Mixed Chelate Compounds of Titanium(III) as Studied by Electron Paramagnetic Resonance and Spectrophotometry

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Titanium(III) possesses low-spin-orbit coupling, and it was recently demonstrated¹⁾ that, when chelated with ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and several other chelating reagents, titanium(III) gives strong EPR signals in an aqueous solution at room temperature. This phenomenon suggests that ions of low-spin-orbit coupling produce EPR signals when strongly coordinated. It was, therefore, decided to investigate several aspects of correlation of complex formation with the EPR signal intensities. An increase in the signal intensity of the titanium(III)-EDTA complex was observed upon the addition of certain organic acids. Complex formation was confirmed for the systems titanium(III)-EDTA with oxalate, tartrate, citrate, and lactate. EPR signals are not exhibited by the titanium(III)-EDTA complex at pH values appreciably lower than 5.7. However, in the presence of any of the above acids, signals are exhibited by the complex at pH 2.5. No signals have been obtained for the titanium(III)-organic acid systems for any of the organic acids tested.

It was noted that complexes formed by titanium(III)-EDTA with three of the above acids show optical absorbance maxima at 720 mμ. No absorbance maximum is shown by titanium(III)-EDTA alone at any pH value.

The aqueous system of metal ion, EDTA, and an organic acid such as tartaric acid has long been utilized in analytical chemistry for chelatometric titrations. The usual understanding of the system has been that the metal-organic acid complex is less stable than the metal-EDTA complex, and that, consequently, when EDTA is added to a solution containing a metal ion and organic acid, the organic acid is displaced to form the more stable EDTA complex. However, the present study gives counter evidence to this interpretation showing that the organic acid is an integral component of the complex.

Experimental

Apparatus and Reagents.—*Electron Paramagnetic Resonance Spectrometer.* — Model JES-118, Japan Electron Optics Company.

Recording Spectrophotometer.—Cary Model 11.

Spectrophotometer.—Hitachi EPU-2 spectrophotometer.

Titanium(III) Chloride Solution.—A pure grade of titanium sponge (courtesy of the Osaka Titanium Corporation, Amagasaki, Japan) was dissolved in hot 6 N hydrochloric acid. An excess of titanium sponge was added to the hydrochloric acid, and additional acid was added as the reaction progressed to prevent the acid concentration from falling to the point where hydrolysis could occur. The solution was decanted from the metal while the vigorous reaction was proceeding in order to prevent the formation of any appreciable quantity of titanium(IV). The solution was maintained in an atmosphere of nitrogen. The final concentration of titanium(III) ion was determined volumetrically by titration with a ceric sulfate solution.

Electron Paramagnetic Resonance Spectrometric Procedure.—Intensity measurements were carried out using the same capillary tube for all determinations. A tube containing DPPH (diphenylpycrylhydrazyl) was taped to the capillary tube as an external standard of signal intensity, and the capillary tube was placed in the same position in the cavity for all determinations. It was found, however, that a comparison of the signal obtained for the sample with that of the DPPH was not a reliable process for determining absolute signal intensities because a slight change in position caused large deviations between the signals of the sample and of the DPPH. Signal intenstity measurements were, therefore, made comparing the peak heights of the signals obtained, which were found to be reasonably reproducible.

Spectrophotometric Procedure. — Solutions of titanium(III) chloride, EDTA, and organic acids were mixed in volumetic flasks, and the pH was adjusted to various values by the addition of ammonium hydroxide. The absorbances were measured using a Hitachi spectrophotometer, and spectrophotometric curves covering the range from 350 to 800 mμ were made using a recording spectrophotometer.

Results and Discussion

Table I lists the conditions used to obtain the EPR spectra and the signal intensity

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1) S. Fujiwara and M. Codell, This Bulletin, 37, 49 (1964).

