

Electron spin resonance studies on titanium(III) chloride in aqueous 2-methyl-2-butanol (*t*-amyl alcohol)

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On addition of small amounts of water (1% to 2%, v/v) to TiCl_3 (0.02 M, pH 1.4 to 1.8) partially dissolved in *t*-amyl alcohol, an electron spin resonance signal ($g_0 = 1.9589 \pm 0.0002$) with well-resolved superhyperfine structure due to water protons is observed (the coupling constant equals 0.187 ± 0.003 mT). Confirmation of splitting to be due to water hydrogens has been obtained by using D_2O in equivalent experiments. Aqueous solutions of $\text{Ti}_2(\text{SO}_4)_3$, TiBr_3 or TiI_3 (0.01 M to 1.0 M, pH 0.8 to 1.8) saturated with *t*-amyl alcohol (ca. 5%, v/v) give no electron spin resonance signal. Addition of NaCl or LiCl (1.0 M) to these solutions produces a signal identical in hyperfine pattern and close in the value of g factor (1.9580 ± 0.0002) to that for TiCl_3 solution. It is proposed that there are axial alkoxide and chloride ions and four equatorial water molecules in the first coordination sphere of this ESR-active Ti(III) complex ion. Approximate spin concentration measurements, made employing deuterated samples, indicate that maximum ESR signal intensity (at ca. 2% added water) represents only $15 \pm 5\%$ of the nominal Ti(III) that is present.

Bolton and his coworkers¹ reported the first observation of proton hyperfine splitting by coordinated water of the electron spin resonance (ESR) signal of a transition metal complex. This they observed on recording the ESR spectrum of Ti(III) chloride in acidic aqueous *t*-butanol¹.

Although complete assignment of the structure of the Ti(III) species was not made, it was proposed that at least one *t*-butanol molecule and four water molecules were among the ligands. Computer simulation of the splitting of the central line indicated eight equivalent water hydrogens. The tertiary alcohol was, therefore, located axially with water ligands in equatorial positions, e.g., *trans*- $\text{Ti}(\text{H}_2\text{O})_4(\text{ROH})L$. The remaining ligand L was unspecified. The partially resolved hyperfine structure indicated delocalization of the $3d^1$ electron onto the ligands suggesting partially covalent bonding. Hence, further information was needed to complement the data already obtained on the Ti(III) complex ions in aqueous solutions.

Preliminary experiments confirmed the report on the aqueous *t*-butanol system except that $|a_{\text{Ti}}|$ value obtained was 1.82 mT rather than 1.55 mT reported by Bolton *et al.*¹ However, the poor central line resolution led us to survey other tertiary alcohols. The central line splitting pattern showed significantly better resolution in the case of aqueous TiCl_3 saturated with *t*-amyl alcohol and *t*-amyl alcohol con-

taining small amounts of water. Accordingly, all further investigation was focussed on *t*-amyl alcohol containing solvents.

Materials and Methods

Physical measurements

All the spectra were recorded on a Varian E-6S X-band ESR spectrometer operating at 100 kHz modulation. Frozen solution samples were taken in cylindrical quartz cells (5 mm, o.d.). Solution spectra at room temperature were recorded in standard Varian E-248 flat cells.

The variable temperature measurements employed an apparatus based on the Varian V-4502 approach, constructed from Dewar components supplied by Scanco Quartz (California). A controller similar to the Varian V-6040 was modified to use a platinum-platinum resistance sensor (EO-100, 100 Ω) (Rdf. Corp.). The calibration was achieved using a Hewlett-Packard 2802 A thermometer. Samples maintained at $210 \pm 3\text{K}$ ($\text{CHCl}_3\text{-CO}_2$ slush bath) or at $197.5 \pm 3\text{K}$ (powdered dry ice) were continuously monitored by the digital thermometer probe with the sample adjacent in the coolant.

The g -factors are quoted relative to diphenylpicrylhydrazyl (DPPH) using a solid sample (linewidth $\Delta H_{\text{p-p}} = 0.10 \pm 0.01$ mT, $g = 2.0036 \pm 0.0002$) that was permanently maintained in a dual cavity assembly (Varian E-232). The field shift between the two

cavities had been carefully measured. DPPH powder, to be used as a primary standard in determining g -factors, was prepared by drying at ca. 340 K for 4-5 h. A weighed and powdered sample of DPPH reagent (Aldrich) was used as received. Hyperfine splitting constants were determined relative to a solution of potassium nitrosodisulphonate (Fremy's salt) for which $g = 2.0055 \pm 0.0001$ and the nitrogen hyperfine splitting, $a_N = 1.309 \pm 0.001 \text{ mT}^2$.

