

Electron Spin Resonance Studies and Electronic Structure of $trans\text{-}[\text{Ti}(\text{H}_2\text{O})_4\text{F}_2]^+$

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At pH 1.0–1.6 aqueous titanium(III) solutions containing added fluoride ion exhibit e.s.r. signals of $trans\text{-}[\text{Ti}(\text{H}_2\text{O})_4\text{F}_2]^+$, $g = 1.9460 \pm 0.0005$, $a_{\text{Ti}} = 17.9 \pm 0.2$ G. The variation in the intensity of the optical and e.s.r. spectra with added fluoride ion indicate >90% conversion to the complex at $[\text{Ti}]:[\text{F}] = 1:2$. The *trans* geometry of the complex is established from the spectrum in D_2O , a 1:2:1 triplet with $a_{\text{T}} = 7.5 \pm 0.5$ G, and from the axial symmetry (D_{4h}) apparent in the frozen solution spectrum, $g_{\parallel} = 1.968$, $g_{\perp} = 1.932$.

The optical spectrum shows two bands assigned to the ${}^2B_{2g} \rightarrow {}^2B_{1g}$ (15 200 cm^{-1}) and ${}^2B_{2g} \rightarrow {}^2A_{1g}$ (23 300 cm^{-1}) transitions. Calculations based on the e.s.r. and optical spectra suggest covalent character in the in-plane π and σ bonding of the complex.

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A des pH allant de 1.0 à 1.6, des solutions aqueuses de titane(III) contenant des ions fluorures ajoutés, montrent un signal r.p.e. du $[\text{Ti}(\text{H}_2\text{O})_4\text{F}_2]^+$ *trans*, $g = 1.9460 \pm 0.0005$, $a_{\text{Ti}} = 17.9 \pm 0.2$ G. On note une variation de l'intensité des spectres optique et r.p.e. lorsqu'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 *trans* en se basant sur le spectre dans le D_2O alors qu'on observe un triplet 1:2:1 avec $a_{\text{T}} = 7.5 \pm 0.5$ G et aussi sur l'existence d'une symétrie axiale (D_{4h}) observée pour le spectre de la solution congelée $g_{\parallel} = 1.968$, $g_{\perp} = 1.932$.

Le spectre optique montre deux bandes qui ont été assignées aux transitions ${}^2B_{2g} \rightarrow {}^2B_{1g}$ (15 200 cm^{-1}) et ${}^2B_{2g} \rightarrow {}^2A_{1g}$ (23 300 cm^{-1}). Des calculs basés sur les spectres r.p.e. et optique suggèrent un caractère covalent pour les liaisons π et σ 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 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 $[\text{Ti}(\text{H}_2\text{O})_4\text{F}_2]^+$ ion, **1**, have appeared. Garif'yanov and Semenova (1b) prepared green hydrated complexes $[\text{Ti}(\text{H}_2\text{O})_{6-n}\text{F}_n]^{(3-n)+}$ which exhibited an intense slightly asymmetric resonance line ($g = 1.946 \pm 0.001$; linewidth 20 G)

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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. Waters and Maki (2) briefly referred to preparation of the paramagnetic complex, **1**, in aqueous solution, in conjunction with a report on ${}^{47}\text{Ti}$ and ${}^{49}\text{Ti}$ hyperfine structure in the $\text{Ti}(\text{OCH}_3)_2^{2+}$ 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-separated 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. Glebov 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 $[\text{Ti}(\text{H}_2\text{O})_3\text{F}]^{2+}$ (7).

In the present study, the structure of the paramagnetic complex in such solutions is firmly established as the $trans\text{-}[\text{Ti}(\text{H}_2\text{O})_4\text{F}_2]^+$ ion on

the basis of detailed e.s.r. studies in H_2O and D_2O . 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 N HCl or H_2SO_4 . An N_2 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 (1c). In preparing solutions of the $[Ti(H_2O)_6F_2]^+$ complex by addition of NaF or KF, pH adjustment was made by addition of the appropriate concentrated acid. For study in heavy water, concentrated $TiCl_3$ solution was added to D_2O (Merck) such that the sample contained 98% D_2O .

