An Electron Paramagnetic Resonance and Spectrophotometric Study of Titanium(III)-Chelate Compounds with Nitrilotricarboxylic Acid and Its Derivatives

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The EPR hyperfine structure of titanium(III) has recently been obtained with several chelating agents,[1] and the chemistry of mixed chelate compounds of titanium(III), EDTA and several complexing organic acids has recently been elucidated,[2] where titanium(III)-EDTA and oxalic, tartaric, citric, and lactic acids have been shown to form complexes which give EPR signals and can be spectrophotometrically identified. It has also been recently shown[3] that a complex formed between titanium(III), zinc and tartaric acid gives an EPR signal of two peaks.

The effect of varying numbers of carboxyl groups on chelating agents of a similar structure seemed of considerable interest, since experience with several chelating agents has shown that those agents with the largest numbers of coordinating groups are the most likely to give EPR signals showing the hyperfine structure of titanium(III). The chelating agents investigated were nitrilotriacetic acid (NTA) $N(CH_2COOH)_3$, hydroxyethyliminodiacetic acid (HEID) $N(CH_2COOH)_2CH_2CH_2\cdot OH$, Bishydroxyethyl glycine (BHEG) $N(CH_2\cdot CH_2OH)_2CH_2COOH$, and iminodiacetic acid (IDA) $HN(CH_2COOH)_2$. NTA gives the largest EPR signals, while IDA, which contains $-H$ in place of $-CH_2CH_2OH$ in HEID, gives the smallest signals.

EPR spectra were obtained using capillary tubes containing solutions prepared by admixing the constituents and adjusting the pH. In the spectrophotometric establishment of the combining ratios of titanium(III) to NTA and HEID in an acid solution, the concentration range of the chelating agents was limited because of the slight solubility of the excessive agents.

Apparatus and Reagents.—The electron paramagnetic resonance spectrometer used was a model JES-118 manufactured by the Japan Electron Optics Company. The recording spectrophotometer used was a Cary Model 11. The spectrophotometers used were Hitachi, model EPU-2 and Hirama, model IIB, filter electrophotocolorimeters.

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 in order 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 then maintained in an atmosphere of nitrogen. The final concentration of titanium(III) ions was determined volumetrically by titration with a ceric sulfate solution.

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

2) S. Fujiwara, K. Nagashima and M. Codell, ibid., in press.

3) S. Fujiwara, K. Nagashima and M. Codell, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 85, 305 (1964).

Chelating Reagents. — The NTA and IDA used were commercial first-grade reagents (Wako Junyaku Co., Tokyo). The HEID and BHEG were synthetized for this investigation (courtesy of Daiichi Seiyaku Co., Ltd., Tokyo).

Titanium(III)-NTA Complexes. — Nitrilotriacetic acid (NTA) forms a complex with titanium(III), which is quite stable and which gives the largest EPR signals of the group studied in this investigation (Fig. 1). A 0.1 M titanium(III) solution of this complex gives signals at pH 1.7, although at pH 1.5 no signal was obtained. The signals become larger with increasing pH values up to approximately 4. Above pH 4, however, the signal intensity remains almost constant to a pH value of approximately 10.

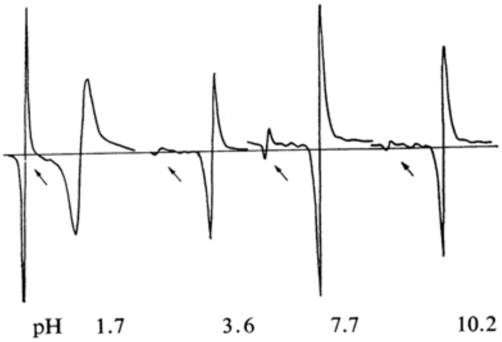

Fig. 1. EPR spectra for Ti(III)-NTA complexes. The concentration of Ti(III) is 0.2 M and the concentration of NTA is 0.4 M. The pH was adjusted with NaOH. Arrows designate DPPH.

Figure 2 shows a complex at pH 1 which gives a blue solution and exhibits a maximum absorbance at 600 $m\mu$, and another complex at pH 4.7 which gives a greenish yellow solution with a maximum absorbance at 710 $m\mu$.

