THE COORDINATION CHEMISTRY AND ELECTROCHEMISTRY OF CHROMIUM(III) COMPLEXES OF THIOBIS(ETHYLENENITRILO)TETRAACETIC ACID

Thesis by

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To my Dad

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ABSTRACT

The product of the reaction between $Cr(ClO_4)_3$ and the ligand, thiobis(ethylenenitrilo)tetraacetic acid (TEDTA), was very dependent on the pH of the reaction mixture. Two monomeric isomers and several dimeric species were identified. Characterization of the various Cr(III) complexes of TEDTA included an examination of their pH behavior, visible and ultraviolet absorption spectra, substitutional lability with excess azide ion, behavior on a Selectacel anion exchange column, reaction with heavy metal cations and methyl mercury cation, infra-red spectra and distinctive electrochemistry. Comparisons of the behavior of the Cr(III)-TEDTA complexes with those of the Cr(III) complexes of related ligands, including EDTA, oxybis(ethylenenitrilo)tetraacetic acid (EEDTA) and pentamethylenedinitrilotetraacetic acid (PMDTA), were very helpful. Based on these data, it was concluded that both *cis* and *trans* isomers (with respect to the nitrogens) were formed. In the *trans* isomer, the sulfur is forced to be close to the Cr(III) center and coordination occurs. At pH 5-9, solutions of the pentadentate *cis* isomer are a mixture of the monomeric complex and an acetate bridged dimer. Confirmation of dimer formation and a value for the dimerization constant were obtained from potential step experiments. The structure of the dimer was strongly supported by the cyclic voltammetry which indicated the presence of two non-equivalent metal centers in the complex. The other dimeric species were highly charged and their IR spectra suggested that they were oxo-bridged.

The electrochemistry of both the *cis* and *trans* isomers and the acetate bridged dimer was investigated in detail. Cyclic voltammetry and electrocapillary measurements indicated that *trans*-$\mathrm{CrTEDTA^-}$ was much more strongly adsorbed on mercury electrodes than was *cis*-$\mathrm{CrTEDTA(OH_2)}$, *cis*-$\mathrm{CrTEDTA(OH_2)^-}$ or the acetate bridged dimer, and that free TEDTA was not adsorbed. Experiments with CrEEDTA showed that it was not adsorbed, indicating that the Cr(III)-TEDTA complexes were attached to the electrode through the sulfur. Quantitative measurements of the adsorption confirmed all of this. The adsorption of *trans*-$\mathrm{CrTEDTA^-}$ increased abruptly over a very narrow range of bulk concentrations and was strongest at positively charged electrodes. The potential dependence was corroborated by the fact that the charge on the electrode in the presence of the complex was more positive. The concentration and potential dependences are attributed to back bonding from Cr(III) to the thioether sulfur which σ-donates electron density to the electrode.

The abrupt change in the surface coverage over a narrow charge of bulk concentration indicates that the adsorption of *trans*-CrTEDTA$^-$ is cooperative.

Chronocoulometric measurements of the adsorption of the *cis* isomer at pH 4 and 7 demonstrated that the neutral complex was more strongly adsorbed than the anions especially at more negative potentials. The adsorption appeared to increase as the electrode potential was made more negative. However, the electrocapillary curves were discrepant. Electrode charge measurements supported the electrocapillary data. The adsorption of the *cis* complex depressed the double layer capacitance at all potentials. This behavior is similar to that of organic adsorbates. Although the non-adsorption of the free ligand was attributed to steric difficulty in exposing the sulfur atom to the electrode, the fact that the La(III) and Zn(II) complexes of TEDTA were also not adsorbed shows that the role of Cr(III) in inducing the adsorption of TEDTA in the *cis* isomers is complicated.

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CHAPTER I

COORDINATION CHEMISTRY OF CHROMIUM(III) WITH THIOBIS(ETHYLENENITRILO)TETRAACETIC ACID (TEDTA)

INTRODUCTION

As part of a continuing investigation of the chemical factors which induce certain classes of complex ions to attach themselves to the surfaces of electrodes by spontaneous adsorption (1-5), we have sought ligands which can induce the adsorption of the widest possible variety of metal cations. Halide and pseudohalide anions are effective in inducing the adsorption of many d^{10} cations (6-9), but large excesses of free ligand are usually necessary to stabilize these rather weak, labile complexes. As a result, analysis of the surface coordination chemistry involved is complicated by competition between these anions and their metal complexes for adsorption sites on the electrode surface. Thiocyanate anion induces the adsorption of certain of the transition metal cations (5), but the extent of adsorption is strongly dependent on the *d* electronic configuration of the transition metal-isothiocyanate complex and competitive ligand adsorption remains a problem with all substitutionally labile complexes. An attractive solution to this problem is to choose a ligand of high denticity and affinity for metal cations so that large ligand excesses are not required to achieve essentially complete complexation. EDTA(ethylenedinitrilotetraacetic acid) is a good example of such a ligand, but with the exception of cobalt (10), EDTA complexes of most metal cations show little or no tendency to adsorb on the surface of mercury electrodes. In seeking a molecule with chelating capabilities similar to those of EDTA but with a much greater tendency towards adsorption on mercury surfaces, we investigated the sulfur-containing analog of EDTA, thiobis(ethylenenitrilo)tetraacetic acid (TEDTA), (1,7-diaza-4-thiaheptane-1,1,7,7,-tetraacetic acid), $S[CH_2CH_2N(CH_2COOH)_2]$. Many metal complexes of this ligand exhibit a propensity to adsorb on mercury surfaces. This chapter concentrates on the unusual coordination chemistry displayed by chromium(III) complexes of TEDTA.

EXPERIMENTAL

APPARATUS

pH Titrations were performed using a Beckman Model 76 Digital pH Meter. Single wavelength absorbance measurements were done on a Beckman DU Spectrophotometer. UV-Visible spectra were recorded on a Cary Model 17 or 118 Spectrophotometer. Elemental analyses were performed by the Caltech microanalytical laboratory unless otherwise specified. Cyclic voltammograms were obtained using either a conventional multipurpose electrochemical instrument based on operational amplifiers which was constructed in this laboratory or a Princeton Applied Research Model 173 Potentiostat/Galvanostat, Model 175 Universal Programmer and Model 179 Digital Coulometer. Voltammograms were recorded on a Tektronix Model 564 CRO. All measurements were made at 25±2° C.

MATERIALS

Reagent grade chemicals were used without further purification. Methyl mercuric hydroxide was obtained as a 1.27 M aqueous solution from Alfa. All solutions were prepared with triply distilled water. Stock solutions of sodium perchlorate were prepared by neutralizing 60% $HClO_4$ with sodium carbonate (11). Stock solutions of chromium(III) perchlorate were prepared by reducing CrO_3 with excess

H_2O_2 in perchloric acid and boiling to remove unreacted H_2O_2. These stock solutions were made 0.5 to 1 $\underline{M}$ in $HClO_4$ to minimize the formation of chromium(III) polymers. The extent of a polymer formation was monitored spectrophotometrically following the method of Altman and King (12). Standardization of Cr(III) solutions involved oxidation to chromate and comparison of the absorbance at 375 nm with a standard potassium chromate solution (13).

SYNTHESIS OF THIOBIS(ETHYLENENITRILO)TETRAACETIC ACID, (TEDTA)

The synthetic procedure of Smolin and coworkers (14) was followed with the following modifications and precautions:

Preparation of Thiobis(ethylamine). The reaction between H_2S and ethyleneimine is *extremely exothermic* and considerable caution was exercised during the introduction of H_2S. The rate of addition of H_2S was such that the temperature of the reaction mixture could be easily maintained at 17-20° C with an ice-water bath. If the pot temperature drifted above 25°, the reaction became autocatalytic. Control of the reaction rate was regained by discontinuing the addition of H_2S and introducing N_2.

To facilitate monitoring of the rate of consumption of H_2S, a U-tube filled with mineral oil was connected to the top of the chilled water (5°) condensor fitted to the reaction vessel. As the addition of H_2S was judged complete when the weight of the reaction vessel had increased by the theoretical amount, provision was made to isolate and close off the pot (via the conventional use of stopcocks) before removing it to the scale. The yield observed was always 60-70% in excellent agreement with that reported (14).

Preparation of the Tetraacid. The yield of the tetraacid was strongly dependent on the rate of addition of base and chloroacetic acid. The yield was 40% greater when the addition rate was such that maintenance of the temperature at 40-50° did not require external heating than when gentle heating was necessary. Although the reaction is somewhat exothermic, an external source of heat was required to maintain the pot temperature at the recommended 40° overnight.

Water was added when necessary to dissolve the reagents. Sulfuric acid was used to acidify the solution, instead of the recommended HCl, to take advantage of the lower solubility of $NaHSO_4$. Acidification lead to a somewhat viscous solution of high ionic strength from which the desired product did not readily crystallize. The following procedure proved necessary to remove the excess salt present.

The acidified reaction mixture was allowed to stand overnight at room temperature in a large crystallizing dish. The crystals of $NaHSO_4$ which formed were removed and discarded (losses of the tetraacid arising from coprecipitation with $NaHSO_4$ were minimal). The filtrate was diluted four-fold with distilled water, the pH adjusted to *ca.* 2 by addition of H_2SO_4 if necessary, and the overnight evaporation repeated. The solid film which formed on the bottom of the crystallizing dish was broken up, the solution agitated and the yellow, and now rather viscous, supernatant was diluted again three- to four-fold with water. After refrigeration for *ca.* 2 hours, crystalline product amounting to 60% of the total yield was obtained. The dilution-evaporation procedure was repeated twice. The product was filtered, washed several times with cold water and dried at 110° for 24 hours. Total overall yield: 33%. Elemental analysis (%): C (40.65); H (5.48); N (7.75). Calculated for $C_{12}H_{20}O_8N_2S$: C (40.90); H (5.72); N (7.95).

The purity of the unrecrystallized material was verified by acidimetric titration of a sample with standard sodium hydroxide. The observed equivalent weight was 177.1 compared with the theoretical value of 176.2.

PREPARATION OF PENTAMETHYLENEDINITRILOTETRAACETIC ACID, (PMDTA)

This ligand was synthesized from 1,5-diaminopentane (Aldrich) and chloroacetic acid using essentially the same procedure described above for TEDTA.

Purification of the crude product by decolorization and multiple recrystallizations from both water and dilute HCl yielded colorless, well-formed crystals. Unfortunately, this improvement in the appearance of the product was not accompanied by a corresponding improvement in the analytical data (Table 1). Based on an average of the carbon and nitrogen analyses of a sample from treatment 4, the calculated purity of the product was 74.8%. The observed equivalent weight of a sample from treatment 4 was 117.5 which compared to the theoretical value of 167.2, indicated that this sample was 70.3% pure. Titration of a sample of PMDTA from treatment 4 with standard Zn^{+2} solution in the presence of ammonia buffer and Eriochrome Black T yielded results consistent with the elemental analyses and equivalent weight determination. The impurity was some hydrogen-containing non-titrateable, non-complexing, inorganic

Table 1

Elemental Analysis Data for PMDTA[a]

	Sample	Treatment	%C	%N	%H	C:N:H
1.	Crude Product	Washed 6-7X with H_2O, dried in dessicator at <10 mm Hg for 2 days and then in oven at 110° for 2 days.	34.44	6.30	5.71	13.1:2.0:25.8
2.	PMDTA after 1st treatment above	Decolorized, 2X recrystallized from H_2O, washed crystals 3X with H_2O and then dried under vacuum for 3 days.	34.96	6.02	5.79	13.2:2.0:26.1
3.	PMDTA after 1st treatment above	Decolorized, recrystallized from 0.1 M HCl, washed crystals 2X with H_2O, dried overnight in vacuum dessicator, then dried overnight at 78° over $CaCl_2$.	34.76	6.19	5.76	13.1:2.0:25.9
4.	Decolorized, recrystallized, PMDTA from treatments 2 and 3 above	Recrystallized from 0.05 M HCl, washed 2X with 0.05 M HCl, recrystallized again from 0.05 M HCl, washed several times with ice water and then oven dried at 105° for 5 days.	34.90 34.34[b]	6.01 6.65[b]	5.70 5.70[b]	13.2:2.0:25.7 12.9:2.1:25.7

[a] Calculated for $C_{13}H_{22}N_2O_8$: %C (46.70); %N (8.38); %H (6.63).

[b] Elemental analysis by Spang Microanalytical Laboratory, Eagle Harbor, MI.

material which did not appear to interfere with the preparation of Cr(III) complexes from the impure ligand.

PREPARATION OF CHROMIUM(III)-CHELATE COMPLEXES

CHROMIUM(III) COMPLEXES OF TEDTA

Two isomeric complexes, I and II, were prepared:

Isomer I. Dilute ($\leqslant$25 m$\underline{M}$) stock solutions of this isomer were prepared by adding a stoichiometric amount of TEDTA to a solution of $Cr(ClO_4)_3$ at pH $\leqslant$1.80 and heating to *ca.* 90° for 1 1/2 hours. The completeness of the complexation reaction was verified by raising the pH of an aliquot of the reaction mixture above 5. A blue precipitate (chromic hydroxide) resulted until complexation was complete. Solutions of Isomer I were stored at pH 1.5 without detectable decomposition for 30 days. Prolonged storage at pH values below 1 resulted in decomposition of the complex, which was reflected by a reduction in the intensity of the violet color of these solutions.

Isomer II. Stock solutions (10 m$\underline{M}$) of this isomer were prepared from solutions of Isomer I by raising the pH to 4-4.5 and maintaining it within this range while the solution was boiled for an additional 3 hours. The resulting red-violet solution was cooled to room temperature and the pH increased to 6.8-7.0. The visible spectrum of this solution, which was nearly identical to that of a pure solution of Isomer II, is shown in Figure 1. Complete conversion to Isomer II occurred after a few weeks at room temperature and pH 6.8-7.0. Alternatively, a solution of pure Isomer II can be obtained immediately by the anion exchange procedure described below. Solutions of Isomer II were stored at pH 6.8-7.0 and appeared to be stable indefinitely.

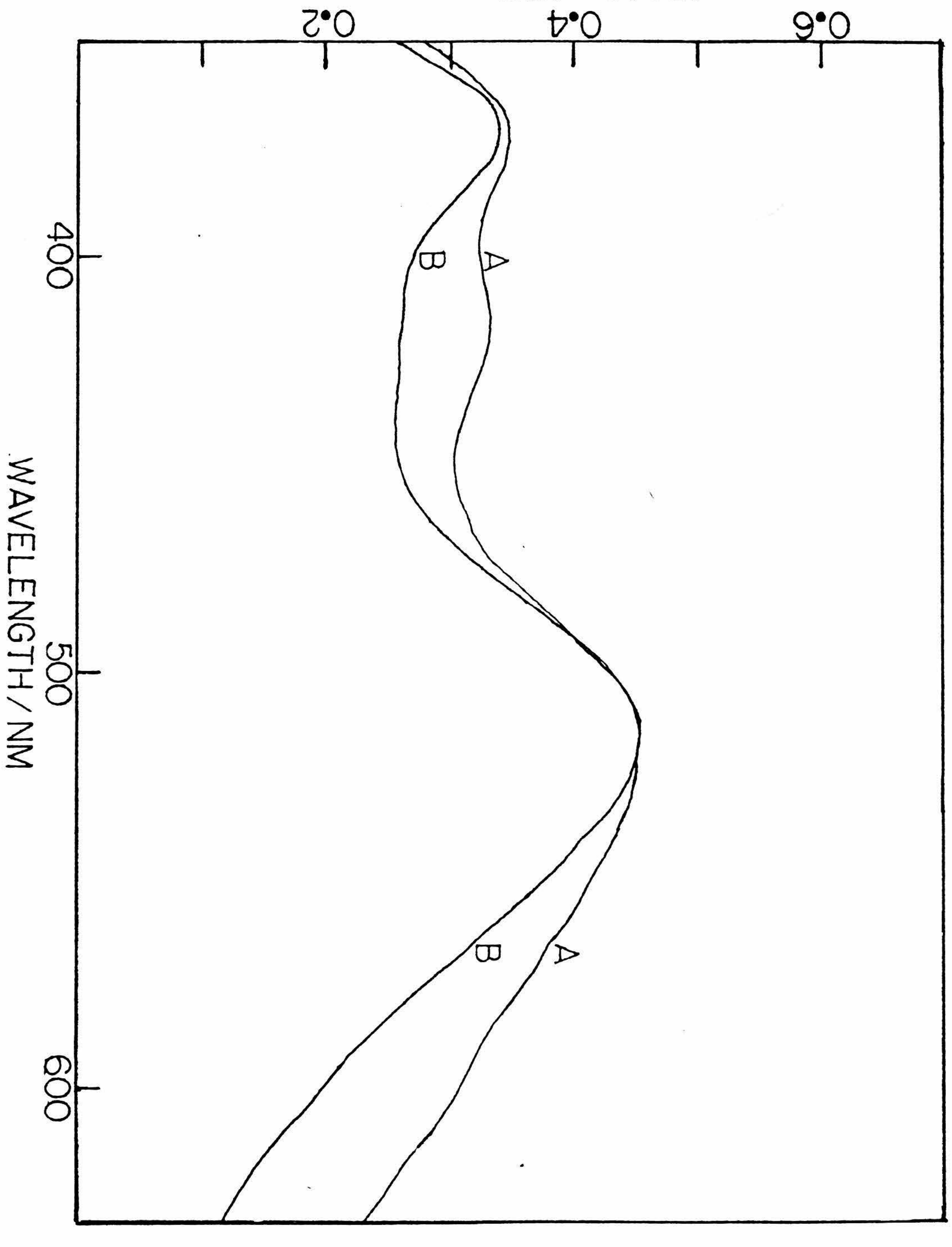
Complex III. Stock solutions (10 m*M*) of this complex were prepared by heating an aqueous mixture containing equimolar quantities of $Cr(ClO_4)_3$ and TEDTA at an initial pH of 3.2 for an hour at 90°. Reaction of TEDTA with $Cr(NO_3)_3 \cdot xH_2O$ resulted in the formation of Complex III even if the pH were initially set to 1.5. The reddish-violet solution could be stored at pH 2 for *ca.* a week.

CHROMIUM(III) COMPLEXES OF OXYBIS(ETHYLENENITRILOTETRAACETIC ACID (EEDTA)

$Cr(ClO_4)_3$ and EEDTA (Ciba-Geigy: from a ten year old stock in this laboratory; the material is apparently no longer commercially available) were mixed in stoichio-

FIGURE 1

Visible Spectra of Solutions of Isomer II. Curve A is the spectrum of the Isomer II reaction mixture after it had cooled to room temperature and the pH had been raised to 6.89. Curve B is the spectrum of a pure solution of Isomer II at pH 6.9 (11.3 m*M*), which had been equilibrating for more than 6 weeks. The spectra were superimposed at the low energy maximum.


ABSORBANCE
0.2
0.4
0.6
WAVELENGTH / NM
400
500
600
A
B
A
B

metric quantities in water (pH 1.8). The mixture was heated for 1 1/2 hours at 90° C. The resulting blue-green solution turned violet on cooling and was stored at pH 4 where it appeared to be stable indefinitely.

CHROMIUM(III) COMPLEXES OF PMDTA

Two isomers were prepared, one violet and one peach in color.

Violet Isomer. A stock solution of the violet isomer was obtained by heating a small excess of the ligand with $Cr(ClO_4)_3$ at pH 1.8 for *ca.* one hour. (The ligand purity was taken into account.)

Peach Isomer. A solution of the violet isomer was adjusted to and kept at pH 5-6 and boiled for 2 hours. The solution became red in color. This red solution was divided -- one half was maintained at room temperature and pH 6.4 and the other half was heated at pH 6.4-6.6 for an additional 20 hours. The color of the solution gradually changed to peach. This solution appeared indefinitely stable at room temperature and pH 6.5-6.6. The red solution at pH 6.4 did not change visibly in over 4 months at room temperature.

ION EXCHANGE RESINS

Selectacel DEAE anion exchange resin was purified according to reference 15 and converted to the perchlorate form by stirring with 1 M $HClO_4$. A column (2.2 x 10 cm) of the resin was rinsed thoroughly with distilled water before use.

AG 1 X-8 and AG 50W X-8 resins were purified by overnight oxidation with a strongly alkaline solution of H_2O_2, followed by several washes with 1 M HCl and distilled water. The AG 1 X-8 (2.2 x 13 cm) and AG 50W X-8 (2.2 x 16 cm) columns were thoroughly rinsed with distilled water before use.

PROCEDURES FOR pH TITRATIONS

The substitutional inertness of chromium(III) complexes made it necessary to heat mixtures of each ligand and $Cr(OH_2)_6^{3+}$ until complexation equilibrium was complete before commencing each titration. For the titrations of Isomer I and Cr(III)-EEDTA the procedure was as follows: A stoichiometric quantity of the solid ligand in the tetraacid form was added to a 10 mM solution of $Cr(ClO_4)_3$ which also contained a slight excess of perchloric acid. The mixture was heated for *ca.* 60-90 minutes at 90° while maintaining its volume by addition of distilled water. The resulting homogeneous solution (pH 1.5-1.7) was cooled to room temperature. For Isomer I, completeness of conversion was verified by spectral examination. The solution was then titrated with standard 0.010 M NaOH. The concentration of perchloric acid present in the stock solution of $Cr(ClO_4)_3$ was determined by a similar titration following the conversion to the CrEDTA complex, which is known to produce four moles of protons per mole of Cr(III) for titration to the first end point (16).

For Isomer II, a slightly different procedure was followed: After preparing a 10 mM solution of Isomer I as described above, the pH of the solution was raised to 4-4.5 by addition of a measured volume of standard 0.01 M NaOH solution. The mixture was heated to 95° C and the pH was maintained at 4-4.5 by continual quantitative additions of NaOH. After three hours, the solution was cooled to room temperature and titrated with standard NaOH. The visible spectrum of this solution at pH 7 was nearly identical to that of pure Isomer II (*cf.* prep. of Isomer II). The data from pH 3.8 to 2.8 were obtained by back titration with standard 0.01 N HCl.

ANALYSIS OF THE SOLID ADDUCT OF MERCURIC ION AND ISOMER II

A 34% excess (over 1:1) of standard 50 mM $Hg(ClO_4)_2$ (pH 1.4) was added to a 10 mM solution of Isomer II; the resulting mixture was centrifuged and samples of the colorless supernatant were carefully withdrawn for Hg^{+2} analysis. The mercury content of these samples was determined by addition of excess EDTA and back titration of the unreacted EDTA with a standard solution of Zn^{+2}.

The precipitate was collected and dried under vacuum for the chromium analysis. A weighed sample of the pink solid was dissolved in water by addition of excess EDTA. This solution was made alkaline and the chromium content assessed by oxidation to chromate as previously described.

RESULTS

PREPARATION, PURIFICATION AND ATTEMPTED ISOLATION

The product of the reaction between $Cr(ClO_4)_3$ and TEDTA depended on the pH of the reaction mixture as summarized in Scheme 1. When the pH was maintained below 1.8 during heating, a violet complex (Isomer I) was obtained which turned blue-green when the pH was adjusted to pH 7 at room temperature. If the initial pH of the reaction mixture was in the vicinity of 3, heating produced a solution which was redder than is characteristic of Isomer I. These reddish-violet solutions (Complex III) turned gray rather than blue-green at pH 7-8 and appeared to contain dimeric Cr(III) complexes which slowly converted to pure Isomer I at pH 1-1.5. If $Cr(NO_3)_3$ was used, Complex III was obtained even at pH 1.5.

Isomer I was converted to Isomer II by adjusting the pH to 4-4.5 and heating to 95° for several hours. Figure 2 shows the spectral changes that occurred during this transformation. Isomer II spontaneously reverted to Isomer I overnight at $pH<1$. Raising the pH of a hot solution of Isomer I above 5 and heating at pH 5-6 led again to the dimers, which were not readily converted to Isomer II. The observed spectral changes are shown in Figure 3.