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 $Cu(H_2O)_6^{2+}$, $Cr(NH_3)_6^{3+}$, $Mn(H_2O)_6^{2+}$, and $VO(H_2O)_5^{2+}$. Approximate digital calculation was used to determine the integrated intensity of the signal (8). Frozen solutions were obtained by rapidly quenching the sample in liquid nitrogen, maintaining the sample in the Varian E-246 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 $Ti(H_2O)_6^{3+}$ 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. 1a. When prepared in D_2O by the same route, the e.s.r. signal now showed a distinct triplet splitting through interaction with two equivalent ^{19}F nuclei, thus indicating the stoichiometry titanium(III):fluoride of 1:2, Fig. 1b. Spectral parameters for this complex are given in Table I. At higher gain, the satellite

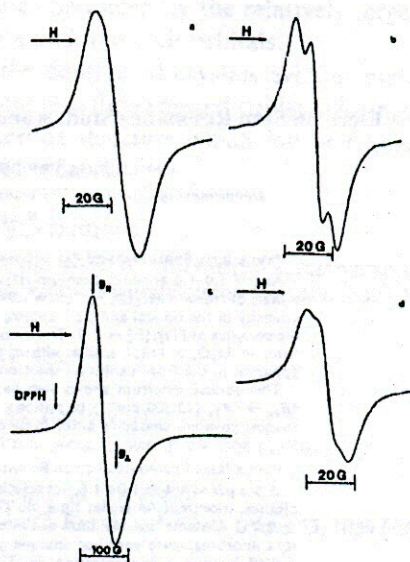


Fig. 1. Electron spin resonance spectra of TiF_2^+ ions in aqueous solution (pH 1.0): (a) $TiCl_3$ (0.02 M), NaF (0.06 M) in H_2O , 25°C; (b) $TiCl_3$ (0.02 M), NaF (0.06 M) in D_2O , 25°C; (c) $TiCl_3$ (0.01 M), NaF (0.03 M) in H_2O , frozen solution at 77 K; (d) $TiCl_3$ (0.06 M), NH_4F (0.06 M) in D_2O , 25°C.

lines from ^{47}Ti and ^{49}Ti 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 $TiCl_3$. 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 I. Electron spin resonance data for $trans-[Ti(H_2O)_4F_2]^+$

Parameter	Value
$g_{ }$	1.968 ± 0.002
g_{\perp}	1.932 ± 0.002
$g_{0^{\circ}}$	1.9460 ± 0.0005
a_{Ti}	17.9 ± 0.2 G
$a_{F\uparrow}$	7.5 ± 0.5 G
a_{H}	$0.2 - 0.4$

$g_{0^{\circ}}$ (calculated) = 1.944; by expression 13.

\uparrow Measured from $[Ti(D_2O)_4F_2]^+$.

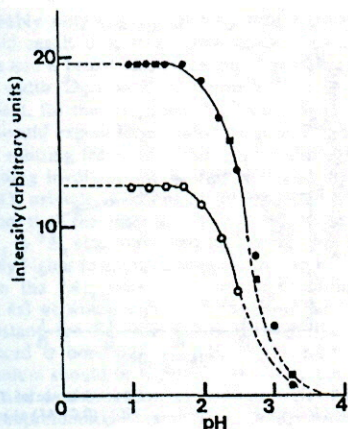


FIG. 2. pH dependence of proposed TiF_2^+ ion. Upper curve, e.s.r. signal intensity: ●, H_2O ; ■, D_2O , relative to reading at pH 1.0. Lower curve, absorbance at 660 nm: ○, relative to reading at pH 1.0. $\text{TiCl}_3 = 0.02 M$, $\text{NaF} = 0.06 M$.