TABLE I. EPR SIGNAL INTENSITIES OF MIXED TITANIUM CHELATE COMPOUNDS

Ti(III) molarity	pH	EDTA ratio	Organic acid ratio	Relative peak height
			Oxalic	
0.1	2.5	1	1	6.2
0.1	3.7	1	1	33.0
0.1	4.3	1	1	51.0
0.1	5.7	1	1	64.0
0.1	5.7	1	0.5	35
0.1	5.7	1	2	65
0.1	5.7	1	3	67
0.1	5.7	0.5	1	19
0.1	5.7	2	1	64
0.1	7.5	1	1	55
0.1	8.4	1	1	57
0.2	9.4	1	1	64
0.2	10.2	1	1	31
			Tartaric*	
0.1	5.7	1	1	6.8
0.1	5.7	1	2	12.8
0.1	5.7	1	3	19
0.1	5.7	1	4	24
0.1	5.7	1	5	27
0.1	5.7	3	1	6.1
0.2	3.5	1	1	5.4
0.2	6.4	1	1	9.9
0.2	9.4	1	1	55
			Citric	
0.2	5.7	1	0.8	3.7
0.2	5.7	1	1	4.2
0.2	5.7	1	2.5	7.5
			Lactic	
0.1	3.2	1	1	0.4
0.1	5.7	1	1	3.5
0.1	5.7	1	2	4.0
0.1	5.7	1	3	4.5
		No addition of organic acid		
0.2	4.3	1		No signal
0.2	5.7	1		0.4
0.2	6.3	1		0.5
0.2	7.4	1		1.5
0.2	12.2**	1		6.0

* At pH 9.6 another signal appears and the signal intensity cannot be accurately measured.

** Adjusted with NaOH.

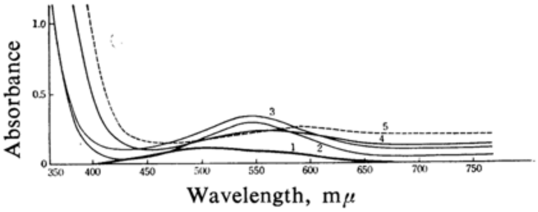

Fig. 1. Absorbance spectra of Ti(III), and Ti-(III)-EDTA at varying pH values.
Curve (1): $TiCl_3$ in 1:10 HCI
Curves (2), (3), (4), and (5): Ti(III)-EDTA (1:1.2 ratio)
Curve (2): pH 2.5, Curve (3): pH 5.0,
Curve (4): pH 8.0, Curve (5): pH 9.1
Ti(III) concentration for all curves: 0.03M

measurements of complexes.

The Titanium(III)-EDTA System.—Curves 2, 3, and 4 of Fig. 1 show the absorption spectra obtained for the titanium(III)-EDTA complex at various pH values, where the concentration of titanium(III) chloride was maintained constant at a titanium(III) to EDTA ratio of 1 to 1.2. Curve 1 shows the absorbance of titanium(III) chloride in an acid solution. From pH 2.5 to pH 8, distinct maxima at 550 mμ are observed for the titanium(III)-EDTA complex. At pH 8 the curve is considerably changed, but it still shows a maximum absorbance at 550 mμ, and a distinct shoulder can be seen at 600 mμ. At pH 9.1 a maximum absorbance at 580~600 mμ is observed. These curves suggest that another complex forms at higher pH values and that it absorbs from 580 to 600 mμ. From Fig. 2 it can be seen that the EPR spectra correspond with this assumption, since an increased intensity is seen for the second peak at higher pH values. The EPR spectrum shown for pH 12.2 was obtained for a solution adjusted with sodium hydroxide; a different piece of DPPH was used for this spectrum than for the other spectra shown in Fig. 2. It is seen that, at this pH, only the second peak is obtained. At pH 13, the complex begins to decompose, and the signal intensity is considerably decreased within a short period. At a pH of about 7, a second peak appears which increases in intensity at higher pH values. This phenomenon is observed whether ammonium hydroxide or sodium hydroxide is used to adjust the pH. The g value for the peak obtained at pH 12.2 is 1.956±0.002. The g value for the first peak is 1.960±0.002, which is in agreement with those of other titanium chelate compounds.[1]

From the above discussion it is apparent that two species of titanium(III)-EDTA complexes exist in neutral and basic solutions, and from the following considerations, we must assume the existence of another titanium(III)-EDTA complex in an acid solution which does not give an EPR signal.

An infrared study[2] has recently shown the presence of five species of EDTA in an aqueous solution, and the existence of acid complexes of metal ions and EDTA has been demonstrated in many instances. From the results of

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[2] D. T. Sawyer and J. E. Tackett, *J. Am. Chem. Soc.*, **85**, 314 (1963).

