Electron Paramagnetic Resonance Studies of Titanium(III) Ions with Complexing Compounds

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The nuclear hyperfine structure of titanium(III) was first observed by Waters and Maki¹⁾ using titanium(III) complexes formed by the interaction of equimolar quantities of titanium(III) chloride in methanol and sodium methylate in methanol and slightly more than two equivalents of hydrogen fluoride in methanol to one equivalent of titanium(III) chloride in methanol. The spectra which were obtained in the methanol solution at $-45°C$ consisted of eight lines, which is in accordance with the predictions of Jeffries²⁾ who determined through nuclear magnetic resonance measurements that ^{47}Ti and ^{49}Ti have spins of 5/2 and 7/2 respectively. The spectrum obtained by Waters and Maki is highly unsymmetrical, with peak intensities decreasing at higher fields.

A symmetrical hyperfine spectrum of titanium(III) was obtained by McGarvey³⁾ at 77°K using a single crystal of aluminum acetylacetonate containing a small amount of titanium acetylacetonate. A signal for titanium(III) in solution has been observed by Shien and Boss⁴⁾ using the $(\pi\text{-}C_5H_5)_2Ti(C_2H_5)$ complex in toluene at 300°K, and by Avvakumov, Garif'yanov and Semenova⁵⁾ using supercooled solutions of $TiCl_3 \cdot 6H_2O$ and $Ti_2(SO_4)_3 \cdot 4H_2O$ in alcohol and glycerine at 200, 77°K, and 300°K. The *g* values were measured, as were the *g* values at 200 and 77°K of the solid salts, used in the above solutions⁶⁾ (see Table II). The hyperfine spectrum of titanium(III) arises from the interaction of the unpaired 3d electron with the nucleus. The eight lines of the hyperfine pattern are formed by the contributions of the ^{47}Ti and ^{49}Ti isotopes with spins of 5/2 and 7/2 respectively; two of them are overlapped by the large central line from ^{46}Ti, ^{48}Ti, and ^{50}Ti with zero spins.

It was decided to investigate the EPR spectra of other titanium(III) solutions at about 9000 Mc. in order to determine if the hyperfine spectra could be obtained in an aqueous solution and at room temperature. Because of their known ability to form chelate complexes, we chose the complexing agents listed in Table I, which also lists the conditions for preparing the samples.

The spectra obtained in this investigation are the first examples of the hyperfine structure of the complexes of paramagnetic ions to be observed in aqueous solutions.

The features of the simple and hyperfine spectra of several of the chelate compounds were considerably changed by varying the pH values by varying the quantities of complexing agents.

Results and Discussion

The spectra for the titanium(III)-NTA complex is unique in showing practically no change when the pH values are changed from 3 to 10.2. At lower pH values the hyperfine structure diminishes in intensity, until at pH 1.90 very little of the hyperfine structure is discernible. The disappearance of the hyperfine pattern may result from 3d-electron exchange among titanium ions or from the rapid relaxation of titanium nuclear spins.

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1) E. L. Waters and A. H. Maki, *Phys. Rev.*, **125**, 233 (1962).

2) C. D. Jeffries, ibid., **92**, 1262 (1953).

3) B. R. McGravey, *J. Chem. Phys.*, **38**, 388 (1963).

4) J. C. W. Chien and C. R. Boss, *J. Am. Chem. Soc.*, **83**, 3767 (1961).

5) V. I. Avvakumov, N. S. Garif'yanov and E. I. Semenova, *Zhur. Eskptl. i. Teoret. Fiz.*, **39**, 1215 (1960).

6) V. I. Avvakumov, N. S. Garif'yanov, S. G. Salikhov and E. I. Semenova, *Fiz. Tverdogo Tele*, **3**, 2111 (1961).

