Electron Spin Resonance Studies and Electronic Structure of \(\text{trans-}[\text{Ti(H}_2\text{O)}_6\text{F}_2]^+\)

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At pH 1.0-1.6 aqueous titanium(III) solutions containing added fluoride ion exhibit e.s.r. signals of \(\text{trans-}[\text{Ti(H}_2\text{O)}_6\text{F}_2]^+\), \(g = 1.9460 \pm 0.0005, \alpha N = 17.9 \pm 0.2\). The variation in the intensity of the optical and e.s.r. spectra with added fluoride ion indicates >90% conversion to the complex at \([\text{Ti}]:[\text{F}] = 1:2\). The \textit{trans} geometry of the complex is established from the spectrum in \(\text{D}_2\text{O}, \alpha = 1.2:1\) triplet with \(\alpha N = 7.5 \pm 0.5\), and from the axial symmetry (\(D_2\alpha\)) apparent in the frozen solution spectrum, \(g = 1.968, g = 1.932\).

The optical spectrum shows two bands assigned to the \(\delta B_{xz} \rightarrow \delta B_{xy}\) (15 200 cm\(^{-1}\)) and \(\delta B_{xz} \rightarrow \delta B_{x y}\) (23 300 cm\(^{-1}\)) transitions. Calculations based on the e.s.r. and optical spectra suggest covalent character in the in-plane \(\pi\) and \(\sigma\) bonding of the complex.


A des pH allanti de 1.0 à 1.6, des solutions aqueuses de titan(III) contenant des ions fluorures ajoutés, montrent un signal r.p.e. du \(\text{Ti(H}_2\text{O)}_6\text{F}_2]^+\) -\(\text{trans}, g = 1.9460 \pm 0.0005, \alpha N = 17.9 \pm 0.2\). On note une variation de l'intensité des spectres optique et r.p.e. lorsque l'on ajoute des ions fluorures; cette variation indique que la conversion vers le complexe est plus grande que >90% lorsque la concentration de \([\text{Ti}]:[\text{F}] = 1:2\). On a établi que le complexe possède la géométrie \textit{trans} en se basant sur le spectre dans le \(\text{D}_2\text{O}\) alors qu'on observe un triplet 1:2:1 avec \(\alpha N = 7.5 \pm 0.5\) et aussi sur l'existence d'une symétrie axiale (\(D_2\alpha\)) observée pour le spectre de la solution congelée \(g = 1.968, g = 1.932\).

Le spectre optique montre deux bandes qui ont été assignées aux transitions \(\delta B_{x z} \rightarrow \delta B_{x y}\) (15 200 cm\(^{-1}\)) et \(\delta B_{x z} \rightarrow \delta B_{x y}\) (23 300 cm\(^{-1}\)). Des calculs basés sur les spectres r.p.e. et optique suggèrent un caractère covalent pour les liaisons \(\pi\) et \(\sigma\) dans le plan du complexe.

[Traduit par le journal]

Introduction

Through analysis of the e.s.r. spectra of titanium(III) complexes considerable information concerning the nature of the bonding can be obtained. Provided that the orbital angular momentum is quenched sufficiently by the effects of the coordinating ligands, the 3d\(^1\) configuration of titanium(III) gives rise to an e.s.r. signal. Analogous systems are found in the \(\text{VO}^2^+\) ion 3d\(^1\) and in the case of copper(II) where a "hole" in the d shell occurs. Detailed e.s.r. studies on complexes of the latter two species have been extensively reported. However, many fewer comprehensive examinations of titanium(III) complexes have been published (1-6).

