all these complexes probably adopt a facial configuration of Cl ligands. This assumption is supported by the fact that for all these complexes the rapid spin– lattice relaxation does not allow one to observe the EPR spectra at room temperature, in contrast with the complexes $TiCl_3(C_4H_8O)_3$ and $TiCl_3(CH_3CN)_3$ with meridional arrangement of Cl ligands where the EPR spectra at room temperature can be observed [3].

Considering all the above facts, the character of EPR spectra of the complexes $TiCl_3(C_2H_5OH)_4$, $TiCl_3(1\text{-}C_3H_7OH)_3$, $TiCl_3(1\text{-}C_4H_9OH)_3$ and $TiCl_3(2\text{-}C_4H_9OH)_3$ is more consistent with a facial than with a meridional configuration of Cl ligands. The structure of these complexes can only be established with final validity by X-ray structural analyses.

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