Frozen solutions (measured only at 77 K) were obtained by rapidly quenching the sample in liquid nitrogen, maintaining the sample in the Varian E-246 insert Dewar. Details of temperature variation experiments are included with the results.

Spin concentrations

Spin concentrations were measured by a comparison of the derivative signal for the unknown with that for a standard sample containing a stable paramagnetic species. Such a method compensates for variations due to instrument drift when spectra are being measured over an extended period of time. The cavity Q -factor was kept constant by using the same solvent and same flat cell for both standard and unknown. However, a limitation on the accuracy of the comparison is imposed, by the necessity of removing and repositioning flat cell while changing the sample. The spin concentration (C) is given by the following equation,

$$C = K \frac{A_x}{A_{st}} \cdot \frac{g_{st}^2}{g_x^2} \cdot \frac{S(S+1)_{st}}{S(S+1)_x}$$

where x indicates the unknown sample and st indicates the standard, A is the area under absorption curve (arbitrary units as long as they are the same for the unknown and the standard). S and g are the spin quantum and g -factor of the paramagnetic species, respectively.

K is mainly an instrumental constant and may be defined as

$$K = \frac{R_x(\text{scan}_x)^2}{R_{st}(\text{scan}_{st})^2} \cdot \frac{G_{st} M_{st}}{G_x M_x}$$

where scan is the horizontal scale; G is the gain; M is the modulation amplitude; and

$$R = \frac{\sum D_i}{D_k}$$

where D_k is the degeneracy of the line for which the area was measured and $\sum D_i$ is the sum of the degeneracies of all the lines in the spectrum.

The C relation applies provided that the same incident microwave power is used, there is no power saturation or unknown, and the same sample cell,

solvent and temperature are used. The areas and concentrations were evaluated by means of a desk calculator that performed an integration, with baseline correction, and computed the concentrations from the C expression.

Further details of the measuring procedure and associated controls for precision and accuracy are given by Premović³.

Preparation of titanium(III) solution and complexes

Ti(III) solution was prepared by dissolving the metallic sponge (Fisher) with gentle heating in approximately 1-2 M hydrochloric or sulphuric acid. An N_2 atmosphere was employed to minimize oxidation of Ti(III) ion. Alternatively, Fisher reagent grade Ti(III) chloride solution (20%) or BDH reagent grade Ti(III) sulphate solution (15%) was used directly without qualitative change in any of the results reported in this paper.

Ti(III) bromide and iodide solutions in aqueous acid were also prepared using the following methods:

(I) Ti(III) carbonate was precipitated from Ti(III) chloride or sulphate solution and thoroughly washed with water until no further chloride or sulphate ion was detected. Ti(III) carbonate was then dissolved in conc. hydrobromic or hydroiodic acid and diluted to the desired concentration⁴.

(II) Dilute reagent grade Ti(III) chloride or sulphate solution was transferred to the top of an ion-exchange column (i.d. 50-80 mm) containing 150 g (dry) 100-200 mesh Dowex AG 50-X12 cation exchange resin. The column was loaded with the metal ion by passing the dilute solution until the effluent had the violet colour. The column was then washed free of chloride or sulphate by extended washing with oxygen-free distilled water. The Ti(III) was then immediately removed from the column by a 2 M solution of the desired acid.

(III) This method was employed for preparation of Ti(III) iodide solution only. Addition of a concentrated solution of potassium iodide to the blue solution of Ti(III) chloride in methanol precipitated potassium chloride⁵. Methanol was removed by several evaporations to dryness employing water as the solvent in the second and subsequent cycles. The solution was then filtered.

The concentrations of anions were varied by either addition of the Fisher reagent grade salts (sodium chloride, potassium bromide, potassium iodide and sodium sulphate) or concentrated acids (37.5% HCl, 48% HBr, 56% HI, 98% H_2SO_4). For study in heavy water, the appropriate diluted Ti(III) solution was added to heavy water (Merck 98%) such that

the final sample contained from 1% to 98% of water as required.