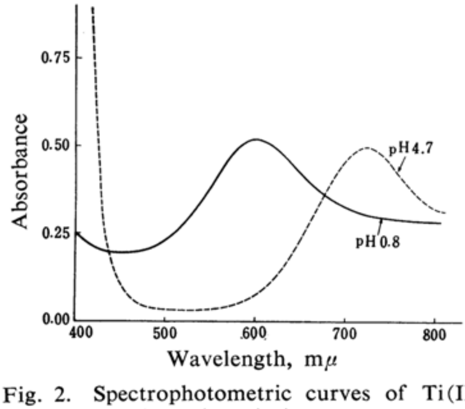

Fig. 2. Spectrophotometric curves of Ti(III)-NTA complexes in solution.

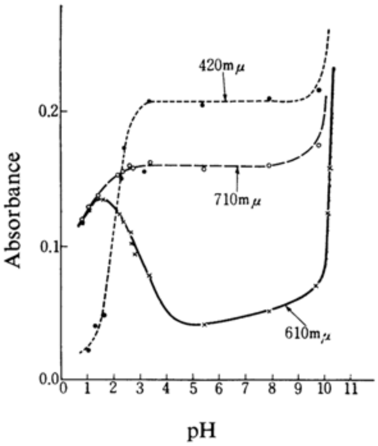

Fig. 3. Change of optical absorbance of Ti(III)-NTA solutions containing tartaric acid with change in pH values.

Figure 3 shows the change in the optical absorbance of each maximum with the changing pH value. The maximum, which occurs at 600 $m\mu$, increases with an increase in the pH value up to about pH 1.5, and then decreases from about pH 1.5 to about pH 4. A red filter whose absorbance curve reaches a peak at approximately 610 $m\mu$ was used to determine the above maximum. The points for pH values higher than 3.5 were extrapolated because of interference from the peak which shows a maximum absorbance at 710 $m\mu$. The maximum which occurs at 710 $m\mu$ increases with the increase in pH values. It attains the highest value at pH 3.5 and shows no further change with the increase in pH until a pH value of a little above 9 is attained, whereupon a rapid increase in absorbance occurs with the further increase in pH value.

The establishment of the ratios of titanium(III) to NTA are shown in Figs. 4a through

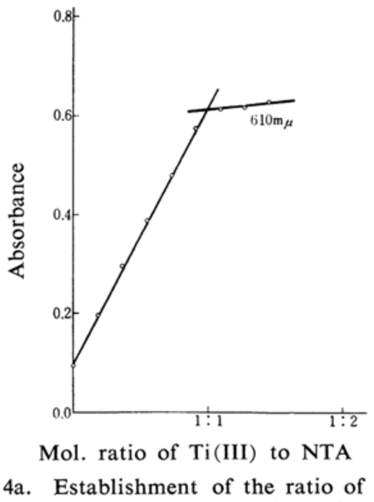

Fig. 4a. Establishment of the ratio of Ti(III) to NTA at pH 1.5 by the molar ratio method. Higher concentrations of NTA were not tested because of the limited solubility.

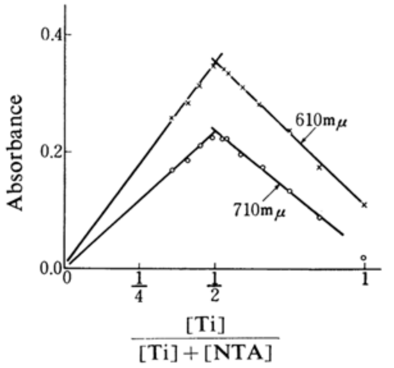

Fig. 4b. Establishment of the ratio of Ti(III) to NTA at pH 1.0 by the method of continuous variation.

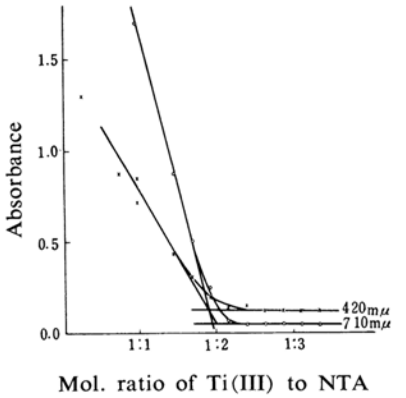

Fig. 4c. Establishment of the ratio of Ti(III) to NTA at pH 9.0 by the molar ratio method.