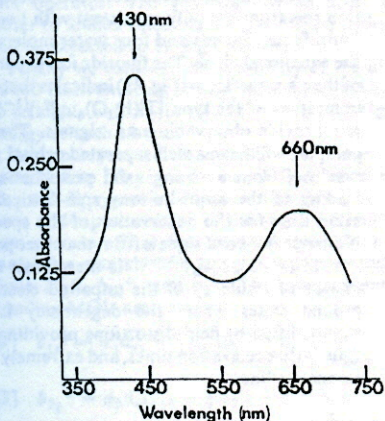


FIG. 3. Optical spectrum of TiF_2^+ in aqueous solution at pH 1.3; TiCl_3 (0.1 M), NaF (0.25 M).

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 ($\epsilon \sim 3.4$) and 660 nm ($\epsilon \sim 2$) (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 $[\text{Ti}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ 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.



Qualitatively, precipitation produced a rose-white solid in contrast to the brown-black mass observed in the hydrolysis of TiCl_3 solution.

Variation of the e.s.r. signal intensity, Fig. 4b, indicated that $[\text{Ti}(\text{H}_2\text{O})_4\text{F}_2]^+$ 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 $100 \pm 10\%$ 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 $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ bands was being monitored. At a mole ratio higher than 1:6 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 (1), or a second coordination shell effect of fluoride ion.

The evidence for $\text{Ti}(\text{H}_2\text{O})_4\text{F}_2^+$ 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 TiCl_3 in D_2O on addition of ammonium fluoride at a 1:1 mole ratio (Glebov's conditions for the supposed $[\text{Ti}(\text{H}_2\text{O})_5\text{F}]^{2+}$ species in H_2O) again shows the symmetrical 1:2:1 triplet, Fig. 1d. Therefore the species present must actually be $[\text{Ti}(\text{D}_2\text{O})_4\text{F}_2]^+$. Of some interest is the markedly lower resolution of the triplet splitting in the Ti^{3+} - NH_4F sys-

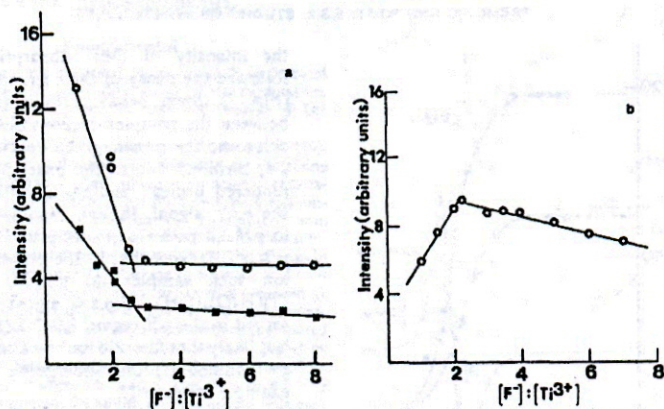


FIG. 4. Dependence of TiF_2^+ concentration on added fluoride ion. (a) Variation of absorbance of TiF_2^+ at: O, 430 nm; ●, 660 nm; $TiCl_3$ (0.15 M) at pH 1.3; (b) Variation in e.s.r. signal intensity, $TiCl_3$ (0.01 M) at pH 1.1.

tem, relative to the higher resolution shown in Fig. 1b for a $Ti^{3+} \cdot NaF \cdot D_2O$ sample. When titanium(III) concentration was varied from 0.01 to 0.1 M in the presence of NH_4F , the line broadening persisted, indicating the effect was not due to concentration dependent relaxation processes. Since spatially NH_4^+ exactly replaces an H_2O^{2+} unit in water structure (11), we tentatively ascribe 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 $TiCl_3 \cdot NaF$ in H_2O is shown in Fig. 1c (Table I). 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 $g_{||}$ and g_{\perp} (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 $[Ti(H_2O)_4F_2]^+$ 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 fluorine 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 $[Ti(H_2O)_{6-n}F_n]^{(3-n)+}$ 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 $[Ti(H_2O)_{6-n}F_n]^{(3-n)+}$ is then direct confirmation of residency of the unpaired electron 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*- $[Ti(H_2O)_4F_2]^+$ ion is D_{4h} . We propose that the ground electronic state is $^2B_{2g}$ (unpaired electron in b_{2g}^* (d_{xy}) 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_g state (e_g^*1 (d_{xz}) and e_g^*2 (d_{yz}) 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_2O) at 25 °C is only 5 G.