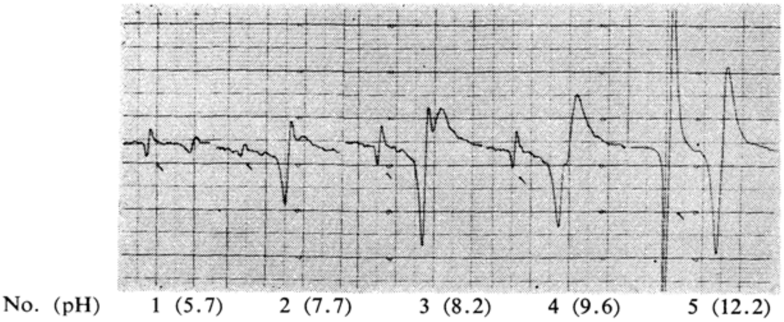


Fig. 2. EPR spectra for the Ti(III)-EDTA complex.
Spectra 1, 3 and 4 were obtained at twice the sensitivity setting of spectra 2 and 5.
Ti(III) concentration for all spectra : 0.02 M. Arrows designate DPPH.

TABLE II. Ti(III)-EDTA SPECIES IN SOLUTION

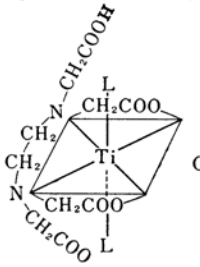
Formula	Formation in	Absorbance maxima	Remark
(Ti(III)-EDTAH$_2$ L$_2$)	(I) acid solution	550 mμ	No EPR signal
(Ti(III)-EDTAH L)	(II) neutral solution	550 mμ	EPR signal $g=1.960$
(Ti(III)-EDTA)	(III) basic solution	580 to 600 mμ	EPR signal $g=1.956$

previous investigations[2–5] and from our own experimental results, the three species listed in Table II are proposed to represent the complexes which exist in the solutions studied.

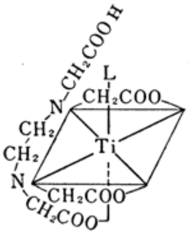
In Table II, EDTAH$_2$, EDTAH and EDTA represent ions where two, three, and four hydrogen ions are removed from the EDTA molecule containing four acid groups. L represents ligands other than EDTA, such as H_2O, Cl^-, and NH_3.

From the EPR spectra (Fig. 2), it appears that, at the approximate range pH 5 to 7, equilibrium mixtures of I and II exist, because the first peak becomes smaller with the decreasing pH and disappears at a pH of about 5, but the existence of a chelate is well established by the reasons given below. At pH 7 to 10, equilibrium mixtures of II and III exist. The same mixtures indicated above by the EPR spectra may be deduced from the spectrophotometric curves (Fig. 1), if we assume that the II complex shows a maximum absorbance at 550 mμ and the III complex, at 580 $\sim$600 mμ, and that the shape of the curves for the I and II complexes are similar to that of the I complex in exhibiting lower absorbance. At lower pH values, a complex forms in solution which gives no EPR signal under the experimental conditions used. It was shown spectrophotometrically at pH 2.5 that a high concentration of this complex exists. It was also experimentally demonstrated that a complex of titanium(III)-EDTA forms in an acidic solution. This was accomplished by first forming the complex of titanium(III) with nitrilotriacetic acid (NTA) at pH 3.5. An intense EPR signal is obtained from this complex at this pH. An identical solution was then prepared, to which EDTA of a molar concentration twice that of titanium was added; the solution adjusted to pH 2.5. No signal was exhibited by this solution. The solution of titanium(III)-NTA was green, while that containing EDTA was purple, which is the color of pure titanium(III)-EDTA solutions at this pH. At pH values of 1 or 2, the color of solutions containing titanium(III) and EDTA, or titanium(III), EDTA, and NTA are the same, while the color of solutions containing titanium(III)-NTA are blue. It was also noticed that a solution containing the intensely-colored titanium(III)-acetylacetonate complex is decolorized upon the addition of EDTA. These phenomena appear to offer good evidence that the titanium(III)-EDTA complex is more stable than the titanium(III)-NTA or the titanium(III)-acetylacetonate complexes.