Several accounts describing the spectrum of the \(\text{[Ti(H}_2\text{O)}_6\text{F}_2]^+\) ion, 1, have appeared. Garif'yanov and Semenova (1b) prepared green hydrated complexes \(\text{[Ti(H}_2\text{O)}_6\text{F}_2]^+\) which exhibited an intense slightly asymmetric resonance line \((g = 1.946 \pm 0.001, \text{linewidth 20 G})\) over the concentration range from 0.01 to 0.001 M titanium(III). Assignment of species as the complex 1 was made without any detailed optical or other experimental study. Watera and Maki (2) briefly referred to preparation of the paramagnetic complex, 1, in aqueous solution, in conjunction with a report on \(\text{[Ti}]\) and \(\text{[T]}\) hyperfine structure in the \(\text{[Ti(OH)}_3]^2+\) spectrum. Of particular note are the references in both of these studies to a strong axial perturbation by the coordinating ligands. Such an axial perturbation creates a well-separatated orbital singlet ground state and a long spin-lattice relaxation time. The result is a relatively narrow line and a much reduced g-tensor anisotropy in this complex. Olegov has reported calculation of the electronic energy levels of a series of titanium(III) complexes, and speculated on the assignment of the e.s.r. absorption in the aqueous titanium(III) solution containing added F\(^-\) ion as being \([\text{Ti(H}_2\text{O)}_6\text{F}_2]^+\) (T).

In the present study, the structure of the paramagnetic complex in such solutions is firmly established as the \(\text{trans-}[\text{Ti(H}_2\text{O)}_6\text{F}_2]^+\) ion on
the basis of detailed e.s.r. studies in H₂O and D₂O. A simple theory of the electronic structure of the complex is developed that is consistent with its observed physical properties.

**Experimental**

All spectra were recorded on a Varian E-6S X band e.s.r. spectrometer operating at 100 kHz modulation. Samples were contained in standard Varian E-248 aqueous solution cells.

Sample preparation was as previously described (19). The titanium(III) solutions were prepared by dissolving the metallic sponge (Fisher) with gentle heating in approximately 1 M HCl or H₂SO₄. An N₂ atmosphere was employed to minimize oxidation of titanium(III) ion. Alternatively Fisher Reagent titanium(III) chloride solution (20%) was used directly without qualitative change in any results. Titanium(III) solutions in aqueous acid containing fluoride or bromide as the anion were prepared by dissolving titanium(III) carbonate in the appropriate concentrated acid (HBr or HF) and diluting to the desired concentration. Titanium(III) carbonate was prepared by the method of Semenova (15). In preparing solutions of the Ti₂(H₂O)₆F₂⁺ complex by addition of NaF or KF, pH adjustment was made by addition of the appropriate concentrated acid. For study in heavy water, concentrated TICl₃ solution was added to D₂O (Merck) such that the sample contained 98% D₂O.

The g factors are quoted relative to DPPH, g = 2.0036, employing a Varian E 232 dual cavity assembly in which the field shift between the cavities had been carefully determined. The integrated intensity of the 1st derivative signal was used to calculate the absolute concentration of the paramagnetic species by reference to standard samples of Cr(H₂O)₆⁺⁺, Cr(NH₃)₅⁺, MoO₃(H₂O)₅⁺⁺, and VO(H₂O)₅⁺⁺. Approximate digital calculation was used to determine the integrated intensity of the signal (3). Frozen solutions were prepared by rapidly quenching the sample in liquid nitrogen, maintaining the sample in the Varian E-248 insert Dewar.

The u.v. and visible spectra were recorded on a Cary Model 17 instrument.

**Results**

By adding slightly more than 2 equiv. of fluoride ion (aqueous HF, KF, or NaF) to a violet solution of the Ti(H₂O)₆F²⁺ ion prepared from the sulfate, chloride, or bromide (0.1 M) we obtained a green solution that exhibited a rather broad e.s.r. absorption signal. One can discern the presence of unresolved hyperfine structure compatible with a triplet (1:2:1) splitting, Fig. 1e. When prepared in D₂O by the same route, the e.s.r. signal now showed a distinct triplet splitting through interaction with two equivalent ¹⁹F nuclei, thus indicating the stoichiometry titanium(III):fluoride of 1:2. Spectral parameters for this complex are given in Table 1. At higher gain, the satellite

![Graph](https://via.placeholder.com/150)

**Fig. 1.** Electron spin resonance spectra of TiF₃⁺ ions in aqueous solution (pH 1.0): (a) TiCl₃ (0.02 M), NaF (0.06 M) in H₂O, 25°C; (b) TiCl₃ (0.02 M), NaF (0.06 M) in D₂O, 25°C; (c) TiCl₃ (0.01 M), NaF (0.03 M) in H₂O, 25°C; (d) TiCl₃ (0.06 M) in D₂O, 25°C.

lines from ¹⁹F and ³⁵Ti interaction were evident in both spectra, and revealed the same fluorine hyperfine splitting.

