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AFML-TR-67-25

SYNTHESIS AND STUDY OF MONO-o-PHENANTHROLINE CHROMIUM (III) PERCHLORATE

PAUL M. MASLONA, 1/LT, USAF

TECHNICAL REPORT AFML-TR-67-25

FEBRUARY 1967

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AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
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FOREWORD

This report was prepared by the Analytical Branch, Materials Physics Division, Air Force Materials Laboratory. The work was initiated under Project No. 7360, "The Chemistry and Physics of Materials," Task No. 736005, "Compositional, Atomic and Molecular Analysis," and administered by the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, Paul M. Maslona, 1/Lt, USAF, Project Engineer.

This report covers work performed from July 1966 to December 1966. The manuscript was released by the author in January 1967 for publication as a Technical Report.

The author gratefully acknowledges the assistance of Joseph Walsh, S.M., of the Department of Chemistry, University of Dayton, Dayton, Ohio, in performing the polarographic measurements, and his understanding of the problem.

This technical report has been reviewed and is approved.

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ABSTRACT

The mono-o-phenanthroline chromium (III) perchlorate complex is prepared by two separate methods, (1) direct addition of the base to the metal ion in acid solution and heating, and (2) the use of Cr(II) to catalyze the reaction. The desired complex is then isolated by ion-exchange methods, and determined by spectrophotometric and elemental microanalytical procedures. Polarographic information is also given.

(Distribution of this abstract is unlimited.)

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SECTION I

INTRODUCTION

1. PURPOSE OF THE INVESTIGATION

It has been shown previously that some chromium complexes containing strong field ligands are reduced more reversibly at the Dropping Mercury Electrode (D.M.E.) than those of other complexes. It has also been observed that these complexes exhibit charge transfer bands near the visible portion of the spectrum (References 1 and 2). A chromium complex of a strong field ligand which shows this near-visible charge transfer band is Cr(III) (o-phen) $(H_2O)_4$ (Reference 3), (o-phen = o-phenanthroline). The purpose of this investigation was to synthesize this complex and to study its polarographic half-wave potential.

2. BACKGROUND

a. The Heterocyclic Diamines

The heterocyclic diamines, o-phenanthroline and 2,2'-dipyridine, have played an important part in the development of coordination chemistry (Reference 4). The ligands have absorption bands in the ultraviolet, well separated from those of the metal (Reference 5). This fact, plus the large absorption coefficient and high stability of the complexes, makes it possible to follow product formation spectrophotometrically (Reference 5). The fact that the ligands form neutral or mildly basic aqueous solutions and are only slightly soluble in water is a minor drawback. The slight solubility can be overcome by using the acid salt of the ligand which readily dissolves (Reference 3). The effect of protonation of the nitrogen atoms of the diamines on the ultraviolet spectra must be known prior to reaction in acid solution since the shift in absorption bands toward the visible could be interpreted as complex formation. This pH dependent shift was studied by Perkampus and Kohler (Reference 6) who also studied seven related phenanthrolines. Favini (Reference 7) correlated the ultraviolet spectra of m,p,o-phenanthrolines in different solvents, including H_2SO_4, with some discussion as to the nature of the observed bands. Kinetic studies have been made on the transition metal complexes of the ligands by Holyer, et al. (Reference 5). Steinhaus and Margerum (Reference 8) studied the effect of halide substitution on the replacement of coordinated water in the Ni(II) (o-phen) complex. Stability constants for o-phenanthroline and 2,2'-dipyridine were determined with hydrogen ions and various bivalent metal ions by Anderegg (Reference 9) who used a potentiometric method. The rates of complex formation and water exchange of o-phenanthroline and Ni(II), Co(II), and Fe(II) were given by Langford and Gray (Reference 10), who found an analogy to the anion reaction of $Co(NH_3)_5OH_2^{+3}$. The water-exchange process is faster in most cases.

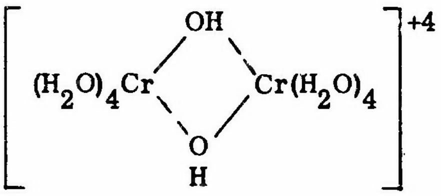
o-Phenanthroline has been widely used in the colorimetric determination of iron as the Fe(III) complex whose maximum absorption band is at 508 m μ (Reference 11). Secrest, et al. (Reference 12), have used this method for the determination of o-phen in alcoholic solutions by adding iron to the solution. Close agreement was found in the procedure.