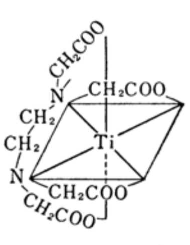
The following structures are proposed to represent the compounds which exist in the solutions studied :



I



II



III

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[3] G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 459 (1948).

[4] K. Saito and H. Terrey, *J. Chem. Soc.*, **1956**, 4701.

[5] D. C. Olson and D. W. Margerum, *J. Am. Chem. Soc.*, **82**, 5602 (1960).

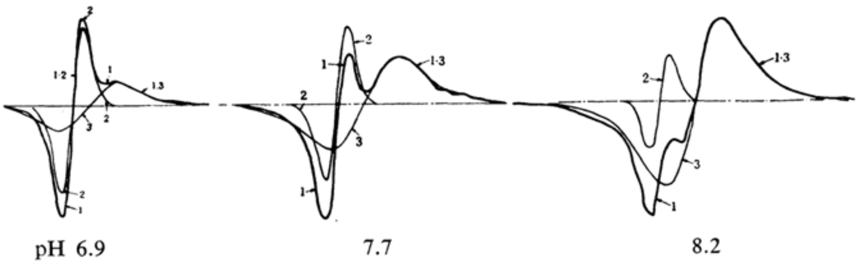


Fig. 3. Procedure for the analysis of signals with two peaks.
Curve 1 is the original spectrum.
Curves 2 and 3 are the reconstructed curve.

Structure I shows the possible complex where EDTA acts a tetradentate. Structure II, in which EDTA acts as a pentadentate, is proposed for the species which exists in neutral solution giving an EPR signal, but the absorbance seen in Fig. 1 is similar to that obtained in acid solutions. The proposed structure III, in which EDTA is a hexadentate, is obtained in a low concentration at pH values above 7, although at pH 10, it appeaes to be the only species in the solution. At pH 7 to 10, a mixture of the two complexes represented by structures II and III appear to be present in the solution.

An analysis was made of the signal of the two peaks obtained for the complex titanium(III)-EDTA at pH 7 to 9, were the concentration of titanium is 0.094 M and the ratio of titanium to EDTA is 1 to 2. The process used in this analysis is shown in Fig. 3; the peaks were first separated into two signals, assuming a normal Maxwell-Boltzmann distribution curve. Each curve was integrated, and the areas under the curves were calculated. The assumption was made that the ratio of the areas represent the ratio of the II and III complexes. Table III lists the results of this analysis. From the information obtained in this analysis, the equilibrium constant can be calculated for the following reaction:

TABLE III. RELATIVE AREAS OF RECONSTRUCTED CURVES AND CALCULATED EQUILIBRIUM CONSTANT FOR THE SYSTEM Ti(III)-EDTA (II AND III IN TABLE II)

pH	Relative areas of separated and integrated curves	*Ke* (mol./l.), calculated
6.9	1 : 1.8	2.07×10^{-7}
7.7	1 : 6.8	1.35×10^{-7}
8.2	1 : 24	1.49×10^{-7}
8.6	1 : 30	0.72×10^{-7}

$$\text{Ti(III)-EDTAH} \rightleftharpoons \text{Ti(III)-EDTA}^- + \text{H}^+$$

$$K_e=\frac{(\text{Ti(III)-EDTA}^-)\ (\text{H}^+)}{(\text{Ti(III)-EDTAH})}$$

The temperature and salt concentrations were not maintained constant for the data obtained for Table III. Although the calculated K_e values shown in Table III are not in excellent agreement, the effect of the temperature and such foreign salts as ammonium chloride and sodium chloride, which usually affect the stability of chelates, must be taken into consideration. The values obtained are of the same order, which strongly indicates that this method of analyzing signals is valid and that the assumed chelate species, II and III, exist in fact.

The Titanium(III)-EDTA-Oxalate System.—The EPR signal intensity and the spectrophotometric absorbance at 720 mμ for the titanium(III)-EDTA system are considerably increased upon the addition of certain organic acids. These effects were studied, and the formation of mixed chelate species was proved.