SCHEME 1

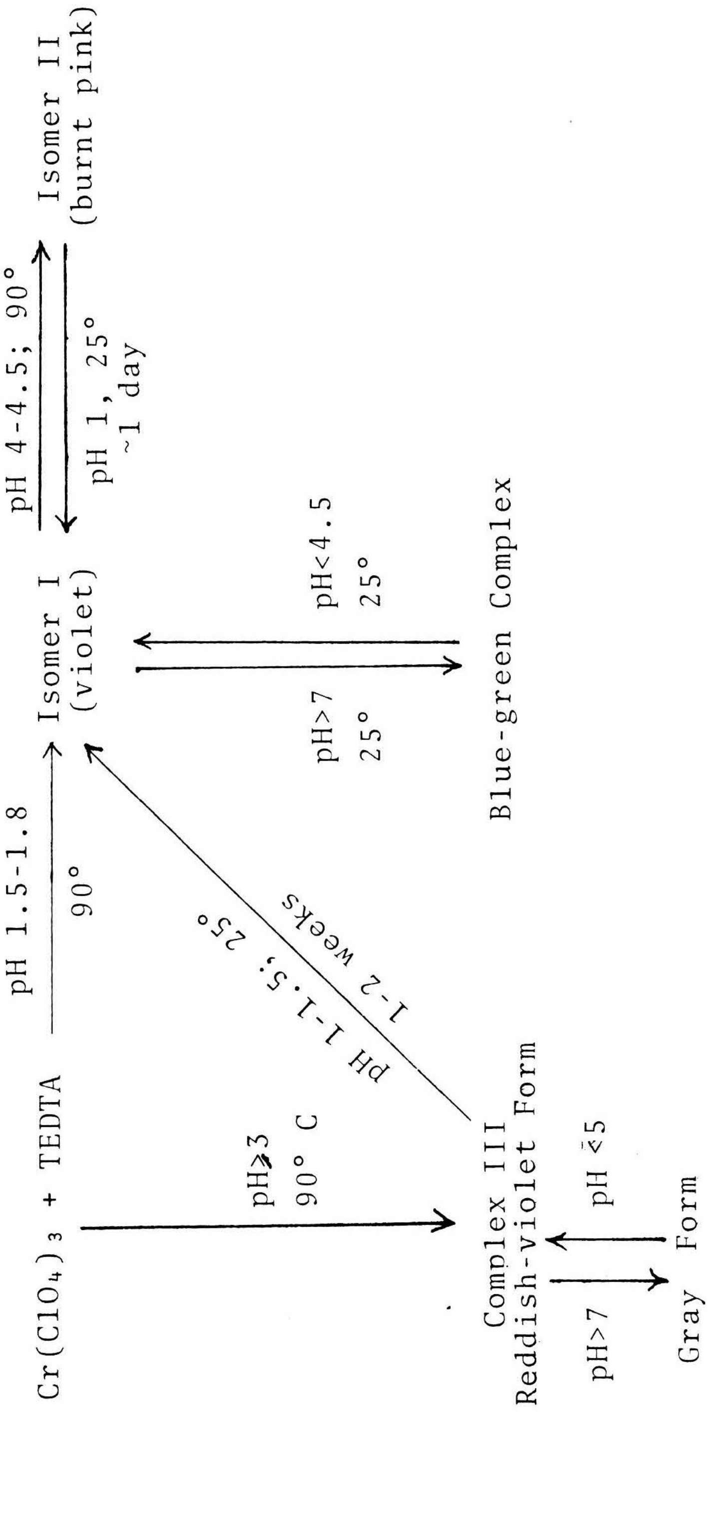

Cr(ClO₄)₃ + TEDTA
pH 1.5-1.8
90°
Isomer I
(violet)
pH 4-4.5; 90°
pH 1, 25°
~1 day
Isomer II
(burnt pink)
pH>7
25°
pH<4.5
25°
Blue-green Complex
pH≥3
90° C
pH 1-1.5; 25°
1-2 weeks
Complex III
Reddish-violet Form
pH>7
pH ≲5
Gray Form

FIGURE 2

Spectral Changes during the Preparation of Isomer II. Curves 1-8 are the spectra of aliquots removed from a reaction mixture *ca.* 10 mM in Cr(III)-TEDTA at the following intervals: Curve 1, prior to raising the pH to 4-4.5 (pH 1.29); Curve 2, after 1/2 hour (pH 5.03); Curve 3, after 1 hour (pH 4.14); Curve 4, after 1 3/4 hours (pH 4.38); Curve 5, after 3 hours, (pH 4.08); Curve 6, after 2 1/2 hours at room temperature, before heating was resumed; Curve 7, after 4 hours total heating (pH 4.24); Curve 8, after raising pH of aliquot 7 to 6.99.

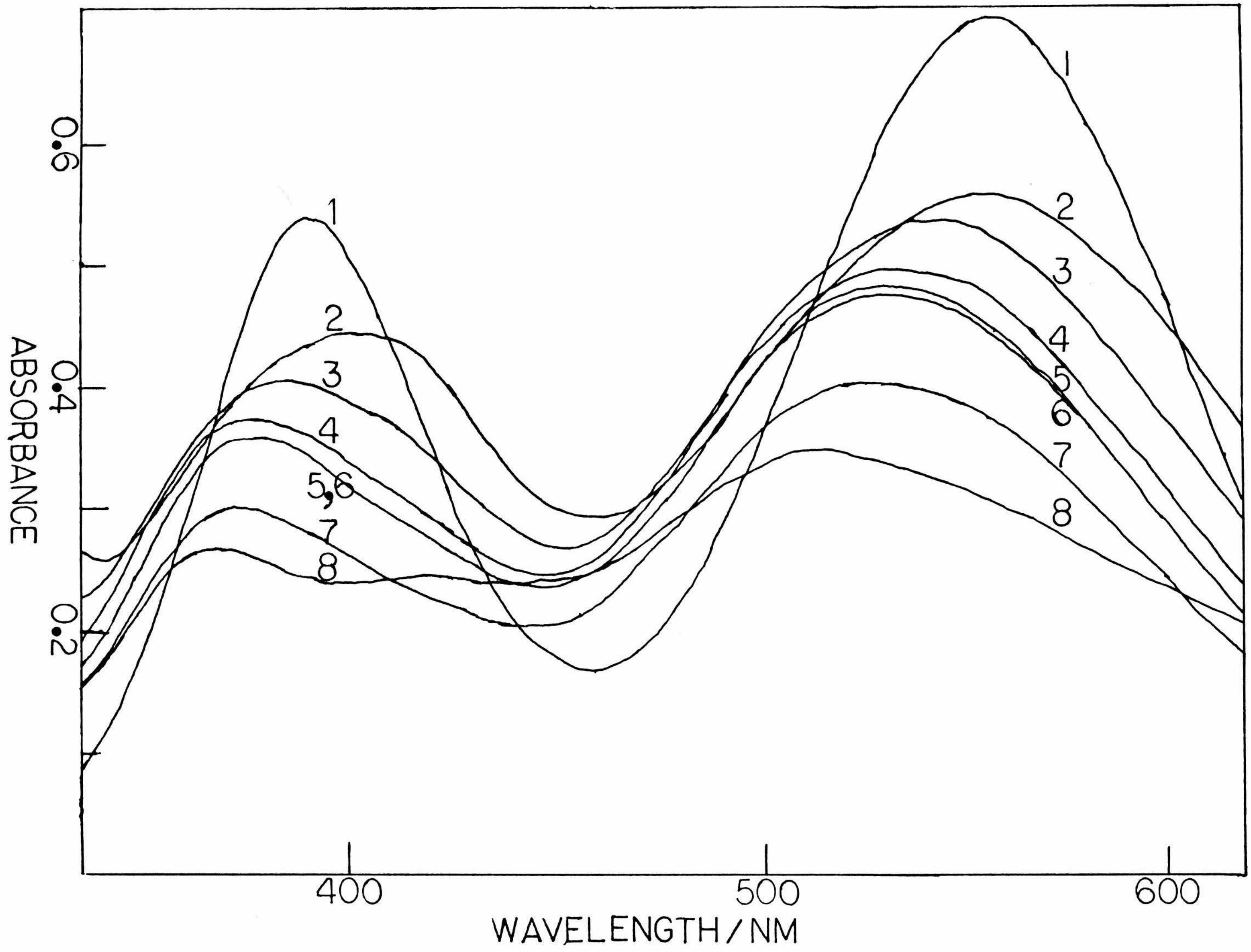
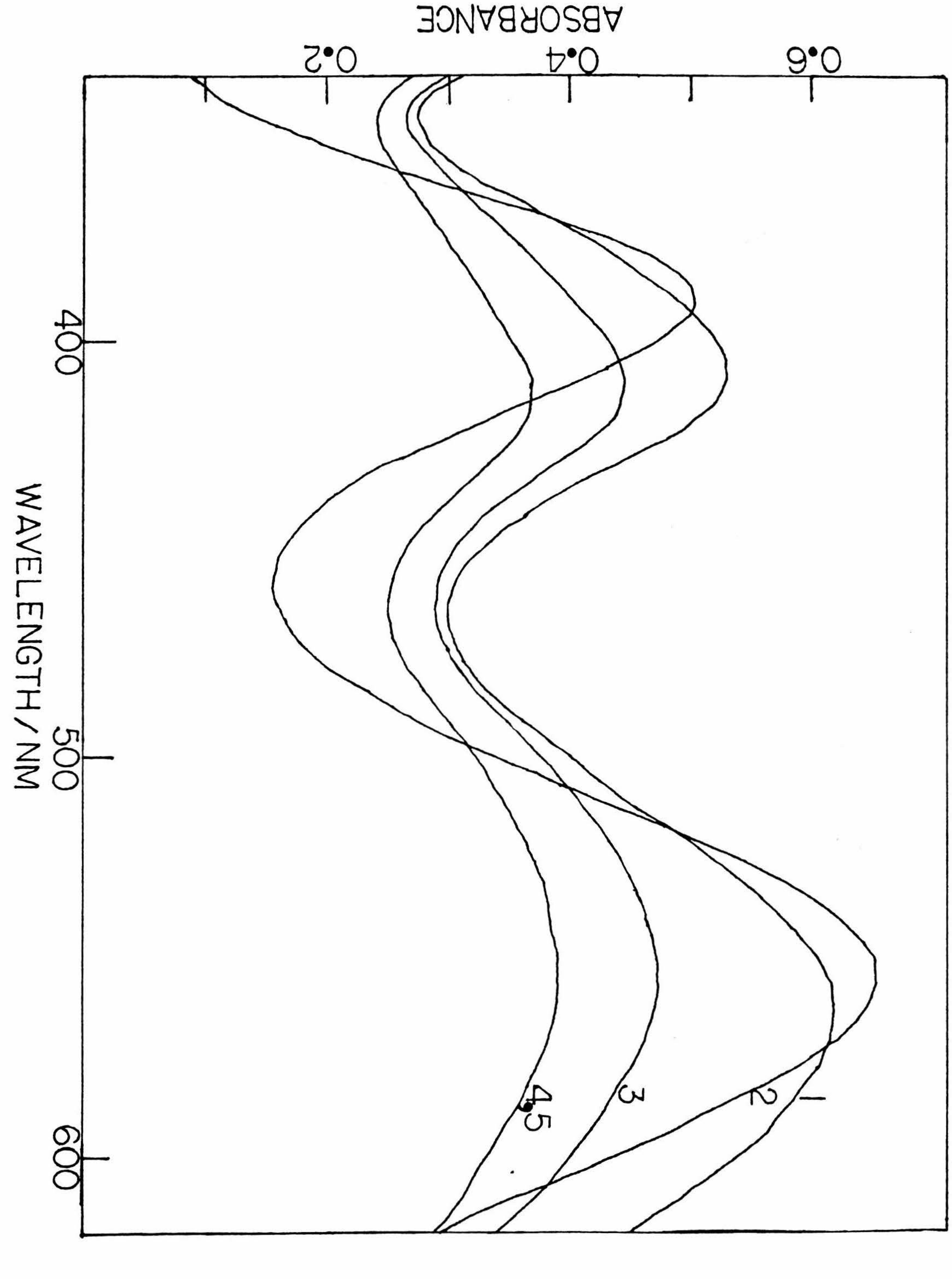

ABSORBANCE
0.6
0.4
0.2
400
500
600
WAVELENGTH/NM
1
2
3
4
5,6
7
8
1
2
3
4
5
6
7
8

FIGURE 3

Spectral Changes during the Preparation of Complex III. Curves 1-4 are the spectra of aliquots removed from a reaction mixture *ca.* 10 mM in Cr(III)-TEDTA at the following intervals: Curve 1, prior to raising the pH to 5-6 (pH 1.58); Curve 2, immediately after raising the pH of the hot reaction mixture (pH 5.30); Curve 3, after 1 hour (pH 5.12); Curve 4, after 5 hours total heating (pH 5.40); Curve 5, aliquot 4 after 3 days at room temperature and pH 6.94.


ABSORBANCE
0.2
0.4
0.6
WAVELENGTH / NM
400
500
600
1
2
3
4,5

Isomers I and II and Complex III were readily separated on a Selectacel DEAE anion exchange column in the ClO_4^- form. Isomer I exhibited no affinity for this resin and was rapidly eluted with either 0.01 N $NaClO_4$ or 0.01 N $HClO_4$. By contrast, Isomer II and the gray form of Complex III were tightly bound in a narrow band which was eluted with 1 M $NaClO_4$; Isomer II moved somewhat faster than gray Complex III and, thus, they could be separated.

Attempts to isolate Isomer I as the acid or lithium salt and Isomer II as the potassium or sodium salt by preparation of concentrated solutions (0.1-0.5 M) from which their precipitation could be effected by the addition of ethanol were unsuccessful. Both powders obtained for Isomer I gave poor elemental analyses. The violet powder obtained as the acid form of Isomer I was insoluble in water and dissolved only slowly in hot, 0.2 M $HClO_4$. Both preps for Isomer II yielded burgundy colored solutions which gradually blackened at pH >9. One solution of the potassium salt (0.1 M), which was allowed to reflux 30 hours at pH 7, became extremely viscous and gelled on cooling to room temperature. All of these materials were probably polymeric.

Ricard (17) has reported that the formation of Cr(III) polymers of long chain (n - 3,4,6) diaminoalkyltetracarboxylic acids was favored by prolonged heating of concentrated solutions (⩾0.1 M) at pH >5. Hydrolytic cleavage of these polymers was effected by heating at 50° in 0.05 M $HClO_4$. Hamm (16) reported that all efforts to isolate the potassium salt of either the violet or blue forms of $CrEDTA^-$ failed and that extremely viscous, oily materials always resulted.

As we lusted for the crystal structure of Isomer II, we persisted in trying to coax its crystallization. Dilute (10 mM) stock solutions of Isomer II were allowed to concentrate by evaporation at pH 7 at room temperature, but clear gels were always obtained. Pink powders could be obtained from these transparent gels by washing them successively with ethanol and ether; however, these were always contaminated with $NaClO_4$ and possibly some excess TEDTA. Attempts to purify Isomer II by recrystallization as either the sodium, ammonium, tetramethylammonium or tetraethylammonium salts from either water or a mixed water-ethanol system by evaporation at room temperature or by slow, controlled cooling were unsuccessful. Typically, opaque, semi-fluid gels were obtained in which were suspended small, dark particles.

In one experiment with the tetraethylammonium salt, a nearly transparent, viscous fluid containing solid particles was obtained after standing overnight at 4° C.

$N(CH_3)_4Br$ can be removed by sublimation at 0.1 mmHg at 150° (19). We have succeeded in separating NH_4Br from a solid mixture of HCrEDTA and NH_4Br at 0.1 mmHg and 60°. The lower temperature is preferred in order to minimize complications from the thermal matrix reaction of the chromium complex and the halide salt (19,20).

Ogino, Chung and Tanaka reported the preparation of solid, monomeric complexes of Cr(III)-diaminoalkyltetra-acetate complexes by using chromous ion to drive the complexation reaction without heating (21). This procedure was followed for Cr(III)-TEDTA. After the addition of Cr(II), the reaction mixture gradually turned deep blue and a blue solid precipitated from solution. No change was observed when the vessel was opened to the air. On standing overnight, the solution turned violet (probably aquation of the blue, chloro complex). The precipitated solid, which was filtered off and washed with ethanol and ether, was pale bluish-violet in color when dry and insoluble in water. Roto-vaping led to a deep blue, glassy solid which was also insoluble in water.

CHARACTERIZATION OF Cr(III)-TEDTA COMPLEXES

Characterization of the Cr(III) complexes of TEDTA included an examination of their pH behavior, visible and UV absorption spectra, substitutional lability with excess N_3^-, behavior on Selectacel anion exchange resin, reactivity with heavy metal ions and methyl mercury cation, limited IR evidence and distinctive electrochemistry. For purposes of comparison, the Cr(III) complexes of two other ligands related to TEDTA were also studied: oxybis(ethylenenitrilo)tetraacetic acid (EEDTA), (more properly, 1,7-diaza-4-oxaheptane-1,1,7,7,-tetraacetic acid) and pentamethylenedinitrilotetraacetic acid (PMDTA), (1,5-diazapentane-1,1,5,5-tetraacetic acid), in which the thioether group in TEDTA is replaced by an ether linkage and a methylene group, respectively.

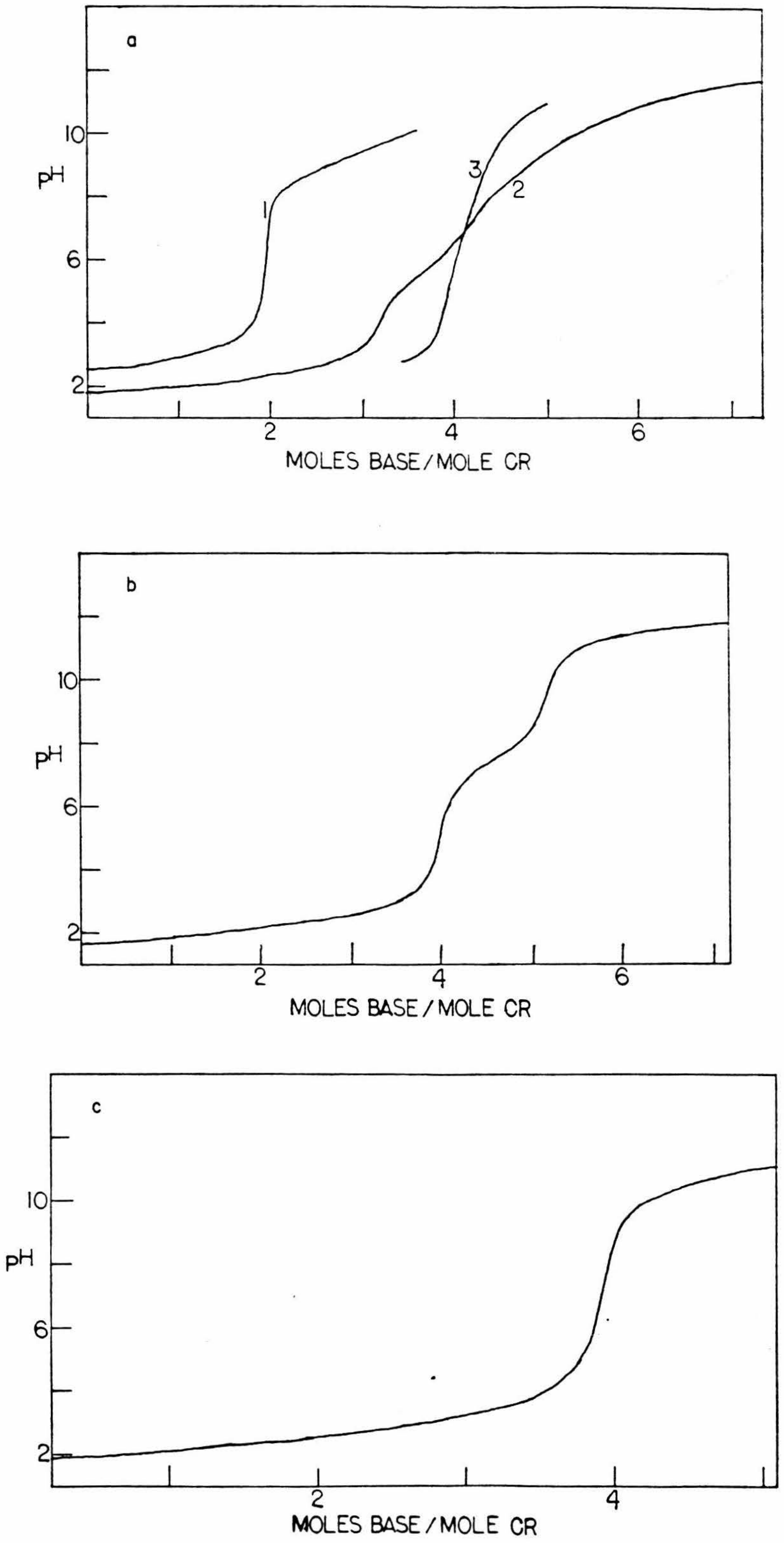
pH BEHAVIOR

pH Titrations. The two isomers of CrTEDTA were subjected to acid-base titrations (as described in the Experimental Section) in order to examine the metal coordination and ligand denticity. Because the reaction of the ligand with substitutionally inert Cr(III) was driven largely to completion by heating before the pH titrations were conducted, the titration curves do not reflect the equilibrium pH dependence of the Cr(III)-ligand reaction.

With Isomer II, the single inflection in the titration curve (Figure 4a, Curve 3) near pH 7 corresponded

FIGURE 4

pH Titration Curves. All solutions were 10 m*M* except as otherwise noted. Part a: Curve 1, free TEDTA (*ca.* 3 m*M*); Curve 2, Isomer I; Curve 3, Isomer II (5 m*M*). Part b: Cr(III)-EDTA. Part c: Cr(III)-EEDTA.


a
10
pH
6
2
1
3
2
2
4
6
MOLES BASE / MOLE CR
b
10
pH
6
2
2
4
6
MOLES BASE / MOLE CR
c
10
pH
6
2
2
4
MOLES BASE / MOLE CR

to the consumption of 4.1 moles of base per mole of Cr(III), 3.9 moles of which were added during the reaction. Therefore, either all four carboxylate groups are coordinated to Cr(III) or any uncoordinated carboxyl group has a pK_a too low to be distinguishable from the titration of a strong acid. During the titration, the originally pink solution of Isomer II changed color only slightly, becoming somewhat more orange at pH 10. However, on standing overnight at a pH ⩾11, the solution took on the green color characteristic of Isomer I at this pH.

Solutions of Isomer I produced titration curves with two less well defined inflections (Figure 4a, Curve 2). The positions of these inflections corresponded reasonably well to the points where 3 and 4 moles of base per mole of Cr(III) had been consumed. (The precise values were 3.1 and 4.1, respectively.) The first three protons titrated as strong acids, but the fourth proton titrated over a somewhat wider pH range and appeared to correspond to a weak acid with a pK_a near 5.5.

The color of the solution of Isomer I varied extensively during the titration: The solution retained its original violet color up to *ca.* pH 4.3 but became progressively bluer at higher pH values and was green above pH 11. The blue-green solution present at pH 7 returned to its original violet color only slowly when the pH of the solution was adjusted quickly to 3, whereas the green solution at pH 11 immediately turned violet.

In the Cr(III)-EDTA complex only three of the four carboxylate groups are coordinated to Cr(III); the sixth coordination position is occupied by a water molecule (16, 22-25). This complex yielded a titration curve (Figure 4b) containing two sharp inflections which corresponded to 4 and 5 moles of base added per mole of Cr(III). The solution remained violet, turning blue only after sufficient base had been added to substantially convert the aquo complex to the hydroxy complex (16,23-25); the observed pK_a of the coordinated water molecule was 7.50 in excellent agreement with the literature value of 7.52 (16). At pH $\geq$12, the solution was green. This green color has been ascribed to the formation of the dihydroxy complex (23). Titration of a solution of the Cr(III)-EEDTA complex (Figure 4c) resulted in a simple titration curve with a single inflection corresponding to the titration of 4 moles of protons per mole of chromium(III). The solution was violet at pH values below 3.5 and blue-green above pH 4.5. The blue-green form of the complex regained its violet color only slowly at room temperature when the pH was decreased to 2.5.

Although a potentiometric pH titration of Complex III was not done, its color as a function of pH was noted. It was reddish-violet up to pH 5.6, gray at pH 7-11 and turned green on standing at pH >12.

As with CrTEDTA, two geometrical isomers of CrPMDTA appear to exist. A violet isomer formed at low pH, underwent color changes identical to those exhibited by Isomer I as the pH was increased. A peach-colored isomer formed at higher pH values behaved similarly to Isomer II, exhibiting only minor variations in color between pH 2 and 11.

pH Hysteresis Experiments. In order to further investigate the hysteresis phenomena noted above, a series of experiments was performed to determine whether there was any difference in the amount of base required to increase the pH from pH 2, 3 or 4 to 8 compared to the amount of acid required to restore the pH to its original value. The results are summarized in Table 2. These data demonstrate that 30 to 35% of the acid groups titrated were not immediately available for reprotonation when the pH was returned to 3 or 4, respectively. However, when the solution was strongly acidified (pH $\leqslant$2), these groups were released and could be reprotonated. Similar experiments with Isomer II and Complex III revealed no hysteresis in their pH behavior.

Table 2

	pH Change	mmoles of Titrant Consumed	$\frac{\text{Quantity of Base Used}}{\text{Quantity of Acid Used}}$
Isomer I[1]			
	2.00 → 8.10	0.879	1.03
	8.10 → 2.00	0.902	
	3.06 → 8.10	0.556	1.43
	8.10 → 3.07	0.390	
	4.16 → 8.10	0.472	1.54
	8.10 → 4.12	0.307	
Isomer II[2]			
	1.98 → 8.17	0.116	0.94
	8.27 → 1.99	0.124	
	3.04 → 8.17	0.0267	1.03
	8.27 → 3.03	0.0260	
	3.56 → 9.17	0.0156	0.93
	8.27 → 3.53	0.0167	
Complex III[3]			
	2.02 → 8.07	0.450	0.91
	8.07 → 2.02	0.492	
	3.12 → 8.07	0.254	0.94
	8.07 → 3.10	0.269	

[1] Sample: 25.00 ml of a solution 10.02 m$\underline{\text{M}}$ in complex.

[2] Sample: 5.00 ml of a solution 10.44 m$\underline{\text{M}}$ in complex + 3.00 ml triply distilled water.

[3] Sample: 20.00 ml of a solution 9.87 m$\underline{\text{M}}$ in complex.

Equilibrium Distribution of Cr(III)-TEDTA Species as a Function of pH. In order to gain a greater understanding of the relationship between the various Cr(III)-TEDTA complexes, a series of experiments was performed to determine their equilibrium distribution as a function of pH. Three sets of five jars were each filled with 15 ml of a 10 m$\underline{M}$ solution of either Isomer I, predominantly Isomer II or predominantly Complex III and the pH was set to 1.5, 3.0, 5.0, 7.0 or 9.0. These solutions were allowed to equilibrate at room temperature over a period of four months. The pH was checked periodically and readjusted when necessary. It was assumed that equilibrium was attained when no changes were observed in the pH, color and visible spectrum of the solution for at least a week. A summary of the data is presented in Table 3. Spectra for each series of solutions are shown in Figures 5a, b and c for Isomer I, Isomer II and Complex III, respectively.

The percentage of Isomers I and II present at equilibrium at pH 3 and 5 was calculated from the data in both Figures 5a and 5b using the observed absorbances at 558 and 512 nm. The results of these calculations are presented in Table 4. The equilibrium distribution of Isomers I and II as a function of pH from pH 1.5-7 is shown in Figure 6.

