

Electron Spin Resonance Studies in Aqueous Solution: Titanium(III) in the pH Region 1.0–3.5

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In aqueous solutions of titanium(III) between pH 1.0 and 3.5 a single line e.s.r. signal is recorded with $g = 1.9408 \pm 0.001$ and linewidth 95 ± 3 G. Evidence is presented in support of a hydrolyzed metal ion complex $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ as the likely active species.

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En solutions aqueuses de titane(III), entre des pH variant de 1.0 à 3.5, on enregistre un signal d'une seule raie r.p.e. avec $g = 1.9408 \pm 0.001$ et de largeur 95 ± 3 G. On fournit des données indiquant que l'ion métallique complexe hydrolysé $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ est l'espèce active probable.
[Traduit par le journal]

Introduction

The titanium(III) ion ($3d^1$) exists in acidic aqueous solution as the hexaquo ion $\text{Ti}(\text{H}_2\text{O})_6^{3+}$. In spite of the unpaired electron that is present, no e.s.r. signal is observed for this species. Such an observation is fully consistent with the octahedral crystal field symmetry of the ion. In the orbitally degenerate ground state, ${}^2T_{2g}$, the spin angular momentum is cancelled by the residual orbital angular momentum, leading to the expectation that $g \approx 0$ (1, 2). Although small axial or rhombic distortions can partially quench the orbital angular momentum, spin-lattice relaxation time is too short to detect the e.s.r. signal. Reduction of the symmetry of the ion to tetragonal or lower leaves essentially only the spin angular momentum, and hence a signal with g close to the free electron (2.0023) and with a narrow linewidth expected. The complexes $\text{Ti}(\text{CH}_3\text{O})_2^+$ and TiF_2^+ in methanol solutions have such a distortion of the octahedral field, and exhibit e.s.r. signals (3). Other examples of e.s.r. spectra from titanium(III) complexes have been published (4–8).

We now wish to report the observation of an e.s.r. spectrum from aqueous solutions of TiCl_3 , $\text{Ti}_2(\text{SO}_4)_3$, and TiI_3 in the pH interval 1.0–3.5. Our experiments indicate that the signal arises from one of the equilibrium forms of the partially hydrolyzed titanous ion $\text{Ti}(\text{OH})^{2+}$, most reasonably either the species $[\text{TiO}(\text{H}_2\text{O})_5]^+$ or $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_4]^+$.

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.

The titanium(III) solutions were prepared by dissolving the metallic sponge (Fisher) with gentle heating in approximately 1 N HCl or H_2SO_4 respectively. In all cases a nitrogen atmosphere was employed to minimize oxidation of the titanous species. Alternatively Fisher reagent titanium(III) chloride solution (20%) was used directly as received without qualitative change in any results. Titanium(III) iodide was prepared in methanol by the procedure of Giggenbach and Brubaker (9). Methanol was eliminated by several evaporations to dryness employing water as the solvent in the second and subsequent cycles.

The g factors are quoted relative to DPPH, $g = 2.0036$. Relative spin concentrations were estimated from the product of the peak-to-peak height of the first derivative signal and the square of the maximum slope width. Absolute concentrations were estimated by comparison with standard aqueous manganous chloride. The u.v./visible spectra were recorded on a Cary Model 17 instrument.

Results and Discussion

Detailed examinations of the behavior of dilute aqueous titanium(III) solutions in the pH region between 0.0 and 3.5 indicate that $\text{Ti}(\text{H}_2\text{O})_6^+$ and $\text{Ti}(\text{OH})^{2+}$ are the dominant species with insignificant amounts of further hydrolyzed ions present below pH 3.5 (10–12). Applying e.s.r. spectroscopy we observe the existence of a paramagnetic signal from dilute titanous ion in aqueous solutions of pH 1.0–3.5. The e.s.r.

TABLE 1. Electron spin resonance data for complex ions

Proposed complex ion*	g factor ± 0.001	ΔH_{pp} $\pm 2 \text{ G}^\dagger$	Total unpaired spins (%)
$[\text{TiO}(\text{H}_2\text{O})_5]^+$ or $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_4]^+$	1.9408	95 \ddagger	~ 2
$[\text{TiO}(\text{D}_2\text{O})_5]^+$ or $[\text{Ti}(\text{OD})_2(\text{D}_2\text{O})_4]^+$	1.9411	72	~ 2

*Total concentration of Ti^{3+} was between 0.001 to 0.500 M in the pH region between 1.5 to 3.5.