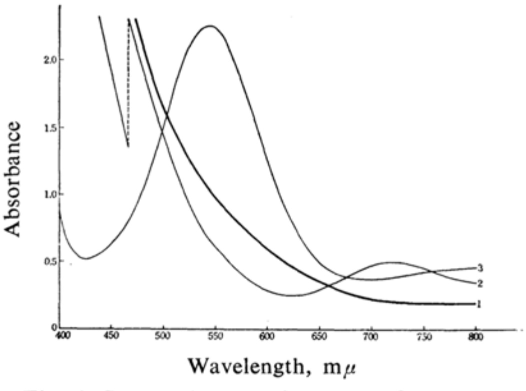


Fig. 4. Spectrophotometric curves for the Ti(III)-EDTA-oxalate system at pH 5.7.
Curve (1) Ti(III)-oxalate (1 : 3 ratio), Ti(III) concentration: 0.03M
Curve (2) Ti(III)-EDTA-oxalte (1 : 1 : 1 ratio), Ti(III) concentration: 0.6M
Curve (3) Ti(III)-EDTA (1 : 1 ratio), Ti(III) concentration 0.16 M

Three curves are shown in Fig. 4. Curve 1 is for the absorbance exhibited by the yellow-brown product formed between titanium(III)

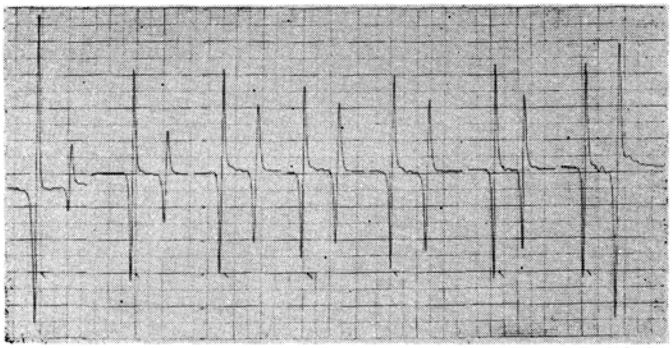
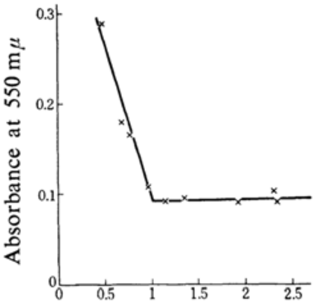


Fig. 5. EPR spectra for the Ti(III)-EDTA-oxalate complex.
Spectrum 1 was obtained at three times the sensitivity and spectrum 7 was obtained at four times the sensitivity settings of the other spectra shown in this figure. Ti(III) concentration for spectrum 7 : 0.02 M. The Ti(III) concentration for all other spectra : 0.01M. Arrows designate DPPH.

and oxalic acid. The molar ratio of titanium(III) to oxalic acid is 1 to 3. No EPR signal is given by this complex at any pH value. The optical absorbance of this compound continues to increase with a decrease in the wavelength. Curve 2 is that of an equal molar ratio of titanium(III) and EDTA ; the maximum absorbance is seen at 550 mμ. Curve 3 is that of the amber-colored product of an equal molar ratio of titanium(III), EDTA, and oxalic acid, where the concentration of titanium(III) and EDTA is the same as for curve 2. No absorbance maximum at 550 mμ, such as is characteristic of the titanium(III)-EDTA complex, is observed. These curves undoubtedly prove the formation of a compound of three components; could not be a mixture of two complexes, such as the titanium(III)-EDTA and titanium(III)-oxalate complexes.



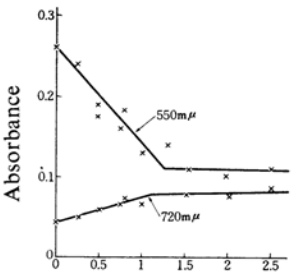
Molecular ratio of EDTA to Ti(III)

Fig. 6. Molecular ratio method for the determination of the ratio of EDTA in the Ti(III)-EDTA-oxalate complex at pH 5.7. Concentration of Ti(III) : 0.06 M. Concentration of oxalic acid : 0.18 M.

