

## Ti<sup>47</sup> and Ti<sup>49</sup> Hyperfine Structure in the Electron Spin Resonance of Titanium (III) Complexes\*

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Satellite lines have been resolved in the solution electron spin resonance spectra of two complexes of titanium (III). These lines arise from hyperfine interaction of the unpaired electron with the odd isotopes of titanium, Ti<sup>47</sup> and Ti<sup>49</sup>. The nuclear spins of the two isotopes are found to be  $\frac{5}{2}$  and  $\frac{7}{2}$ , respectively, in agreement with earlier nuclear induction intensity measurements. The Ti hyperfine constants for the two complexes are almost identical (50.0 Mc/sec). The two complexes studied are a one-to-one complex between titanium (III) and the OCH<sub>3</sub><sup>-</sup> ion, and the

TiF<sub>2</sub><sup>+</sup> ion. The preparation of these complexes is discussed. In the case of the TiF<sub>2</sub><sup>+</sup> ion, an additional hyperfine interaction is observed with the two fluorine nuclei. The splitting constant for the fluorine interaction is 21.1 Mc/sec.

The optical spectra of these complexes show large splittings of the *d*-electron levels which are believed to be the result of strong axial perturbations by the coordinating ligands. These splittings lengthen the electron spin lattice relaxation time sufficiently to permit the resolution of the satellite lines.

JEFFRIES<sup>1</sup> has assigned to the isotopes Ti<sup>47</sup> and Ti<sup>49</sup> nuclear spins of  $\frac{5}{2}$  and  $\frac{7}{2}$ , respectively. This assignment was carried out indirectly, by means of nuclear induction intensity measurements, and as far as we know, has never before been confirmed by the observation of hyperfine multiplet structure in optical spectra or electron spin resonance (ESR) spectra. We have now observed such multiplet splittings in the ESR spectra of two titanium (III) complex ions and can confirm that the earlier assignment is correct.

Solutions of anhydrous TiCl<sub>3</sub> in various anhydrous alcohols have been studied chemically and spectroscopically, and are believed to consist of octahedrally solvated titanium (III) ions.<sup>2</sup> No ESR signals have been detected in these solutions. Starting with methanol solutions of TiCl<sub>3</sub> prepared by the method of Hartmann *et al.*<sup>2</sup> we have prepared two other complexes of the titanium (III) ion which exhibit sufficiently narrow ESR absorption lines to permit the resolution of the titanium odd isotope contact hyperfine interaction in

solution. The first complex is yellow and may be prepared by adding one equivalent of NaOCH<sub>3</sub> to one equivalent of TiCl<sub>3</sub> in methanol. It has been identified as a one-to-one complex by observing that the intensity of the ESR signal goes through a maximum when one equivalent of NaOCH<sub>3</sub> has been added. An ESR spectrum of this complex ion is shown in Fig. 1.

The titanium isotopes responsible for the satellite lines in Fig. 1 are Ti<sup>47</sup>, 7.32% abundant, and Ti<sup>49</sup>, 5.46% abundant.<sup>3</sup> The remaining even-even isotopes, Ti<sup>48</sup> and Ti<sup>50</sup>, account for the strong central line. Jeffries measured the gyromagnetic ratios of the two odd isotopes and found them practically identical<sup>1</sup>:

$$\gamma(\text{Ti}^{49})/\gamma(\text{Ti}^{47}) = 1.00026 \pm 0.00002.$$

Thus the magnitude of the hyperfine splitting of each of these isotopes will be the same. We observe the superposition of 6 lines from an isotope of spin  $\frac{5}{2}$  and 8 lines from an isotope of spin  $\frac{7}{2}$ . The measured intensity ratio of line 2 to line 1 is  $3.0 \pm 0.3$ ; the intensity ratio expected from assigning spin  $\frac{5}{2}$  to Ti<sup>47</sup> and  $\frac{7}{2}$  to Ti<sup>49</sup> is 2.8. The observed hyperfine structure consequently verifies Jeffries' conclusion.

We find that the linewidth of the hyperfine component depends upon *m<sub>I</sub>*; this is a behavior observed in a number of other transition metal complexes and arises from the anisotropy in the *g* tensor and in the hyperfine tensor.<sup>4</sup> The magnetic data for this complex are tabulated in Table I.

Similar results (see Table I) have been obtained with a second titanium (III) complex, the TiF<sub>2</sub><sup>+</sup> ion. This ion, which is green, is prepared by adding slightly more than two equivalents of HF in anhydrous methanol to one equivalent of the blue solution of TiCl<sub>3</sub> in methanol. The spectrum shows in addition to the Ti<sup>47</sup> and Ti<sup>49</sup> interaction, a triplet splitting of each component by an interaction with two equivalent F<sup>19</sup> nuclei, thus establishing the chemical stoichiometry. This ion may also be prepared in water by similar means.