The pH dependence of the intensity of the e.s.r. absorption is shown in Fig. 2 for a 0.01 M solution derived from TiCl₃. From a constant maximum level under acidic conditions (pH 1.0–1.6) the signal steadily diminishes until it is no longer observed at pH 3.5.

**Table 1.** Electron spin resonance data for trans-[Ti(H₂O)₆F²⁺]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ω₁</td>
<td>1.958 ± 0.002</td>
</tr>
<tr>
<td>Ω₂</td>
<td>1.912 ± 0.002</td>
</tr>
<tr>
<td>Ω₃</td>
<td>1.940 ± 0.0005</td>
</tr>
<tr>
<td>σ₁</td>
<td>17.9 ± 0.2 G</td>
</tr>
<tr>
<td>σ₂</td>
<td>7.5 ± 0.5 G</td>
</tr>
<tr>
<td>σ₃</td>
<td>0.2 - 0.4</td>
</tr>
</tbody>
</table>

*Calculated = 1.944; by expression 13, Measured from [TiCl₃·2H₂O]⁺.*
Fig. 2. pH dependence of proposed TiF₆³⁺ ion. Upper curve, e.s.r. signal intensity: □, H₂O; ■, D₂O, relative to reading at pH 1.0. Lower curve, absorbance at 650 nm; ○, relative to reading at pH 1.0. TiCl₃ = 0.02 M, NaF = 0.05 M.

Fig. 3. Optical spectrum of TiF₆³⁺ in aqueous solution at pH 1.5; TiCl₃ (0.1 M), NaF (0.25 M).

In the pH range 1.0-2.5 the green aqueous solution derived from titanium fluoride, chloride, bromide, or sulfate exhibited the same optical spectrum in the presence of 2.5-4.0 equiv. of fluoride ion, with maxima at 430 nm (ε ≈ 3.4) and 660 nm (ε ≈ 2) (see Fig. 3). The decay in the intensity of these absorptions smoothly followed the decay of the e.s.r. signal to pH 2.5 (Fig. 2). Such behavior indicates an identity between the complex responsible for the green color and the paramagnetic species. Beyond pH 2.5, turbidity due to the onset of precipitation rendered optical readings unreliable. However the e.s.r. signal, though diminishing, persisted to pH 3.3 with sharp precipitation occurring at pH > 3.5. Note that in the presence of fluoride ion such samples no longer exhibited the [Ti(H₂O)₆F₆]³⁺ e.s.r. signal normally observed in the pH region 1.0-3.5 (18). Therefore, it is likely that fluoride ion remained coordinated to titanium(III) ions undergoing hydrolysis, for example reaction 1.

[1] [Ti(H₂O)₆F₆]³⁺ + OH⁻ ⇌ [Ti(H₂O)₅F₅(OH)]⁻

Qualitatively, precipitation produced a rose- red solid in contrast to the brown-black mass observed in the hydrolysis of TiCl₃ solution.

Variation of the e.s.r. signal intensity, Fig. 4b, indicated that [Ti(H₂O)₆F₆]³⁺ was one of the most stable complexes in solution. A relatively sharp breaking point was observed near a ratio of 1:2, and the depression of e.s.r. signal intensity with further increase in fluoride ion was gradual. Measurement of the integrated intensity of the maximum signal (see Experimental) indicated that 100 ± 10% of the titanium(III) was in the complex. Changes in absorbance at 430 and 660 nm, Fig. 4a, were compatible with the e.s.r. observations, though now loss of intense Ti(H₂O)₆F₆ bands was being monitored. At a mole ratio higher than 1:2 we observe a small shift of the 430 nm band to higher wavelength (450 nm) with 10% higher extinction coefficient. This observation is consistent with either significant population of higher complexes (I), or a second coordination shell effect of fluoride ion.