Next, for the ${}^2B_{1g}$ state (b_{1g}^* ($d_{x^2-y^2}$) orbital) we would expect larger isotropic proton hyperfine splitting from the water ligands through σ bonding involving the b_{1g}^* orbital and the a_1 (H_2O) orbitals. Also one might expect g_{\perp} to be higher than the observed value (1.932), since the ${}^2B_{1g} \rightarrow {}^2E_g$ electronic transition would be relatively higher in energy compared to ${}^2B_{2g} \rightarrow {}^2E_g$.

In the ${}^2A_{1g}$ state (a_g^*1 and a_g^*2 orbitals; d_{z^2} , $4s$) we would expect a higher isotropic h.f.s. constant for fluorine nuclei through the enhanced σ bonding. In addition the h.f.s. for titanium should be higher. In D_{4h} symmetry the d_{z^2} and $4s$ orbitals belong to the same irreducible representation and a direct contribution of spin density at the metal nucleus is allowed. For the ${}^2A_{1g}$ state, we would expect g_{\parallel} 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_{\perp} value would also be closer to 2.0023 since the ${}^2A_{1g} \rightarrow {}^2E_g$ transition will be expected to be high in energy.

Finally we consider the possibility of the unpaired 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 ${}^2B_{2g}$ 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 representations b_{1g}^* , b_{2g}^* , and e_g^* . The relevant antibonding MO's are

$$[2] \quad b_{1g}^* = \alpha_1 d_{xy} - \frac{1}{2} \alpha_1' [p_y^4 + p_x^4 - p_y^3 - p_x^4]$$

$$[3] \quad b_{2g}^* = \alpha_2 d_{x^2-y^2} - \frac{1}{2} \alpha_2' [-\sigma_x^4 + \sigma_y^4 + \sigma_x^3 - \sigma_y^4]$$

$$[4] \quad e_g^*1 = \epsilon d_{xz} - \frac{1}{2^{1/2}} \epsilon' [p_x^5 - p_x^6] - \frac{\epsilon''}{2^{1/2}} [p_x^4 - p_x^3]$$

$$[5] \quad e_g^*2 = \epsilon d_{yz} - \frac{1}{2^{1/2}} \epsilon' [p_y^5 - p_y^6] - \frac{\epsilon''}{2^{1/2}} [p_y^4 - p_y^3]$$

It is assumed that each of the oxygen ligand atoms has available $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals and each fluorine $2p_x$, $2p_y$, and $2p_z$ for the formation of MO's with titanium $3d$ orbitals. The six ligands are placed on the $\pm x$, $\pm y$, and $\pm z$ axes and are labelled by superscripts starting with 1 on the $+x$ axis and proceeding counterclockwise with the 5th and 6th ligands (fluorine) placed on the $+z$ and $-z$ axes respectively. In the above states the σ' are hybrid orbitals on oxygen given by expression 6 with a plus sign indicating the ligands on the positive x , y axes

$$[6] \quad \sigma' = np^i \pm (1 - n^2)^{1/2} s^i$$

and a minus sign those ligands on negative x , y axes. A value of n equal to $(\frac{3}{5})^{1/2}$ corresponds to sp^2 hybridization on the ligand atom.