TABLE I. PREPARATION OF SAMPLE SOLUTIONS

Complexing agent	Name	Formula	pK_{a_i} $i=1,2,3,4$	Quantity added per 10 ml.	Control of pH by addition of	Additional reagent
NTA	Nitrilotriacetic acid	$N(CH_2COOH)_3$	1.9, 2.5, 9.7	0.3 g.	NH_4OH	
HEID	Hydroxyethyl-iminodiacetic acid	$N(CH_2COOH)_2 \cdot CH_2CH_2OH$	2.2, 8.7	0.3 g.	NH_4OH	
BHEG	Bis-(2-hydroxyethyl)-glycine	$N(CH_2CH_2OH)_2 CH_2COOH$	8.08	0.3 g.	NH_4OH	(1) Tartaric acid (2) No tartaric acid
TEOHA	Triethanolamine	$N(CH_2CH_2OH)_3$	7.90	—	Complexing agent itself	Tartaric acid
DEA	Diethylamine	$NH(CH_2CH_3)_2$	11.0	—	Complexing agent itself	Tartaric acid
NBA	*N*-Butylamine	$H_2N(C_4H_9)$		—	Complexing agent itself	Tartaric acid
EDTA	Ethylendiamine-tetraacetic acid disodium salt	$C_2H_4 \cdot \{N(CH_2COOH) \cdot (CH_2COONa)\}_2$	2.2, 8.0, 5.2, 10.3	0.3 g.	NH_4OH	(1) Tartaric acid (2) No tratraic acid
AAC	Acetylacetone	$CH_3COCH_2COCH_3$		3 ml. saturated soln.	NH_4OH	
TEA	Triethylamine	$N(CH_2CH_3)_3$	10.8	—	Complexing agent itself	Tartaric acid

The titanium(III)-NTA spectra are unsymmetrical and similar to those obtained by Waters and Maki. The other complexes studied exhibited remarkable changes at higher pH ranges. The stability of this complex probably results from the three carboxyl groups of NTA, which allows the molecule to enter into a three-dimensional system with titanium(III) with little probability of interaction with the nitrogen of NH_4 when an excess of ammonium hydroxide is added. In less stable titanium(III) complexes, titanium(III) hydroxide tends to precipitate at higher pH values.

The cause of the unsymmetrical hyperfine structure of this spectrum may be deduced from the suggestion made by McConnell[7] and confirmed experimentally by Rogers and Pake[8] regarding the observed broadening of the hyperfine spectrum of VO(III) ions in an aqueous solution. This condition can also exist with the solutions used in this investigation.

$$1/T_2 \approx \lambda_c(\Delta g \beta H_0 + b m_I)^2/h^2$$

where b is $A_\parallel - A_\perp$; the other symbols possess their usual meanings. The above equation generally predicts a different width contribution for each hyperfine line. The minimum width should occur for the m_I value which causes the bracket to approach a minimum.

The spectra for the titanium(III)-HEID complex show a hyperfine structure which is far less intense than but which has the same unsymmetrical features as the previously-discussed complex. This hyperfine structure is only discernible at pH ranges from about 5.0 to 7.9. At appreciably higher or lower pH values, no hyperfine structure is exhibited by the complex. Since HEID contains only two carboxyl groups, the three-dimensional system which was thought to be obtained with the NTA complex is less likely to be obtained with this complex.

With BHEG, which contains only one carboxyl group, no hyperfine structure is obtained at any pH value. This complex is not as stable as either of the above complexes, and titanium(III) hydroxide begins to precipitate at a pH of approximately 9.0. Upon the addition of tartaric acid, however, the precipitation is prevented and a signal at higher pH values can be obtained.

The spectrum for the titanium(III)-EDTA

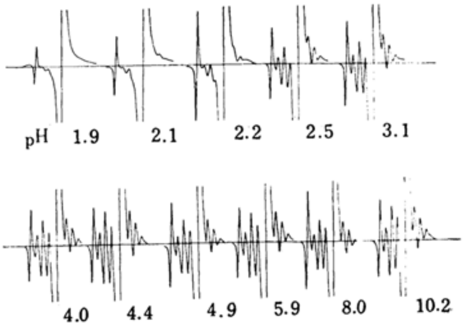

Fig. 1. Spectra for the Ti(III)-NTA complex. The concentration of $TiCl_3$ is 0.11 M. The field increases from left to right. The initial peak is that of DPPH.

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[7] H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).

[8] R. N. Rogers and G. E. Pake, ibid., **33**, 1107 (1960).

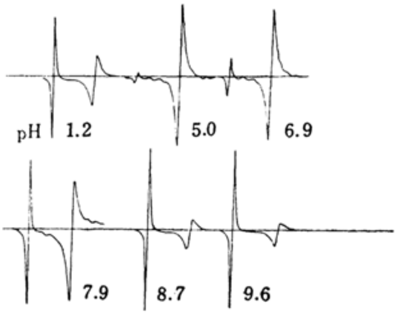

Fig. 2. Spectra for the Ti(III)-HEID complex. The concentration of $TiCl_3$ is 0.11 M. The field increases from left to right. The initial peak is that of DPPH.