Reagent grade (either Fisher or Aldrich) alcohols were used without further purification.

The final concentration of Ti(III) ions was determined volumetrically by titration with a ceric sulphate solution using *o*-phenanthroline as indicator. Typical values obtained for either stock solutions or solutions prepared by dissolving the metal lay in the range 95-97%.

Results and Discussion

ESR observations

The concentration range of *t*-amyl alcohol in water was limited by the solubility of the alcohol in water. In the acidified salt solutions that were used, saturation occurred at approximately 5 volume per cent *t*-amyl alcohol. As a result, essentially two media could be conveniently employed: (a) aqueous solutions saturated with alcohol, and (b) alcohol containing 1-2% water.

(a) *Aqueous solution*—When aqueous solution of $\text{Ti}_2(\text{SO}_4)_3$, TiI_3 or TiBr_3 (0.02 M; pH, 1.8) was saturated with alcohol no signal was observed. However, a saturated (0.02 M) TiCl_3 solution provided the ESR spectrum shown in Fig. 1. Addition of a molar concentration of NaCl or LiCl to the Ti sulphate, bromide or iodide sample produced an ESR signal identical in hyperfine pattern and g -factor. In water alone at pH 1.0, the dominant $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ species had no detectable ESR signal. Clearly, the complex ion must contain both *t*-amyl alcohol and chloride ion ligands.

(b) *t*-Amyl alcohol solution—Anhydrous TiCl_3 was only very slightly soluble in the pure alcohol. In any event no signal was recorded from the supernatant alcohol. On addition of small amounts of water, TiCl_3 partially dissolved and an ESR signal was obtained that attained maximum intensity at approximately 2% added H_2O . Alternatively, concentrated aqueous TiCl_3 could be added directly to the alcohol. Identical samples prepared using $\text{Ti}_2(\text{SO}_4)_3$ or

TiBr_3 gave no signal. A 1% (v/v) solution having TiCl_3 concentration approximately 0.02 M gave a spectrum similar to that of the aqueous sample, again with resolved hyperfine splitting (Fig. 2). The hydrogen coupling constant in alcohol was 0.187 ± 0.003 mT. Bolton reported a value of 0.180 mT in aqueous solution containing *t*-butanol¹. The equally spaced splitting pattern showed seven of the nine lines expected for eight equivalent hydrogens. The $m_l = 3/2$ line showed the best resolution of the super-hyperfine multiplets (Fig. 3). Second derivative presentation, not available on the E6S system, could reveal the wing lines. Similar resolution was achieved using 1% water in the acetylenic alcohol $\text{CH}_3 \equiv \text{C} - \text{COH}(\text{CH}_3)\text{CH}_3$ with $a_H = 0.185 \pm 0.003$ mT. The aqueous *t*-amyl alcohol system provided poorer resolution (Fig. 1), but later improved spectra were obtained using an aqueous solution saturated with the six-carbon tertiary alcohol $(\text{CH}_3\text{CH}_2)_2\text{COH}(\text{CH}_3)$, $a_H = 0.185 \pm 0.003$ mT. The g -factor in the *t*-amyl alcohol solvent, 1.9589 ± 0.0002 , was also measurably higher than

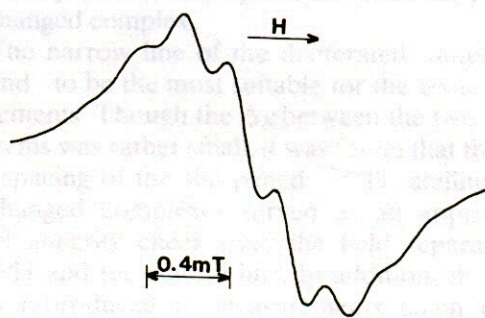


Fig. 2—ESR spectrum of $[\text{Ti}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_{11}\text{O}^-)\text{Cl}]^+$ ions [TiCl_3 (0.02 M) in *t*-amyl alcohol containing 1% (v/v) H_2O].