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

$$[7] \quad \mathcal{H} = \beta_e g_{\parallel} H_z S_z + \beta_e g_{\perp} (H_x S_x + H_y S_y) + A S_z I_z + \beta (S_x I_x + S_y I_y)$$

where

$$[8] \quad g_{\parallel} = 2.0023 - \frac{8\lambda\alpha_1^2\alpha_2^2}{\Delta E_{x^2-y^2}} \times \left[1 - \frac{1}{2} \frac{\alpha_1'\alpha_2'}{\alpha_1\alpha_2} T(n) - \left(\frac{\alpha_2'}{\alpha_2} \right) S - \left(\frac{\alpha_1'}{\alpha_1} \right) \Pi_1 \right]$$

$$[9] \quad g_{\perp} = 2.0023 - \frac{2\lambda\alpha_1^2\epsilon^2}{\Delta E_{xz}} \times \left[1 - \frac{1}{2^{1/2}} \left(\frac{\epsilon'\alpha_1'}{\epsilon\alpha_1} \right) - \left(\frac{\alpha_1'}{\alpha_1} \right) \Pi_1 - \frac{1}{2^{1/2}} \left(\frac{\epsilon'}{\epsilon} \right) \Pi_1 \right]$$

The complete expression for g_{\perp} contains an additional term within the square brackets namely

$$- \frac{1}{2^{1/2}} \left(\frac{\epsilon''}{\epsilon} \right) \Pi_2$$

that arises from out-of-plane π bonding with oxygen $2p_z$ orbitals. In view of the low energy of $2p_z$, the contribution of this term will be negligible and it is omitted from the final expression 9 for g_{\perp} .

$$[10] \quad A = P \left[-\alpha_1^2 \left(\frac{4}{7} + K_0 \right) - \frac{8\lambda\alpha_1^2\alpha_2^2}{\Delta E_{x^2-y^2}} - \frac{6\lambda\alpha_1^2\epsilon^2}{\Delta E_{xz}} \right]$$

$$[11] \quad B = P \left[\alpha_1^2 \left(\frac{2}{7} - K_0 \right) - \frac{11}{7} \cdot \frac{\lambda \alpha_1^2 \epsilon^2}{\Delta E_{xx}} \right]$$

The parameter $\lambda = 154 \text{ cm}^{-1}$ is the spin-orbit coupling constant for the free ion in the appropriate valence state, K_0 is the Fermi contact term for the titanium nucleus, and $\Delta E_{x^2-y^2}(\Delta E_{(2B_{2g} \rightarrow 2B_{1g})})$ and $\Delta E_{zz}(\Delta E_{(2B_{2g} \rightarrow 2E_g)})$ are the transition energies to the $2B_{1g}$ and $2E_g$ states respectively. The parameter $P = -25.7 \times 10^{-4} \text{ cm}^{-1}$ for $^{47,49}\text{Ti}^{3+}$ was obtained by extrapolation (13, 14), as defined by expression 12 where r is average orbital radius.

$$[12] \quad P = g_N \beta_e \beta_N \langle r^{-3} \rangle_{av}$$

In eqs. 8 and 9, the integral $T(n)$ is taken over all ligand functions and S , Π_1 , and Π_2 are the group overlap integrals.

$$S = 2 \langle d_{xy} | p_y^1 \rangle$$

$$\Pi_1 = 2 \langle d_{x^2-y^2} | \sigma^1 \rangle$$

$$\Pi_2 = 2 \langle d_{xz} | p_x^3 \rangle$$

Expressions 10 and 11 can be written as follows after substituting from expressions 8 and 9 neglecting small contributions to A and B (≤ 0.05).

