

Electron Spin Resonance Studies on $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ in Frozen Aqueous Solutions of Titanium(III) Chloride, Bromide, Iodide, and Sulfate

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Strongly acidic aqueous solutions of titanium(III) chloride, bromide, iodide, or sulfate (0.02 M metal ion) provide no detectable e.s.r. signal at room temperature. In the frozen solution (77 K) an identical spectrum is observed from each sample with $g_{\parallel} = 1.994 \pm 0.001$ and $g_{\perp} = 1.896 \pm 0.001$. A maximum signal is observed at 6–8 M added anion, indicating not all titanium(III) species are e.s.r. active. Analysis indicates that the local symmetry of the $\text{Ti}^{3+}(\text{3d}^1)$ ions providing the signal is D_3 . It is proposed that these ions are $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ species located in sites in the ice structure subject to a strong asymmetric electric field from nearby counter ions. Since the spectrum is independent of anion, the counter ions are unlikely to be in the first or second coordination shell of the Ti^{3+} .

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Lors de l'examen par r.p.e. à température de la pièce, de solutions fortement acides de chlorure, de bromure, d'iodure et de sulfate de titane(III) (0.02 M en ion métallique) on n'observe aucun signal. Dans des solutions congelées (77 K) on observe un spectre identique pour chaque échantillon avec $g_{\parallel} = 1.994 \pm 0.001$ et $g_{\perp} = 1.896 \pm 0.001$. On observe un signal maximum par addition de 6–8 M d'anions; ceci indique que toutes les espèces de titane(III) ne sont pas actives en r.p.e. Une analyse indique que la symétrie locale des ions $\text{Ti}^{3+}(\text{3d}^1)$ fournissant le signal est D_3 . On propose que ces ions sont des espèces $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ situées dans des sites de la structure de la glace qui sont sujets à des champs électriques asymétriques très forts provenant des ions antagonistes voisins. Puisque le spectre est indépendant de l'anion, il semble improbable que les ions antagonistes soient dans la première ou dans la deuxième sphère de coordination du Ti^{3+} .

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Introduction

The ground state of a d^1 ion such as Ti^{3+} is 2D , separated in the free ion by a rather large energy, $80\,378\text{ cm}^{-1}$ from the first excited state 2S (the $3d^1 \rightarrow 4s^1$ transition) (1). An ideal octahedral ligand field (O_h symmetry) splits the 2D state into a low lying ${}^2T_{2g}$ state and an upper ${}^2E_{g}$ state. The acidic aqueous solutions of the titanium(III) halides, TiCl_3 , TiBr_3 , and TiI_3 , have been studied both chemically and spectroscopically, and are believed to contain only octahedrally solvated titanium ions, $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ (2–4).

The broad weak band in the optical spectrum of the $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ ion is assigned to the ${}^2T_{2g} \rightarrow {}^2E_{g}$ transition (5). One interesting feature of the spectrum is the asymmetric character of the visible absorption band. This band consists of a broad maximum at $21\,000\text{ cm}^{-1}$ with a pronounced shoulder at $\sim 17\,000\text{ cm}^{-1}$. The splitting is considered to arise from a nuclear configurational instability in the excited state *i.e.* from the Jahn–Teller effect (6). The ideal

octahedral ion $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ cannot be stable because of the threefold degeneracy of the ${}^2T_{2g}$ ground state, and a tetragonal distortion is required so that a nondegenerate ground state exists *i.e.* (${}^2B_{2g}$). However the theoretical background of the Jahn–Teller effect gives no direct information concerning the magnitude of the deviation from octahedral symmetry, or a choice between a static distortion and a dynamic equilibrium between limiting structures. It is however expected that the splitting of the ${}^2T_{2g}$ ground state will be smaller than that of the excited ${}^2E_{g}$ state.

No e.s.r. signals have been detected in solutions of $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ ions at room temperature since the residual angular momentum in the ${}^2T_{2g}$ ground state cancels the spin angular momentum. Eventual small axial or other distortion might possibly partially "quench" the orbital angular momentum, but the expected rather short T_1 (spin–lattice relaxation time) will render the e.s.r. signal undetectable.

We now report the appearance of identical

e.s.r. signals in frozen aqueous solutions of $TiCl_3$, $TiBr_3$, and TiI_3 at 77 K which we assign to $Ti(H_2O)_6^{3+}$ ions under the influence of a strong asymmetric electric field generated indirectly by the negative counter ions present.¹ A similar signal is observed from a frozen $Ti_2(SO_4)_3$ solution.

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 5 mm cylindrical quartz cells and frozen by plunging into liquid nitrogen. Spectra were recorded while the sample was cooled in a Varian E-243 insert Dewar accessory.