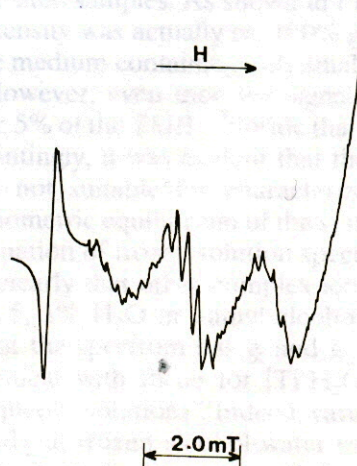


Fig. 3—ESR spectrum of $[\text{Ti}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_{11}\text{O}^-)\text{Cl}]^+$ ions, solution as in Fig. 2, showing fine structure of $^{47,49}\text{Ti}$ satellite line ($m_l = 3/2$).

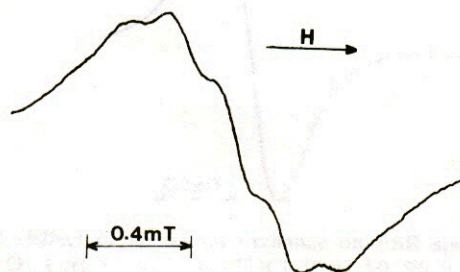


Fig. 1—ESR spectrum of $[\text{Ti}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_{11}\text{O}^-)\text{Cl}]^+$ ions [TiCl_3 (0.02 M) in H_2O containing 5% (v/v) *t*-amyl alcohol, pH 1.8].

that for the sample in the aqueous phase, $g_0 = 1.9580 \pm 0.0002$.

(c) *Deuterated solvent*—Confirmation of the splitting to be due to water hydrogen was obtained by using D_2O in equivalent experiments. In Fig. 4a, the spectrum of an aqueous phase sample containing just 5% (v/v) D_2O showed nearly complete loss of the hyperfine splitting. At 10% D_2O the signal showed no trace of hyperfine structure, but retained virtually the same overall signal linewidth. Even at 33% D_2O (Fig. 4b) the measured linewidth (0.62 mT) was further reduced only by 11%. In 98% D_2O (Fig. 4c) the linewidth was reduced to 0.30 mT indicating significant unresolved hyperfine structure in the D_2O/H_2O mixtures. The effect of a small amount of D_2O (e.g. 5%) on the linewidth may ap-

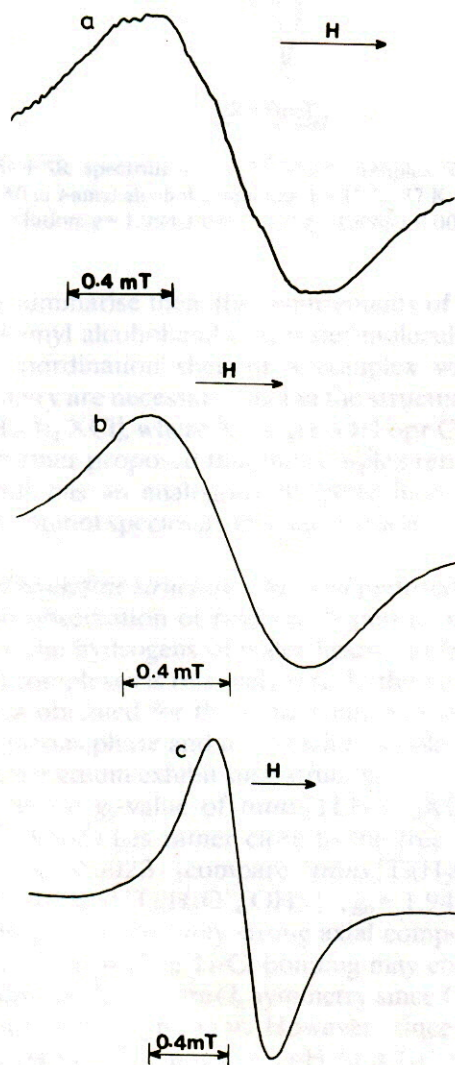


Fig. 4—Effect of deuterium exchange on ESR spectrum of $[Ti(H_2O)_4(C_5H_{11}O^-)Cl]^+$ ions $[TiCl_3 (0.02 M), 5\% (v/v) t\text{-amyl alcohol}]$ in: (a) 20:1 mixture of $H_2O:D_2O$; (b) 2:1 mixture of $H_2O:D_2O$; and (c) $D_2O (98\%)$.

pear to be too great at first glance. However, exchange of a single deuterium alters the coupled spins to an odd number, exactly interposing a spectrum of identical splitting with an even number of lines. Rapid effective loss of resolution occurs. Combination of 8, 7, 6 and 5 protons, etc., in a range of partially exchange complexes present at 33% D_2O provided a signal with no hyperfine splitting (Fig. 4b).