4c. Figure 4a shows the molar ratio method for determining the composition of the species which exists at pH 1.5 and which exhibits a maximum absorbance at 600 mμ. The red filter mentioned above was also used for this experiment. Figure 4b shows the method of continuous variation for establishing the ratio of the same species. The ratio is clearly shown to be 1 to 1 by both procedures. Figure 4c shows the molar ratio method for establishing the ratio of the species which appears at pH values between 3.5 and 9. Experiments were carried out at pH 9 in the presence of tartaric acid to prevent the hydrolysis of titanium(III). The strong blue color of the titanium(III)-tartrate compound becomes lighter upon the addition of increasing amounts of NTA. The absorbance curve changes abruptly at a ratio of 1 titanium(III) to 2 NTA, corresponding to the formation of the chelate. The species which exists in this solution shows a maximum absorbance at 710 mμ.

From the above discussion, the following complex species may be proposed;

	Formula	Optical absorbance at	Predominant at pH	g Value (EPR)
(1)	Ti(III)(NTA)$_1$	600 mμ	1.5	unobservable
(2)	Ti(III)(NTA)$_2$	710 mμ	3.5—9	1.961±0.002

The Titanium(III)-HEID Complexes.—Figure 5 shows the absorbance curves of a titanium(III)-HEID solution at different pH values. At pH 1.4 the solution is blue and the maximum absorbance is seen at 590 mμ. At pH 5.0 the solution is yellowish green and the maximum is shown at 720 mμ. At pH 9.2 the solution is purplish and the maximum appears at 540 mμ. Figure 6 shows the change in absorbance with the variation in pH values. It should be noted that the complex which shows a maximum absorbance at 590 mμ exhibits the highest intensity at pH 1.2 (traced with a 610 mμ filter). The complex which shows a maximum absorbance at 720 mμ shows a steady increase in intensity up to a pH value of about 3, and it remains constant to pH 5.5, after which an increase in intensity occurs until a pH of

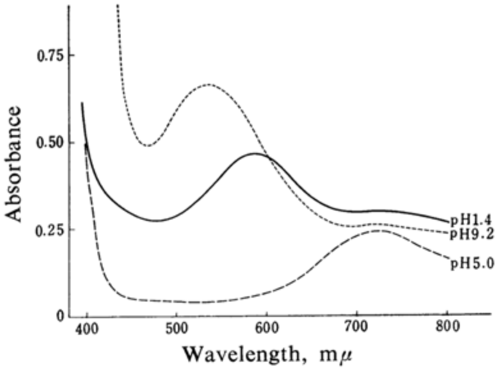

Fig. 5. Spectrophotometric curves of Ti(III)-HEID complexes in solution.

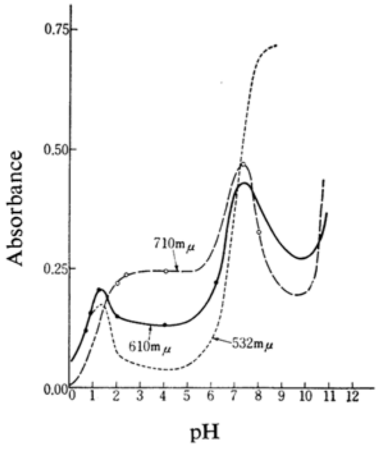

Fig. 6. Change of optical absorbance with pH of Ti(III)-HEID solutions.

about 7 is attained when a 710 mμ filter was used. At pH values above 7 a continual decrease is noted. The peculiar appearance of the curves at pH values above 8 is due to precipitation.

From Fig. 6 it may be seen that the complex which shows a maximum absorbance at 540 mμ (traced by using a 532 mμ filter) exhibits the highest intensity at pH 8, which indicates that this complex is the predominant species at higher pH values.