Table 3

Summary of Data for the Cr(III)-TEDTA pH Equilibrium Experiments

Predominant Starting Species	pH	Observed ΔpH[a]	Original Color	Final Color	Equilibration Time[b]	Isosbestic Points
1. Isomer I	1.5	None	Violet	Violet	0	366 nm (ε29.9)[d]
	3.0	Decreased	Violet	Red-Violet	4 weeks	
	5.0	Decreased	Purple	Pink-Violet	13 weeks	
	7.0	Decreased	Blue	Burnt Pink	16 weeks	513 nm (ε38.5)[e]
	9.0	Decreased	Grayish-Green	Gray-Purple	6 weeks	
2. Isomer II	1.5	None[c]	Reddish-Violet	Violet	1 week	
	3.0	Increased	Reddish-Violet	Red-Violet	4 weeks	
	5.0	Increased	Reddish-Purple	Pink-Violet	4 weeks	372 nm (ε35.1)[e]
	7.0	~Constant	Grayish-Red-Violet	Burnt Pink	4 weeks	
	9.0	Decreased	Gray Red-Violet	Gray-Pink	11 weeks	
3. Complex III	1.5	None[c]	Reddish-Violet	Violet	2 weeks	
	3.0	Increased	Reddish-Violet	Red-Violet	8 weeks	
	5.0	Increased	Grayish-Purple	Pink-Violet	7 weeks	372 nm (ε37.0)[d]
	7.0	Decreased	Grayish-Purple	Burnt Pink	15 weeks	
	9.0	Decreased	Gray-Purple	Gray-Pink	13 weeks	

[a] Observed change in the pH as the solution equilibrated.

[b] Time required to reach equilibrium.

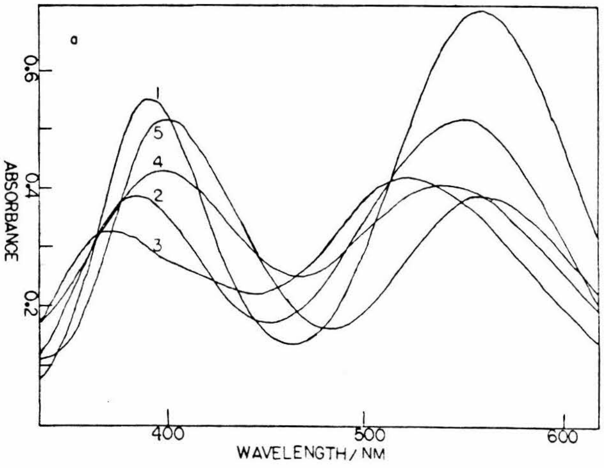
[c] At such high acidities, the pH electrode error was comparable to any variation observed in the solution pH.

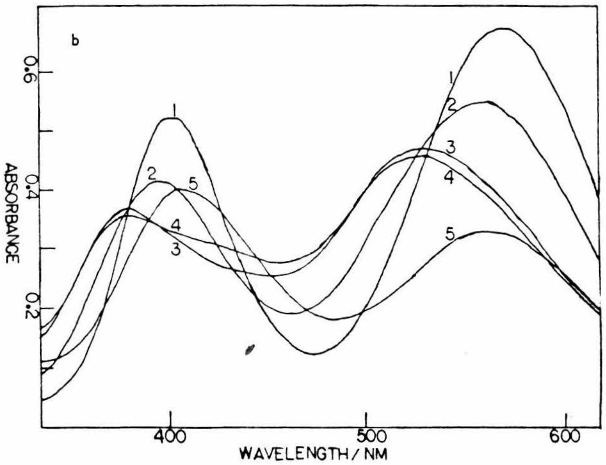
[d] Intersection of spectra for solutions set at pH 1.5, 3.0, 5.0 and 7.0.

[e] Intersection of spectra for solutions set at pH 1.5, 3.0 and 5.0.

FIGURE 5

Spectra of solutions originally *ca.* 10 mM in: Isomer I, Part a; Isomer II, Part b; Complex III Part c, which had been allowed to come to equilibrium at room temperature over a period of over four months with the pH maintained at: pH 1.5, Curve 1; pH 3.0, Curve 2; pH 5.0, Curve 3; pH 7.0, Curve 4; pH 9.0, Curve 5.


a
ABSORBANCE
0.6
0.4
0.2
400
500
600
WAVELENGTH / NM
1
5
4
2
3


b
ABSORBANCE
0.6
0.4
0.2
400
500
600
WAVELENGTH / NM
1
2
5
4
3
1
2
3
4
5

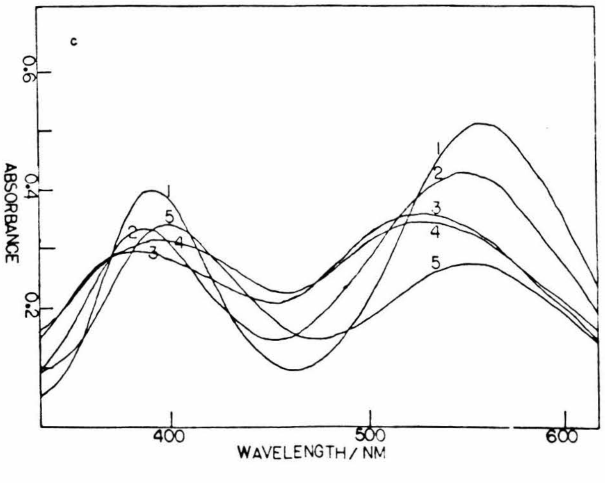

c
ABSORBANCE
0.6
0.4
0.2
400
500
600
WAVELENGTH / NM
1
5
2
4
3
1
2
3
4
5

Table 4

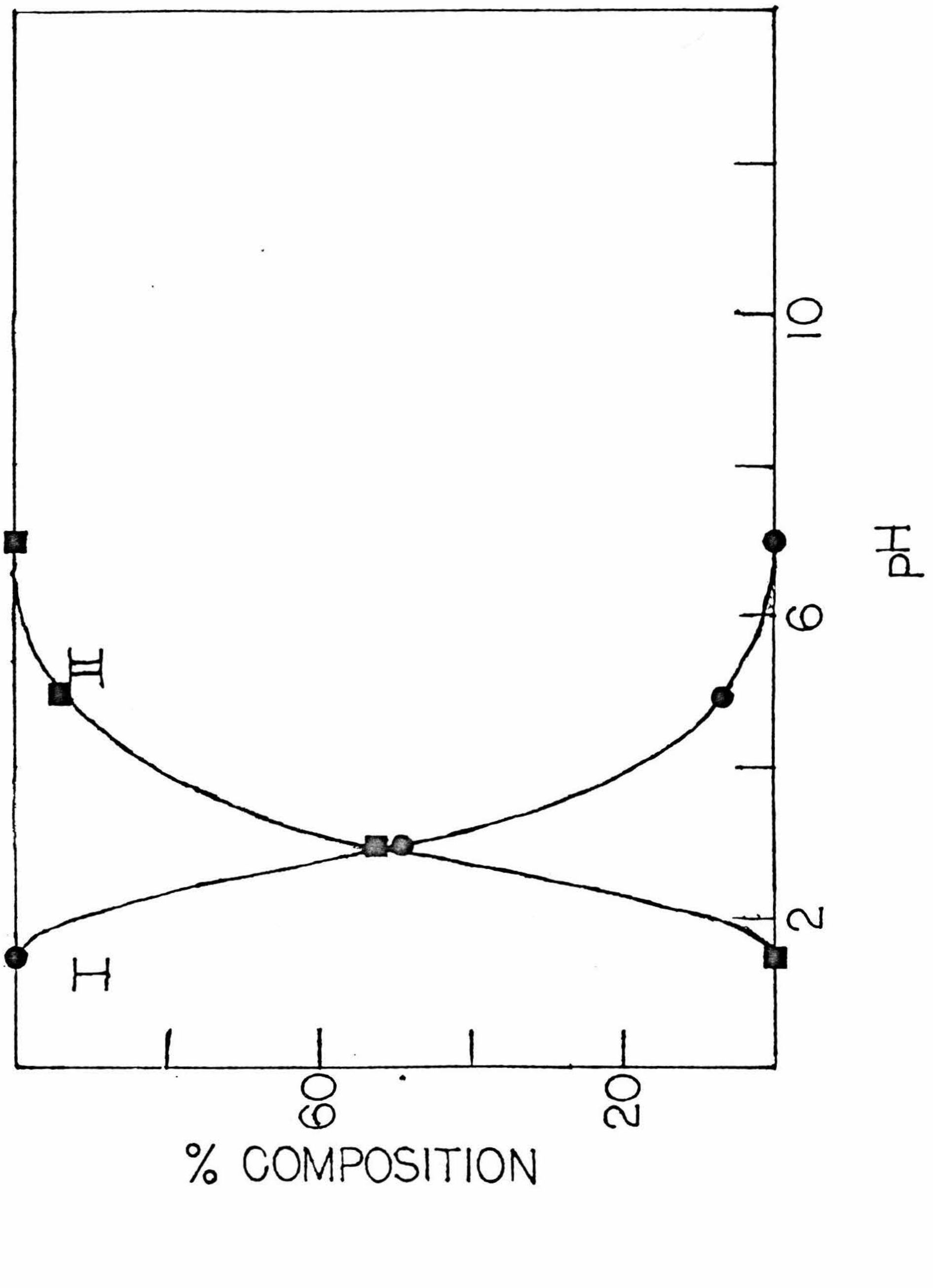
Equilibrium Composition of Cr(III)-TEDTA Solutions[a]

pH	% Isomer I	%Isomer II
3	46.5	53.5
	50.6	49.4
5	5.2	94.8
	8.2	91.8

[a] First set of numbers at a given pH was obtained from an analysis of the spectra in Figure 5a; second set, from Figure 5b. The extinction coefficients used were: at pH 3, $\varepsilon^{I}_{558} = 63.8$, $\varepsilon^{I}_{512} = 37.4$, $\varepsilon^{II}_{558} = 30.3$ and $\varepsilon^{II}_{512} = 40.0$ $\underline{M}^{-1}$ cm^{-1}; at pH 5, same except $\varepsilon^{I}_{558} = 66.0$ $\underline{M}^{-1}$ cm^{-1}.

FIGURE 6

Equilibrium Distribution of Isomers I (●) and II (■) as a function of pH from pH 1.5 to 7.0. Points at pH 3 and 5 were calculated from the spectra in Figures 5a and 5b as described in the text and in Table 4. Points at pH 1.5 and 7 were known from previous experiments.


% COMPOSITION
60
20
pH
2
6
10
I
II

VISIBLE AND UV ABSORPTION SPECTRA

Visible spectra of solutions of Isomers I, II and Complex III as a function of pH are shown in Figures 7, 8 and 9. UV spectra are shown in Figure 10 and λ_{max} values are summarized in Table 5 along with those for the Cr(III)-EEDTA and Cr(III)-PMDTA complexes. Note that only for Isomer II does a UV band appear to be present at 240 nm. For Complex III, this band may be obscured by the intense UV absorption.

REACTIONS WITH AZIDE ION

The water molecule which occupies the sixth coordination position in the pentadentate EDTA complex of Cr(III) is relatively labile and can readily be replaced by another ligand such as acetate (26) or azide (27,28). Tanaka and coworkers (27) found that such anation by azide intensified and red-shifted the two prominent absorption bands of CrEDTA. The two isomers of CrTEDTA were therefore reacted with azide to compare their behavior with that of the EDTA complex.

A 9.4 m$\underline{M}$ unbuffered solution of Isomer II at pH 4.3 was treated with a fifty-fold excess of NaN_3 which produced an immediate increase in the pH to 6.7. Heating this solution to boiling for one hour caused the pH to increase to 8.4 and the originally pink solution took on

FIGURE 7

Visible Spectra of 10 m$\underline{M}$ Solutions of Isomer I: Curve A, pH 4.28 (violet solution); Curve B, pH 7.23 (blue-green solution).

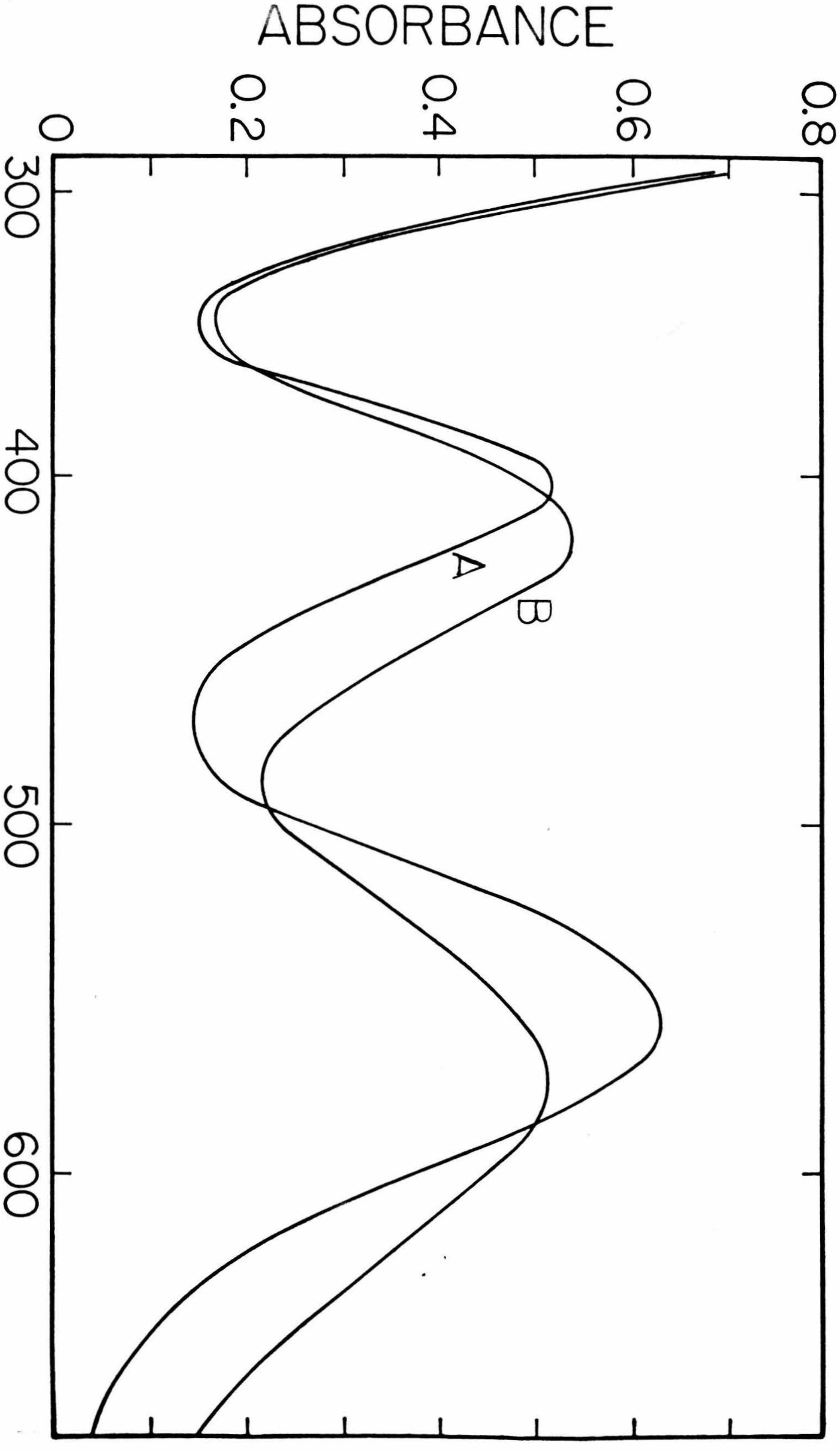

ABSORBANCE
0
0.2
0.4
0.6
0.8
300
400
500
600
nm
A
B

FIGURE 8

Visible Spectra of 10 mM solutions of Isomer II: Curve A, pH 3.01; Curve B, pH 7.15; Curve C, pH 10.78.

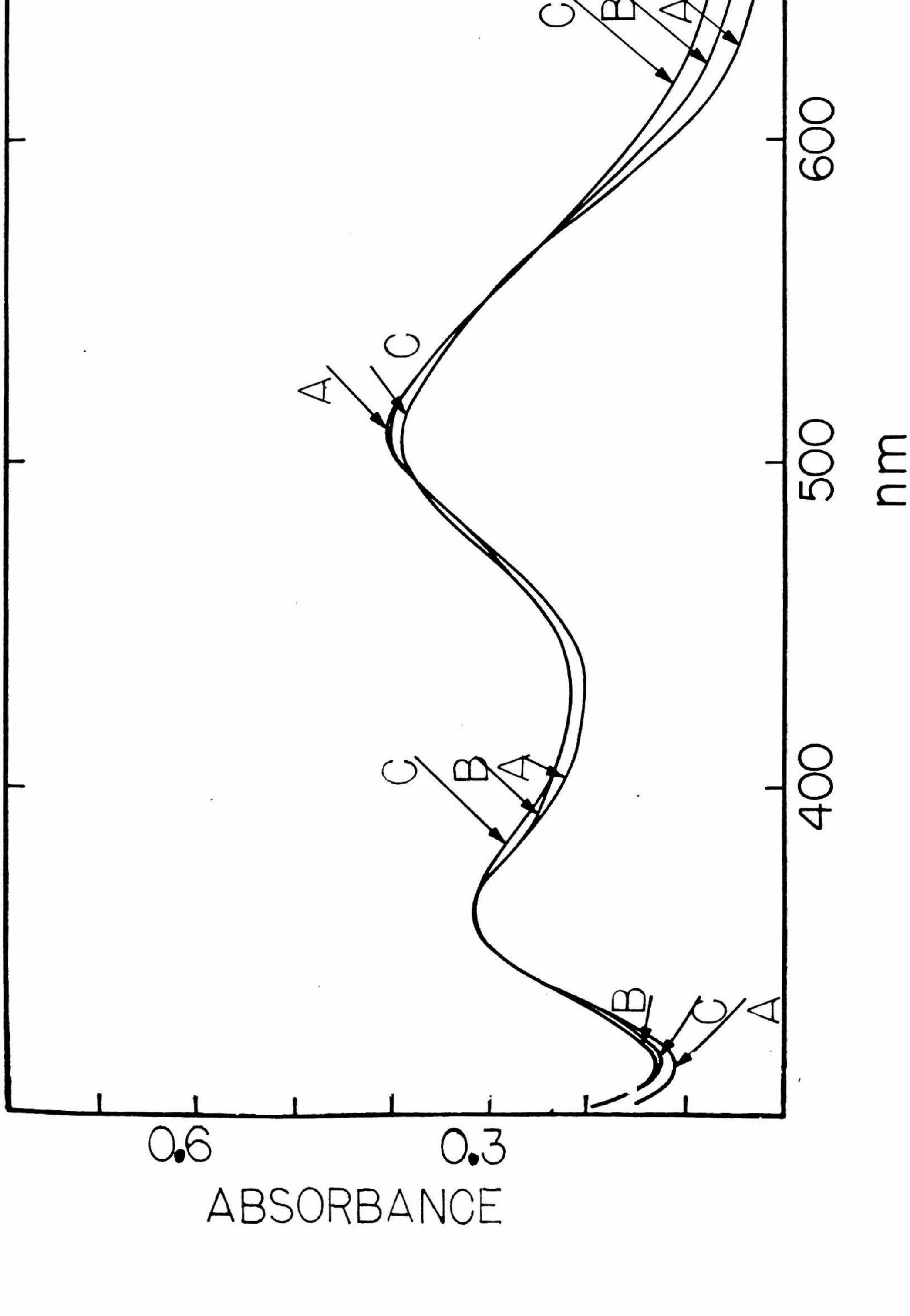

ABSORBANCE
0.6
0.3
nm
400
500
600
A
B
C

FIGURE 9

Visible Spectra of 10 mM Solutions of Complex III. Curve A, pH 1.98 (reddish-violet); Curve B, pH 8.53 (gray).

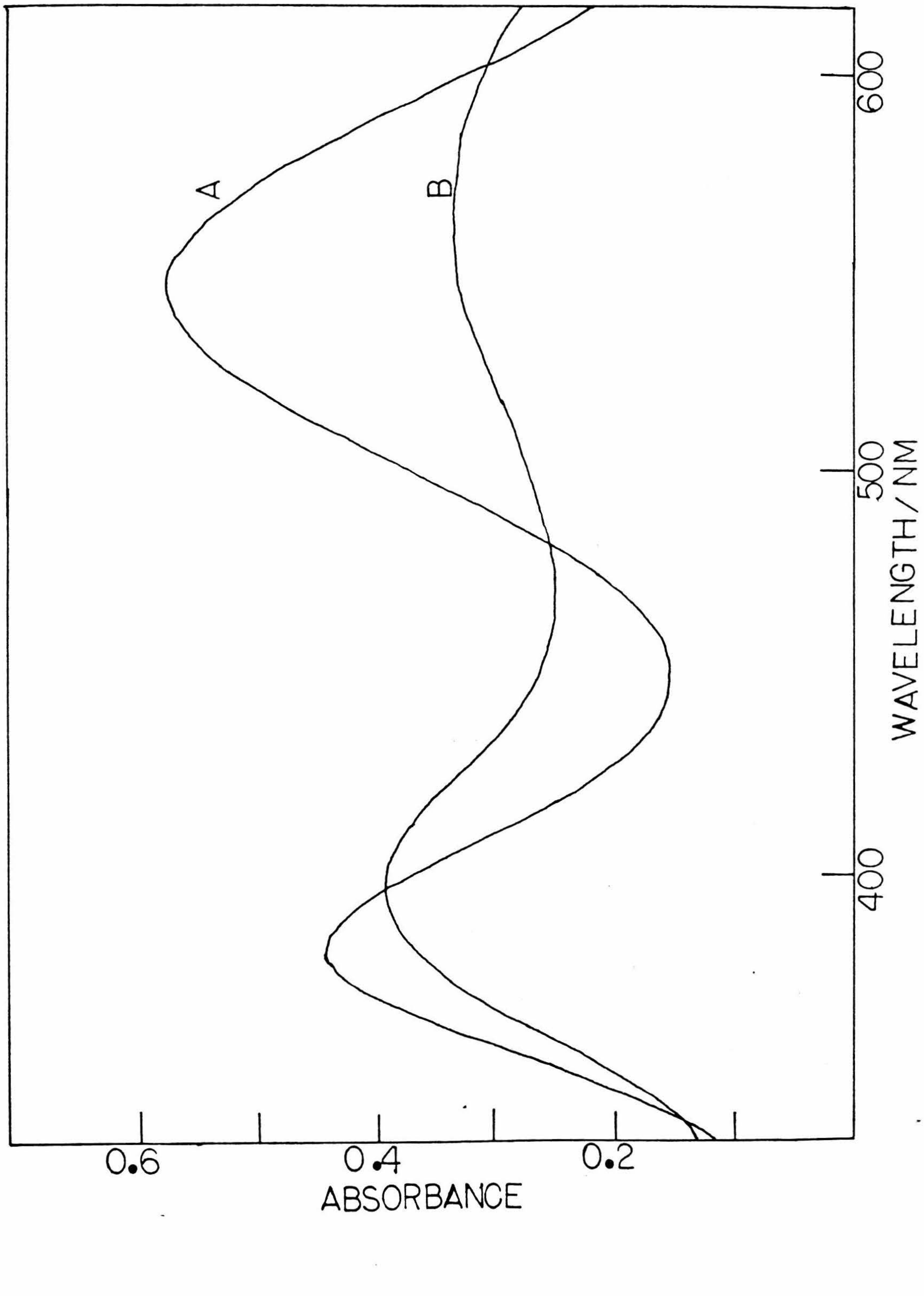

A
B
0.6
0.4
0.2
ABSORBANCE
400
500
600
WAVELENGTH / NM

FIGURE 10

Ultraviolet Spectra of *ca.* 0.2 mM Cr(III)-TEDTA Solutions. Curve A, Isomer I at pH 4.49; Curve B, Isomer I at pH 7.13; Curve C; Isomer II, at pH 7.15; Curve D, Complex III at pH 8.86.