The evidence for Ti(H₂O)₅F₅⁺ is in good agreement with the conclusions of other workers (1, 9, 10) and at variance with the experimental results of Glebov (7). The e.s.r. spectrum obtained from TiCl₃ in D₂O on addition of ammonium fluoride at a 1:1 mole ratio (Glebov's conditions for the supposed [Ti(H₂O)₅F₅⁺] species in H₂O) again shows the symmetrical 1:2:1 triplet, Fig. 1d. Therefore the species present must actually be [Ti(D₂O)₅F₅⁺]. Of some interest is the markedly lower resolution of the triplet splitting in the Ti⁺⁻NH₄⁺ sys-
system, relative to the higher resolution shown in Fig. 1b for a Ti$^{4+}$-NaF-D$_2$O sample. When titanium(III) concentration was varied from 0.01 to 0.1 M in the presence of NH$_4$F, the line broadening persisted, indicating the effect was not due to concentration dependent relaxation processes. Since spatially NH$_4^+$ exactly replaces an H$_2$O$^+$ unit in water structure (11), we tentatively attribute the effect to association of ammonium ion with the complex in the second coordination sphere. Some delocalization of unpaired spin density to the second coordination sphere may provide additional hyperfine splitting.

The spectrum of a frozen solution of TiCl$_3$-NaF in H$_2$O is shown in Fig. 1c (Table 1). From the slight distortion of the linewidth, we conclude axial symmetry for the complex with much reduced g-tensor anisotropy and $^{19}$F hyperfine tensor anisotropy. The values of $g_\perp$ and $g_\parallel$ (Fig. 1c) are assigned as the maximum limits of the anisotropy apparent in the nearly isotropic line that is observed (12). The calculated $g$ factor is found to be in reasonable agreement with the isotropic $g$ factor measured at room temperature.

**Structure Assignment**

The e.s.r. signal arises from the [Ti(H$_2$O)$_4$-F$_3$]$^+$ complex ion, and this species is sufficiently stable to be the predominant form of titanium(III) in solution at [Ti$^{3+}$$]$:[F$^-$$]=1:2.

The equivalence of the two fluoride ligands shown by the single h.f.s. constant, and the axial symmetry apparent from the frozen solution spectrum are only consistent with two axial fluoride ion ligands and four water molecules in the equatorial plane. The fluoride ion dependence of the e.s.r. spectrum (Fig. 4b) indicates that higher complexes of the type [Ti(H$_2$O)$_4$-F$_3$]$^{3+}$$^+$ do not provide observable e.s.r. signals. The $trans$ complex will have a well-separated orbital singlet resulting from a strong axial perturbation and leading to the requisite long spin–lattice relaxation time for the observation of the spectrum. Nonappearance of signals from the other possible ions [Ti(H$_2$O)$_4$-F$_3$]$^{3+}$$^+$ is then direct confirmation of the presence of two unpaired electrons in ground states where the degeneracy is only slightly lifted by field distortions providing short spin–lattice relaxation times, and extremely broad resonance lines.

**Discussion**

The symmetry of the $trans$-[Ti(H$_2$O)$_4$F$_3$]$^+$ ion is $D_4h$. We propose that the ground electronic state is $^2B_2g$ (unpaired electron in $d_{3z^2}$ orbital). The e.s.r. spectrum provides direct confirmation of this assignment when the available alternative energy levels are considered.

If the electron were in an $^2E_2$ state ($e_g^+1$ ($d_{3z^2}$) and $e_g^+2$ ($d_{xy}$) orbitals), the degeneracy
probably only slightly split by field distortion
would result in a short spin–lattice relaxation
time and a broad resonance line. Note here the
line width (D_{1/2}) at 25 °C is only 5 G.