Figures 7a through 7c show the spectrophotometric determination of the ratios of titanium(III) to HEID. Filters which transmit the light of wavelengths close to the absorbance maxima of the complexes were used. The same procedures were applied for these determinations as for the titanium(III) to NTA ratios. Figure 7a shows that at pH 1.2 titanium(III) is combined with HEID in a 1 to 1 ratio. Two species were shown by the EPR spectra (Fig. 8) to exist at this pH, with one of the species being predominant.

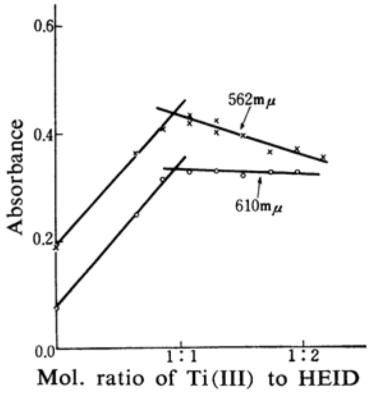

Fig. 7a. Establishment of the ratio of Ti(III) to HEID at pH 1.2 by the molar ratio method.

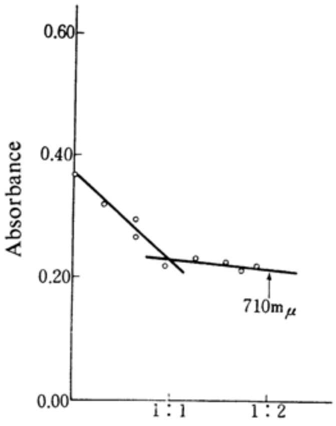

Fig. 7b. Establishment of the ratio of Ti(III) to HEID at pH 4.2 by the molar ratio method.

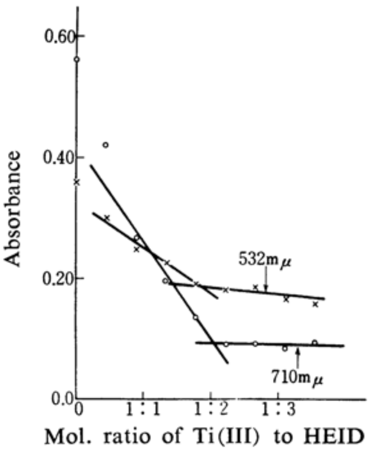

Fig. 7c. Establishment of the ratio of Ti(III) to HEID at pH 9.2 by the molar ratio method.

The minor species, which exhibits a maximum absorbance at 720 mμ and which is stable at higher pH values (pH 3—5.5) was shown, as is illustrated in Fig. 7b, to be in a 1 to 1 ratio. Thus, it must be concluded that the species which exhibits a maximum absorbance at 590 mμ and which is stable at the lower pH values (—pH 1.2) is composed of 1 to 1 proportions of titanium(III) and HEID. Figure 7b shows that at pH 4.2 a species composed of a 1 to 1 ratio is also predominant, while it may be seen in Fig. 7c that, at pH 9, a species composed of a 1 to 2 ratio predominates. The experiments illustrated in Fig. 7c were carried out in the presence of tartaric acid to prevent the hydrolysis of titanium(III). The strong blue color of the titanium(III)-tartrate compound becomes lighter upon the addition of increasing amounts of HEID. The absorbance curve changes abruptly at a ratio of 1 titanium(III) to 2 HEID.

Figures 7a through 7c show the decrease in the absorbances with an increase in the quantities of HEID. This is probably due to the

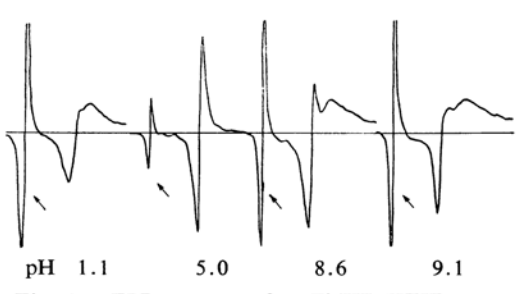

Fig. 8. EPR spectra for Ti(III)-HEID complexes. The concentration of $TiCl_3$ is 0.2 M and concentration of HEID is 0.4 M. The pH was adjusted with NaOH. Arrows designate DPPH.

oxidizing effect of some impurity in the reagent.