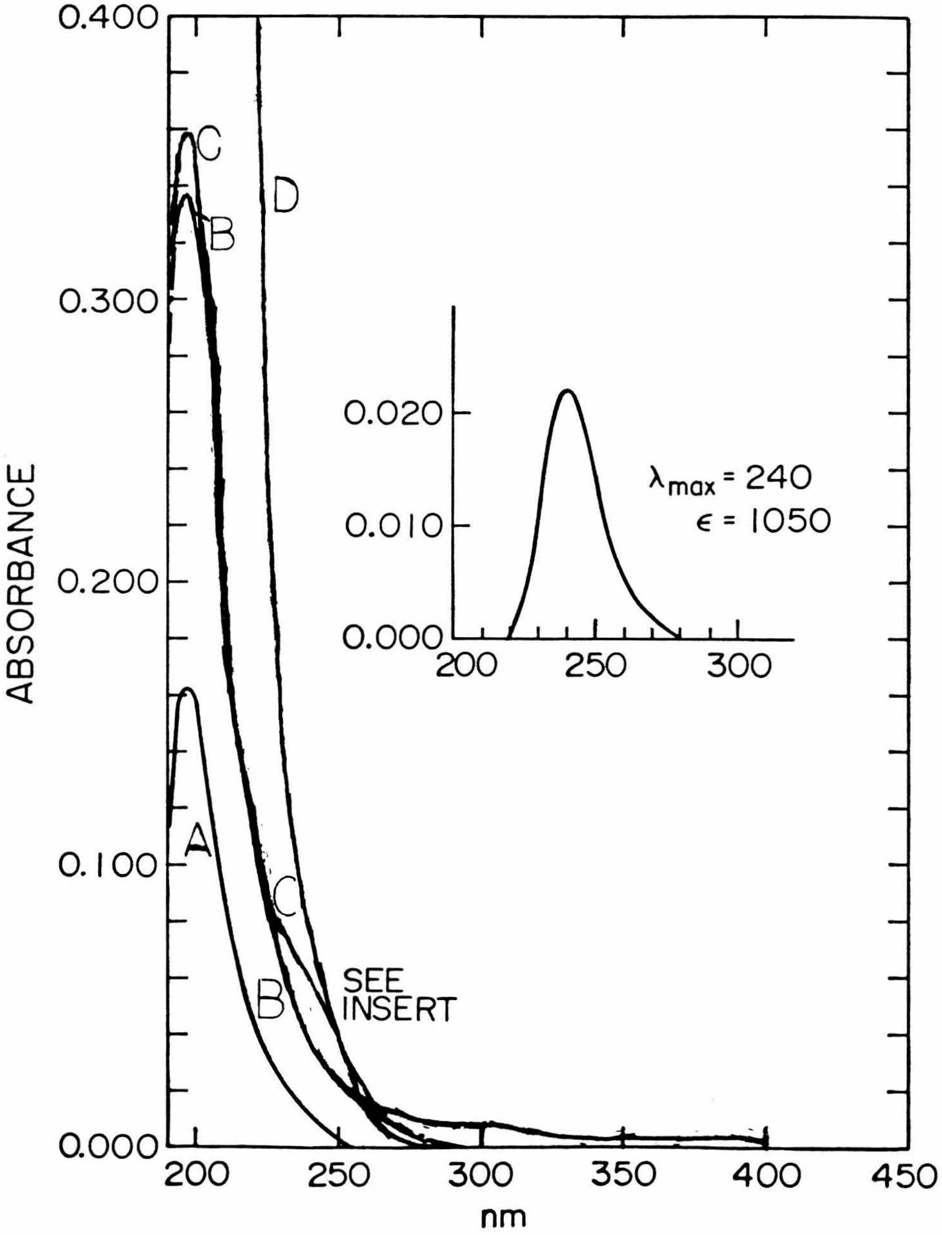

0.400
0.300
0.200
0.100
0.000
ABSORBANCE
200
250
300
350
400
450
nm
A
B
C
D
B
C
SEE INSERT
0.020
0.010
0.000
200
250
300
λ_{max} = 240
ϵ = 1050

Table 5

Absorption Spectral Data[a]

	pH	Color of the Solution	λ_{max} (nm)	ε^b ($M^{-1}cm^{-1}$)
CrTEDTA				
Isomer I	4.28	Violet	558	65
			393	51
	4.49		195	8,650
	7.23	Blue-green	584	54
			414	58
	7.13		195	17,800
Isomer II	3.01	Reddish-pink	513	40
			365	30
			~415(weak max)	--
	4.72		240	1,050
			195	19,100
	7.15	Burnt pink	512	41
			365	31
			~415(weak max)	--
	10.78	Orangish-pink	509	37
			365	29
			~415(weak max)	--
Complex III	1.98	Reddish-violet	554	58
			390	45
			309(sh)	~5
	8.53	Gray	575	37
			407	45
			303(sh)	~9

Table 5 Cont'd

CrEEDTA	1.75	Violet	561 396	53 47
	4.65	Blue-green	585 415 203(sh)	78 78 ~4,800
CrPMDTA				
Violet Isomer	1.46	Violet	557 393	64 51
Peach Isomer	6.40	Peach	514 410^c 370^c	~60% of those for Violet Isomer

[a] Visible spectra were obtained with 10 m$\underline{M}$ solutions of the complexes in 1 cm quartz cells; UV spectra, with 0.2 m$\underline{M}$ solutions in 0.1 cm quartz cells.

[b] Extinction coefficients were calculated per mole of Cr(III).

[c] Split band--maxima of approximately equal intensity.

an orange tint. However, the visible spectrum of the solution matched that of the control. Therefore, Isomer II was not anated by N_3^-. The maxima in the visible absorption spectrum of Isomer I undergo a significant and not completely reversible shift to the red in the pH range from 4.3 to 7 in the absence of N_3^-. Therefore, for the reaction of Isomer I with N_3^-, the solution was carefully maintained at pH 4.25-4.35. Addition of a fifty-fold excess of NaN_3 to a 10 m<u>M</u> solution of Isomer I caused an immediate color change from violet to blue-violet. After two hours standing at room temperature, the visible absorption spectrum exhibited two bands: λ_{max} (ε), 570 nm (102); 414 nm (68 $\underline{M}^{-1}$ cm^{-1}) which were more intense and red-shifted from those of Isomer I (Table 5). After standing overnight, the pH of the solution increased to 4.6 and the absorption spectrum changed: λ_{max} (ε), 582 nm (136); 424 nm (91 $\underline{M}^{-1}$ cm^{-1}). This final spectrum was immune to further increases in pH, but reducing the pH to 1.8 and gentle heating restored the spectrum of pure Isomer I. By heating the reaction solution at 60°, the final spectrum was obtained in one hour. This behavior closely matched that of CrEDTA (27) and strongly indicates that Isomer I also possessed a labile coordination position.

However, anation of Isomer I did not occur even after one hour at 60° C when the solution was adjusted to pH 7 (producing a blue-green solution) before the azide was added.

The substitutional lability of both the reddish-violet and gray forms of Complex III were examined by adding a 50-fold excess of N_3^- to 10 mM solutions of each form. For the reddish-violet form, the initial pH of the blank and the N_3^--containing solutions was 4.60 and 4.58, respectively; for the gray form, 8.54 and 8.39, respectively. Although no hysteresis was observed in the interconversion of the two forms of Complex III, care was taken in these experiments to control the pH during the addition of N_3^-. All the solutions were boiled for 40 minutes.

The color of the N_3^--containing solution of the reddish-violet form turned purple after a few minutes at room temperature. After 5 minutes on the hot plate, the color had changed to an intense, grayish-blue; additional heating had no effect. The pH rose to 6.50 and was lowered to 4.62 without any perceptible change in the color of the solution prior to recording the visible spectrum. Maxima were observed at 585 (ε60) and 433 nm (ε44 M^{-1} cm^{-1}). After standing overnight at pH 4.6, these bands red-shifted to 592 (ε67) and 441 nm

(ε49 $\underline{M}^{-1}$ cm^{-1}). No further changes in the visible spectrum occurred. Interestingly enough, the color of the blank was not constant during the heating period, becoming somewhat redder and less intense. The pH dropped to 2.77 and was raised to 4.30 before running the visible spectrum. All bands blue-shifted: 554 → 537 (ε44), 390 → 378 (ε33 $\underline{M}^{-1}$ cm^{-1}) and 309(sh) → 305(sh) nm (ε constant); the asymmetry of the principal high energy band increased. The pH decrease and these spectral changes are consistent with partial conversion to Isomer II which apparently did not occur in the N_3^--containing solution. Thus, a better blank for comparison with the azide induced spectral shifts was the blank solution before heating (pH 4.24): λ_{max} (ε), 554 (ε52) and 390 (ε41 $\underline{M}^{-1}$ cm^{-1}).

The color of the N_3^--containing solution of the gray form became slightly greener within minutes at room temperature; heating had no effect. The pH rose slightly to 8.55. Maxima were observed at 572 (ε38) and 406 nm (ε50 $\underline{M}^{-1}$ cm^{-1}) at pH 8.40. The spectrum was unchanged after standing for 2 days at room temperature and pH 8.3. Although the positions and extinction coefficients of the maxima were essentially unaltered from those of the gray complex before heating (Table 5), the band shapes had been modified. The high energy azide band became more symmetrical and the width of the low energy band decreased. The greenish tint to the color was due to the increased transmission of light in the 500 nm region by the N_3^--containing solution. Heating had a much larger effect on the color and spectrum of the blank solution. Its color changed to grayish-purple, the visible bands shifting to: λ_{max} (ε) at pH 8.34, 558 (31), 404 (39) and 308(sh) nm (~9 $\underline{M}^{-1}$ cm^{-1}) (*cf.* Table 5). (The pH rose slightly to 8.88.) These changes in the blank are again ascribed to formation of Isomer II. However, the azide result is interesting. Excess azide seems to inhibit the conversion of the gray form of Complex III to Isomer II.

The blue-green form of CrEEDTA was not anated by azide. Unlike Isomer II, the peach isomer of CrPMDTA did react with azide, albeit slowly. The usual conditions were used and the solution heated for 1 1/2 hours. The pH rose from 6.46 to 8.59 as the color changed from peach to brownish-orange. A blank solution set at pH 8.6 and boiled for 1 1/2 hours did not change color. The color of the azide-containing solution darkened slowly on standing for over a week at room temperature and pH 6.6, whereas the blank was unchanged. The spectral data are summarized in Table 6.

Table 6

CrPMDTA + 50-Fold Excess N_3^-

Reaction Time Sequence	Color	pH[a]	λ_{max} (nm)
Before addition of N_3^-	Peach	6.40	370 } split peak 410 } 514
After boiling 1.5 hrs.	Brownish-Orange	6.39	415 (asym. on blue side) 513 } split peak 553 }
After 21 hrs. at room temperature	Blackish-Orange	6.44	415 (asym. on blue side) 560 (asym. on blue side)
After 8 days at room temperature[b]	Gray	6.01	421 (nearly symmetrical) 567 (symmetry increased)

[a] pH of solution during recording of visible spectrum.

[b] Color had been constant for several days.

ION-EXCHANGE BEHAVIOR

Attempts to determine the charges of Isomers I and II from their behavior on ion-exchange resins were only moderately successful. Isomer I behaved as a cation when loaded onto AG 50W X-8 cation exchange resin from a 0.1 M $HClO_4$ solution, but it could be subsequently eluted by washing with dilute (0.1 M) $NaClO_4$. It seems likely that the cationic form existing at pH 1 represents the tetradentate form in which there are two uncoordinated carboxylate groups because CrEDTA exhibits such behavior at low pH (23). Isomer II showed no affinity for either an AG 50W X-8 cation exchange resin or an AG 1 X-8 anion exchange column at pH 4 in 0.1 M $NaClO_4$. The monoanionic CrEDTA complex behaved similarly. The gray form of Complex III behaved as a highly charged anion on an AG 1 X-8 column in the Cl^- form. The band did not move discernably even when washed with 5 M $NaClO_4$. It was finally removed by washing with 1 M HCl.

A solution of Isomer II at neutral pH was loaded onto a Selectacel DEAE anion column in the ClO_4^- form. No movement was discernable after washing for an hour with 0.1 N $HClO_4$

The behavior of the various Cr(III) complexes on Selectacel was investigated. It was found that CrEDTA at pH 5.4 (violet, monoanionic), CrEEDTA at pH 6.95

(blue-green, monoanionic) and Isomer I at pH 7 (blue-green, anionic) banded on loading, were not removed with distilled water and eluted readily with 0.01 N $NaClO_4$ (although the bands broadened considerably). The elution rate of these complexes with 0.01 N $NaClO_4$ matched that of Isomer I at pH 2 (violet, neutral) with 0.01 N $HClO_4$.

Isomer II (pH 7, monoanionic), the gray form of Complex III (pH 8.5, polyanionic) and the peach form of CrPMDTA (pH 6, monoanionic) exhibited considerable affinity for the Selectacel resin. None of these complexes could be moved with 0.01 N $NaClO_4$. Rinsing with 0.1 M $NaClO_4$ broadened these bands somewhat, but did not remove them from the column. Rapid elution and considerable sharpening of these bands resulted on washing with 1 M $NaClO_4$. Isomer II and peach CrPMDTA moved at approximately the same rate with 1 M $NaClO_4$; gray Complex III, somewhat slower. The disparity in the behavior of these two groups of Cr(III) complexes on Selectacel is especially notable because it is independent of complex charge.

REACTIONS WITH HEAVY METAL CATIONS AND METHYL MERCURY CATION

Isomer II reacted with Hg^{+2}, Ag^{+} and Pb^{+2} to produce precipitates. When precipitation was incomplete, the color of the supernatant diminished in intensity, but no change in its hue was observed. Complete precipitation (as judged from the absence of color in the supernatant) occurred when an equimolar quantity of Hg^{+2} had been added. Precipitation was incomplete when less Hg^{+2} was used. The Pb^{+2} solid was soluble in acid. The Hg^{+2} and Ag^{+} precipitates were insoluble in water or acid but dissolved readily in 1 $\underline{M}$ HCl. The Hg^{+2} precipitate was also soluble in excess EDTA and the spectrum of the resulting pink solution matched that of Isomer II. Analysis of the pink Hg^{+2} solid (Experimental Section) yielded a mercury to chromium ratio of one to one. The precipitate formed with Ag^{+} was quite photosensitive and turned dark red from its initial pink color unless protected from the light.

Both the gray and violet forms of Complex III behaved similarly to Isomer II. Complete precipitation was observed when an equimolar quantity of Hg^{+2} was added. The lavender precipitate was insoluble in acid.

Isomer I and the free TEDTA also formed precipitates with Hg^{+2} and Ag^{+}, but complete precipitation required much higher concentrations of the heavy metal cation. The Ag^{+}-Isomer I solid was also light sensitive. The Cr(III)-EEDTA complex in which an oxygen atom replaces the sulfur atom of CrTEDTA exhibited no apparent reaction with Hg^{+2}.

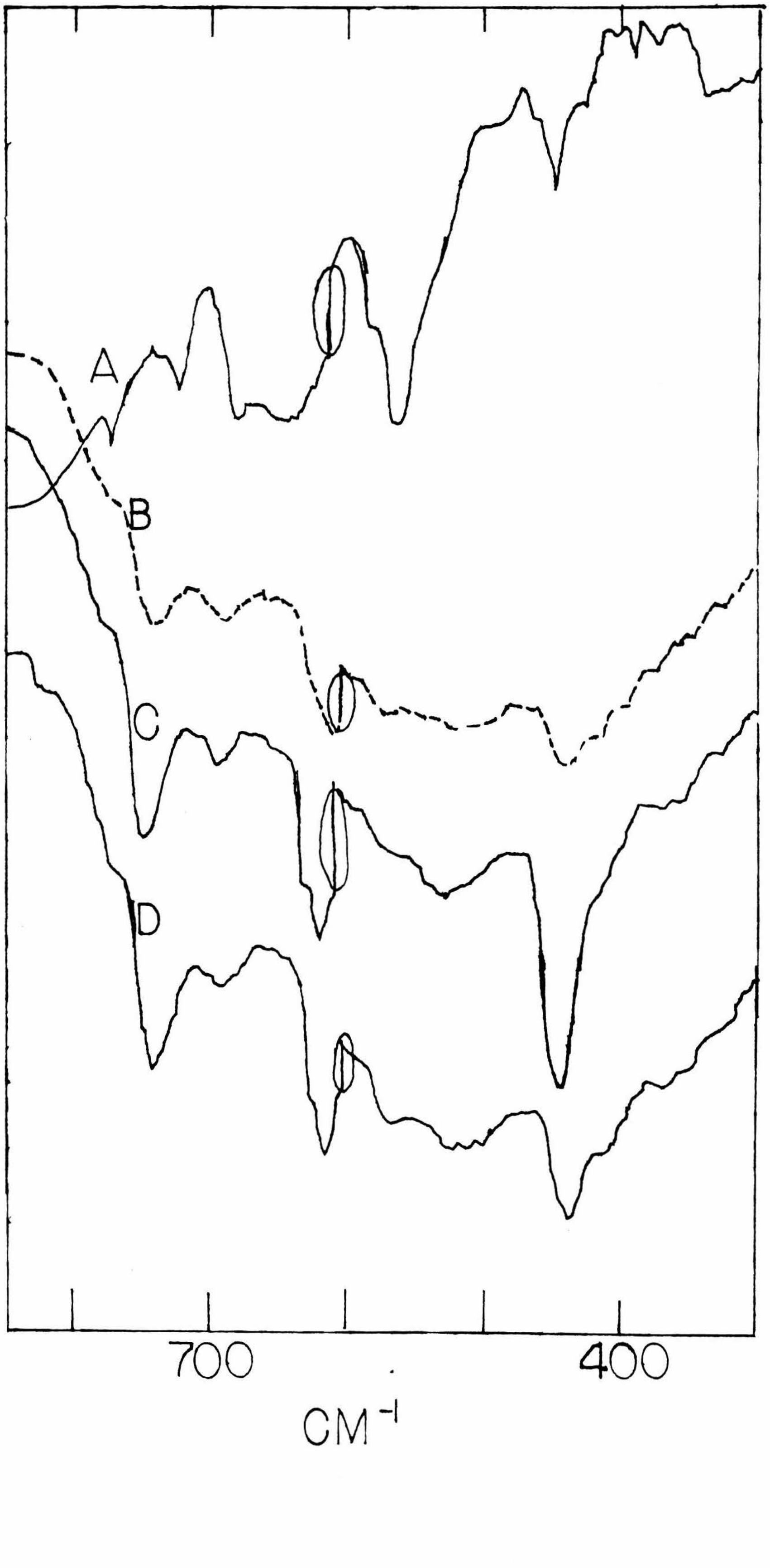
The behavior of Isomers I and II with CH_3Hg^+ paralleled their behavior with Hg^{+2} and Ag^+. A pink precipitate was obtained at pH <4 on addition of excess CH_3HgOH to a solution of Isomer II, but no change in the hue of the supernatant occurred. As the pH of the solution was decreased below 4, smaller quantities of CH_3Hg^+ were needed to precipitate Isomer II. Complete removal of Isomer II from solution was observed at pH 1.6. Dissolution of the pink solid was effected by raising the pH (pK_b of CH_3HgOH = 9.4 (29)) as the complex dissociated. A solution of Isomer I became only slightly turbid after the addition of a 60-fold excess of CH_3Hg^+ at pH 1.6. When the solid had settled, the color of the supernatant was unchanged from that of a pure solution of Isomer I.

IR EVIDENCE

The IR spectra of TEDTA and the Hg^{+2} precipitates of Isomers I, II and Complex III were recorded. Little information was obtained from the carbonyl and N-H stretching regions as the bands were broad and poorly resolved. The most distinctive region was from 850 to 300 cm^{-1} and this portion of each spectrum is reproduced in Figure 11. Notable are the relative intensities of

FIGURE 11

The 850 to 300 cm^{-1} Region of the IR Spectrum (KBr): Curve A, TEDTA; Curve B, Hg^{+2} precipitate of Isomer I; Curve C, Hg^{+2} precipitate of Isomer II; Curve D, Hg^{+2} precipitate of Complex III. Circled part of each spectrum indicates a discontinuity caused by a grating change.


A
B
C
D
700
400
CM⁻¹

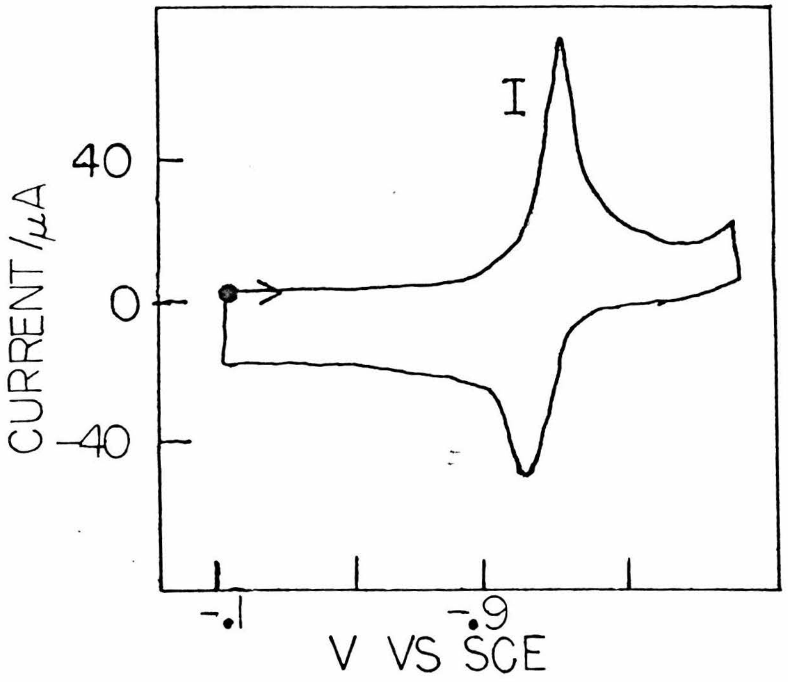
the absorptions at 750 and 700 cm^{-1} (743 and 690 cm^{-1} in Complex III) for Isomer II and Complex III compared with Isomer I, in particular, the intensity of the 750 band is enhanced in the spectra of the former complexes; the presence of a moderately strong band at 620 cm^{-1} in the spectra of Isomer II and Complex III and the absence of this band in the spectrum of Isomer I; and the presence of a weak absorption at 830 cm^{-1} only in the spectrum of Complex III.

ELECTROCHEMISTRY

Isomers I and II were both adsorbed on mercury electrodes but they exhibited marked differences in their electrochemical reductions. Figure 12 shows cyclic voltammograms for both isomers. Isomer II was adsorbed so intensely that the peak potentials for the reduction of the initially adsorbed and the unadsorbed molecules were separated by 110 mV. The much weaker adsorption of Isomer I produced only a single reduction peak with a peak current that increasingly exceeded the diffusion controlled value as the scan rate was increased (30). The cyclic voltammograms of Complex III were very similar to those for Isomer II at the same pH. The cyclic voltammetry of the CrEEDTA complex under the same conditions produced a single reversible wave with no evidence of significant adsorption.

FIGURE 12

Cyclic voltammetry of 1 mM solutions of Isomers I and II at pH 4, scan rate: 10 v/s.


I
40
0
-40
CURRENT /μA
-.1
-.9
V VS SCE

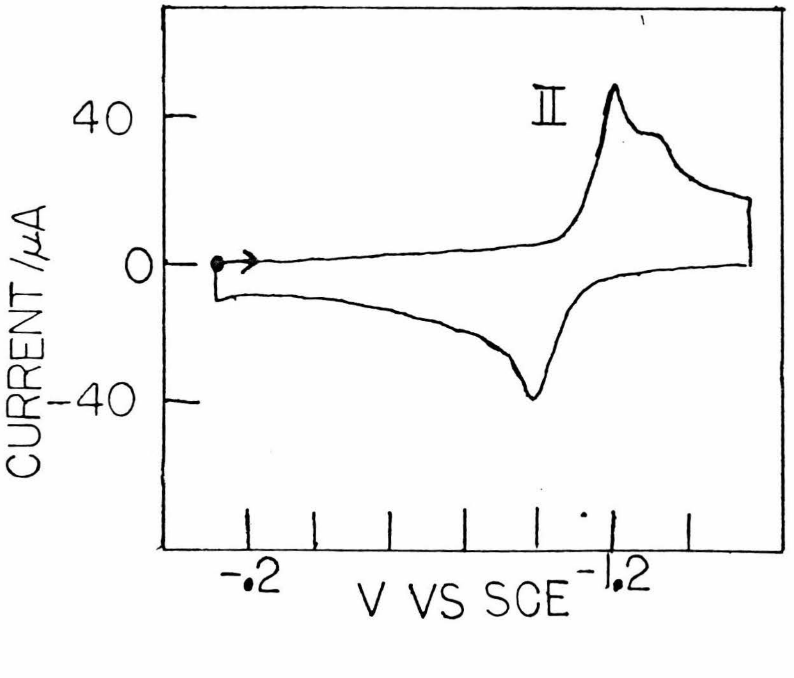

II
40
0
-40
CURRENT /μA
-.2
-1.2
V VS SCE

Table 7 lists representative data on the adsorption of both isomers of CrTEDTA and of CrEEDTA as determined chronocoulometrically (31). As inferred from the cyclic voltammetry, CrEEDTA is not adsorbed. Isomer II is strongly adsorbed and the adsorption of Isomer I is moderate. The adsorption of Isomer II increased as the electrode potential was made more positive. The sign of the potential dependence of the adsorption of Isomer I could not be established unambiguously but the magnitude of the potential dependence was certainly much less than for Isomer II.

Table 7

Adsorption of Cr(III)-EEDTA and Cr(III)-TEDTA Complexes on Mercury[a]

Complex	$\Gamma \times 10^{10}$ moles cm^{-2}
Cr(III)-EEDTA[b]	0
Isomer I[c]	0.30
Isomer II[d]	2.0

[a] Measured at an electrode potential of -0.4 V *vs*. SCE.

[b] 0.94 m$\underline{M}$ CrEEDTA in 0.5 $\underline{M}$ $NaClO_4$, pH 4.6.

[c] 0.024 m$\underline{M}$ Isomer I in 1 $\underline{M}$ $NaClO_4$, pH 4.30.

[d] 0.027 m$\underline{M}$ Isomer II in 1 $\underline{M}$ $NaClO_4$, pH 4.77.

DISCUSSION

The structures we propose for the two isomeric Cr(III)-TEDTA complex are shown in Figure 13. In Isomer I, we believe TEDTA acts as a pentadentate ligand resembling the behavior of EDTA in the CrEDTA complex (16, 22-25). Only three of the four carboxylate groups are coordinated and a water molecule occupies the sixth coordination position on Cr(III). By contrast, in Isomer II, TEDTA is believed to act as a sexadentate ligand with the thioether sulfur atom coordinated to the metal. The evidence and reasoning upon which these proposed structures are based will be elaborated in what follows.

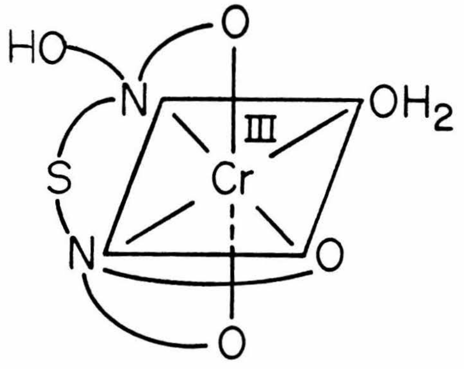
DENTICITY OF THE Cr(III)-TEDTA COMPLEXES

pH BEHAVIOR

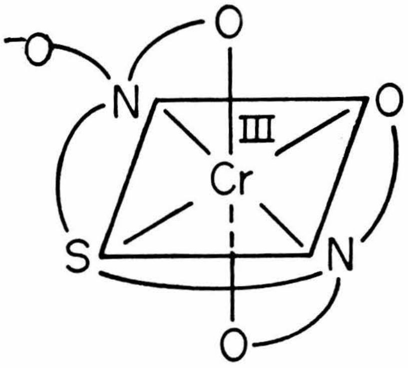
It will be useful to discuss the behavior of the two isomers of Cr(III)-TEDTA by comparison with the extensively studied Cr(III)-EDTA complex. The two inflections in the pH titration curve for the latter complex correspond to the titration of 4 and 5 moles of acid per mole of chromium and they have been identified with the titration of the free protons present along

FIGURE 13

Proposed structures of the two monomeric isomers of Cr(III)-TEDTA.