In Table I it may be seen that the EPR signal intensity of the titanium(III)-EDTA-oxalate complex increases with an increase in the pH value. The fact that a second peak does not appear at higher pH values (Fig. 5), as occurs with the titanium(III)-EDTA system, the titanium(III)-EDTA-tartrate system and the titanium(III)-EDTA-citrate system, is evidence for the presence of only a single complex. Evidence for the stability of the complex is seen in the fact that quantities of oxalic acid in excess of a 1 to 1 molar ratio have no such apparent effect on the signal intensity as is experienced with tartaric, citric and lactic acids (Table I and Fig. 9).

Figure 6 shows the spectrophotometric establishment of the composition of each component of complexes. A plot of the absorbance versus molar ratio of EDTA to titanium(III) is shown for all points. The pH values of these solutions were adjusted to 5.7 with ammonium hydroxide. A sharp break in the absorbance curve at 550 mμ is seen when the molar ratio of titanium(III) to EDTA reaches unity. The same experimental procedure was carried out at pH 2.5, and the same molar ratio for the complexes was found. The less intense EPR signals obtained at lower pH values probably result from the presence of a higher concentration of a complex of the same composition but possessing a different structure, one which does not give an EPR signal.

The determination of the ratio of oxalate in the titanium(III)-EDTA-oxalate complex is shown in Fig. 7. The ratio of titanium(III) to EDTA was maintained constant, varying amounts of oxalic acid were added, and the pH was adjusted to 4.5. A break in the curve at 550 mμ may be seen when the molar concentration of each component of the complex is approximately equal. At 720 mμ the break in the curve, which is not very pronounced, is seen at approximately the same molar concentration.



Molecular ratio of oxalic acid to Ti(III)

Fig. 7. Molecular ratio method for the determination of the ratio of oxalic acid in the Ti(III)-EDTA-oxalate complex at pH 4.5. Concentration of Ti(III) and EDTA: 0.06 M.

Formula IV is proposed for the main species of the titanium(III)-EDTA-oxalate complex present in solution:

$$(Ti^{3+}EDTAH_2^{2-}(COO)_2^{2-})$$
IV

The Titanium(III)-EDTA-Taratrte, -Citrate, and -Lactate Sytems.—As with oxalic acid, tartaric, citric, and lactic acids also affect the titanium(III)-EDTA complex by increasing the EPR signal intensity and permitting the EPR signal to be obtained at lower pH values. The EPR spectra and spectrophotometric curves are shown in Figs. 8 and 9.

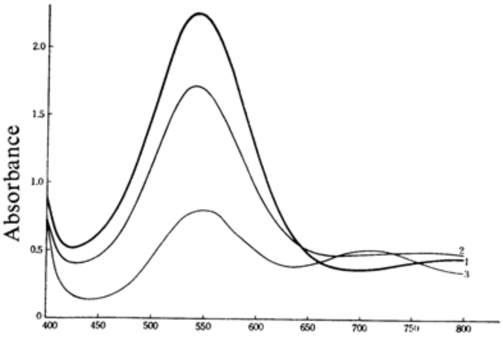


Fig. 8. Spectrophotometric curves for the Ti(III)-EDTA-tartrate system at pH 5.7.
Concentration of Ti(III): 0.16 M
Curve (1) Ti(III)-EDTA (1 : 1 ratio)
Curve (2) Ti(III)-EDTA-tartrate (1 : 1 : 1 ratio)
Curve (3) Ti(III)-EDTA-tartrate (1 : 1 : 3 ratio)

It may be seen in Table I and Fig. 9 that the titanium(III)-EDTA-tartrate EPR signal intensity increases up to a molar ratio of tartaric acid to titanium(III) of at least 50 to 1 under the experimental conditions employed. However, no quantitative measurement of this effect could be made because of the insolubility of some tartrate salts at the ratio of tartaric acid to titanium(III) of 3 to 1.