Figure 8 shows EPR spectra for the titanium(III)-HEID system. To obtain the EPR spectra at very low pH values a concentrated solution must be used, since the signal intensity is so low. At pH 1, two peaks are obtained. As the pH value is increased, however, only one peak is discernible. The signal intensity increases to pH 3.7, after which little change is noted until a pH of 7.5 is reached; a second peak then appears which is favored by higher pH values.

The following species may be proposed to represent the complexes which exist at the various pH values mentioned above.

	Absorbance at	Predominant at pH	*g* Value
(1) $Ti(III)_1$-$(HEID)_1$	590 mμ	1.2	1.952± 0.002
(2) $Ti(III)_1$-$(HEID)_1$	720 mμ	3 to 5.5	1.952± 0.002
(3) $Ti(III)_1$-$(HEID)_2$	540 mμ	>8	1.952± 0.002

Species 1 and 2 represent those species which are similar in composition but which are stable at different pH values and which exhibit different optical absorbances. Species 1 must be an acid complex in which the HEID is bidentate ($HEIDH^{-1}$) and one hydrogen of a carboxylic group remains unionized, and species 2, a complex in which HEID is tridentate and both hydrogens are ionized.

From Figs. 5 and 6 it may be seen that at pH 1 to 1.5 species 1 is predominant, but some absorbance at 720 mμ is observable. The EPR spectrum (spectrum at pH 1.1 of Fig. 8) shows a major species and a minor species which correspond to the species which were spectrophotometrically observed.

Titanium(III)-BHEG, and -IDA Complexes.—The absorbance curves obtained with the blue solutions of titanium(III) and BHEG are always very broad, with a considerable absorbance over the entire visible spectrum. This indicates some hydrolysis which precludes the establishment of formation ratios by the spectrophotometric technique. With titanium(III) and BHEG a very small EPR signal can be obtained at pH 5.2; the signal increases with an increase in pH values up to about 9, after which the signals decrease in size. Only one peak can be obtained, and no definite hyperfine structure is discernible.

Figure 9 shows that the signal obtained with a solution containing BHEG to titanium(III) in a ratio of 6 to 1 is definitely larger than that obtained with a 3 to 1 ratio. The presence of oxalic acid has no apparent effect on the signal size or shape.

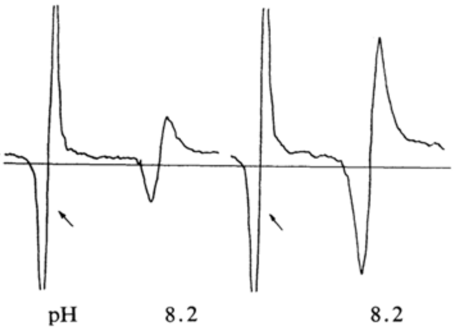

Fig. 9. EPR spectra for the Ti(III)-BHEG complex. The concentration of Ti(III) is 0.2 M and the concentration of BHEG is 0.6 M for the smaller spectrum and 1.2 molar for the larger spectrum. The pH was adjusted with NaOH. The chart speed for this figure is different than that used for Figs. 1 and 8. Arrows designate DPPH.

Solutions containing titanium(III) and IDA are blue and give EPR signals only over the narrow pH range of 7.5 to 9.0. Only one peak can be seen, and all the signals are very small. The presence of oxalic acid has a definite depressing effect on the signal intensity.

Summary

Complexes formed by titanium(III) and agents which are similar in structure but varying in numbers of carboxyl groups have been studied by EPR and spectrophotometry. Among the reagents investigated, NTA, which posesses four coordinating groups, gives the largest EPR signals with a well-developed hyperfine structure. BHEG, which possesses two coordinating groups, gives much smaller signals, and even at the highest sensitivity setting of the instrument, no definite hyperfine structure can be detected. HEID, which posesses three coordinating groups, gives signals with two peaks, which indicates the simultaneous existance of two complexes in the solution. The ratios of the complexes of titanium(III) and NTA and HEID which exist in solution at various pH values have been spectrophotometrically determined.

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