ISOMER I



ISOMER II

with the single, uncoordinated carboxyl group ($pK_1 = 3.1$) followed by the coordinated water molecule ($pK_2 = 7.5$) (16). The originally violet solution becomes blue as the pH traverses the range between the first and second inflection and the monohydroxy complex is formed (reaction 2):

$$\underset{\text{violet}}{\mathrm{CrHEDTA(OH_2)}} + \mathrm{OH^-} \xrightleftharpoons{pK_1=3.1} \underset{\text{violet}}{\mathrm{CrEDTA(OH_2)^-}} + \mathrm{H_2O} \qquad (1)$$

$$\underset{\text{violet}}{\mathrm{CrEDTA(OH_2)^-}} + \mathrm{OH^-} \xrightleftharpoons{pK_2=7.5} \underset{\text{blue}}{\mathrm{CrEDTA(OH)^{-2}}} + \mathrm{H_2O} \qquad (2)$$

This interpretation of the pH behavior of CrEDTA received recent additional support from kinetic measurements by Thorneley, *et.al.* (23).

The titration curve for Isomer II resembles that for CrEEDTA in that only a single inflection is observed which corresponds to the titration of four moles of protons per mole of chromium. This implies the absence of a titrateable, coordinated water molecule and, therefore, that all six of the coordination positions around the metal are occupied by the ligand after four moles of acid have been neutralized. The inertness of the coordination environment to changes in pH is demonstrated for Isomer II by the absence of significant color changes for pH values from

2 to 11 and for CrEEDTA by the slowness of the color change when the pH is reduced from 8 to 3. The reasons for proposing that the sulfur atom of TEDTA occupies the sixth coordination position rather than the fourth carboxylate group, are set out below.

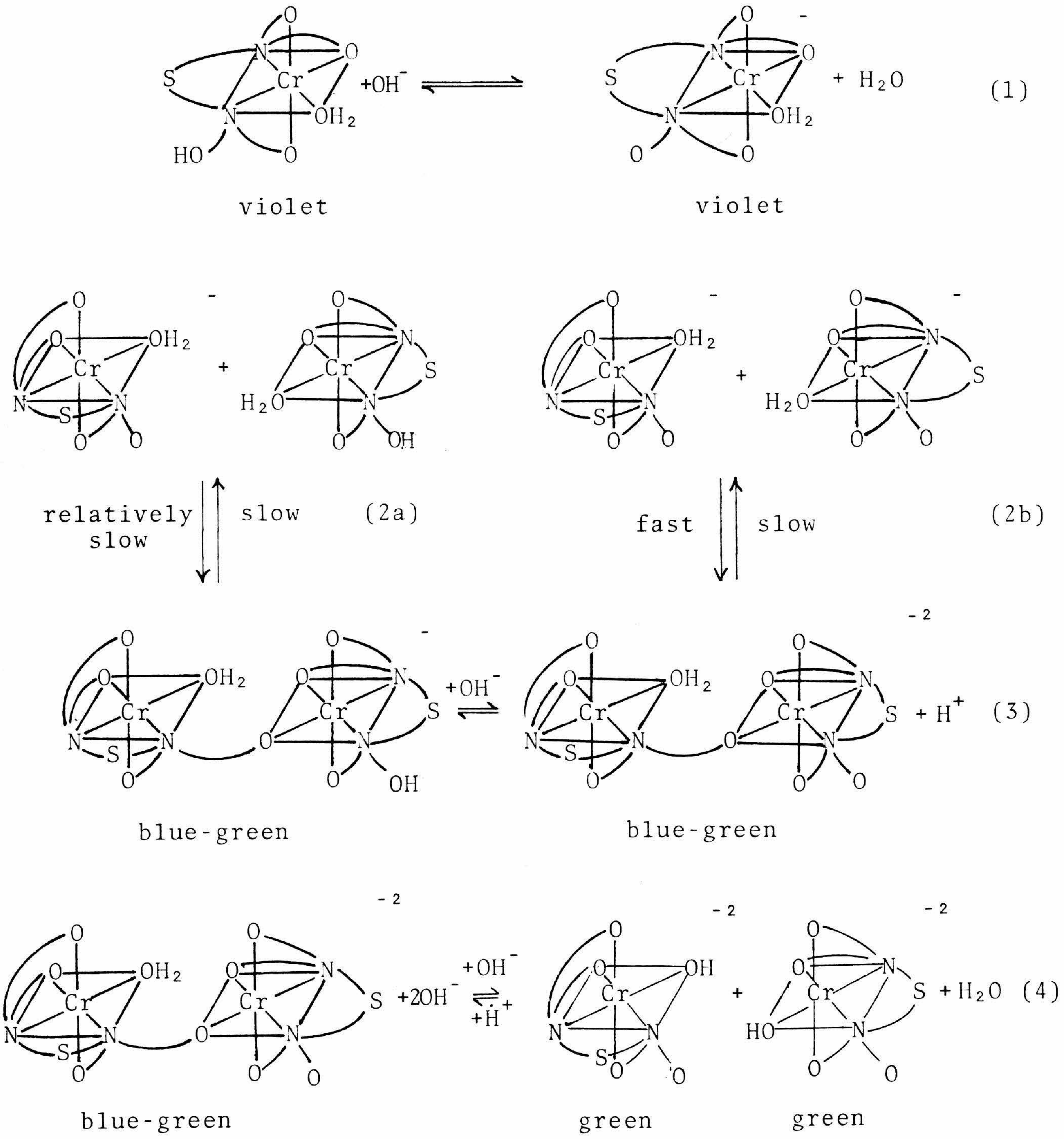
The titration curve for Isomer I (Figure 4a) exhibits two poorly defined inflections marking the consumption of 3 and 4 moles of base per mole of chromium. The drawn out nature of the titration curve and the unusually high pH observed after 3.5 moles of base were added (*ca.* 5.5) (32) suggest a more complicated picture than simply conversion of the violet pentadentate complex to a blue-green hexadentate complex as is observed for CrEEDTA. (Note: The pH after addition of 3.5 moles of base for CrEEDTA was 3.85.)

The ability of the free acetate group in $CrEDTA(OH_2)^-$ to labilize the coordinated water molecule has been well established (26-28). Azide substitution experiments (described above and discussed below) have demonstrated the lability of the coordinated water in the violet form of Isomer I. Therefore, it is proposed that following neutralization of the dangling carboxyl group, the labilized water is displaced by the free acetate arm of another molecule of Isomer I. Then the two possible sources of acid neutralized between 3 and 4 moles of base added are the proton released from the bridging acetate group and the proton on the non-bridging, uncoordinated acetate group. The combined action of these two different acids is believed to be responsible for the absence of a sharp inflection at 4 moles of base added. The addition of a fifth mole of base results in dissociation of the dimer and formation of a green hydroxy complex. The model is summarized in Scheme 2.

Ample support for the proposed model can be found in the literature. Tanaka and co-workers have shown that acetate readily substitutes on $CrEDTA(OH_2)^-$ (26). More recently, Ogino, *et.al.* synthesized several binuclear complexes in which the free acetate arm of $NiEDTA(OH_2)^{-2}$, $CoEDTA(OH_2)^-$ or $CrEDTA(OH_2)^-$ was bound to $[Co(NH_3)_5]^{+3}$ (33). Carboxylate bridged dimers have frequently been proposed to explain the coordination in many metal ion complexes of amino acids (17, 34-36).

Moreover, several additional lines of experimental evidence strongly favor the formulation of the blue-green form of Isomer I as an acetate bridged dimer. The pH hysteresis experiment is corroborative. If none of the dimer had dissociated when the pH was reduced from 8 to 4, 50% less acid would have been required to effect this pH change than base was used in originally raising the pH from 4 to 8. As 35% less acid was used and the color turned bluish-violet, some dissociation occurred. However, these results are also consistent with hexadentate coordination in the blue-green form. But the cyclic

Scheme 2


+OH⁻
+ H2O
(1)
violet
violet
relatively slow
slow
(2a)
fast
slow
(2b)
+OH⁻
+ H⁺
(3)
blue-green
blue-green
+2OH⁻
+OH⁻
+H⁺
+ H2O
(4)
blue-green
green
green

voltammetric behavior cannot be satisfactorily explained in terms of this latter proposal. At pH 7-9 where the solution is blue-green, three cathodic waves were observed for Isomer I -- the first representing reduction of the violet form followed by two, one-electron waves of equal height at more negative potentials. By contrast, the blue-green form of Cr(III)-EEDTA exhibited only a single reversible, one-electron wave from pH 5.5 to 9, which gradually disappeared at higher pH.

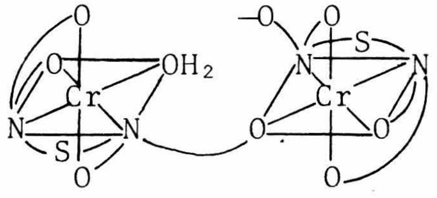
The two more cathodic peaks for Isomer I are assigned to the successive reduction of the two nonequivalent metal centers in the dimer. Assignment of these two waves to reduction of the hexadentate and hydroxy complexes of Isomer I is incompatible with the fact that their peak currents are always equal and with the observation that $CrEDTA(OH)^{-2}$ and the green form of Cr(III)-EEDTA (presumably a mono- or dihydroxy complex) are not reducible. The green form of Isomer II was also irreducible. Potential step experiments as a function of concentration substantiated the existence of a dimer (K_D = 2410 $\underline{M}^{-1}$) (Table 1, Chapter II). A complete discussion of the electrochemistry follows in Chapter II.

The observed conversion of Complex III from reddish-violet to gray implies a change in the coordination of the metal as a function of pH. The ease of this interconversion indicates that it occurs without making or breaking bonds to Cr(III).

REACTIONS WITH AZIDE ION

Isomer I reacts readily with azide to produce spectral changes resembling those obtained with the pentadentate CrEDTA$(OH_2)^-$ complex. This is consistent with the presence of a labile water molecule in the coordination sphere of Isomer I as shown in Figure 13 and Scheme 2. The lack of apparent reaction between the proposed acetate bridged dimer of Isomer I and azide is attributed to the inefficiency of the anchimeric *cis* effect (37) under these conditions.

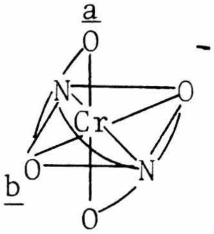
The unbound carboxylate group can labilize the coordinated water *cis* to it by nucleophilic attack. There are two likely geometrical isomers of the dimer; one of these is shown in Scheme 2, the other is shown below:



In the former isomer, *cis* attack is not possible. In the isomer depicted above, although *cis* attack is possible, freedom of rotation of the two halves of the molecule about the bridged group significantly decreases the probability that the two halves of the dimer will be properly oriented for *cis* attack. Considering this orientation problem and the existence of another isomer in which *cis* attack is impossible (Scheme 2), one would predict a much slower and incomplete reaction of azide with the dimer relative to the monomer. Indeed, it seems likely that when the dimer was properly oriented for *cis* attack, formation of a second acetate bridge could also occur.

The failure of Isomer II to react with N_3^- under conditions where Isomer I and $CrEDTA(OH_2)^-$ are readily anated is strong evidence that Isomer II has no open coordination position (Figure 13). Hexadentate coordination is also indicated for the blue-green form of CrEEDTA which also failed to react with N_3^-.

The reaction of the peach isomer of CrPMDTA with azide is superficially inconsistent with the pH behavior of this complex which showed it to be hexadentate. The apparent lability of the coordinated carboxylates may result from the bulkiness of the 8-membered chelate ring in the *trans* isomer which the peach complex is believed to be. As can be seen from the diagram below, the pentamethylene group bridging the two N's crowds acetate groups a and b.



Therefore, these groups might be expected to be somewhat labile. Steric interactions in transition metal complexes have been shown to weaken metal-ligand bonds (38-40). Hamilton and Alexander attributed the considerably higher rate of aquation of *trans*-(RR,SS)-dichloro(1,4,8,11-tetraazaundecane)cobalt(III) relative to the *trans*-(RS) isomer to the greater crowding of the axial chlorides in the (RR,SS)-racemate (40).

The greater lability of the peach CrPMDTA complex compared with Isomer II supports sulfur coordination in Isomer II. PMDTA and TEDTA are virtually the same size (the nitrogen-nitrogen distance in TEDTA is 0.56 Å longer). Therefore, if the two nitrogens and four acetates were coordinated to Cr(III) in Isomer II, it would be expected to undergo anation by azide as does *trans*-CrPMDTA. The failure of Isomer II to react with azide indicates the absence of labilizing steric interactions with the coordinated acetate groups and points to the participation of the sulfur atom rather than a carboxylate group in achieving hexacoordination.

The reddish-violet form of Complex III is readily anated and behaves similarly to Isomer I. Consequently, it is concluded that there is a free acetate group *cis* to a coordinated water in this form of Complex III. However, the results obtained with the gray form are atypical. The absence of a shift in the visible bands indicates that azide substitution did not occur. But, the increased absorbance at the high energy maximum, the increased transmission in the 500 nm region, and the resistance of the gray form to isomerization in the presence of azide imply that azide is interacting with the gray complex in some manner. The nature of this interaction is not understood.

CIS AND *TRANS* ISOMERS OF Cr(III)-TEDTA

In the preceding discussion the existence of *cis* and *trans* (with respect to N's) isomers of Cr(III)-TEDTA has been proposed on the basis of the solution chemistry of the two isomers. Considerable spectral evidence can also be marshalled to support this proposal.

VISIBLE ABSORPTION SPECTRA

Wilkins and Williams have summarized the utility of visible absorption spectroscopy for distinguishing between *cis* and *trans* isomers of transition metal complexes (41). Theory predicts greater splitting of the e and t_2 levels in the *trans* isomer compared to the *cis* isomer. In practice, the *cis* bands are only broadened, whereas, the *trans* bands are actually split and usually, considerably diminished in intensity. For example, the spectrum of *cis*-$Cr(en)_2(OH_2)_2^{+3}$ displays maxima at 366 (ε43.7) and 485 nm (ε67.6 $\underline{M}^{-1}$ cm^{-1}), while for the *trans* isomer, splitting of the low energy band is observed: 361 (ε39.2), 442 (ε39.3) and 508 nm (ε22.5 $\underline{M}^{-1}$ cm^{-1}) (20).

The CrEDTA(OH_2) complex, in which the two nitrogens are known to have the *cis* configuration from crystal structure measurements (22), exhibits a spectrum with two, relatively symmetrical absorptions at 395 and 545 nm. Similar spectra are observed for all forms of Isomer I, both the violet and blue-green forms of CrEEDTA and the violet form of CrPMDTA (Table 5). It therefore seems likely that the nitrogen atoms are *cis* in each of these complexes. The bands in the spectrum of Isomer II and the peach form of CrPMDTA are diminished in intensity, the low energy band is broadened and the high energy band is split. These spectral features are consistent with the nitrogen atoms in these two complexes being *trans* to each other.

Busch and coworkers (42) and Bosnich and coworkers (43) have shown that the stabilities of geometrical isomers are affected greatly by the chelate ring size. In particular, they found that the stability of the *trans* isomer increased as the chelate ring size increased. Jørgensen observed that the lower the ring stability, the lower *Dq* (44). The trends in the spectral data in Table 8 for various hexadentate Cr(III) chelate complexes are consistent with these expectations. As the size of the nitrogen chelate ring increases in the *cis* isomers, the visible bands red-shift, reflecting the decreasing stability of these isomers. The greater distance between the nitrogen atoms in CrPMDTA and CrTEDTA leads to the formation of the *trans* isomer as evidenced by the blue-shift of the visible bands.

BEHAVIOR ON SELECTACEL ANION EXCHANGE RESIN

The remarkable difference between the mobility of Isomer I and a known *cis* complex, $CrEDTA(OH_2)^-$ compared with Isomer II and a probable *trans* complex, peach $CrPMDTA^-$, on Selectacel anion exchange resin supports the assignment of the *cis* configuration to Isomer I and the *trans* configuration to Isomer II.

Table 8

Trends in the Stabilities of Hexadentate Cr(III) Chelate Complexes as a Function of the Nitrogen Chelate Ring Size

Complex	λ_{max} (nm)	Color	Size of the N-N Chelate Ring No. of Members	 Distance Between the N's[a] (Å)	Ref.
cis-CrTRDTA[b]	509,385	Red	6	6.04	45
cis-CrTDTA[c]	556,397	Violet	7	7.58	21
cis-CrEEDTA	585,415	Blue-Green	8	8.90	this work
trans-CrPMDTA	517,420,370	Peach	8	9.12	this work
trans-CrTEDTA	512,415,365	Burnt Pink	8	9.68	this work

[a] Bond distances obtained from the 51st ed. of the Handbook of Chemistry and Physics.

[b] TRDTA is trimethylenedinitrilotetraacetic acid.

[c] TDTA is tetramethylenedinitrilotetraacetic acid.

SULFUR COORDINATION TO Cr(III)

In his review, Jørgensen states that thioethers, which are part of multidentate ligands containing amino groups, are much more attractive to central metal ions which normally display no affinity for R_2S (46). Models show that when the nitrogens are in the *trans* configuration in CrTEDTA, the sulfur is forced into proximity to the Cr(III), thus facilitating its binding. A few examples of thioether sulfur coordination to Cr(III) have been reported (47,48). Additional evidence for sulfur coordination in Isomer II is discussed below.

UV ABSORPTION SPECTRA

The UV absorption spectrum of Isomer II contains a shoulder at 240 nm (ε1050) which is not present in the spectrum of Isomer I or the Cr(III) complexes of EDTA and EEDTA. The intensity of the band suggests that it arises from a charge transfer transition. Sulfur-to-chromium charge transfer would be consistent with the structure proposed for Isomer II (Figure 13). The higher energy of this band compared to those for Cr(III) thiolate complexes, which are generally observed at 265-275 nm (49), is consistent with the lesser reducing power of thioethers compared with thiols. The absence of such a band in the UV spectrum of Isomer I supports the absence of a sulfur-chromium bond in this isomer (Figure 13).

REACTIONS WITH HEAVY METAL CATIONS AND METHYL MERCURY CATION

There is little doubt that the reaction between Isomers I and II and Hg^{+2}, Ag^{+} or CH_3Hg^{+} involves the binding of the cation to the sulfur moiety. Monodentate binding of Hg^{+2}, Ag^{+} and CH_3Hg^{+} to the thioether sulfur atoms in methionine (50,36,51) and S-methylcysteine (51,34) has been established at low pH. The fact that higher concentrations of these cations are required for reaction with Isomer I than with Isomer II is added evidence of the different coordination chemistry exhibited by the thioether sulfur in the two isomers. This difference in behavior may reflect an enhancement of the nucleophilicity of the coordinated sulfur due to the thioether π-accepting electron density (52,53) from Cr(III), thus increasing the attractiveness of the sulfur atom to Hg^{+2}, Ag^{+} and CH_3Hg^{+} (54).

IR EVIDENCE

The similarity of the IR spectra of Isomer II and Complex III in the fingerprint region suggests that they are structurally similar and unlike Isomer I. The band at 620 cm^{-1}, which is present only in the spectra of Isomer II and Complex III, may originate from a Hg-S-Cr stretch as it is absent in the spectrum of the Ag^{+}-Isomer II adduct. The weak band at 830 cm^{-1}, which is present only in the spectrum of Complex III, probably results from a Cr-O stretch of the Cr-O-Cr system (55) and suggests that Complex III is an oxo-bridged dimer. McAuliffe and Perry have reported a weak absorption at 830 cm^{-1} in the IR spectrum of μ-oxodi[bis(methionato)aquochromium(III)], $[H_2O(Met)_2CrOCr(Met)_2(H_2O)]$, which they assigned to a Cr-O stretch within the Cr-O-Cr unit (56).

ELECTROCHEMISTRY

The marked difference in the extent of the reactions of Isomers I and II with CH_3Hg^+ and Hg^{+2} is matched by the difference in their adsorptive attachment to the surface of mercury electrodes (Table 7). The intensity and potential dependence of the adsorption of Isomer I are comparable to those of many organic adsorbates (57). However, the more intense adsorption of Isomer II signals a stronger and more specific interaction with the mercury surface. The binding site is almost certainly the sulfur atom because of the non-adsorption of the very similar CrEEDTA complex. The unusually strong adsorption is believed to be the result of the back donation involved in the formation of the chromium-sulfur bond in Isomer II which "softens" the sulfur atom thus enhancing its adsorbability (58).

To summarize the chemical data on the Cr(III)-TEDTA complexes:

i) The pH behavior and azide experiments indicate that Isomer I is pentadentate with a coordinated water molecule and that Isomer II is hexadentate.

ii) The splitting of the visible bands, their decreased intensity for Isomer II relative to Isomer I and the discrimination on Selectacel between the mobilities of Isomer I and a known *cis* complex, $CrEDTA(OH_2)^-$ compared to Isomer II and a probable *trans* complex, peach $CrPMDTA^-$, suggest that the nitrogens are *cis* in Isomer I and *trans* in Isomer II.

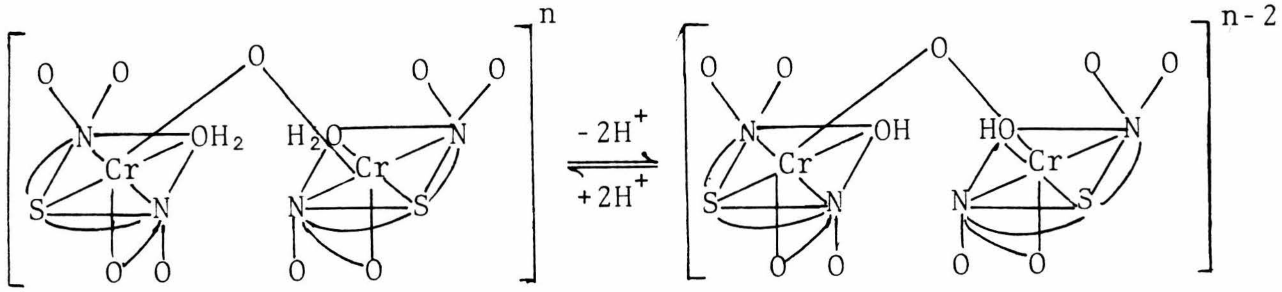
iii) The S → Cr(III) CT band at 240 nm, the inertness of Isomer II relative to hexadentate, *trans*-$CrPMDTA^-$ to reaction with azide, its apparently strong binding to Hg^{+2} and CH_3Hg^+ and strong adsorption on positively charged mercury electrodes are all consistent with the presence of a chromium-sulfur bond in Isomer II.

On the basis of these data, the structures for Isomers I and II in Figure 13 are proposed. That is, Isomer I is *cis*-[thiobis(ethylenenitrilo)tetraacetato]aquochromium(III), *cis*-CrTEDTA(OH_2) and Isomer II is *trans*-[thiobis(ethylenenitrilo)tetraacetato-*S*]chromate(III), *trans*-$CrTEDTA^-$.

With regard to the dimers,

iv) The drawn out titration curve for *cis*-CrTEDTA(OH_2), the sluggishness of conversion of the blue-green form to *cis*-CrTEDTA(OH_2), the lack of reaction of the blue-green form with azide, the electrochemical nonequivalence of the two metal centers, the results of the potential step experiment which were consistent with a dimerization constant of $2410 \pm 140\ \underline{M}^{-1}$ (*cf*. p. 76) are all consistent with the formulation of the blue-green form of *cis*-CrTEDTA(OH_2) as the acetate-bridged dimer, *cis*-[thiobis(ethylenenitrilo)tetraacetato]aquochromium(III)-μ-N-acetato-*cis*-[thiobis(ethylenenitrilo)-tetraacetato]chromate(III), TEDTA(OH_2)Cr(NCH_2COO)CrTEDTA (Scheme 2).

v) For Complex III, the high negative charge of the gray form and the IR band at 830 cm^{-1} suggest that the complex is an oxo-bridged dimer; the asymmetrical visible bands and high affinity for Selectacel suggest that the nitrogens are *trans*; the apparently strong binding with Hg^{+2} and strong adsorption on mercury electrodes as shown by cyclic voltammetry are indicative of chromium-sulfur coordination. The azide experiment demonstrates the presence of a coordinated, labile water molecule in the reddish-violet form. The ready interconversion of the two forms requires that no bonds to Cr(III) are made or broken. Structures for the two forms of Complex III are shown below:



reddish-violet

μ-oxodi(*trans*-[thiobis(ethylenenitrilo)tetraacetato-*S*]-aquochromate(III)),

[*trans*-CrTEDTA(OH_2)$]_2$O

maximum charge: -4

gray

μ-oxodi(*trans*-[thiobis(ethylenenitrilo)tetraacetato-*S*]-hydroxochromate(III)),

[*trans*-CrTEDTA(OH)$]_2$O

maximum charge: -6

DRIVING FORCE FOR THE ISOMERIZATION OF Cr(III)-TEDTA COMPLEXES

Figure 6 shows the pH dependence of the equilibrium between Isomers I and I. During the conversion of Isomer I to Isomer II, it was found that one mole of acid was released per mole of chromium. It is believed that this results from a significant decrease in the pK_a of the fourth carboxylate group when the configuration of the two nitrogen atoms changes from *cis* to *trans*. Although other factors may be involved, the enhancement of the acidity of the uncoordinated acetate group appears to be the source of the free energy which controls the *cis-trans* isomerization of the nitrogen atoms. As a consequence of the nitrogens being *trans*, the sulfur atom is brought into close proximity with the Cr(III) center thus facilitating its coordination. Coordination of the sulfur moiety is no doubt favored by the replacement of the large, eight-membered ring in the *cis* isomer with two, five-membered rings in Isomer II.