Next, for the $^2B_{3g}$ state ($b_{x}^{*}$ ($d_{xy}$, $d_{yz}$) orbital) we
would expect larger isotropic proton hyper-
fine splitting from the water ligands through σ
bonding involving the $b_{y}^{*}$ orbital and the $a_{1}$
($H_{2}O$) orbitals. Also one might expect $g_{1}$ to be
higher than the observed value (1.932), since the
$^2H_{3g} ightarrow ^2E_{g}$ electronic transition would be rel-
tively higher in energy compared to $^2B_{3g} ightarrow ^2E_{g}$.

In the $^2A_{1g}$ state ($a_{1}^{*}$ and $a_{2}^{*}$ orbitals; $d_{4z^2}$, $4s$) we would expect a higher isotropic h.f.s.
constant for fluorine nuclei through the en-
hanced σ bonding. In addition the h.f.s. for
thulium should be higher. In $D_{4h}$ symmetry the $d_{4z^2}$
and $4s$ orbitals belong to the same irreduc-
ible representation and a direct contribution of
spin density at the metal nucleus is allowed. For the
$^2D_{3g}$ state, we would expect $g_{1}$ to be very
close to 2.0023 since the $B_{1g}$ and $B_{2g}$ states cannot
mix with the ground state of $A_{1g}$ symmetry under the perturbation of the angular
momentum operator. The $g_{1}$ value of the ground state would also be
closer to 2.0023 since the $^2A_{1g} ightarrow ^2E_{g}$ transition
will be expected to be high in energy.

Finally, we consider the possibility of the un-
paired electron being in any other metal orbital
to be highly unlikely in view of the expected high-
energy of such states.

We now proceed to examine the assigned
ground state $^2B_{3g}$ in more detail. Only states of
$B_{1g}$ and $E_{g}$ symmetry can mix with this ground
state under perturbation of the angular
momentum operator. Therefore we need consider only
molecular orbitals belonging to the represen-
tations $b_{1}^{*}$, $b_{2}^{*}$, $a_{1}^{*}$, and $e_{1}^{*}$. The relevant anti-

bonding MO's are

2. $b_{1}^{*} = a_{1}d_{xy} - \frac{1}{2} a_{2} [p_{x}^{2} + p_{y}^{2} - p_{z}^{2}]$

3. $b_{2}^{*} = a_{2}d_{x^{2}-y^{2}} - \frac{1}{2} a_{2} [a_{x}^{2} + a_{y}^{2} + a_{z}^{2} - a_{x}^{*}]$

4. $e_{1}^{*} = e_{dx^{2}} - \frac{1}{2} \sqrt{3} e' [p_{x}^{2} - p_{y}^{2} - p_{z}^{2}]$

5. $e_{2}^{*} = e_{dy^{2}} - \frac{1}{2} \sqrt{3} e' [p_{x}^{2} - p_{y}^{2}]$

It is assumed that each of the oxygen ligand
atoms has available 2s, 2p, 2p, and 2p, orbitals
and each fluorine 2p, 2p, and 2p, for the forma-
tion of MO's with titanium 3d orbitals. The six
ligands are placed on the $+x$, $±y$, and $±z$ axes
and are labelled by superscripts starting with 1
on the $+x$ axis and proceeding counterclock-
wise with the 5th and 6th ligands (fluorine)
placed on the $+z$ and $−z$ axes respectively. In
the above states the $a_{1}^{*}$ are hybrid orbitals on
oxygen given by expression 6 with a plus sign
indicating the ligands on the positive $x$, $y$ axes

$[6] \sigma_{1}^{*} = np^{0} ± (1 - n)^{1/3}^{1/3}$

and a minus sign those ligands on negative $x$, $y$
axes. A value of $n$ equal to $(3)^{1/3}$ corresponds to
sp$^{3}$ hybridization on the ligand atom.