The commercial 20% $TiCl_3$ solution (Fisher); or 15% $Ti_2(SO_4)_3$ solution (B.D.H., $[Cl] < 0.02\%$) were used directly. The $TiBr_3$ and TiI_3 salts were prepared by the method of Semenova from the $Ti_2(CO_3)_3$ salt (8). The concentrations of anions were varied by either addition of the reagent grade salts (NaCl, KBr, KI, and Na_2SO_4) or concentrated acids (48% HBr, 37.5% HCl, 56% HI, and 98% H_2SO_4).

The g factors are quoted relative to DPPH $g = 2.0036$, measured by means of a dual cavity assembly.

Results

Strongly acidic solutions of titanium(III) chloride ($pH \leq 1.0$) provide no detectable e.s.r. signal at room temperature. However, a rapidly frozen solution of 0.02 M $TiCl_3$ in 2 M HCl provides the spectrum shown in Fig. 1, assigned to a species with axial symmetry with $g_{\parallel} = 1.994 \pm 0.001$ and $g_{\perp} = 1.896 \pm 0.001$. The result confirms the reported observation of Glebov (7).

We now report that a frozen solution of 0.03 M $Ti_2(SO_4)_3$ in 3.75 M H_2SO_4 provided an experimentally identical spectrum under conditions where chloride ion is totally absent. Moreover both a commercial $Ti_2(SO_4)_3$ solution (B.D.H.) and a solution prepared by dissolving Ti sponge in concentrated H_2SO_4 gave the same result. To further test the sensitivity of the observed spectrum to the nature of the anion we have prepared samples of both the iodide and the bromide salts of titanium(III) (8). The method involves precipitation of titanium(III) carbonate from a $TiCl_3$ solution and thorough water-washing until no further

¹Recently Glebov reported the e.s.r. spectrum of a frozen hydrochloric acid solution of $TiCl_3$ with pronounced g factor anisotropy ($g_{\parallel} = 1.98$ and $g_{\perp} = 1.89$). However the assignment of the structure $Ti(H_2O)_5Cl^{2+}$ made without experimental or theoretical justification overlooks the true significance of the results (7).

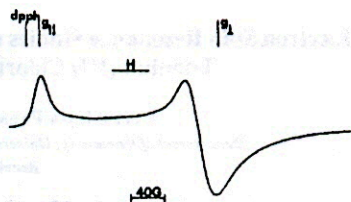


FIG. 1. Electron spin resonance spectrum of $Ti(H_2O)_6^{3+}$ in frozen aqueous solution: $Ti^{3+} = 0.02 M$, $[HCl] = 6 M$, 77 K.

chloride ion is detected. The $Ti_2(CO_3)_3$ is then dissolved in either aqueous HBr or HI to prepare solutions of titanous ion. Frozen solutions (77 K) prepared by this procedure $[Ti] = 0.02 M$, $[I^-]$ or $[Br^-] = 6 M$ showed the same spectrum as recorded for the sulfate or chloride, Fig. 2. Even if a conservative estimate of say 10 mol% residual chloride is assigned to the solid carbonate, the ratio of $[Cl^-]$ to $[I^-]$ in the final solution would still be 10^4 . It seems clear that the species providing the spectrum is independent of the anion selected, and hence does not contain anion in the first coordination shell.

A further convincing series of experiments relied upon the dependence of the signal intensity toward anion concentration. Employing 0.01 M titanium(III), a qualitatively identical spectrum was recorded at 2 M concentration of all the anions. In all cases the intensity gradually increased reaching a maximum at 4–8 M added anion. At elevated anion concentrations ($> 10 M$) further resonances due to additional species were apparent. Then the spectra were clearly different for Cl^- , Br^- , I^- , and SO_4^{2-} , showing a direct influence of the anion in the first coordination shell.

Of all the anions that were examined, sulfate

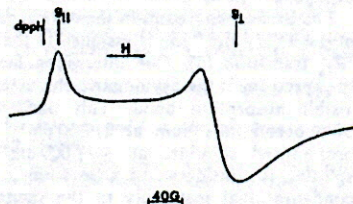


FIG. 2. Electron spin resonance spectrum of $Ti(H_2O)_6^{3+}$ in frozen aqueous solution: $Ti^{3+} = 0.02 M$, $[HI] = 6.9 M$, 77 K.

provided the weakest spectrum with a maximum intensity (7.5 M sulfate) that was only 40% of the strongest signal obtained with the halide ions. However addition of any one of NaCl, KBr, or KI to the sample caused an increase in intensity to the maximum observed with the halide ions alone, again with no change in the spectral parameters (line width or position). These experiments indicate that the studies with TiI_3 and $TiBr_3$ prepared via the carbonate route are indeed independent of chloride ion.