$$[13] \quad A = -KP - \frac{4}{7} \alpha_1^2 \cdot P + (g_{||} - 2.0023)P + \frac{3}{7} (g_{\perp} - 2.0023)P$$

$$[14] \quad B = -KP + \frac{2}{7} \alpha_1^2 P + \frac{11}{14} (g_{\perp} - 2.0023)P$$

where $K = \alpha_1^2 K_0$

For the isotropic solution spectra

$$[15] \quad g_0 = \frac{1}{2} (g_{||} + 2g_{\perp})$$

and

$$[16] \quad a = \frac{1}{2} (A + 2B) = -KP - (g_0 - 2.0023)P$$

The spin density at the titanium nucleus may be given in terms of

$$[17] \quad \chi = \frac{4\pi}{S} \sum_m (|\Psi_m(0)|^2 - |\Psi_m(0)|^2) = -\frac{3}{2} \frac{KP}{g_N \beta_e \beta_N}$$

Electrons in d orbitals cannot contribute directly to χ , but finite values of this parameter result from polarization of the inner filled s orbitals by the unpaired electrons.

The expressions for $g_{||}$ and g_{\perp} 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 ($> 50\,000 \text{ cm}^{-1}$).

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 ^{47}Ti (7.32% abundance; $I = 5/2$) and ^{49}Ti (5.46%; $I = 7/2$) have equivalent gyromagnetic ratio [$\gamma(^{49}\text{Ti})/\gamma(^{47}\text{Ti}) = 1.00026 \pm 0.00002$] 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 (^{46}Ti , ^{48}Ti , ^{50}Ti).

The measured value of the isotropic h.f.s. constant a_{Ti} is $17.9 \pm 0.2 \text{ G}$ (Table 1). Through eqs. 16 and 17 using $P = -25.7 \times 10^{-4} \text{ cm}^{-1}$ we calculate as a result that $\chi = -2.3 \text{ a.u.}$, in agreement with other titanium complexes (2, 3, 5).

However, calculation of the χ value using unrestricted Hartree-Fock methods (15) reveals that polarization of both 2s and 3s are important, 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_g and b_{2g}) derived from the cubic ${}^2T_{2g}$ state since the overlap integrals are zero, for example $\langle 2s | e_g \rangle = 0$. However, charge-transfer from the 2s orbital to vacant metal orbitals derived from the E_g cubic states, 4s and 4p orbitals is possible. The latter orbitals can accept ligand electrons of either spin orientation but exchange with the ${}^2B_{2g}$ 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 a_F for $[\text{Ti(H}_2\text{O)}_4\text{F}_2]^+$ as 7.5 ± 0.5 G (Table 1).

Spin density in the fluorine 2s orbital is given by eq. 18

$$[18] \quad \rho_s = \frac{a_F}{A_{2s}}$$

where

$$[19] \quad A_{2s} = \frac{8}{3} \pi g_e \beta_e g_N \beta_N |\Psi(0)_{2s}|^2$$

is the hyperfine interaction of a single unpaired 2s electron in a fluoride ion. Taking the value for $A_{2s} = 1.57 \text{ cm}^{-1}$ (16) we obtain $\rho_s = -0.0011$ comparable in magnitude to values obtained for other transition metal fluorides (17). Similar ρ_s values are obtained for the TiF_2^+ species in a range of alcoholic solvents (2, 18) where nearly the same isotropic a_F value is observed for two equivalent fluorine nuclei. We infer the same geometry in all the TiF_2^+ 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_2O strongly indicates the existence of proton hyperfine structure from water ligands in the H_2O solution, Fig. 1a. Approximate calculation based on the improved resolution indicates a h.f.s. a_H for four water ligands (8H) of ca. 0.2 to 0.4 G.

Since the proton interaction is observed for the complex it is evident that $\alpha_1' > 0$ and that in-plane π bonding exists. Such bonding permits some spin density at hydrogen through spin-polarization as suggested previously for *trans*- $[\text{Ti(H}_2\text{O)}_4((\text{CH}_3)_2\text{COH})\text{X}]$ (5) and for *trans*- $[\text{Ti(H}_2\text{O)}_4(\text{OH})_2]^+$ (19).