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CHAPTER II

ELECTROCHEMICAL STUDY OF THE ADSORPTION OF THE *CIS* AND *TRANS* ISOMERS OF CHROMIUM(III)-TEDTA ON MERCURY ELECTRODES

INTRODUCTION

In Chapter I, the coordination chemistry of Cr(III) with TEDTA was described and evidence for the formation of both *cis* and *trans* isomers (with respect to the nitrogens) was presented. In the complex having the *trans* configuration, the sulfur atom of the thioether group is forced to lie close enough to the Cr(III) center for a chromium-sulfur bond to be formed. Because of our general interest in ligands which may be used to induce the adsorption of metal cations on electrode surfaces (1-4), the electrochemistry of these two, new complexes of chromium(III) was examined. Striking differences in the cyclic voltammetry and adsorption of the two isomers at mercury electrodes were observed and are described in this chapter.

EXPERIMENTAL

APPARATUS

A small volume (10 ml), two compartment cell was employed which isolated the sodium chloride saturated calomel reference electrode (Sargent-Welch) from the hanging (Brinkmann Instruments, Inc.) or dropping mercury working electrode (dme) and the platinum wire auxiliary electrode. The area of the hanging mercury drop electrode was 0.032 cm^2. The mercury flow rate for the dme was 0.65 mg sec^{-1}. Electrocapillary curves were measured using a digital drop timer previously described (5) in conjunction with a Princeton Applied Research (PAR) Model 174 Polarograph. Cyclic voltammograms were obtained using either a conventional multipurpose electrochemical instrument based on operational amplifiers which was constructed in this laboratory, or a PAR Model 173 Potentiostat/Galvanostat, Model 174 Universal Programmer and Model 179 Digital Coulometer. Voltammograms were recorded on a Tektronix Model 564 CRO and photographed when permanent records were desired. Chronocoulometric determinations of the quantity of adsorbed reactants were performed by means of the computerized data acquisition and analysis system that has been previously described (6).

pH measurements were performed using a Beckman Model 76 Digital pH Meter. All measurements were made at 25±2° C.

MATERIALS

Stock solutions of *cis*-CrTEDTA(OH_2) sodium [*trans*-CrTEDTA] and CrEEDTA were prepared, purified and standardized as described in Chapter I. Spectral measurements were used to verify that the stock solutions were pure. Stock solutions of the chromium(III) complex with EDTA (ethylenedinitrilotetraacetic acid) were prepared by mixing stoichiometric quantities of $Cr(ClO_4)_3$ and the tetraacid in water and heating for 1 hour. Supporting electrolyte solutions were prepared from triply distilled water and consisted of unbuffered 1 M $NaClO_4$ unless otherwise specified. The pH of each solution was adjusted after oxygen was removed by bubbling with prepurified nitrogen.

RESULTS

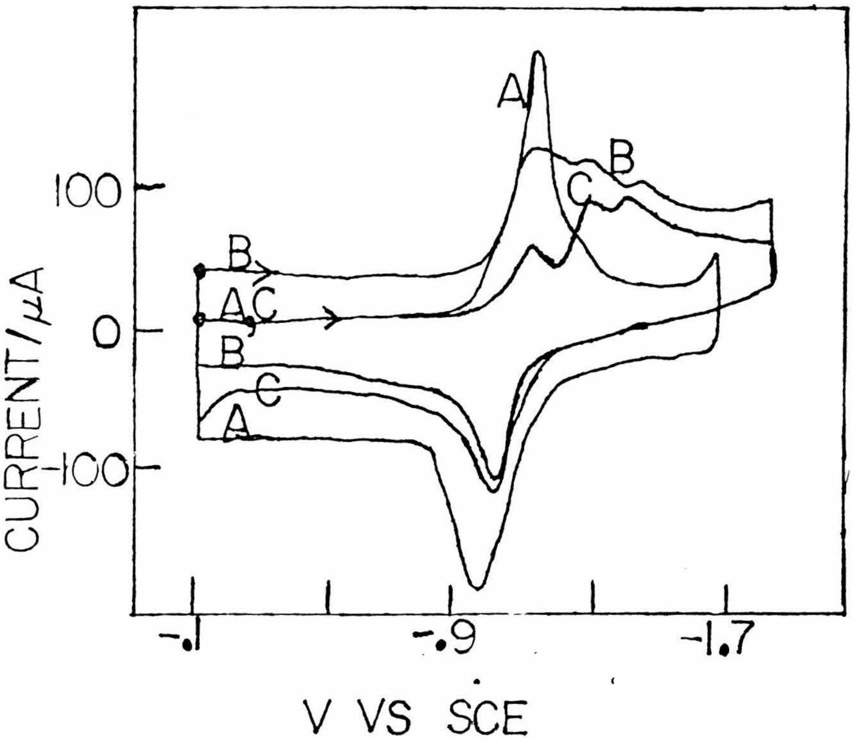
CYCLIC VOLTAMMETRY

Figure 1 shows a series of cyclic voltammograms for *cis*-CrTEDTA(OH_2) at pH 4.0, 5.3 and 7.2. Depending on the pH, as many as three cathodic peaks appeared. As the pH increased, the peak currents of the two more cathodic waves increased at the expense of the first wave. On repetitive scanning at pH 7.2, the waves at -1.26 V and 1.40 V gradually disappeared as the wave at -1.04 V grew. If the electrode was maintained for 30 seconds at -1.60 V before initiating a (positive going) potential scan, the waves at -1.26 V and -1.40 V did not appear in the cathodic half of the cycle. Both CrEDTA(OH_2) and CrEEDTA exhibited a single set of uncomplicated cathodic and anodic voltammetric waves under the conditions where *cis*-CrTEDTA(OH_2) showed multiple cathodic waves.

In order to verify the existence of the proposed acetate bridged dimer (*cf.* Chapter I, pp. 73-76), the following potential step experiment was performed on solutions 0.5, 1.0 and 2.5 m<u>M</u> in *cis*-CrTEDTA(OH_2) at pH 7.3: The potential was stepped from some initial potential to -1.15 V, where only *cis*-CrTEDTA(OH_2) was reduced and to -1.50 V, where both the monomer and dimer were reduced.

FIGURE 1

Cyclic Voltammetry of 1 mM Solutions of Isomer I. Curve A, pH 4.0; Curve B, pH 5.3; Curve C, pH 7.2. Scan Rate: 50 v/s.


A
B
C
B
A
C
B
C
A
100
0
-100
CURRENT/μA
-.1
-.9
-1.7
V VS SCE

The slope of a plot of charge *vs.* $(\text{time})^{\frac{1}{2}}$ for the first step was proportional to the concentration of the monomer whereas, the difference in the slopes for the first and second steps was proportional to the dimer concentration. As the diffusion coefficient of the dimer was expected to be smaller than that of the monomer, both it and the dimerization constant, K_D, were fit to the data. The results of this experiment which are presented in Table 1 strongly support the existence of the dimer.

The peak current for the first reduction wave of *cis*-$CrTEDTA(OH_2)$ is plotted against the square root of the scan rate in Figure 2 along with the calculated behavior for an uncomplicated diffusion limited electron transfer reaction. The increasing deviation between the observed and calculated behavior as the scan rate increases is in the direction expected for initially adsorbed reactants.

Cyclic voltammograms for *trans*-$CrTEDTA^-$ are shown in Figure 3. In contrast with the *cis* isomer, these voltammograms were unaltered as the pH was increased from pH 4 to 10. Two reduction waves were present on the first scan at -1.19 V and -1.30 V. A new reduction wave appeared at -1.04 V on the second cathodic scan and the height of the two original waves diminished. Upon repetitive scanning at a high scan rate (*e.g.* 100 V

Table 1

Evaluation of the Dimerization of *Cis*-CrTEDTA(OH_2) at pH 7.3[a]

Conc. (mM)	Slope at -1.15 V ($\mu C\ cm^{-2}\ s^{-\frac{1}{2}}$)	Slope at -1.50 V ($\mu C\ cm^{-2}\ s^{-\frac{1}{2}}$)	% Monomer	K_D (M-1)
0.5	72.4	156	42.9	2470
1.0	100	273	33.9	2560
2.5	171	586	26.2	2200

Average: 2410±140 M^{-1}

---

[a] The monomer diffusion coefficient was 6 x 10^{-6} $cm^2\ s^{-1}$. The dimer diffusion coefficient obtained from fitting the data was 4.5 x 10^{-6} $cm^2\ s^{-1}$, which is quite reasonable.

FIGURE 2

Scan rate dependence of the peak current of the first reduction wave of *cis*-CrTEDTA(OH_2): 1 m*M*, pH 4. The dashed line represents the behavior of an uncomplicated, diffusion limited electron transfer reaction.

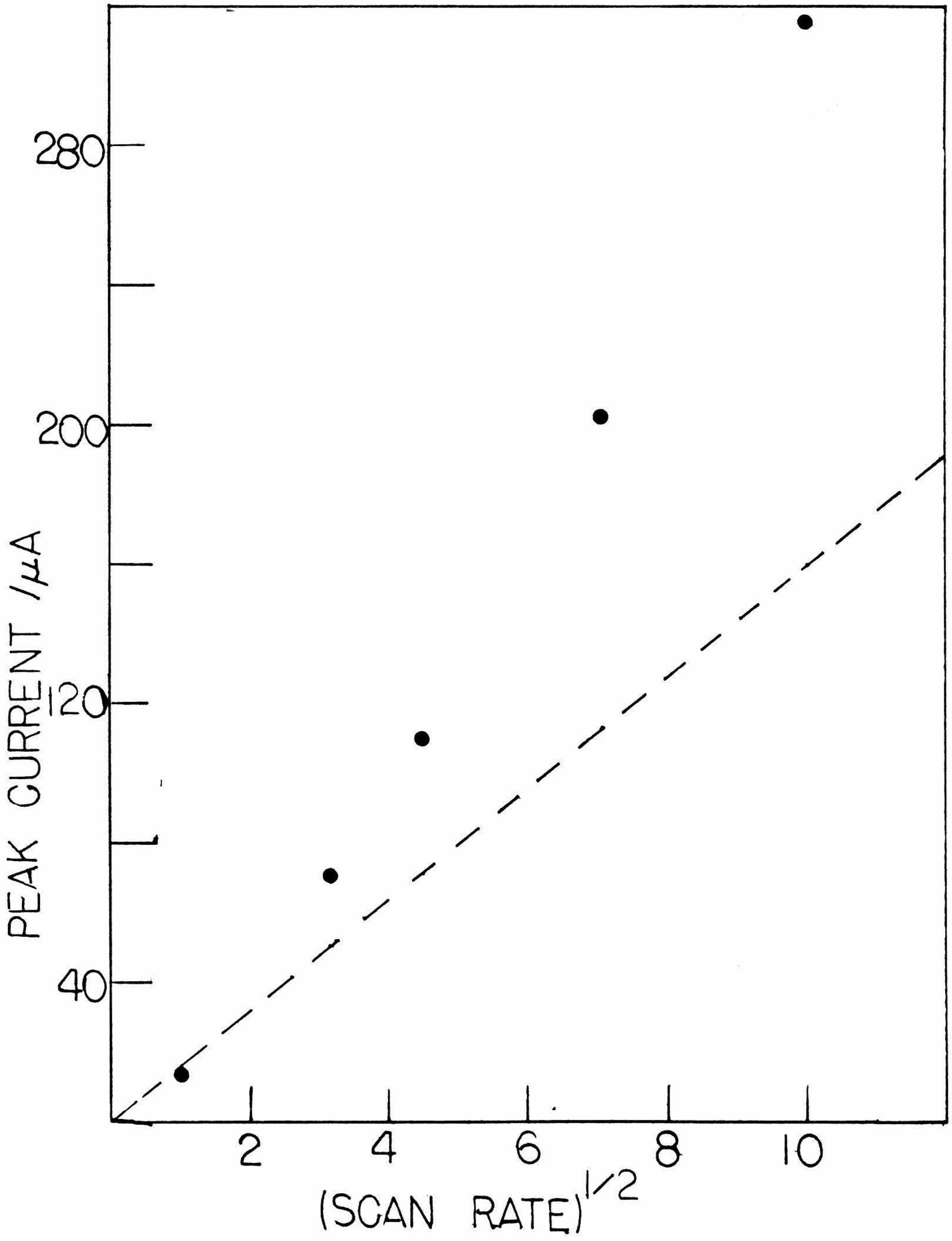
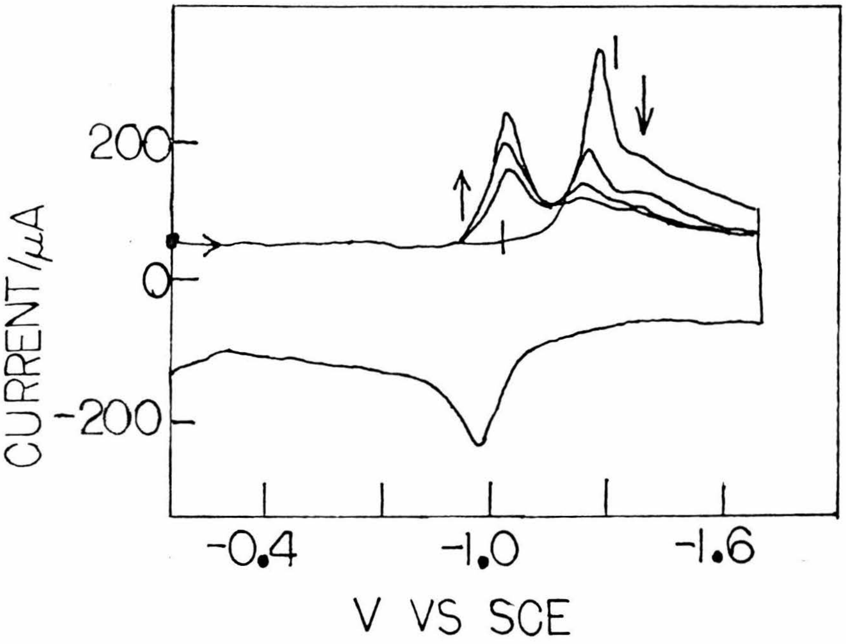

280
200
120
40
PEAK CURRENT /μA
2
4
6
8
10
(SCAN RATE)^1/2

FIGURE 3

Cyclic Voltammetry of 1 mM Solutions of Isomer II at pH 7. Successive scans at 100 v/s. Curve 1 is the first scan.


200
0
-200
CURRENT/μA
-0.4
-1.0
-1.6
V VS SCE

sec^{-1}) a steady-state voltammogram resulted in which the original pair of reduction waves was absent and only the wave at -1.04 V remained. If the electrode was maintained at -1.60 V for 30 seconds before initiating the (positive-going) scan, only the wave at -1.10 V appeared during the cathodic half of the voltammogram.

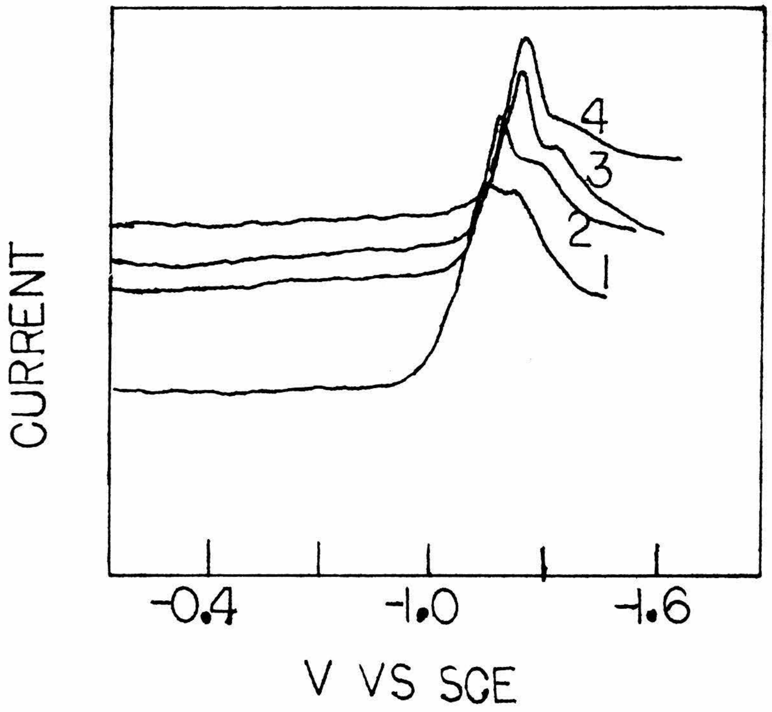
A series of cathodic voltammograms at increasingly higher sweep rates is shown in Figure 4. Note that the reduction wave at -1.19 V grows more rapidly than the wave at -1.30 V as the scan rate is increased. This behavior is consistent with the first wave being assigned to the reduction of reactant which is adsorbed strongly enough to shift its reduction potential from that of the diffusing reactant (7). This interpretation is also supported by the concentration dependence of the voltammograms: Decreasing the concentration of the complex from 1 m*M* to 80 μ*M* produced a proportional decrease in the peak current for the wave at -1.30 V; however, the peak current at -1.19 V decreased by only 20% (adequate time was allowed to assure adsorption equilibrium before the scan was initiated).

ELECTROCAPILLARY CURVES

The prominence of adsorption in the voltammetric behavior of both isomers of Cr(III)-TEDTA led us to

FIGURE 4

Cathodic voltammograms of a 1 mM solution of Isomer II at pH 4 at increasingly faster scan rates: Curve 1, 2 v/s, 5 μA/cm; Curve 2, 10 v/s, 20μA/cm; Curve 3, 50v/s, 50μA/cm; Curve 4, 100v/s, 100μA/cm.


CURRENT
-0.4
-1.0
-1.6
V VS SCE
1
2
3
4

examine the electrocapillary curves for solutions of each complex by measuring the natural drop time of a dme as a function of potential. The resulting electrocapillary curves are shown in Figure 5. The larger change in interfacial tension produced by the *trans* isomer is indicative of its stronger adsorption on mercury as is the relative shift in the position of the electrocapillary maximum (ecm): -0.55 V and -0.65 V for the *cis* and *trans* isomers, respectively.

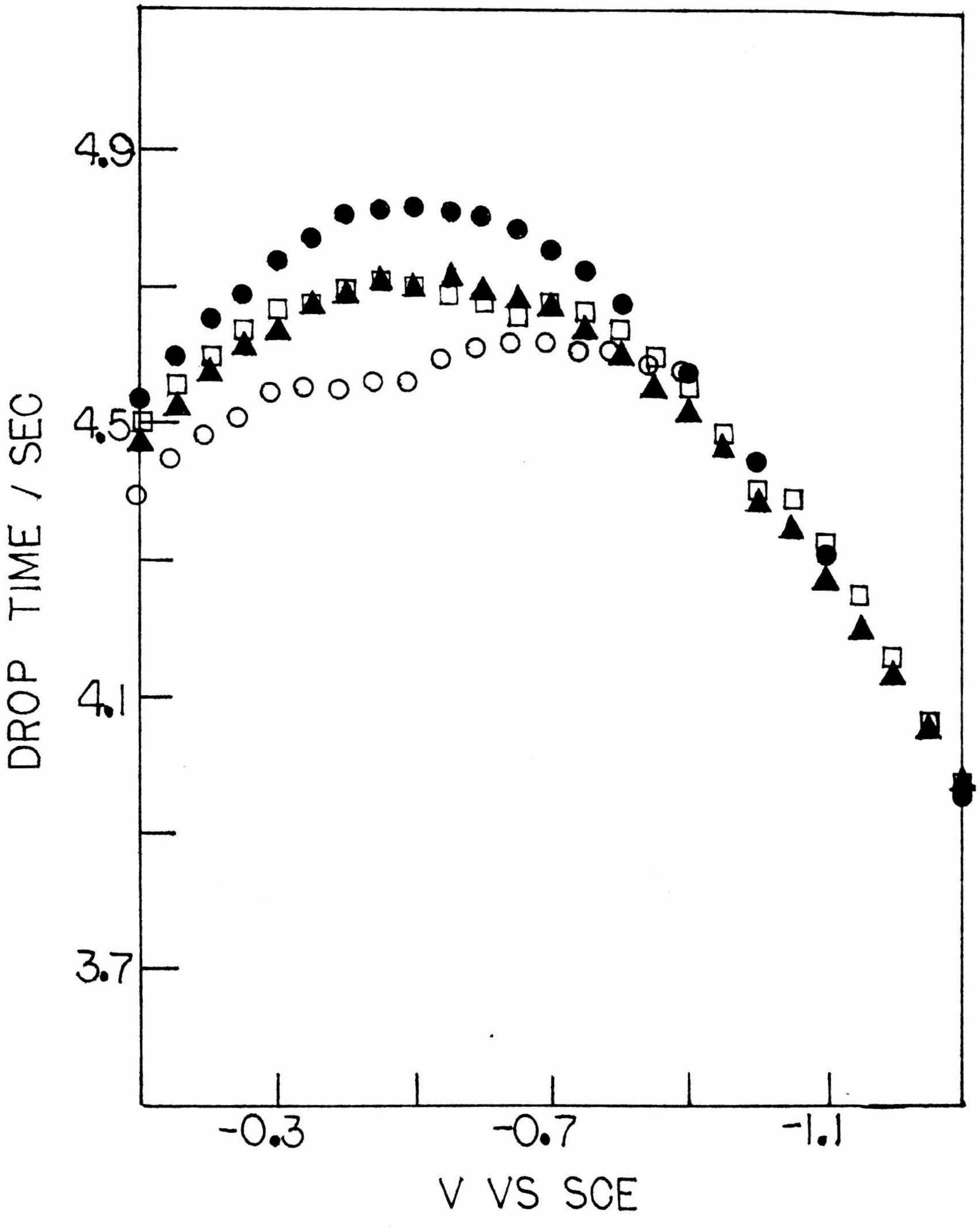
The electrocapillary curve for a 1 m$\underline{M}$ solution of free TEDTA in 0.5 $\underline{M}$ $NaClO_4$ at pH 4.2 was indistinguishable from the curve for 0.5 $\underline{M}$ $NaClO_4$ alone. Thus, the free ligand is adsorbed much less strongly than either of the Cr(III) complexes. The lower adsorbability of the free ligand may reflect greater steric hindrance in exposing the sulfur atom to the electrode surface when the ligand is not wrapped back around the metal to which it is coordinated.

DETAILED STUDY OF THE ADSORPTION OF *CIS*-CrTEDTA(OH_2) AND *TRANS*-$CrTEDTA^-$ ON MERCURY ELECTRODES

Trans-$CrTEDTA^-$. Double potential step chronocoulometry (8) served well as a method for the determination of the quantity of adsorbed *trans*-$CrTEDTA^-$. The ratio of the slopes of the chronocoulometric plots (charge *vs*. the

FIGURE 5

Electrocapillary Curves for Isomers I and II. 1 M $NaClO_4$, (●); 0.93 mM Isomer I, pH 3.90, (□) 0.93 mM Isomer I, pH 7.20, (▲); 0.28 mM Isomer II, pH 3.97, (O).


4.9
4.5
4.1
3.7
DROP TIME / SEC
-0.3
-0.7
-1.1
V VS SCE

square root of a time function) for the reductive and oxidative steps were in good accord with the value expected given the quantity of adsorbed complex, which had been evaluated from the intercepts of these same plots (8). This agreement demonstrated that the chromium(II) complex produced by the reduction of *trans*-CrTEDTA$^-$ was not adsorbed on the electrode at the potential (-1.6 V) at which it was formed.

Figures 6 and 7 display the concentration and potential dependences, respectively, of the adsorption of the *trans* isomer at pH 5. Especially noteworthy are the extremely low concentrations at which the complex is significantly adsorbed and the abrupt changes in coverage that result over a very narrow range of bulk concentration or electrode potential. This feature of the adsorption of *trans*-CrTEDTA$^-$ is better revealed in Figure 8 where the data are plotted using Langmuir coordinates. In each case, the dashed line of unit slope represents a hypothetical system which obeys the Langmuir isotherm. The horizontal distance between the experimental points and the dashed line is a measure of the magnitude of the interactions between the adsorbed molecules. Positive deviations from Langmuir's isotherm signify attractive interactions and negative deviations, repulsive interactions between the adsorbed species. At potentials

FIGURE 6

Concentration Dependence of the Adsorption of *Trans*-$CrTEDTA^-$, pH 5. Initial potential: -.3 V (●); -.5 V (■); -.8 V (▲).