$^\dagger \Delta H_{pp}$ is the peak-to-peak linewidth.

‡ Room temperature. Value decreases to $84 \pm 3 \text{ G}$ at 0°C .

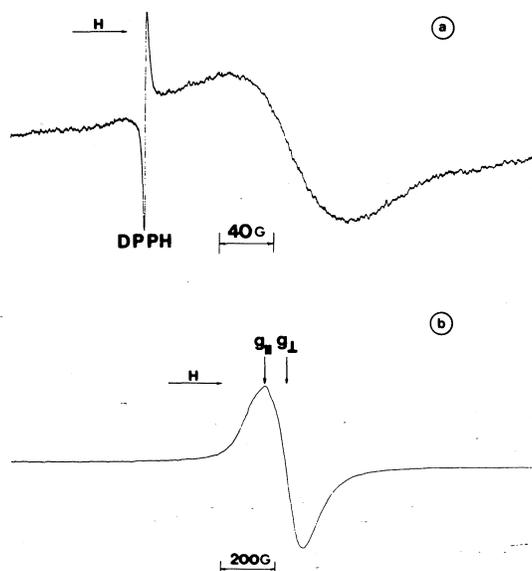


FIG. 1. (a) TiCl_3 , 0.016 M , 25°C ; pH 2.7. (b) TiCl_3 , 0.018 M , 77°K (frozen solution); Solution pH 2.2 D_2O ; $g_{\perp} = 1.925 \pm 0.001$, $g_{\parallel} = 1.961 \pm 0.001$.

spectrum is shown in Fig. 1a and the spectral data are tabulated in Table 1. By approximate calculation, employing graphical integration of the derivative absorption curve, we estimate the maximum concentration of spins contributing to the signal to be *ca.* 2% of the total Ti^{3+} concentration.

Assignment of the basic structural feature of the complex providing the signal is based on the close agreement of its pH dependence with that of the hydrolyzed ion $\text{Ti}(\text{OH})^{2+}$. In Fig. 2 the relative concentration of $\text{Ti}(\text{OH})^{2+}$ both based on the absorption maximum at 465 nm, and based on the titrimetric data of Pecsok and co-worker (10) is compared with the e.s.r. signal.

The close correspondence of the relative intensity of the e.s.r. signal with the titrimetric $\text{Ti}(\text{OH})^{2+}$ concentration in particular, is clearly apparent. Note that precipitation brings a halt to spectrally estimated concentrations at about pH 3.5.

Examination of the effect of the anions Cl^- , SO_4^{2-} , and I^- on the e.s.r. signal sheds further light on the nature of the paramagnetic species. First, the variation of the relative signal intensity with pH is nearly the same for the three species, Fig. 2. Second, the linewidth of the signal is in-

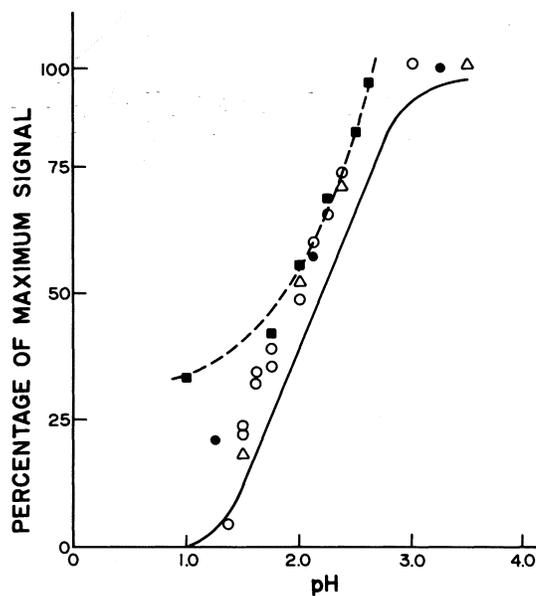


FIG. 2. The pH dependence of $\text{Ti}(\text{OH})^{2+}$ concentration and of relative e.s.r. signal intensity for aqueous solutions of titanium (III). \bullet , TiCl_3 , 0.016 M , e.s.r. signal; \circ , TiCl_3 , 0.008 M , e.s.r. signal; Δ , $\text{Ti}_2(\text{SO}_4)_3$ 0.005 M , e.s.r. signal; - - - \blacksquare , $\text{Ti}(\text{OH})^{2+}$, λ_{max} 465 nm, absorbance; — \circ , $\text{Ti}(\text{OH})^{2+}$, titrimetric, calculated as per ref. 10.