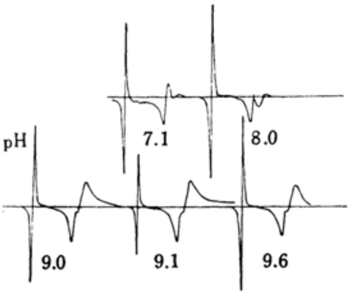

Fig. 3. Spectra for the Ti(III)-EDTA complex. The concentration of $TiCl_3$ is 0.11 M. The field increases from left to right. The initial peak is that of DPPH.

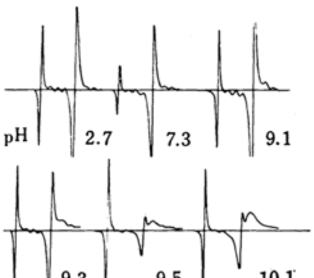

Fig. 4. Spectra for the Ti(III)-EDTA-tartaric acid complex. The concentration of $TiCl_3$ is 0.11 M. The field increases from left to right. The initial peak is that of DPPH.

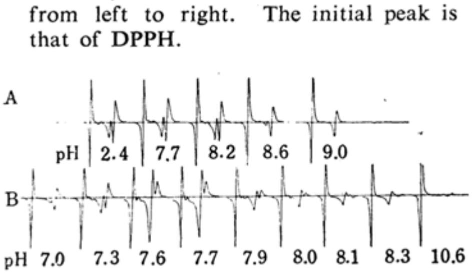

Fig. 5. Spectra for the Ti(III)-TEOHA-tartaric acid complex. The concentration of $TiCl_3$ is (A) 0.044 M. and (B) 0.088 M. The field increases from left to right. The initial peak is that of DPPH.

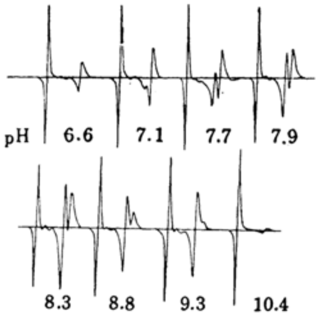

Fig. 6. Spectra for the Ti(III)-TEA-tartaric acid complex. The concentration of $TiCl_3$ is 0.11 M. The field increases from left to right. The initial peak is that of DPPH.

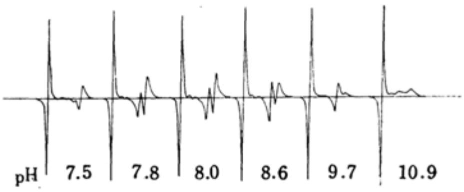

Fig. 7. Spectra for the Ti(III)-DEA-tartaric acid complex. The concentration of $TiCl_3$ is 0.088 M. The field increases from left to right. The initial peak is that of DPPH.

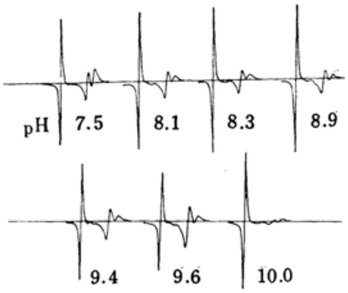

Fig. 8. Spectra for the Ti(III)-NBA-tartaric acid complex. The concentration of $TiCl_3$ is 0.11 M. The field increases from left to right. The initial peak is that of DPPH.

complex is especially interesting because of the different spectra obtained with and without the addition of tartaric acid. With no tartaric acid, the spectra (Fig. 3) shows a less hyperfine structure, but evidence for more than one complex is clearly seen. Two peaks are observed for all pH values but are more pronounced at the pH values of 7 and 8. With the addition of tartaric acid, the spectrum exhibits an observable hyperfine structure in which each component of the hyperfine lines is broadened at higher pH values. At pH 9.5, another peak without a hyperfine structure appears at higher