For the *t*-butyl alcohol complex, the estimation of Johnson *et al.* (5) gave a total spin density of ~ 0.22 on four equatorial water molecules with $a_H = 1.8$ G in their case. On this basis in *trans*- $[\text{Ti(H}_2\text{O)}_4\text{F}_2]^+$, the total spin density on the water ligands is in the range 0.03–0.06. However, the use of the Q_{OH}^H factor in the former study (5) is open to question in view of the determination through ^{17}O labelling that $\text{Cu(II)(H}_2\text{O)}_6$ has $p = 0.22$ 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

$$[20] \quad g_{\parallel} = 2.0023 - \frac{8\lambda}{\Delta E(^2B_{2g} \rightarrow ^2B_{1g})} \cdot K_{\parallel}$$

$$[21] \quad g_{\perp} = 2.0023 - \frac{2\lambda}{\Delta E(^2B_{2g} \rightarrow ^2E_g)} \cdot K_{\perp}$$

where

$$[22] \quad K_{\parallel} = \alpha_1'^2 \alpha_2'^2 \left[1 - \frac{1}{2} \frac{\alpha_1' \alpha_2'}{\alpha_1 \alpha_2} T(n) - \left(\frac{\alpha_2'}{\alpha_2} \right) S - \left(\frac{\alpha_1'}{\alpha_1} \right) \Pi_1 \right]$$

$$[23] \quad K_{\perp} = \alpha_1'^2 \alpha_2'^2 \left[1 - \frac{1}{2^{1/2}} \left(\frac{\alpha_1' \alpha_2'}{\alpha_1 \alpha_2} \right) - \left(\frac{\alpha_1'}{\alpha_1} \right) \Pi_1 - \frac{1}{2^{1/2}} \left(\frac{\alpha_2'}{\alpha_2} \right) \Pi_1 \right]$$

The values of K_{\parallel} and K_{\perp} 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 $0 \leq K_{\parallel}, K_{\perp} \leq 1$, 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 $\lambda(154 \text{ cm}^{-1})$ is available for titanium(III) covalency might better be expressed by eq. 24.

[24] Covalency factor

$$= \left[\frac{K \lambda(\text{covalent})}{\lambda(\text{ionic})} \right] = \frac{\Delta g \cdot \Delta E}{n \lambda(\text{ionic})}$$

where n = symmetry dependent integer, $n = 8$ for D_{4h} ; $\Delta g = 2.0023 - g_{\parallel}$ (g_{\perp}); ΔE = 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 $\sim 15\,200 \text{ cm}^{-1}$ (660 nm) and $23\,300 \text{ cm}^{-1}$ (430 nm) either one might correspond to the $^2B_{2g} \rightarrow ^2B_{1g}$ transition, expression 20. We find that expression 24 gives a value of 0.45 for the low energy ($15\,200 \text{ cm}^{-1}$) 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 $15\,200\text{ cm}^{-1}$ band is then assigned to ${}^2B_{2g} \rightarrow {}^2B_{1g}$ and the higher energy band to the ${}^2B_{2g} \rightarrow {}^2A_{1g}$ 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 H_2O ligands is clearly consistent with significant in-plane π bonding. We should stress that the actual value of K_{\parallel} will be somewhat higher (ca. 0.60) if a reduction in λ due to covalency of 30% is assumed.

By first postulating an ideal ionic case e.g. $\lambda = 154\text{ cm}^{-1}$ and $K_{\perp} = 1$ 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 as 0.6–0.8. Then $\Delta E({}^2B_{2g} \rightarrow {}^2E_g)$ falls to $2500\text{--}3200\text{ cm}^{-1}$. On the other hand the relatively low energy of the ${}^2B_{2g} \rightarrow {}^2A_{1g}$ transition ($23\,300\text{ cm}^{-1}$) is consistent with the expected low covalent σ bonding between the metal ion and the axial fluorines. The marked stability of the $\text{trans-}[\text{Ti}(\text{H}_2\text{O})_4\text{F}_2]^+$ ion is also consistent with substantial metal–fluorine π bonding.

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