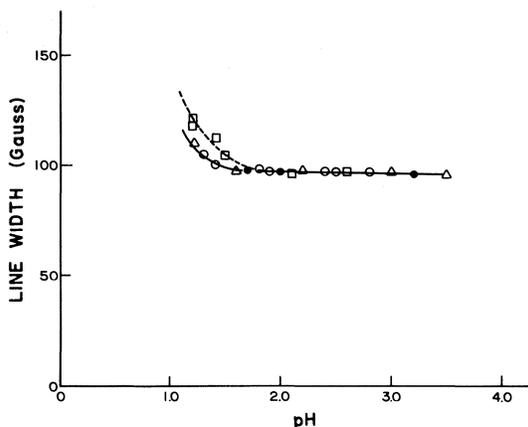
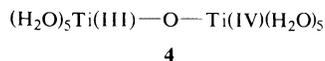
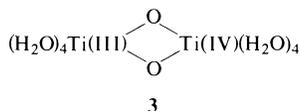


FIG. 3. Electron spin resonance signal linewidth for aqueous titanium(III) solutions, 25°C. ●, TiI_3 , 0.016 M ; ○, TiCl_3 , 0.008 M ; △, $\text{Ti}_2(\text{SO}_4)_3$, 0.005 M ; □, TiCl_3 , 0.080 M .

dependent of anion above pH 1.6 as shown in Fig. 3. Finally, the intensity of the signals in the case of the chloride and iodide do not change on increasing the anion concentrations to 2.0 M in samples of 0.001 M titanous ion, in keeping with their low complexation constants (10–12). In contrast, increased sulfate (2.0 M) destroyed the signals in chloride, iodide, or sulfate samples. We ascribe the effect to complexation of the e.s.r. "active" species by added sulfate. In summary, the anion is not required in the primary coordination sphere, indeed in the case of sulfate it diminishes signal intensity. Moreover since we see no change in g value or linewidth, Fig. 3, even though crystal field effects of the anions should be significantly different, we conclude that the anion is not present in the e.s.r. active complex.

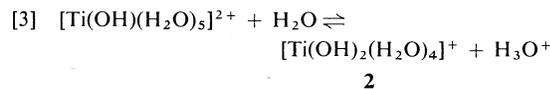
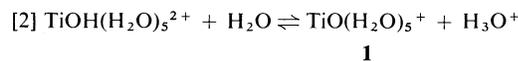
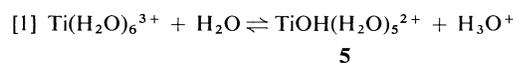
The possibility that the species was a dimeric or polymeric oxygen bridged form of Ti(III) and Ti(IV), **3** and **4** were considered.



However no increase in signal intensity was achieved by either deliberate addition of excess Ti(IV) ions or purposeful partial oxygenation of a TiCl_3 test solution at pH 2.5. We note that the internuclear separation of the metal ions in a

bridged species precludes a Ti(III)—Ti(III) dimer in view of the expected rapid spin-spin relaxation processes. Likewise spin exchange with Ti(IV) might be expected to broaden any signal from species **3** and **4** making them unlikely candidates for the e.s.r. active species. Moreover, at concentrations from 0.01 to 0.500 M , a direct variation in signal intensity with increasing titanium(III) was observed.

Clearly the structural possibilities reduce to aquated and hydrolyzed titanium(III) ions **1**, **2**, and **5**, as produced in reactions 1–3.



Since **5** is the predominant form of titanium in these solutions, it cannot be the e.s.r. "active" species that is present at only 2% of the nominal metal concentration. The complex ion **1** is more attractive since it will be present in low concentration but linearly related to titanium concentration and independent of anion.