TABLE II. *g* Values of Ti(III) complexes

Complexing agent	Concn. of $TiCl_3$ (molarity)	pH	*g* value ±0.002
Acetylacetone	0.011 and 0.022	1.7 to 2.6	1.946
NTA	0.11	1.9, 8.0, 10.2	1.962
NTA	0.11	2.1, 2.2, 2.5, 3.1, 4.0, 4.4, 4.9, 5.9	1.961
HEID	0.11	1.2	1.952
HEID	0.11	5.0, 7.9	1.953
HEID	0.11	6.9	1.950
HEID	0.11	9.6	1.954
BHEG	0.11	3.3, 3.7, 3.9	1.957
BHEG	0.11	8.9, 9.2	1.954
BHEG	0.11	9.6, 10.1	1.953
EDTA (no tartaric acid)	0.11	1.1, 7.1	1.958
EDTA (no tartaric acid)	0.11	8.0, 9.0, 9.1, 9.6	1.956
EDTA (tartaric acid)	0.11	2.7, 7.3, 9.1, 9.3	1.957
EDTA (tartaric acid)	0.11	9.5, 10.1	1.956

Complexing agent	Concn. of $TiCl_3$ (molarity)	pH	Peak a	Peak b
TEOHA	0.044	7.4, 8.2, 8.6, 8.8, 9.0	1.970	1.964
TEOHA	0.088	7.0, 7.6, 7.7, 7.9, 8.1, 8.3	1.970	1.964
TEA	0.11	6.6	1.969	(1 peak)
TEA	0.11	7.1, 7.7, 7.9, 8.3, 8.8, 9.3	1.970	1.965
TEA	0.11	10.4	1.970	(1 peak)
DEA	0.088	7.5, 7.8, 8.0, 8.6, 9.7	1.970	1.964
NBA	0.088	7.5, 8.1, 8.3, 8.9, 9.4, 9.6, 10.0	1.970	1.964

$(\pi\text{-}C_5H_5)_2Ti(C_2H_5)$ in toluene	1.94 (300°K)[4]
$TiCl_3\cdot 6H_2O$ (solid salt)	1.91 (77° and 200°K)[6]
$Ti_2(SO_4)_3\cdot 4H_2O$ (solid salt)	1.91 (77° to 200°K)[6]
$TiCl_3\cdot 6H_2O$ (ethanol solution)	1.9±0.1 (Room temp.)[5]
Ti(III) : CH_3OH (methanol solution)	1.9532±0.0005 (−45°C)[1]
TiF_2^+ (methanol solution)	1.9465±0.0004 (−45°C)[1]

fields. At pH 10.1, the increase in the intensity of the second peak indicates a change in the equilibrium mixture of the two complexes.

The principles of the complex formation of titanium(III) with TEOHA (Fig. 5), TEA (Fig. 6), DEA (Fig. 7), and NBA (Fig. 8) are similar. A hyperfine structure is seen with all the complexes. The spectra clearly show the presence of two different complexes for each complexing agent. The concentration of one complex with respect to the other depends upon the amount of complexing agent which has been added, rather than upon the pH of the solution. This is shown with the different equilibrium mixtures of complexes obtained using different concentrations of titanium(III) with TEOHA at pH 7.7 (Fig. 5). Since the concentration of titanium(III) in one case is double that of the other, a different complex is dominant. The *g* values for this group (Table II) are all 1.974±0.002, which is excellent evidence for the fact that the orbital character of the ground electronic doublet of titanium(III) remains the same with these compounds for all pH values. Similar conditions appear to exist with NTA, HEID, BHEG, and EDTA, as is shown in Table II, where *g* varies from 1.950 to 1.962. The *g* value for titanium(III) acetylacetonate is 1.946, which is a fairly sizable shift from that of the other complexes. It is interesting to note that the *g* values are little changed with different complexing agents and varying pH values. This shows that the contributions of the spin orbit coupling are little changed despite the fact that different colors are obtained.

The titanium(III) used in this investigation was a commercial grade in hydrochloric acid and contained zinc in excess of a 1 : 1 ratio to titanium. Recent work has shown that zinc is necessary in order to obtain spectra with complexing agents which do not contain carboxyl groups. Somewhat similar spectra can be obtained with a mixture of titanium(III), tartaric acid and zinc.

Summary

The EPR spectra of a number of titanium(III) complex compounds have been obtained at room temperature and in aqueous solutions; these compounds show either a hyperfine structure alone or a mixture of hyperfine and simple structures. The *g* values for the various complexes have been determined and compared. This technique should provide a simple method for studying the state in solution of the complexes of several other metals and their isotopes.

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