Upon the addition of tartaric acid to the titanium(III)-EDTA complex, the EPR signal intensity continues to increase. It is shown

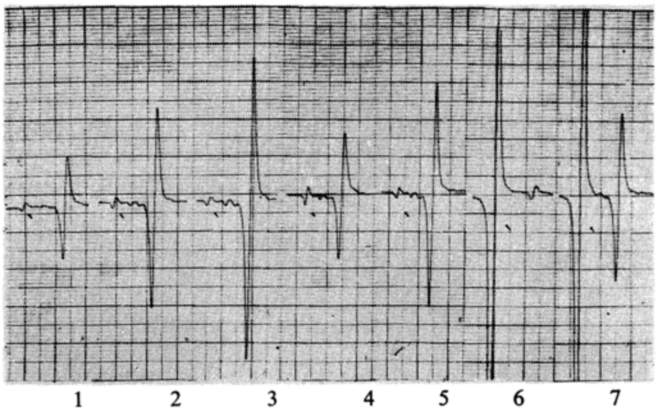


Fig. 9. EPR spectra for the Ti(III)-EDTA-tartrate, -citrate, and -lactate complexes. The sensitivity setting used for spectra 4, 5, 6 and 7 was twice that used for spectra 1, 2 and 3. Arrows designate DPPH.

Spectrum No.	Acid	Ti(III) : EDTA : Acid	Molar Concn. of Ti(III)	pH
1	Tartaric	1 : 1 : 1	0.1	5.7
2	Tartaric	1 : 1 : 2	0.1	5.7
3	Tartaric	1 : 1 : 3	0.1	5.7
4	Citric	1 : 1 : 1	0.2	5.7
5	Citric	1 : 1 : 2.5	0.2	5.7
6	Lactic	1 : 1 : 1	0.2	3.2
7	Lactic	1 : 1 : 3	0.1	5.7

spectrophotometrically in Fig. 8 that, when tartrate ions are present in a 3 to 1 ratio to titanium(III) and EDTA, the concentration of the complex as exhibited by the absorbance at 720 mμ is the same as that shown for the oxalate complex. It may be noted that the EPR signal intensity never reaches half the intensity of the signal obtained for the oxalate complex. The unexpectedly high absorbance which occurs for this complex at 720 mμ may be due to a greater absorbance of the tartrate complex over that of the oxalate complex.

The continuous increase of the EPR signal and in the optical absorbance at 720 mμ with the increase in tartrate ion concentration indicates a lower stability for the three-component complex containing tartrate, but no definite ratio of the complex can be established by these techniques. In this three-component system, the complex obviously exists in pH-dependent and organic acid concentration-dependent equilibria.

With succinic and acetic acids, no maxima are exhibited at 720 mμ, and the absorbance for the entire curve is the same as for the titanium(III)-EDTA complex alone. No EPR signals are obtained for the titanium(III)-EDTA complex in the presence of these acids at low pH values, which appears to show that these acids do not form complexes similar to the titanium(III)-EDTA-oxalate complex.

The spectrophotometric curve for lactic acid falls between curves 1 and 2 in Fig. 8, which indicates that this acid forms a less stable complex than tartaric and citric acids, and we were unable to observe any increase in absorbance at 720 mμ. An EPR signal with lactic acid is obtained at pH 3.2, where the complex with EDTA alone does not give a signal. These spectrophotometric results correspond well with those obtained by EPR.

With the complex formed with citric acid, a spectrophotometric curve is obtained which is very close to curve 1 in Fig. 8. Moreover, the EPR signal obtained for the citrate complex at pH 5.7 is much more intense than that obtained for the titanium(III)-EDTA complex at this pH. These indicate a behavior of citrate similar to that of tartrate with the titanium(III)-EDTA system. At a pH of about 9, a second peak appers for the titanium(III)-EDTA-citrate complex, and at a pH of about 10, a second peak appears for the titanium(III)-EDTA-tartrate complex. A study of the latter system has been reported on in a previous paper.[1)]

Summary

An electron-paramagenetic resonance and spectrophotometric study has been made of the composition of mixed chelate compounds of titanium(III) - ethylenediaminetetraacetic acid (EDTA) and organic acids. The existence of three titanium(III)-EDTA complexes in solution has been established. The complex formation of titanium(III)-EDTA with oxalate, tartrate, citrate and lactate has been confirmed, and the ratio of the oxalate has been established. Structures for the complexes have been proposed, probable equilibrium mixtures of complexes at various pH values have been discussed and new procedures have been proposed for the detection of chelate compounds in solution.

The assistance of Miss Tokuko Seki with the calculations of the equilibrium constans of the complexes is gratefully acknowledged.

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