As expected, loss of hyperfine structure also occurred when D_2O was used to prepare the complex in alcoholic solution. Solid $TiCl_3$ (0.1 g) was suspended in 20 ml of *t*-amyl alcohol-OD (approximately 75-85% minimum $C_5H_{11}OD$ prepared by equilibrating with D_2O) and 0.2 ml D_2O (98%) was added. After thorough agitation, the undissolved $TiCl_3$ was allowed to settle. The resultant spectrum had a single narrow line ($\Delta H_{p-p} = 0.30$ mT). Once again, if 20 ml of $C_5H_{11}OH$ was employed (e.g., approximately 1:1, $H_2O:D_2O$ is created after exchange) the linewidth increased to 0.60 mT. In fact, the spectrum was then identical with that in Fig. 4b (save for the shift in g value) showing the same remarkably smooth absorption curve for the partially exchanged complex.

The narrow line of the deuterated samples was found to be the most suitable for the g -value measurements. Though the Δg between the two solvent systems was rather small, it was found that the regular spacing of the sharpened $^{47,49}Ti$ satellite in the exchanged complexes served as an approximate field linearity check over the field separation of DPPH and the central line. In addition, the g -shift was reproduced in measurements taken months apart.

(d) *Concentration of active species*—Approximate intensity measurements were best made employing deuterated samples. As shown in Fig. 1 and Fig. 2, the intensity was actually ca. 100% greater in the alcoholic medium containing only small amounts of water. However, even then the signal represented only $15 \pm 5\%$ of the $Ti(III)$ chloride that was present. Disappointingly, it was evident that the active species was not suitable for characterization of the complexiometric equilibrium of the system.

Examination of frozen solution spectrum at 77 K showed clearly that other complex ions were present (Fig. 5, 1% H_2O in *t*-amyl alcohol). It may be noted that the spectrum has g_0 and g_1 values almost identical with those for $[Ti(H_2O)_6]^{3+}$ ion in frozen aqueous solutions⁶. Indeed, variable temperature study of frozen alcohol-water solution again showed a sharp disappearance of the signal in the region 193 K to 213 K, as the ESR signal associated with $[Ti(H_2O)_6]^{3+}$ ions³.

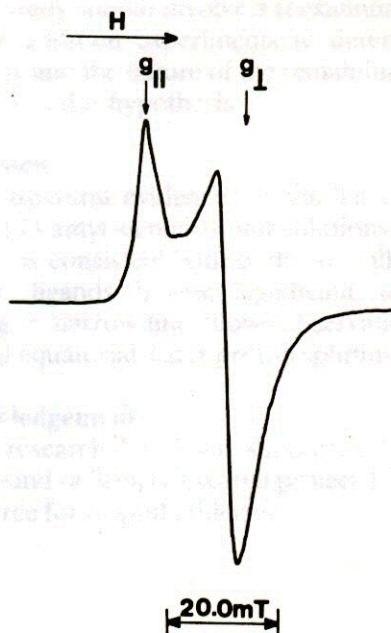


Fig. 5—ESR spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex ions $[\text{TiCl}_3$ (0.02 M) in *t*-amyl alcohol containing 1% H_2O , 77 K, frozen solution: $g = 1.994 \pm 0.002$ and $g = 1.896 \pm 0.001$]

To summarise then, the requirements of chloride ion, *t*-amyl alcohol and four water molecules in the first coordination shell of a complex with axial symmetry are necessarily met in the structure, *trans*- $[\text{Ti}(\text{H}_2\text{O})_4 \text{XCl}]$, where $\text{X} = \text{C}_5\text{H}_{11}\text{OH}$ or $\text{C}_5\text{H}_{11}\text{O}^-$. It is further proposed that the complex reported by Bolton¹ has an analogous structure incorporating one *t*-butanol species in an axial position.

Metal hyperfine structure and axial perturbation

The observation of resolved hyperfine structure due to the hydrogens of water ligands in transition metal complexes is relatively rare. In this study ESR spectra obtained for the same complex ion both in the aqueous phase and in a much less polar tertiary alcohol medium exhibit such structure.