Our tentative assumption was that the species was $Ti(H_2O)_6^{3+}$ located in a site in the solid where a distortion of the local symmetry of the Ti^{3+} ions was created by nearby anionic species. As further tests of this hypothesis we have varied the $Ti(III)$ concentration from 0.01 to 0.1 M with no appearance of resonances due to triplet $Ti^{3+} \cdots Ti^{3+}$ species over a wide-field sweep. Moreover we have observed that changing halide ion concentration by adding the salts (KI, KBr, or NaCl) gave the same effect as adding the corresponding concentration of the mineral acid. Therefore no specific effect of other cations (Na^+ , K^+ , H^+) on the e.s.r. active ions is indicated.

Discussion

The appearance of an e.s.r. signal in the frozen solutions of the titanous salts clearly indicates that a distortion of the pure octahedral O_h symmetry of the $Ti(H_2O)_6^{3+}$ species has occurred. Two lines of evidence can be used to identify the nature of the effect: (i) dependence of the signal on the chemical constitution of the sample, (ii) parameters of the observed spectrum.

There is no doubt that the signal is independent of the anion in the series Cl^- , Br^- , I^- , and SO_4^{2-} . Since dissolution of the pure metallic sponge in either concentrated reagent H_2SO_4 or in analyzed grade HCl gave samples with identical spectra, no systematic spurious impurity is suspected either. Since signal intensity increases with anion concentration, we conclude *not all* Ti^{3+} ions are located in the same environment. Clearly then we are not dealing with a (hypothetical) temperature dependent relaxation process of the $Ti(H_2O)_6^{3+}$ species that would render its spectrum observable at 77 K. Bearing in mind the uncertainty of even approximate concentration comparison in the frozen solution samples we estimate that less than 50% of the nominal $Ti(III)$ concentra-

tion is e.s.r. active in the sample giving the most intense spectrum. In any event the fact that signal intensity *does increase* on addition of anion shows that 100% of the titanium(III) ions present do not contribute to the signal at low anion concentration.

The absence of specific effect of the anions on the spectrum leads us to suggest that while these counter ions are stabilized in water structures in the vicinity of the metal ion, they do not form a part of the first or second coordination shells. Although all four ions (Cl^- , Br^- , I^- , and SO_4^{2-}) are spherically symmetric their ionic radii and charge density are sufficiently different to project some spectral differences if neighboring (second shell) effects on the d^1 ions were primarily responsible for the distortion from octahedral symmetry. Hence, we favor the remaining alternative; that the ice structure requirements of closely situated anions and cations in turn cause a distortion of the local symmetry of the $Ti(H_2O)_6^{3+}$ unit located in that ice structure. Accordingly at low anion concentration fewer $Ti(H_2O)_6^{3+}$ would be at the required separation from a counter ion to be affected by its presence.

However the actual local symmetry of the Ti^{3+} ion in the structure is a rather complex question. In the following discussion we consider several important possibilities and compare the predicted spectrum with that actually observed.

D_{4h}

In D_{4h} symmetry, the five orbitals of a $3d^1$ configuration split into four energy states: ${}^2B_{2g}(d_{xy})$, doubly degenerate ${}^2E_g(d_{xz}, d_{yz})$, ${}^2B_{1g}(d_{x^2-y^2})$, and ${}^2A_{1g}(d_{z^2})$. Consider that the Ti^{3+} ion is an octahedral ligand field of six water ligands with a small tetragonal distortion, i.e. D_{4h} symmetry with ${}^2B_{2g}$ as the ground state. The corresponding expression for g_{\parallel} is

$$g_{\parallel} = 2.0023 - \frac{8\lambda}{\Delta E({}^2B_{2g} \rightarrow {}^2B_{1g})} \cdot \phi_{\parallel}$$

where $\lambda = 154 \text{ cm}^{-1}$, ΔE refers to the electronic transition from the ${}^2B_{2g}$ to the ${}^2B_{1g}$ state, and ϕ_{\parallel} is a complex function employed to estimate covalency. The magnitude of ϕ is mainly determined by the appropriate molecular orbital coefficients. However the value of ϕ lies between 0 and 1 tending to unity as the σ and π bonding becomes more ionic, and conversely. Assuming

that we are dealing with a nearly purely ionic case *i.e.* $\phi_{\parallel} \rightarrow 1$ we can easily calculate (from $g_{\parallel}(\text{exp}) = 1.994 \pm 0.001$) that $\Delta E(^2B_{2g} \rightarrow ^2B_{1g})$ would be as high as $154\,000 \text{ cm}^{-1}$. Since we would expect the energy of this transition to be in the range $15\,000\text{--}22\,000 \text{ cm}^{-1}$ (1-5) we must anticipate an unrealistically high covalency, *e.g.* $\phi_{\parallel} = 0.10$ to 0.15 to accommodate this possibility.