The appropriate effective spin Hamiltonian
for Ti$^{3+}$ in a tetragonal field is given by ex-
pression 7

$[7] \mathcal{H} = g_{1} \mathcal{H}_{1} S_{1} + g_{2} \mathcal{H}_{1} \left( S_{1} S_{2} + S_{1} S_{3} \right) + g_{3} \mathcal{H}_{1} I_{1} + \left( S_{1} I_{1} + S_{2} I_{1} + S_{3} I_{1} \right)$

where

$[8] g_{1} = \frac{2.0023}{\Delta_{E_{1g}} - \frac{\Delta_{E_{1g}}}{\Delta_{E_{1g}}} x \left[ 1 - \frac{1}{2} \sigma_{a} \sigma_{c} \right] \left( \sigma_{a} \sigma_{c} \right)}$

$[9] g_{1} = \frac{2.0023}{\Delta_{E_{1g}}} \Delta_{E_{1g}} x \left[ 1 - \frac{1}{2} \sigma_{a} \sigma_{c} \left( \sigma_{a} \sigma_{c} \right) \right]$

The complete expression for $g_{1}$ contains an
additional term within the square brackets

$- \frac{1}{\Delta_{E_{1g}}} \left( \sigma_{a} \sigma_{c} \right)$

that arises from out-of-plane $\pi$ bonding with
oxygen 2p orbitals. In view of the low energy of
2p, the contribution of this term will be negli-
gible and it is omitted from the final expression
for $g_{1}$.

$[10] A = \mathcal{P} \left[ -\sigma_{c} \frac{1}{\Delta_{E_{1g}}} + \frac{1}{\Delta_{E_{1g}}} \right]$

$- \frac{\Delta_{E_{1g}}}{\Delta_{E_{1g}}} \Delta_{E_{1g}} x \left[ 1 - \frac{1}{2} \sigma_{a} \sigma_{c} \left( \sigma_{a} \sigma_{c} \right) \right]$
Electrons in d orbitals cannot contribute directly to $\chi$, but finite values of this parameter result from polarization of the inner filled s orbitals by the unpaired electrons. The expressions for $g_s$ and $g_d$ are deficient in that they do not contain terms for the charge-transfer (c.t.) states. These c.t. terms are of the same general form as those for the d-d states. For the present complex, one predicts that these will be of minor importance since it is clear from the optical spectrum that c.t. transitions if present occur at fairly high energy ($\approx 50,000$ cm$^{-1}$).

It is worth noting that in the derivation of the above expressions several other approximations have been made including omission of spin-orbit coupling of the ligand atoms and ligand-ligand overlap.

**Hyperfine Interactions**

**Titanium**

The titanium isotopes $^{48}$Ti (7.32% abundance; $I = 5/2$) and $^{47}$Ti (84.88%; $I = 7/2$) have equivalent gyromagnetic ratio $\gamma(48$Ti)/$\gamma(47$Ti) = 1.00026 $\pm$ 0.00002) and give rise to a familiar pattern of two overlapping spectra of six and eight lines respectively, appearing as satellites of the main intense central line ($^{48}$Ti, $^{47}$Ti, $^{49}$Ti).

The measured value of the isotropic h.f.s. constant $a_I$ is $17.9 \pm 0.2$ G (Table I). Through eqs. 16 and 17 using $P = -25.7 \times 10^{-14}$ cm$^2$ and $a = 0.05$, we calculate from a result that $\chi = -2.3$ a.u., in agreement with other titanium complexes (2, 3, 5).

However, calculation of the $\chi$ value using unrestricted Hartree-Fock methods (15) reveals that polarization of both 2s and 3s orbitals, with negative contributions from the 3s orbital. In these calculations covalency has been found to be important.