Since the g_0 -value of *trans*- $[\text{Ti}(\text{H}_2\text{O})_4 \text{XCl}]$ complex (1.9585) lies rather close to the free electron value of 2.0023 (compare *trans*- $[\text{Ti}(\text{H}_2\text{O})_4 \text{F}_2]^+$, $g_0 = 1.9467$ and $[\text{Ti}(\text{H}_2\text{O})_4(\text{OH})_2]^+$, $g_0 = 1.941$ ⁸), one can propose a relatively strong axial component of the ligand field. The Ti-Cl bonding may contribute to distortion from pure O_h symmetry since Cl^- is an accepted strong π -donor. However, since neither the $[\text{Ti}(\text{H}_2\text{O})_5 \text{Cl}]^{2+}$ nor the $[\text{Ti}(\text{H}_2\text{O})_4 \text{Cl}_2]^+$ complex ion³ seems to give an observable ESR spectrum at room temperature, an important and specific role is indicated for the *t*-amyl alcohol in the axial position. In analogy to VO^{2+} , we could expect a much stronger axial perturbation (by an alkoxide axial ligand) in

trans- $[\text{Ti}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_{11}\text{O}^-)\text{Cl}]^+$ than that in *trans*- $[\text{Ti}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_{11}\text{OH})\text{Cl}]^2$. One may suggest that some multiple bond character between Ti(III) and the alkoxide axial ligand, analogous to that for the vanadium-oxide bond, may exist. The increased negative charge on the oxygen would also facilitate more covalent σ - and π -bonding.

In summary, it is proposed that simultaneous effects of both the alkoxide group and chloride ion lead to the rather strong axial perturbation.

The observation of discrete hydrogen splitting in the ESR spectrum requires that both the aquation and proton exchange rates be slow compared to the frequency separation of the hyperfine components. In Fig. 2, especially, we note that line broadening due to either exchange process has not become significant, i.e., mean lifetime of the hydrogen in the aquo ligand is of the order 10^{-6} s (ref. 9). Previous work based on NMR technique indicates that $\tau_m = 5 \times 10^{-6}$ s for an alcohol ligand in the TiCl_3 complex in methanol¹⁰. Any destabilizing steric effect of the alcohol is then not reflected in a marked increase in lability of the water ligands.

At high acid concentration, loss of hyperfine splitting does occur in spectra recorded in both aqueous and alcohol media. In alcohol medium (Fig. 3), with 1% (v/v) added aqueous TiCl_3 (20% technical stock TiCl_3), we recorded a nominal pH of 0.8 that has no direct correspondence with aqueous samples. However, addition of a further 3% (v/v) HCl completely eliminated the hyperfine structure.

In water, hyperfine structure disappeared below pH 1.4 although the complex could be observed as a single line at pH values as low as 0.8. At pH 1.0 it was possible to work at TiCl_3 concentrations in the range 0.01–1.0 M. No further line broadening due to spin-spin exchange effects was observed. These observations are a basis for study of proton exchange rates of aquo ligands. For example, the $a_{\text{H}}(\text{OH})$ splitting in the CH_2OH species (0.096 mT) was lost at pH 1, leading to a value of acid-catalysed exchange $k = 1.8 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ (ref. 10).

Finally, Waters and Maki recorded a spectrum of Ti(III) chloride in dry methanol after addition of one equivalent of methoxide ion¹¹. The narrow line, Ti hyperfine coupling (1.82 mT) and isotropic g -value (1.9532) that they reported are clearly comparable to the parameters obtained in the tertiary alcohol/1% H_2O solvent. Goldberg and coworkers published spectra of TiCl_3 in methanol containing small amounts of water¹². The spectral parameters of the principal line were: $g_0 = 1.9548$, $a_{\text{Ti}} = 1.835$ mT and linewidth (peak to peak), $\Delta H_{p-p} = 0.29$ mT.

The axial perturbation due to alkoxide and chloride ligands may be common to all these systems.

Further study should involve a reexamination of the alkoxide addition experiments to determine their generality and the nature of the remaining ligands in order to test this hypothesis.

Conclusion

The structural evidence for the Ti(III) complex formed in *t*-amyl alcohol-water solutions containing Cl^- ion, is consistent with both axial alkoxide and chloride ligands having significant σ - and π -bonding. A narrow line allows observation of well-resolved equatorial water proton splitting.

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