In an octahedral field with elongated tetragonal distortion (D_{4h} symmetry) the ground state might be expected in some cases to be $^2A_{2g}(\text{d}_{xy})$ and corresponding expressions for the g_{\parallel} and g_{\perp} are

$$g_{\parallel} = 2.0023$$

$$g_{\perp} = 2.0023 - \frac{6\lambda}{\Delta E(^2A_{1g} \rightarrow ^2E_{2g})} \cdot \phi_{\perp}$$

Now we expect g_{\parallel} to be close to the free electron value, but $\Delta E(^2A_{1g} \rightarrow ^2E_{2g})$ would have to be assigned an improbably low value $\leq 8700 \text{ cm}^{-1}$. Normally the transition lies between $25\,000$ and $45\,000 \text{ cm}^{-1}$.

On the basis of the above discussion, we tentatively reject D_{4h} as the local point symmetry.

D_{2d}
Consideration of a $3d^1$ ion in a tetrahedral field with tetragonal distortion (D_{2d} symmetry) would involve nearly equivalent expressions and subsequent analysis would be qualitatively identical to D_{4h} .

D_{2h}
The d^1 ion in an octahedral field with a small rhombic distortion (D_{2h} symmetry) has five energy states: $^2B_{1g}$, $^2B_{2g}$, $^2B_{3g}$, and two 2A_g states. Now the e.s.r. spectrum cannot exhibit true axial symmetry. The difference between g_x and g_y arises from the difference in energy between the $^2B_{2g}$ and $^2B_{3g}$ states.

$$g_z = g_{\parallel} = 2.0023 - \frac{8\lambda}{\Delta E(^2B_{1g} \rightarrow ^2A_{1g})} \cdot \phi_z$$

$$g_x = 2.0023 - \frac{2\lambda}{\Delta E(^2B_{1g} \rightarrow ^2B_{3g})} \cdot \phi_x$$

$$g_y = 2.0023 - \frac{2\lambda}{\Delta E(^2B_{1g} \rightarrow ^2B_{2g})} \cdot \phi_y$$

Since our observed spectrum indicates that $g_x \approx g_y$, then clearly the objection to D_{2h}

becomes analogous to the arguments presented for D_{4h} (*vide supra*).

D_3
If the ligand field is determined primarily by the six oxygen atoms of the water ligands an approximately octahedral symmetry with a small axial trigonal distortion (D_3 symmetry) can also be considered.

In this symmetry the five orbitals are split into three energy states, one belonging to the A_1 representation and the other two to the E_1 representation. The appropriate combinations are

$$A_1 \quad d_0$$

$$E_1 \quad \begin{cases} \sqrt{2/3}d_{-2} + \sqrt{1/3}d_1 \\ \sqrt{2/3}d_2 + \sqrt{1/3}d_{-1} \end{cases}$$

$$E_2 \quad \begin{cases} \sqrt{1/3}d_{-2} - \sqrt{2/3}d_1 \\ \sqrt{1/3}d_2 - \sqrt{2/3}d_{-1} \end{cases}$$

If pure octahedral symmetry exists, the energies of the A_1 and E_1 states are lowest and equal. A small axial distortion lifts the degeneracy and makes either A_1 or E_1 the ground state. If we are dealing with D_3 symmetry then our experimental g values are only consistent with A_1 as the ground state (if E_1 were the ground state both g_{\parallel} and g_{\perp} are predicted to be close to zero).

Consider A_1 as the ground state and assuming that we are dealing with a purely ionic case with $\Delta E(A_1 \rightarrow E_1) \gg \lambda$ we have

$$g_{\parallel} = 2.0023$$

$$g_{\perp} = 2.0023 - \frac{2\lambda}{\Delta E(A_1 \rightarrow E_1)} - \frac{4\lambda}{\Delta E(A_1 \rightarrow E_2)}$$

On the basis of this expression and assuming $\Delta E(A_1 \rightarrow E_2)$ is in the range $15\,000\text{--}22\,000 \text{ cm}^{-1}$ (*i.e.* by analogy to $\Delta E(^2B_{2g} \rightarrow ^2B_{1g})$ in D_{4h} symmetry) one calculates that $\Delta E(A_1 \rightarrow E_1) < 5600 \text{ cm}^{-1}$. Since the experimental value of g_{\parallel} is rather lower than the free electron value, the assumption implicit in the above expression (*i.e.* $\Delta E(A_1 \rightarrow E_1) \gg \lambda$ for $\lambda = 154 \text{ cm}^{-1}$) is not strictly valid, and $\Delta E(A_1 \rightarrow E_1)$ may be much lower than 5600 cm^{-1} .

Notwithstanding, the experimental g values are undoubtedly more consistent with D_3 local symmetry of the titanium(III) complex unit giving the spectrum than with the other possibilities that have been discussed.

On the basis of present data we are unable to make comment on the nature of the ice structure involved, for either anion or cation; or indeed whether the distortion of the field about the Ti(III) arises from the location of the ions near a phase boundary of two forms of ice structure.

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