**Fluorine**

The fluorine 2s orbitals have no interaction with the orbitals ($e_s$ and $b_{3u}$) derived from the cubic $T_d$ state since the overlap integrals are zero, for example $\langle 4s|e_s\rangle = 0$. However, charge transfer from the 2s orbital to vacant metal orbitals derived from the $E_u$ cubic states, 4s and 4p orbitals is possible. The latter orbitals can accept ligand electrons of either spin orientation but exchange with the $b_{3u}$ state will increase the transfer probability for electrons of the same spin as the titanium(III) 3d$^1$ unpaired electron.
Hence negative spin density is achieved in the fluorine 2s orbital.
In the present study we obtained an isotropic h.f.s. constant $\alpha_F$ for \( [\text{Ti}((\text{H}_2\text{O})_4)\text{F}_3]^+ \) as 7.5 $\pm$ 0.3 G (Table I).
Spin density in the fluorine 2s orbital is given by eq. 18
\[
\rho_F = \frac{\alpha_F}{A_{2s}}
\]
where
\[
A_{2s} = \frac{8}{3} \pi \kappa \beta \alpha_0 \alpha_0 \alpha_0 \alpha_0 \alpha_0 \alpha_0 \alpha_0 \alpha_0 \alpha_0
\]
is the hyperfine interaction of a single unpaired 2s electron in a fluoride ion. Taking the value for $A_{2s} = 1.57$ cm$^{-1}$ (16) we obtain $\rho_F = -0.0011$ comparable in magnitude to values obtained for other transition metal fluorides (17). Similar $\rho_F$ values are obtained for the TiF$_4^-$ species in a range of alcoholic solvents (2, 18) where nearly the same isotropic $\alpha_F$ value is observed for two equivalent fluorine nuclei. We infer the same geometry in all the TiF$_4^-$ species. Moreover, the magnitude of the hyperfine splitting is consistent with the axial (trans) geometry assumed from the frozen solution spectrum; since equatorial (cis) fluorine splitting should be enhanced by greater covalent interaction with the ligand.

Hydrogen (Water Ligands)

Resolution of the fluorine h.f.s. in D$_2$O strongly indicates the existence of proton hyperfine structure from water ligands in the H$_2$O solution, Fig. la. Approximate calculation based on the improved resolution indicates a h.f.s. $\alpha_H$ for four water ligands (8H) of $\alpha_H$ 0.2 to 0.4 G.

Since the proton interaction is observed for the complex it is evident that $\alpha_H > 0$ and that in-plane $\pi$ bonding exists. Such bonding permits some spin density at hydrogen through spin-polarization as suggested previously for trans-\( [\text{Ti}((\text{H}_2\text{O})_4)(\text{CH}_3\text{COO})]^+ \) (5) and for trans-\( [\text{Ti}((\text{H}_2\text{O})_4)(\text{OH})_2]^+ \) (19).

For the $n$-butyl alcohol complex, the estimation of Johnson et al. (5) gave a total spin density of $\sim 0.22$ on four equatorial water molecules with $\alpha_H = 1.8$ G in their case. On this basis in trans-\( [\text{Ti}((\text{H}_2\text{O})_4)(\text{CH}_3\text{COO})]^+ \), the total spin density on the water ligands is in the range 0.03–0.06. However, the use of the $Q_{\text{OH}}^n$ factor in the former study (5) is open to question in view of the determination through $^1$O labelling that Cu(TI)(H$_2$O)$_2$ has $\rho = 0.22$ on oxygens while no evidence of hydrogen hyperfine splitting is seen (20).