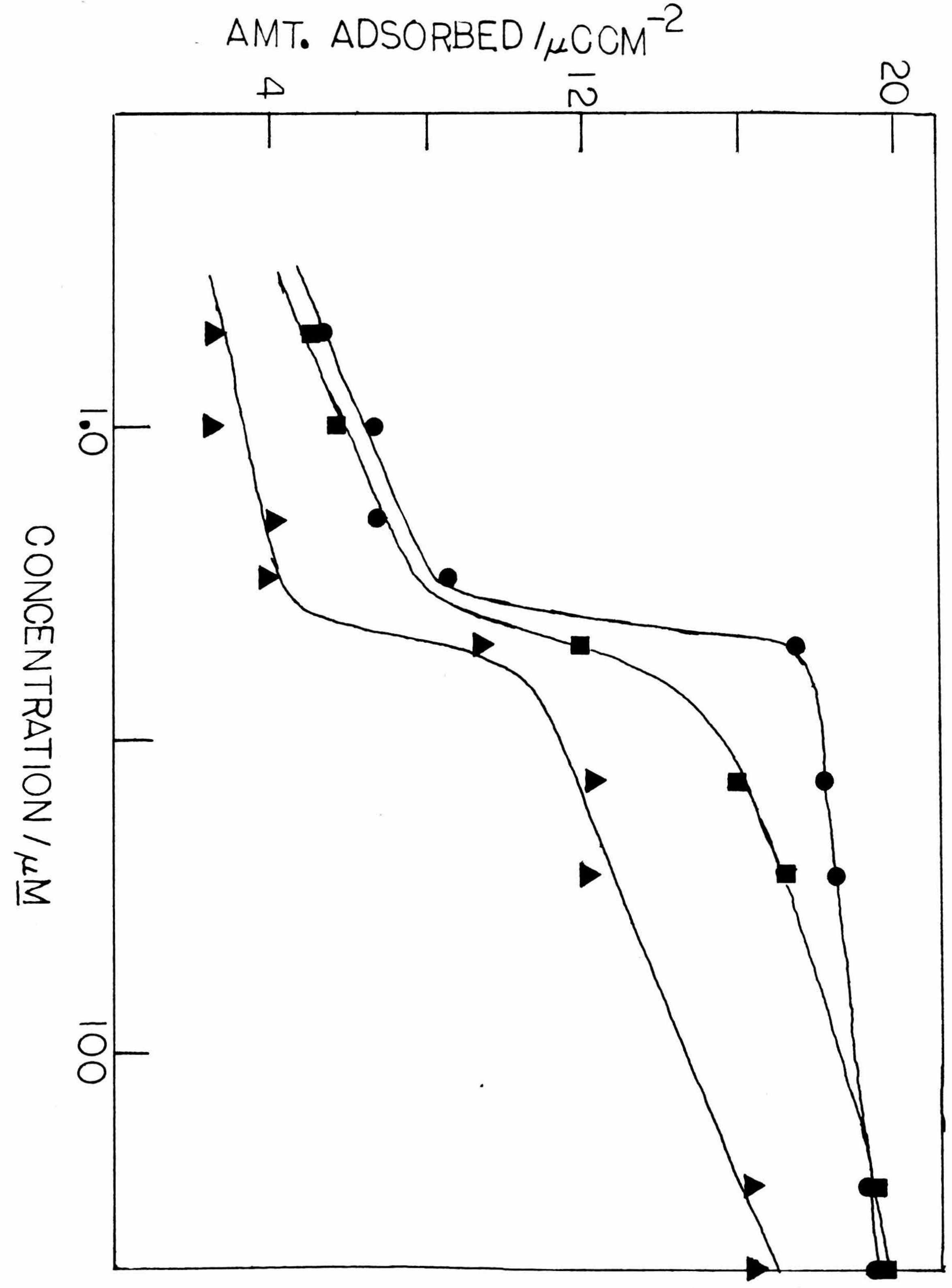

AMT. ADSORBED /μCCM⁻²
4
12
20
CONCENTRATION /μM
1.0
100

FIGURE 7

Potential Dependence of the Adsorption. 0.027 mM *trans*-CrTEDTA$^-$, pH 5 (■). 0.24 mM *cis*-CrTEDTA(OH_2), pH 4 (●).

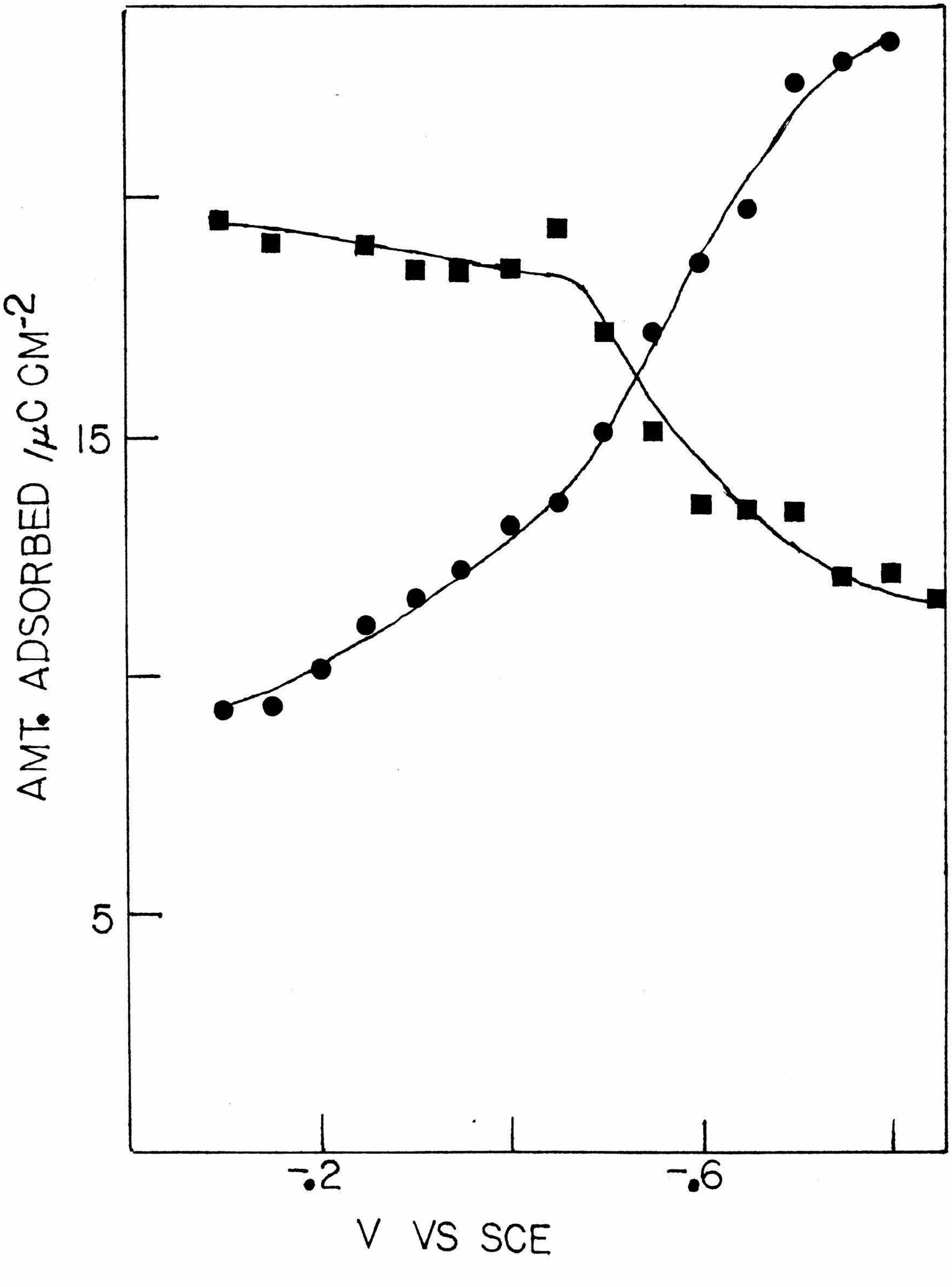
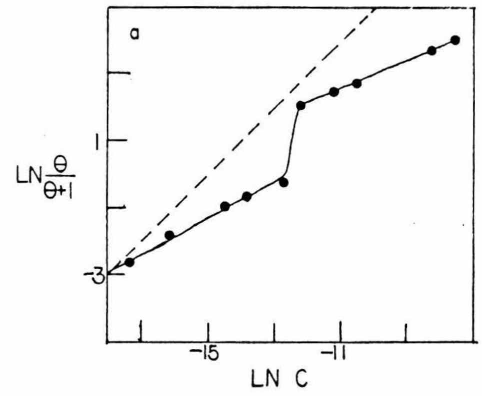
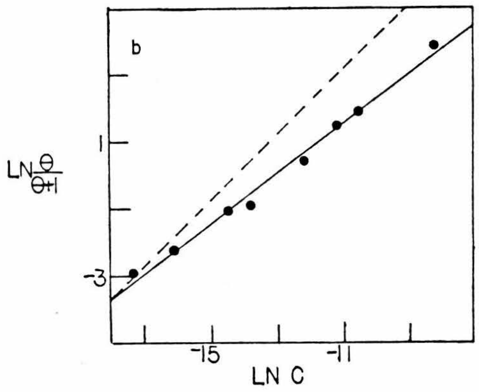
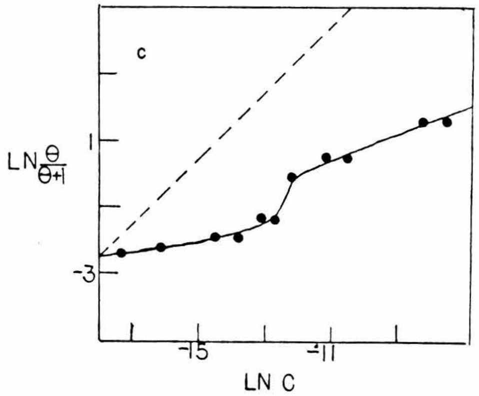

AMT. ADSORBED /µC CM^{-2}
15
5
-.2
-.6
V VS SCE

FIGURE 8

Langmuir Plots for *Trans*-CrTEDTA$^-$ at pH 5. Initial potential: Part a, -.3 V; Part b, -.5 V; Part c, -.8 V. Dashed line represents a hypothetical system which obeys the Langmuir isotherm.


a
1
-3
LN θ/(θ+1)
-15
-11
LN C


b
1
-3
LN θ/(θ+1)
-15
-11
LN C


c
1
-3
LN θ/(θ+1)
-15
-11
LN C

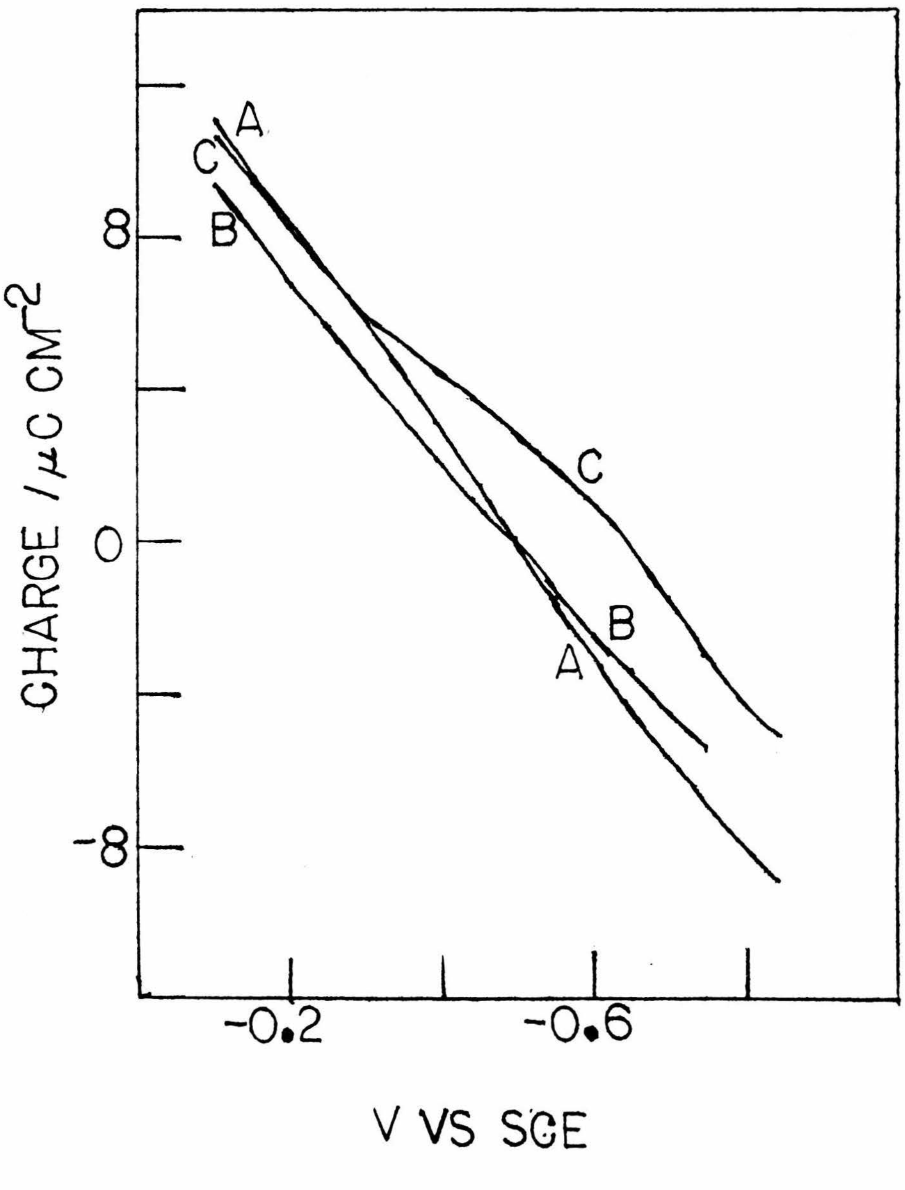
positive of the point of zero charge (pzc in 0.27 m<u>M</u> *trans*-CrTEDTA$^-$ was -0.641 V.) where the electrode bears a net positive charge, the repulsiveness of the intermolecular interactions abruptly decreases over the very narrow range of bulk concentration (3 to 5 μ<u>M</u>) where full coverage is achieved (Figure 8a). At potentials near the pzc, this discontinuity is not evident in the Langmuir plot (Figure 8b). At potentials negative of the pzc, the interactions are so extremely repulsive at low bulk concentrations that the apparent reduction in these forces which accompanies the sudden increase in surface coverage(between 3 and 5 μ<u>M</u>) is reflected in a slight discontinuity in Figure 8c. These adsorption data could not be fit to a single, continuous coverage independent Frumkin isotherm (accounts for interactions between the adsorbed molecules) (9).

Enhancement of the ligand field at the nitrogen atom in $CrNCS^{+2}$ on binding Hg^{+2} has been demonstrated (10) and attributed to increased chromium to ligand π-bonding (11). Similar arguments have been advanced to explain the stronger adsorption of *cis*-$Cr(OH_2)_4(NCS)_2^+$ than of free SCN^- at comparable concentrations on positively charged mercury surfaces (12). We believe that back donation is responsible for the marked preference of *trans*-CrTEDTA$^-$ for positive electrodes shown in Figure 7. Greater adsorption at constant composition at more positive electrode potentials requires that the electrode charge increase at constant potential (13). Consequently the electronic charge densities in the presence and absence of *trans*-CrTEDTA$^-$ were evaluated. The total charge flowing into a dme during the growth of each drop was measured and the faradaic and nonfaradaic components separated according to previously described procedures (14). The results are plotted in Figure 9. The pzc shifted from -0.492 V to -0.641 V in accordance with the greater positive charge on the electrode in the presence of *trans*-CrTEDTA$^-$. Since the adsorption is essentially potential independent at potentials positive of the pzc (*cf.* Figure 7), the charge on the electrode at these potentials is only slightly affected by the presence of the complex.

The chronocoulometric plots of charge *vs.* (time)$^{\frac{1}{2}}$ for *trans*-CrTEDTA$^-$ at concentrations greater than 3 μ<u>M</u> were curved. The curvature was most pronounced at the most positive potentials and decreased as the bulk concentration increased. The initial slope was larger than the diffusion controlled slope and approached it after *ca.* 5 msec. Such behavior has been previously

FIGURE 9

Electrode Charge-Potential Curves. Curve A, 1 M $NaClO_4$, pH 4; Curve B, 1mM *cis*-CrTEDTA(OH_2), pH 4.15; Curve C, 0.27 mM *trans*-$CrTEDTA^-$, pH 3.89.


CHARGE /μC CM^{-2}
8
0
-8
-0.2
-0.6
V VS SCE
A
C
B
C
B
A

observed in these laboratories and was caused by slow reduction of the adsorbed complex (15).

To determine if *trans*-Cr(III)TEDTA$^-$ is rapidly desorbed at -1.6 V before it is reduced, its desorption at -1.1 V was examined. Using a solution 27 μM in complex at pH 6.3, the potential was stepped from -0.1 V or -0.5 V, where the reactant was initially adsorbed, to -1.1 V, where significant desorption, but no faradaic reaction occurred and then to -1.5 V, where reduction of both the attached and diffusing reactant was fast. The charge-time data obtained were analyzed according to the treatment of Osteryoung and Christie (16). The data were consistent with instantaneous desorption at -1.1 V followed by the diffusion-controlled establishment of a new adsorption equilibrium. Since approximately 60% of the initially adsorbed reactant was desorbed at -1.1 V, it is highly probable that all of the complex is rapidly desorbed at -1.6 V.

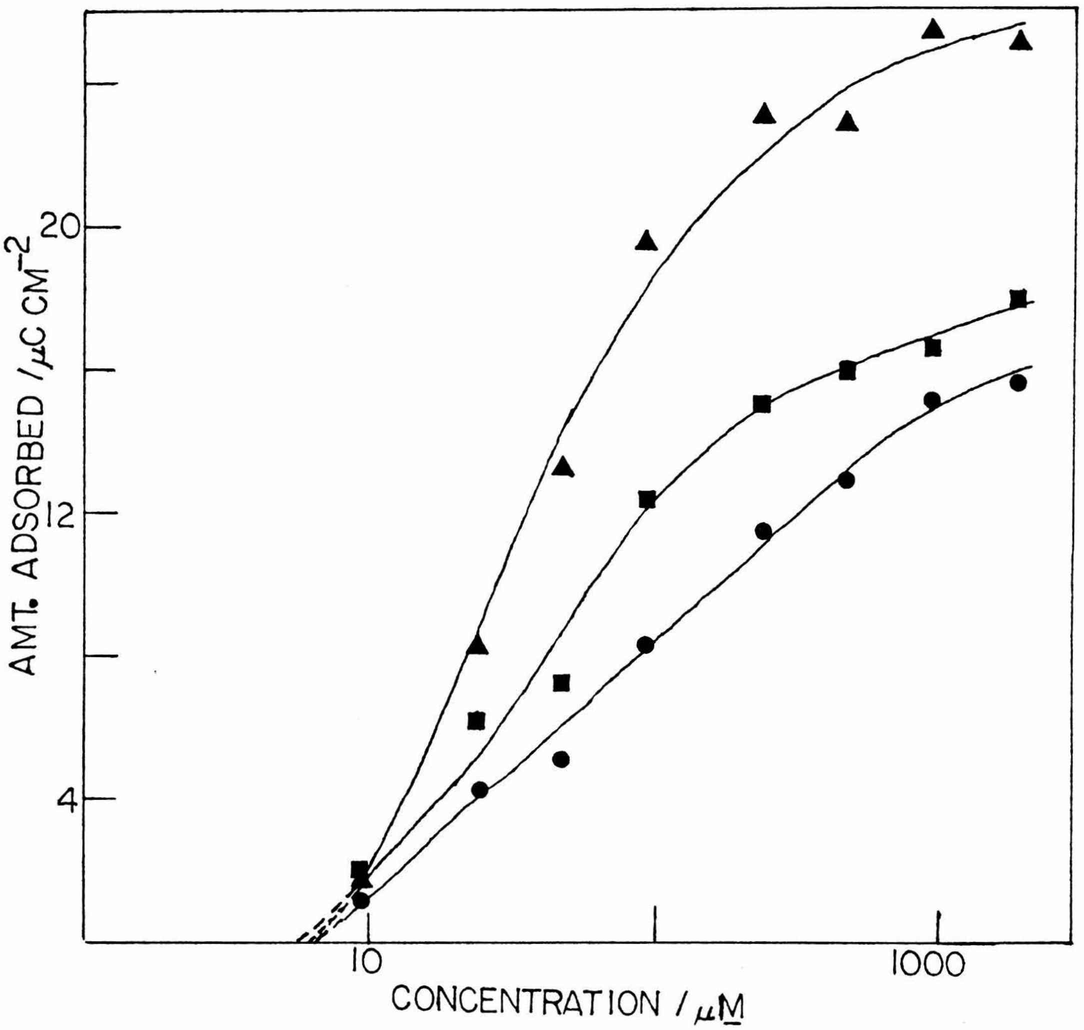
Cis-CrTEDTA(OH_2). Double potential step chronocoulometry was not useful for the evaluation of the quantity of adsorbed *cis*-Cr(III)TEDTA(OH_2) at pH 4 because the resulting chromium(II) complex appeared to remain adsorbed throughout the duration of the reductive step. This adsorption of the electrode reaction product was evident from the intercept and slope of the chronocoulometric plots for the oxidation step which were too high and too low, respectively. It was ascertained that the persistence of the chromium(II) complex on the surface was not the result of its spontaneous adsorption at equilibrium by performing a chronocoulometric experiment with the initial electrode potential maintained at a value (-1.4 V) where the chromic complex was reduced and then stepping the potential to a more positive value (-0.5 V) where the chromous complex was oxidized at a diffusion controlled rate. Chronocoulometric plots (charge *vs.* $(\text{time})^{\frac{1}{2}}$) for such experiments had intercepts which were much smaller than those for the oxidative half of a double potential step experiment and were, in fact, within ten percent of the double layer charging blank for the pure supporting electrolyte. Therefore, although the chromium(II) complex produced by reduction of *cis*-CrTEDTA(OH_2) at pH 4 is not adsorbed at equilibrium at -1.4 V, its rate of desorption is somewhat slow.

The slow desorption of the chromous complex forced us to use the difference in the intercepts of the chronocoulometric plots in the presence and absence of *cis*-CrTEDTA(OH_2) to estimate its adsorption. Values for the apparent adsorption obtained in this way are plotted in Figure 10. The *cis* isomer seems to be much more weakly adsorbed than the *trans* isomer and the maximum obtainable coverage appears to be a rather sensitive function of the electrode potential, at least at the highest bulk concentration employed (2 m$\underline{M}$).

However, there is a discrepancy between the apparent potential dependence of the adsorption shown in Figure 7 and the slope of the electrocapillary curve for the *cis* isomer shown in Figure 5. If the adsorption really increased as the electrode potential was made more cathodic, it is required by thermodynamics that the electrode charge become more negative (13). However, the slope of the electrocapillary curve for the *cis* isomer at any potential, which is proportional to the electrode charge, is less negative than that of the blank. To corroborate the electrocapillary behavior, the electrode charge was measured as a function of potential in a solution 1 m$\underline{M}$ in *cis*-CrTEDTA(OH_2) at pH 4.1 as described above. The data are plotted in Figure 9 and confirm the conclusions reached by inspection of the electrocapillary curves.

FIGURE 10

Concentration Dependence of the Apparent Adsorption of *Cis*-CrTEDTA(OH_2), pH 4. Initial potential: -.3 V (●); -.5 V (■); -.8 V (▲).


AMT. ADSORBED / μC CM^{-2}
20
12
4
10
1000
CONCENTRATION / μM

The apparent adsorption of *cis*-CrTEDTA(OH_2) was also measured at pH 7. Representative data are listed in Table 2. All of the adsorption observed at pH 7 can be explained in terms of the monomer alone at total Cr concentrations below 0.05 mM. However, at higher concentrations, a significant fraction of the *cis* isomer is dimerized. As the scan rate dependence of the dimer waves indicates that the dimer is adsorbed, both the monomer and dimer contribute to the total quantity of adsorbed complex at pH 7. At pH 7, the uncoordinated carboxyl group is deprotonated and the originally neutral *cis* complex is now anionic. As the data in Table 2 show, these complexes are less strongly adsorbed than the uncharged monomer at all potentials, but the greatest difference is observed at the most negative potentials as would be expected for anionic adsorbates.

Table 2

Apparent Adsorption of *cis*-CrTEDTA(OH_2) on Mercury (10^{10} x mol cm^{-2})

$[Cr]_T$ (mM)	Dimer Conc.[a] (mM)	Monomer Conc.[a] (mM)	Acetate Bridged Dimer (pH 7) -.3 V	-.5 V (V *vs.* SCE)	-.8 V	Monomer (pH 4)[b] -3 V	-5 V (V *vs.* SCE)	-8 V
1.88	0.67	0.53	1.1	1.2	1.4	1.3	1.7	2.4
0.94	0.30	0.35	0.96	1.1	1.3	---	---	---
0.47	0.12	0.22	0.82	0.90	1.2	1.2	1.6	2.4
0.24	0.049	0.14	0.55	0.61	0.92	---	---	---
0.094	0.012	0.070	0.43	0.57	0.79	---	---	---
0.047	0.0038	0.040	0.44	0.47	0.59	0.54	0.75	1.4
0.024	0.0011	0.022	0.24	0.32	0.32	0.45	0.65	0.87
0.0094	0.00019	0.0090	0.17	0.21	0.27	0.12	0.21	0.18

[a] Calculated using $K_D = 2410\ \underline{M}^{-1}$

[b] Quantities of adsorbed complex reported are for bulk concentrations of the *cis* monomer which are as close as possible to those calculated to be present, *e.g.* for 0.53 mM, the values reported are those measured at 0.47 mM.