Moreover in analogy to VO^{2+} , we can expect a much stronger axial perturbation by the oxide ligand in $[\text{TiO}(\text{H}_2\text{O})_5]^+$ than by OH^- in the dominant complex **5**. However, in the particular case of VO^{2+} , e.s.r. and spectroscopic studies (13–15) have convincingly demonstrated that the local point symmetry of vanadium in $[\text{VO}(\text{H}_2\text{O})_5]^+$ is C_{4v} and that the unpaired electron lies in the d_{xy} orbital (${}^2B_{2g}$). Hence axial π bonding is possible, effectively giving rise to a triple bond between the vanadium and the unique oxygen atom. Therefore the axial component to the ligand field will lead to a high deviation from O_h symmetry. The isotropic g factor for the complex $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ is 1.964 (13–15) and indicates a strong axial field and a relatively small anisotropy in the g value. In contrast, the active titanium species described here has a lower g value (1.9408), and moreover, a rather large linewidth (see Discussion below). Accordingly, although not recognized in the solution studies (9–11) we feel that the complex **2** $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_4]^+$, is a more likely candidate than the $[\text{TiO}(\text{H}_2\text{O})_5]^+$. The dihydroxy species

will have the necessary axial perturbation, but much less than the alternative TiO^+ species.

To test further the nature of the e.s.r. active species we have prepared TiCl_3 in D_2O at pH 2.2, observing a decrease in linewidth at 0.008 M from 96 to 72 G. The change is assigned to replacement of the hydrogens of water ligands by deuterium, narrowing the resonance line by removing the larger hyperfine interaction with the protons.¹ For example, Johnson *et al.* (8) have reported a splitting of 1.8 G for each proton in four water ligands of a titanium(III) complex with *t*-butyl alcohol. If the present complex **2** has four water ligands and two OH groups, as formulated, we can project a total contribution of *ca.* 20 G from this source. A slight change in coupling constant would clearly accommodate the whole of the line narrowing that is observed. Clearly the comparable proton hyperfine coupling in our complex and that of Johnson *et al.* (8) is consistent with a similar degree of delocalization of the d electron onto the water ligand in both instances.

Linewidth Effects

The spectrum of the frozen solution in D_2O at 77 °K provides evidence for the axial symmetry expected for complexes **1** and **2** (Fig. 1*b*). From the values of $g_{\perp} = 1.9250 \pm 0.001$ and $g_{\parallel} = 1.9606 \pm 0.001$, one calculates $g_0 = \frac{1}{3}(g_{\parallel} + 2g_{\perp}) = 1.9368 \pm 0.002$ which compares favorably with the value recorded in solution 1.9411 ± 0.001 . The possibility of species such as $\text{Ti}(\text{OH})_3$ and the unsymmetrical bridged species **3** and **4** are ruled out by this observation. Finally, we observe no resonance lines indicative of dimeric titanium(III) species with triplet character. One is struck by the relatively narrow line (*ca.* 115 G) observed in the randomly oriented frozen sample. Consideration of the linewidth at room temperature 72 ± 3 G would indicate that the basic resonance linewidth has actually decreased.

There are several sources that contribute to the relaxation of the e.s.r. signal. Electric quadrupole effects are negligible in magnitude. Anisotropic processes and intermolecular interactions are eliminated by the nature of the temperature

¹The broad resonance line obscures resolution of both proton and ⁴⁷Ti or ⁴⁹Ti coupling with the electron spin.

dependence of the linewidth and by the lack of effect of the anion or metal ion concentration. Over the range 0.001 to 0.500 M of titanium(III) concentration no change in linewidth is observed (Fig. 3). Accordingly, we can conclude that the linewidth is determined mainly by the relaxation processes within the coordination shell of the ion.

It seems plausible that vibrational spin-orbit processes are responsible for the linewidth, and that there is a near degeneracy of the electronic levels. Observation of significant narrowing on going from room temperature to 0 °C (see Table 1) and the relatively narrow linewidth of the randomly oriented sample at 77 °K in D_2O (see Fig. 1*a* and *b*), is consistent with excitation energies of the order kT .

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