Optical Spectrum and $g$-Values

The expressions 8 and 9 can be rewritten in the form
\[
\text{[20]} \quad g_\parallel = 2.0023 - \frac{8\alpha}{\Delta E(B_{2g}^+ \rightarrow B_{1u}^+)} \cdot K_4
\]
\[
\text{[21]} \quad g_\perp = 2.0023 - \frac{2\alpha}{\Delta E(B_{2g}^+ \rightarrow B_{1u}^+)} \cdot K_4
\]
where
\[
\text{[22]} \quad K_4 = \frac{\alpha_1^2 \alpha_2^2}{\alpha_1^2 + \alpha_2^2} \left[ 1 - \frac{1}{2} \frac{\alpha_1^2 \alpha_2^2}{\alpha_1^2 + \alpha_2^2} \right] S - \left( \frac{\alpha_1^2}{\alpha_1^2 + \alpha_2^2} \right)^{1/2} \cdot \left( \frac{\alpha_1^2}{\alpha_1^2 + \alpha_2^2} \right)^{1/2}
\]
\[
\text{[23]} \quad K_4 = \frac{\alpha_1^2 \alpha_2^2}{\alpha_1^2 + \alpha_2^2} \left[ 1 - \frac{1}{2\alpha_1^2} \frac{\alpha_2^2}{\alpha_1^2} \right] S - \left( \frac{\alpha_2^2}{\alpha_1^2 + \alpha_2^2} \right)^{1/2} \cdot \left( \frac{\alpha_2^2}{\alpha_1^2 + \alpha_2^2} \right)^{1/2}
\]
The values of $K_4$ have been regarded as the "orbital-reduction factors" (21) and these parameters are usually employed to estimate covalency. It is clear from expressions 8 and 9 that $0 \leq K_4$, $K_4 \leq 1$, and that both factors tend to one as the corresponding bonding tends to be ionic and vice versa.

Since only the limiting ionic value for $\lambda(154$ cm$^{-1}$) is available for titanium(III) covalency might better be expressed by eq. 24.

Covalency factor
\[
\text{[24]} \quad \frac{\lambda(\text{covalent})}{\lambda(\text{ionic})} = \frac{\Delta E \cdot \Delta E}{\lambda(\text{ionic})}
\]
where $n = \text{symmetry dependent integer, } n = 8$ for $D_{4h}$; $\Delta E = 2.0023 - g_\parallel (g_\parallel)$; $\Delta E = \text{energy of appropriate electronic transition}$.

Clearly if $\lambda(\text{covalent})$ is actually lower than $\lambda(\text{ionic})$ calculated values of the "covalency factor" will be lower than $K$ itself.

Since the optical spectrum shows two electronic bands at $\sim 15 200$ cm$^{-1}$ (660 nm) and 23 300 cm$^{-1}$ (430 nm) one either might correspond to the $^2B_{2g}^+ \rightarrow ^2B_{1u}^+$ transition, expression 20. We find that expression 24 gives a value of 0.35 for the low energy (15 200 cm$^{-1}$) possibility and 0.68 for the high energy transition. Taking into consideration the high charge density (low effective ionic radius) of the axial fluoride ligands, simple crystal field theory would pre-
dict a tetragonally compressed octahedron (22). Accordingly, the 15 200 cm⁻¹ band is then assigned to $2B_2g \rightarrow 2B_1u$ and the higher energy band to the $2B_2g \rightarrow 2A_{1u}$ transition. Since the covalency parameter is only 0.45 we conclude that both in-plane π bonding and σ bonding are relatively covalent. It is improbable that only one or other is highly covalent. Observation of hydrogen hyperfine splitting from H₂O ligands is clearly consistent with significant in-plane π bonding. We should stress that the actual value of $K_2$ will be somewhat higher (ca. 0.60) if a reduction in κ due to covalency of 30% is assumed.

By first postulating an ideal ionic case e.g. $\lambda = 154$ cm⁻¹ and $K_2 = 1$ we can calculate the upper limit of the energy of the $2B_2g \rightarrow 2E_g$ transition as 4300 cm⁻¹, eq. 21. However we note that fluoride ion is characterized by its π donor properties (23), suggesting that the overall covalency factor could be conservatively estimated at 0.6–0.8. Then $\Delta \varepsilon (2B_2g \rightarrow 2E_g)$ falls to 2500–3200 cm⁻¹. On the other hand the relatively low energy of the $2B_2g \rightarrow 2A_{1u}$ transition (23 300 cm⁻¹) is consistent with the expected low covalent σ bonding between the metal ion and the axial fluorines. The marked stability of the $\text{trans-}[\text{Ti(H}_2\text{O)}_5\text{F}_2]^{1+}$ ion is also consistent with substantial metal-fluorine π bonding.

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