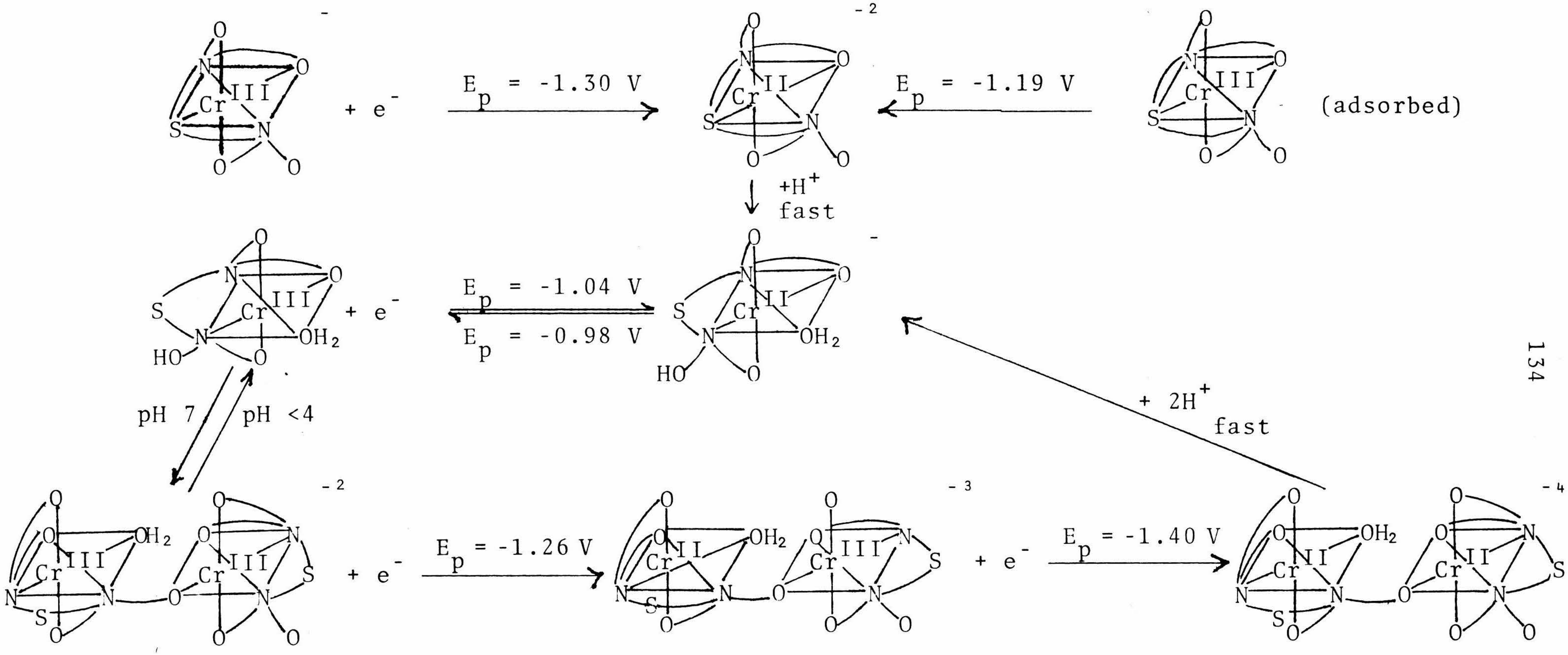
DISCUSSION

CYCLIC VOLTAMMETRY

The cyclic voltammetric behavior of the two isomers shown in Figures 1 and 3 can be explained by means of the combination of electrode and chemical reactions summarized in Scheme 1. In Figure 1, the reversible one-electron wave at -1.04 V results from the reduction of *cis*-CrTEDTA(OH_2) and is the only wave observed at pH 4, where the complex exists in its neutral, monomeric form. At pH 7, the two other one-electron waves at -1.26 V and -1.40 V, which are of equal size, represent the reduction of the acetate-bridged dimer. The electrochemical nonequivalence of the two Cr(III) centers is a reflection of the difference in their coordination environments. By contrast, the symmetrical dimer, $(EDTA\text{-}Fe(III))_2O^{-4}$, exhibits only a single, two-electron wave (17).

The observation of a wave for each Cr(III) also dictates the order of their reduction. The metal donating the bridging acetate group must be reduced first. If the other Cr(III) center were reduced first, the bridging O-Cr bond would be labilized, the dimer would dissociate and only two cathodic waves would have been observed -- one for the monomer and a single, one-electron wave for the dimer. Moreover, as the coordination environ-

Scheme 1


-
+ e⁻
E_p = -1.30 V
-2
E_p = -1.19 V
(adsorbed)
+H⁺
fast
-
E_p = -1.04 V
E_p = -0.98 V
+ e⁻
pH 7
pH <4
+ 2H⁺
fast
-2
+ e⁻
E_p = -1.26 V
-3
+ e⁻
E_p = -1.40 V
-4
Cr
III
II
N
O
S
OH_2
HO

ment of the metal donating the bridging group is less affected by the formation of the dimer, it is reasonable that its reduction potential would be shifted less from the monomer potential. Dissociation of the dimer follows reduction of the second metal center as shown by the gradual growth of the monomer wave and disappearance of the dimer waves on successive scans.

Reduction of either adsorbed or diffusing *trans*-Cr(III)-TEDTA$^-$ produces *trans*-Cr(II)TEDTA^{-2} which rapidly relaxes to *cis*-Cr(II)TEDTA(OH_2)$^-$, as evidenced by the anodic wave at -0.98 V and the appearance of a new cathodic wave at -1.04 V on the second scan (Figure 3). The greater stability of *cis*-Cr(II)TEDTA(OH_2)$^-$ is demonstrated by the fact that after the electrode was held at -1.6 V for 30 s., only *cis*-Cr(III)TEDTA(OH_2) was reduced during the cathodic half of the sweep.

The concentration and scan rate dependence of the peaks at -1.19 V and -1.30 V indicate that the first wave originates from the reduction of the strongly adsorbed complex and the second, from reduction of the diffusing complex. The reduction of attached complex at a less negative potential than the diffusing complex is attributed to the strength of the Hg-S bond and consequent weakening of the S-Cr bond, facilitating the stretching of the Cr-S bond to reach the transition state.

ADSORPTION BEHAVIOR

The electrocapillary curve for *cis*-CrTEDTA(OH_2) at pH 4 (Figure 5) indicates that the depression of the interfacial tension in the presence of the adsorbed complex was the greatest near the pzc (-0.486 V in 1 m<u>M</u> *cis*-CrTEDTA(OH_2)). Moreover, the electrode charge measurements show that the double layer capacitance is depressed at all potentials by the adsorption of the *cis* isomer. These results suggest that *cis*-CrTEDTA(OH_2) is behaving as an organic adsorbate (18) and that the apparent increase in the adsorption of *cis*-CrTEDTA(OH_2) at more cathodic potentials is misleading. The lack of adsorption by CrEEDTA demonstrates the complex is attached to the electrode through the sulfur. The accessibility of the sulfur atom to the electrode is enhanced by the coordination of the ligand to Cr(III). Therefore, the reason that free TEDTA is not adsorbed is probably because of the steric difficulty of exposing the sulfur moiety to the mercury electrode. However, the role of Cr(III) in inducing the adsorption of TEDTA on mercury is more complicated since the La(III) and Zn(II) complexes of TEDTA were not adsorbed.

At pH 7, where part of the *cis* complex exists as the acetate bridged dimer, both the monomer and dimer contribute to the total apparent adsorption (Table 2). The scan rate dependence of the dimer waves is consistent with its adsorption. The much weaker adsorption of these complexes at the more cathodic potentials at pH 7 results from the electrostatic repulsion of the negative ions from the negatively charged electrode.

The adsorption of *trans*-$CrTEDTA^-$ on mercury electrodes is extraordinarily strong and comparable to that of $Cr(NCS)_6^{-3}$, which it is believed forms three bonds to the electrode (19). This isomer exhibits a marked preference for positive electrodes (Figure 7) which probably arises from the capacity of the thioether sulfur to π-accept *d* electrons (20,21) from Cr(III) and σ-donate electron density to the electrode. The resulting increase in the ligand field stabilization energy which accompanies this shift in electron density is the driving force for the adsorption of the *trans* isomer (1b, 12). Clearly, this mechanism would operate most effectively at positively charged electrodes.

The abrupt change in coverage observed over the very narrow range of bulk concentration (Figure 6) indicates that the adsorption is cooperative. The sudden onset of strongly attractive interactions is indicated by the discontinuity in the Langmuir plot

(Figure 8a). At -.3 V, the cooperative mechanism apparently operates very effectively and saturation is almost achieved at 5 μM (Figure 6). At -.5 V where the electrode is less positively charged, back bonding is less efficient, the electrostatic repulsion between the negatively charged adsorbed molecules is more important and higher bulk concentrations are required to achieve the same surface concentration. When the electrode is negatively charged (at -.8 V), back bonding is least effective and the electrostatic repulsion of *trans*-$CrTEDTA^-$ from the electrode strongly interferes with its adsorption.

To summarize, the lack of adsorption of $CrEEDTA^-$, in which the sulfur atom of TEDTA is replaced by oxygen, demonstrates that the sulfur is the site of attachment of the Cr(III)-TEDTA complexes to the electrode. Steric hindrance in exposing the sulfur moiety to the electrode probably prevents free TEDTA from adsorbing on mercury. Although these steric problems are greatly reduced by the coordination of ligand around a metal ion, the non-adsorption of the La(III) and Zn(II) complexes of TEDTA shows that additional factors are involved in the adsorption of *cis*-$CrTEDTA(OH_2)$ on mercury. Back bonding by Cr(III) enhances its ligand field stabilization energy and is responsible for the marked preference of *trans*-$CrTEDTA^-$

for positive electrodes. A cooperative adsorption mechanism accounts for the abrupt charge in coverage of the electrode by *trans*-CrTEDTA$^-$ over a very narrow range of bulk concentrations.

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CHAPTER III

DIGITAL DEVICE FOR PRECISE DETERMINATION OF DROP TIMES AT DROPPING MERCURY ELECTRODES*

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[†] Contribution No. 5526

INTRODUCTION

Thermodynamic information on the adsorption of ions and molecules at mercury electrodes is often obtained from electrocapillary curves (1). The necessary values of the interfacial tension can be determined directly by means of a capillary electrometer or evaluated from measurements of the natural drop time of a dropping mercury electrode (2). The tedious experimental aspects of the former approach are well known. The latter procedure is more attractive because it is experimentally simpler and readily automated (2-6) Several methods for detecting drop fall have been proposed previously (5). The two most common employ photoelectric or impedance measurements to detect the end of drop life.

Corbusier and Gierst (2) were among the first to suggest the photoelectric method, which requires that the capillary be positioned very precisely in the light beam. However, their device and several of those based on impedance measurements (3,4) do not allow the lifetimes of consecutive drops to be measured. In this note, a simple, digital timer is described which provides a rapid, convenient means for determining the lifetimes of up to 1024 consecutive drops. The potential of the electrode can be controlled by a standard, commercial polarograph. (A Princeton Applied Research Model 174 Polarographic Analyzer was utilized, but any polarograph having a current measuring circuit with an output which can be adjusted for d.c. level and polarity would be acceptable.)

The experimental arrangement for measuring drop times is the same as that for recording a polarogram. The current output of the polarograph is connected directly to the input terminal of the drop timer. Since the device can be set to time up to 1024 consecutive drops at each potential, drop lifetimes can be determined very accurately. Once started, the timer runs continuously without operator intervention and displays the number of clock pulses elapsed during the last run while performing the next one. This permits the operator to record the result of each run while the next run is in progress. The digital output of the timer is well suited for interfacing to a computer if even greater automation were desired.

EXPERIMENTAL

DESCRIPTION OF THE INSTRUMENT

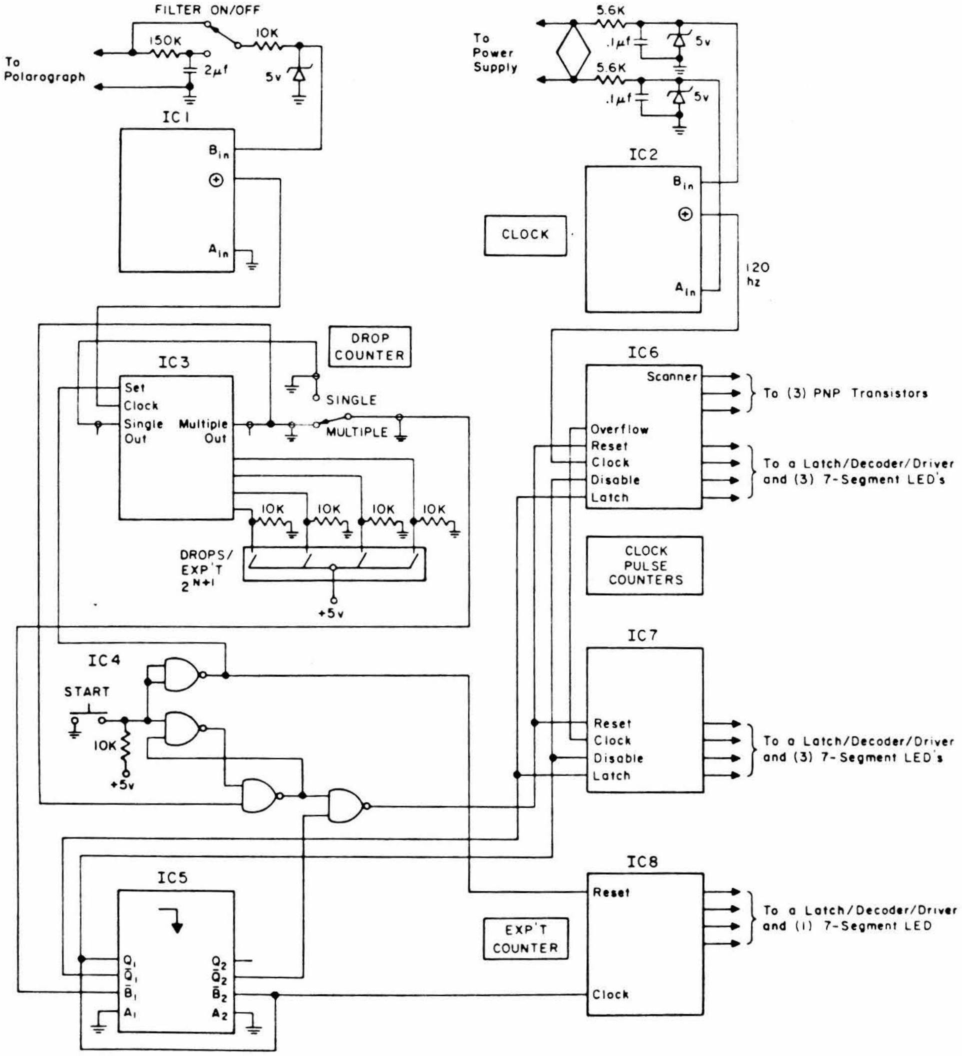
The drop timer is shown schematically in Figure 1. The abrupt change in current which accompanies the detachment of each drop from the capillary is used to sense the end of drop life. The input signal to the timer is sharpened by a Schmitt trigger, IC1, which is set to fire when the negative edge of the signal at its input crosses the threshold level of +2.6 V. (Since the timer accepts only positive input voltages, it is necessary to reverse the polarity of the current output when the current changes sign).

The clock frequency is 120 hz. The unrectified, 60 hz signals from the transformer secondary are differentiated and fed to separate inputs of the Schmitt trigger, IC2. Normally, as one input is high while the other is low, the exclusive OR output is high. However, just before and after the voltage reverses direction (twice per cycle), both inputs are low causing the exclusive OR output to change state, thus generating the clock pulses. The inputs of both IC1 and IC2 are protected by Zener diodes (5 volt).

An experiment is initiated by depressing the START button sometime during the growth of a drop. This clears

FIGURE 1

Schematic Diagram of Drop Timer. All integrated circuits are Motorola CMOS devices. IC1 and IC2 are dual Schmitt triggers, MC14583; IC3 is a programmable timer, MC14536; IC4 is a quad 2-input NAND gate, MC14011; IC5 is a dual monostable multivibrator, MC14528; IC6 and IC7 are three-digit BCD counters, MC14553; IC8 is a BCD counter, MC14510. Not shown are the latch/decoder/drivers, MC14511, and the 7-segment LED's MAN-74, which are conventionally wired.

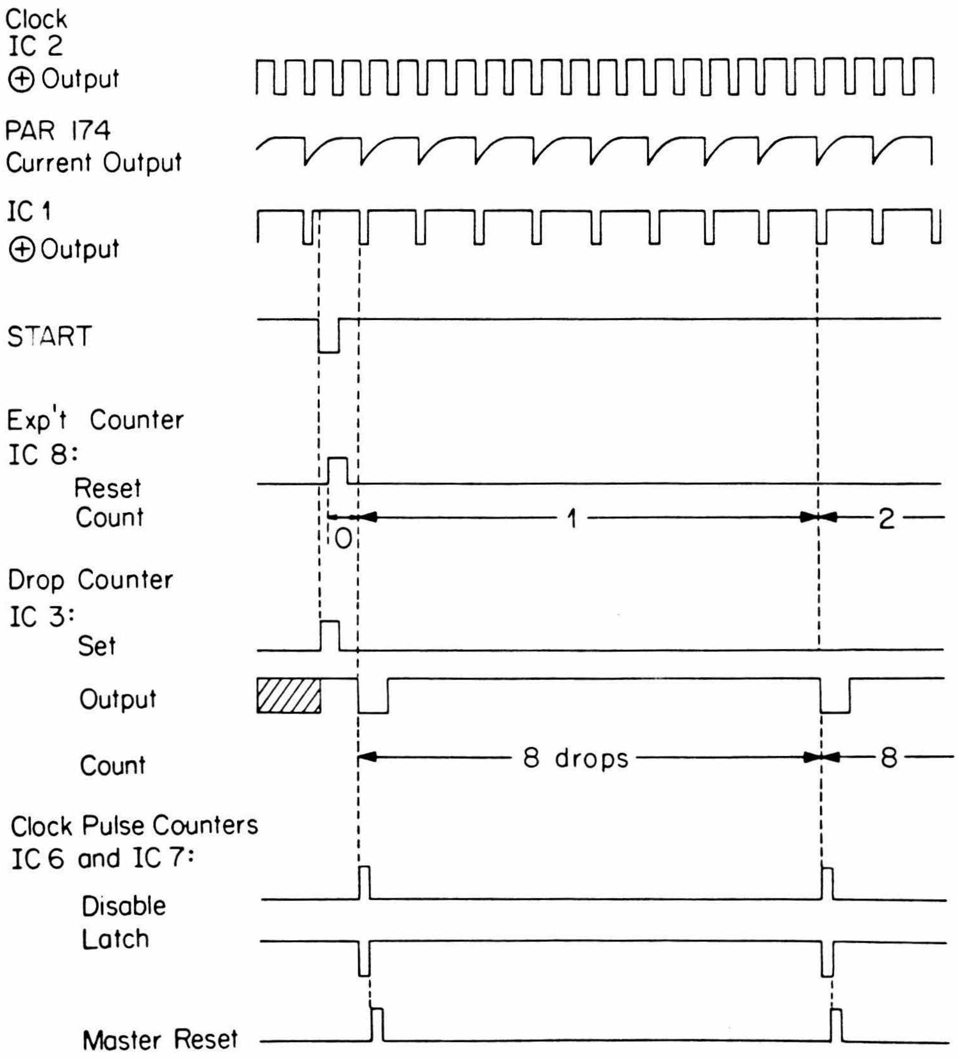

FILTER ON/OFF
150K
10K
2μf
5v
To
Polarograph
IC1
B in
⊕
A in
To
Power
Supply
5.6K
.1μf
5v
5.6K
.1μf
5v
IC2
B in
⊕
A in
CLOCK
120
hz
DROP
COUNTER
IC3
Set
Clock
Single
Out
Multiple
Out
SINGLE
MULTIPLE
10K
10K
10K
10K
DROPS/
EXP'T
2 N+1
+5v
IC6
Scanner
Overflow
Reset
Clock
Disable
Latch
To (3) PNP Transistors
To a Latch/Decoder/Driver
and (3) 7-Segment LED's
CLOCK
PULSE
COUNTERS
IC4
START
10K
+5v
IC7
Reset
Clock
Disable
Latch
To a Latch/Decoder/Driver
and (3) 7-Segment LED's
IC5
Q1
Q̄1
B̄1
A1
Q2
Q̄2
B̄2
A2
IC8
Reset
Clock
EXP'T
COUNTER
To a Latch/Decoder/Driver
and (1) 7-Segment LED

IC8 and when the drop falls, IC3, IC6 and IC7 are reset, IC8 is incremented by one and the counting begins. When the preset number of drops has been counted, the output of IC3 undergoes a brief negative transition which triggers the firing of IC5, thus disabling IC6 and IC7 and updating the two digital readouts which display the number of clock pulses counted and the number of times the measurement will have been repeated at the conclusion of the current run. The relative timing of these events is shown in Figure 2. The execution time of the device is *ca.* 10-15 μsec which represents a negligible correction for electrodes with natural drop times of several seconds.

The low pass filter shown in Figure 2 was employed to reduce 60 hz noise (RC = 0.3 sec). The presence of the filter caused the apparent lifetimes of each drop to increase by a constant amount (*ca.* 0.02 sec).

FIGURE 2

Timing Diagram. The purpose of this figure is to show the relative timing of the indicated events. However, the time scales for the various events are not necessarily the same. For example, the clock pulses (IC2) are separated by 8.33 msec, whereas the pulses from the exclusive OR output of IC1 occur only every 3-7 sec.


Clock
IC 2
⊕ Output
PAR 174
Current Output
IC 1
⊕ Output
START
Exp't Counter
IC 8:
Reset
Count
0
1
2
Drop Counter
IC 3:
Set
Output
Count
8 drops
8
Clock Pulse Counters
IC 6 and IC 7:
Disable
Latch
Master Reset

RESULTS AND DISCUSSION

CHARACTERISTICS AND PROPERTIES OF THE TIMER

As the clock frequency employed in this device is 120 hz, the uncertainty in the lifetime of a single 5 sec. drop is *ca.* 0.2%. Such precision in the measurement of individual drop times is comparable to that reported by Corbusier and Gierst (2) but not as high as has been achieved with some of the previously described devices (3,5,6). However, when the lifetimes of many drops are averaged, the accuracy and precision of the present timer are very high indeed.

A precision time mark generator (Tektronix Model 180 A) was used as the input source to test the inherent accuracy and precision of the drop timer. For marks separated by 5 sec. and counting 8 marks per run, the interval could be measured to within 0.2%. In twenty replicate experiments a precision of ±0.008% was observed. The time mark generator was also used to test the ability of the timer to measure short time intervals. For marks exactly 0.01 sec. apart, the timer yielded an interval of 0.010006 sec. after counting 512 marks.

ELECTROCAPILLARY DATA

The timer was used to measure the electrocapillary curve for 0.5 M $NaClO_4$ (pH 4.2) at 25° C. At least three runs consisting of the measurement of eight drop times were performed at each potential. Even near the pzc the drop time could be measured with a precision better than ±0.1% by using the most sensitive current range on the PAR 174 (7).

The data are plotted in Figure 3 along with the surface tension data of Parsons and Payne for aqueous 0.5426 M $HClO_4$ at 25° C (8). The agreement between the two sets of data is excellent. Thus, the greater convenience of the drop timer described herein has been achieved without sacrificing the quality of the electrocapillary data obtained. Of course, all methods based on drop time measurements share the limitation that adsorption equilibrium must be reached rapidly for the drop time to be a reliable measure of the equilibrium interfacial tension.

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CREDIT

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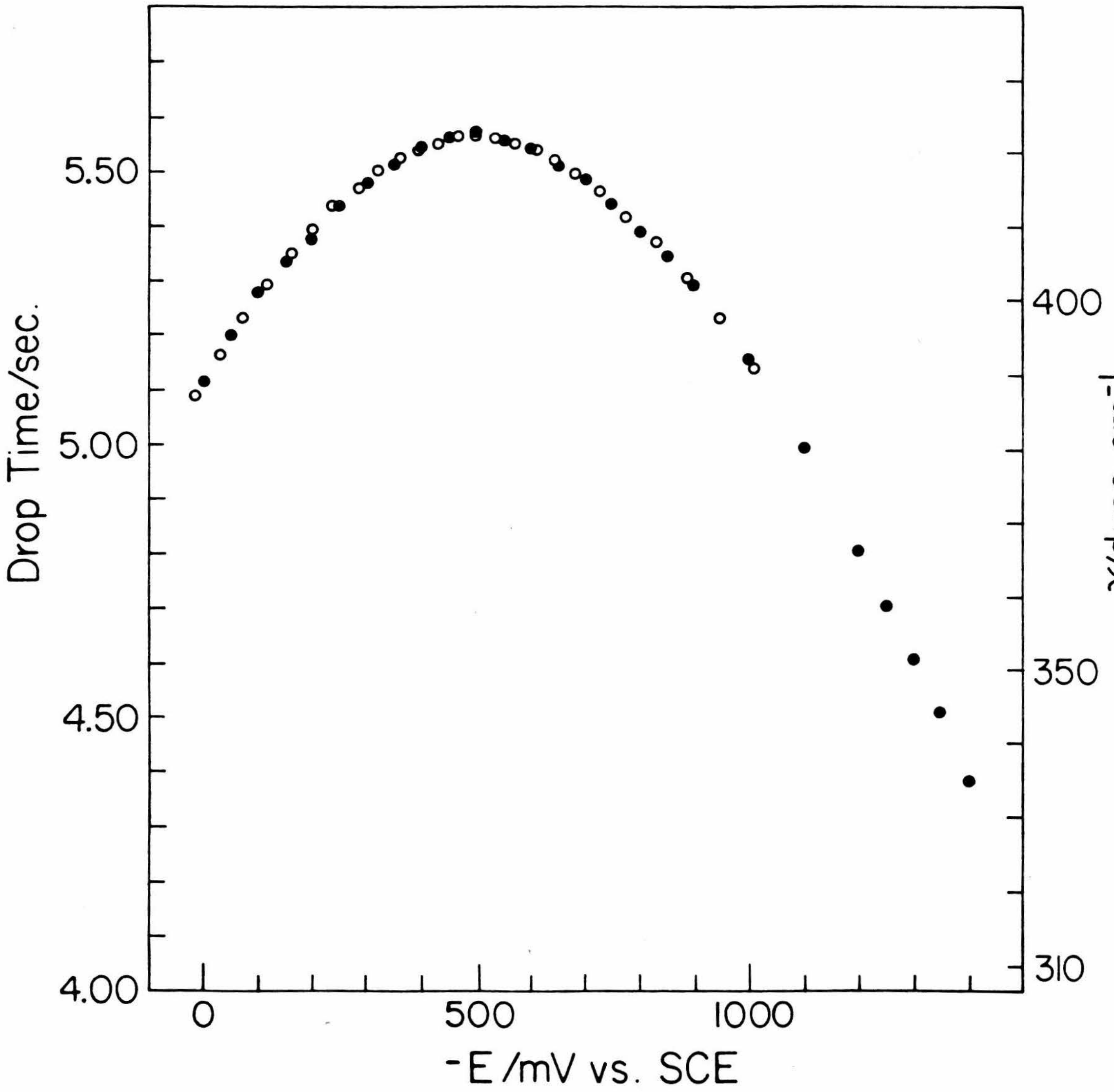
FIGURE 3

Comparison of electrocapillary data obtained from differential capacitance and drop time measurements. (●) - This work; (O) - Taken from Parsons and Payne (8). The two data sets were superimposed at the electrocapillary maximum.


Drop Time/sec.
5.50
5.00
4.50
4.00
γ/dyne cm^{-1}
400
350
310
0
500
1000
-E/mV vs. SCE

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