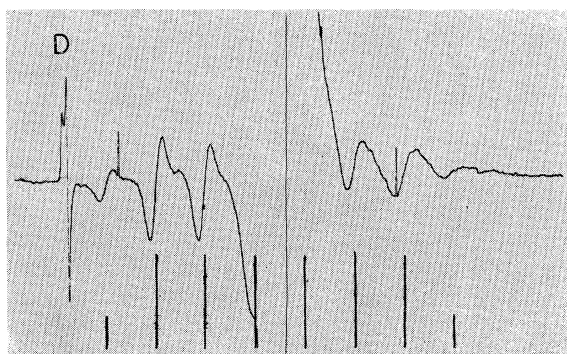


FIG. 1. The ESR spectrum of 0.005*M* Ti(III):CH<sub>3</sub>O<sup>-</sup> at 9.358 kMc/sec. The field increases from left to right. The spectra were obtained at -45°C and the resonance indicated by *D* comes from some paramagnetic material in the walls of the quartz Dewar. The separation between the satellite lines is  $18.2 \pm 0.2$  gauss.

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<sup>1</sup> C. D. Jeffries, *Phys. Rev.* **92**, 1262 (1953).

<sup>2</sup> H. Hartmann, H. L. Schläfer, and K. H. Hansen, *Z. anorg. u. allgem. Chem.* **284**, 153 (1956).

<sup>3</sup> J. E. Hogg, *Can. J. Chem.* **32**, 1039 (1954).

<sup>4</sup> R. N. Rogers and G. E. Pake, *J. Chem. Phys.* **33**, 1107 (1960); H. M. McConnell, *J. Chem. Phys.* **25**, 709 (1956).

TABLE I. Isotropic hyperfine constants and  $g$  factors in Ti(III) complexes. All measurements were carried out at  $-45^\circ\text{C}$ .

Ion/solvent	$g$	$A_{\text{Ti}}$ (Mc/sec)	$A_F$ (Mc/sec)	$ \chi $ (a.u.)
Ti(III):CH <sub>3</sub> O <sup>-</sup> /CH <sub>3</sub> OH	1.9532 $\pm 0.0005$	49.7 $\pm 0.5$	...	2.58
TiF <sub>2</sub> <sup>+</sup> /CH <sub>3</sub> OH	1.9465 $\pm 0.0004$	50.0 $\pm 0.9$	21.1 $\pm 0.3$	2.64

We have observed large splittings in the optical absorption spectra of these ions and believe them to be the result of strong axial perturbations by the coordinating ligands. These axial fields leave a well separated orbital singlet ground state and thus lengthen the electron spin-lattice relaxation time. The results are narrow lines and a much reduced  $g$ -tensor anisotropy in these complexes. Details of the  $g$ -tensor anisotropy, as determined by measurements on rigid glasses, as well as the optical spectra of these complexes will be reported elsewhere.

The spin density at the Ti nucleus may be given in

terms of the  $\chi$  defined by Abragam *et al.*<sup>5</sup>:

$$\chi = \frac{4\pi}{S} \langle \delta(\mathbf{r}) S_z \rangle_{S_z=S} = \frac{3}{4} \frac{A_{\text{Ti}}}{g_N \beta_N \beta}.$$

Here we have omitted small contributions to  $A_{\text{Ti}}$  from the  $g$ -tensor anisotropy.

The values of  $\chi$ , in atomic units, reported in Table I are very similar to those of other ions of the first transition series.<sup>5,6</sup> The origin of this isotropic hyperfine interaction is probably that postulated by Wood and Pratt,<sup>7</sup> and by Heine,<sup>6</sup> i.e., a polarization of the  $s$  electrons by the single unpaired  $3d$  electron through an exchange interaction.

#### ACKNOWLEDGMENT

We are greatly indebted to Professor R. V. Jones for pointing out to us the existence of the green fluoride complex.

<sup>5</sup> A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955).

<sup>6</sup> V. Heine, Phys. Rev. **107**, 1002 (1957).

<sup>7</sup> J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957); see also R. E. Watson and A. J. Freeman, *ibid.* **120**, 1134 (1960).

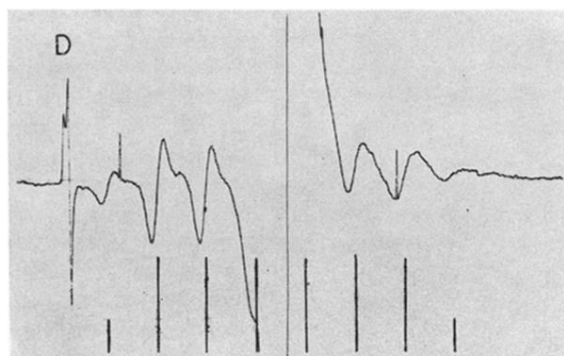


FIG. 1. The ESR spectrum of  $0.005M$   $Ti(III):CH_3O^-$  at  $9.358$  kMc/sec. The field increases from left to right. The spectra were obtained at  $-45^\circ C$  and the resonance indicated by  $D$  comes from some paramagnetic material in the walls of the quartz Dewar. The separation between the satellite lines is  $18.2 \pm 0.2$  gauss.