Perhaps the most important factor for using the diamines in complex formation is their ability to produce large crystal field splitting of the "d" orbitals on metal ions. These orbitals, in the case of octahedral complexes, undergo a perturbation resulting in three stabilized and two destabilized orbitals. The energy separation between these two types of orbitals is designated 10 Dq, and can be determined by spectral studies (Reference 13). Ligands which produce large values of 10 Dq are referred to as strong field ligands, and form extremely stable complexes. Unusual oxidation states, such as Cr(II) $(CN)_6^{-4}$, can be stabilized by complexation with strong field ligands (Reference 14). The large size of the diamines also makes it possible, by varying the size of the central metal ion, to produce the mono, bis, and tris form; the tris species on a small central ion would not be stable due to steric factors.

b. Chromium and Chromium Complex Formation

Chromium (III) is one of the best known and most extensively studied metal ions in coordination chemistry (Reference 15). For octahedral complexes of identical ligands, such as Cr(III) $(NH_3)_6$, the ground state has the configuration $(t_{2g})^3$ and also shows two higher levels $(t_{2g})^2(e_g)$ and $(t_{2g})(e_g)^2$ in the spectra and shows complete agreement between calculated and experimental values (Reference 16).

Virtually all chromium compounds are strongly colored, and detectable in some cases to one ppm. One of the important methods of analysis for chromium is the formation of the s-diphenyl carbazide complex which shows a maximum absorption at 540 mμ, and an extinction coefficient at 3.14 x 10^4 at this wavelength (Reference 17). Other methods, using complex formation, included reaction with sodium 1,8-dihydroxynaphthalene3,6-disulfonate, benzidine and aniline (Reference 18). Since chromium is commonly determined in aqueous solutions, and has many color reactions, no data are available on analytical methods using ultraviolet methods. $Cr(H_2O)_6^{+3}$ in NO_3^- and ClO_4^- solutions can be converted by heating or OH^- addition to the olated species readily. $Cr(OH)(H_2O)_5^{+2}$ forms first, and upon heating,



is produced.

Upon oxalation, $(H_2O)_5Cr\text{-}O\text{-}Cr(H_2O)_5^{+4}$ forms. Continued OH^- addition to $Cr(OH)(H_2O)_5^{+2}$ forms $Cr(OH)_3(H_2O)_3$ which precipitates and rearranges to $Cr_2O_3 \cdot XH_2O$. $Cr(H_2O)_6^{+3}$ is violet in color and shows two absorption peaks which are pH, temperature, and concentration dependent at 580 mμ and 420 mμ (Reference 19).

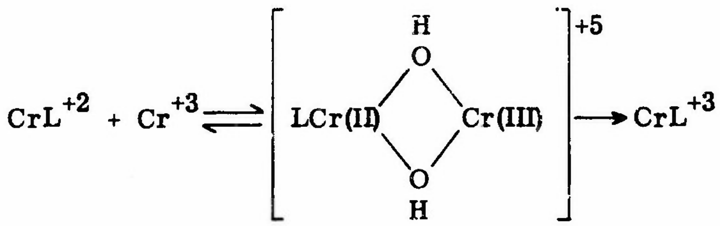
Hunt and Taube (Reference 20), and Swaddle et al. (Reference 21), have shown through radio isotope methods that both hexaquochromium (III) and hexammine chromium (III) hold their six ligand molecules distinct from solvent for many hours. Substitution of one of the ligands of Cr(III)$(X)_6$ is exceedingly slow or does not occur at all. A ligand field stabilization energy computation (Reference 22) indicates that d^3 systems are more resistant to distortions leading to five or to seven coordinate intermediates than other systems, hence the inertness (slow ligand exchange) of the complexes. It is for this reason that complex synthesis using Cr(III)$(H_2O)_6$ as a starting material is an extremely slow process and therefore not a very popular method of formation of the desired Cr(III) complex. However, this method is of some value when anhydrous Cr(III) salts are used, when the reaction is carried out in nonaqueous solutions, or by heating the ligand and $Cr(H_2O)_6^{+3}$ for long periods of time (Reference 3). Broomhead and Dwyer (Reference 23) produced the monodipyridine and o-phenanthroline Cr(III) complex by reaction of the base with excess anhydrous metal halide in dimethylformamide (DMF), and boiling, showing the use of all three methods to increase reaction rate.

A more popular method is the use of Cr(II) to catalyze the reaction. This procedure can be carried out using Cr(III) ligand and amalgamated zinc in acid solution under an inert gas. In this reaction, Cr(II) is formed when Cr(III) is reduced by metallic zinc. The Cr(II) being labile (rapid ligand exchange), forms the Cr(II) complex readily, and subsequently undergoes electron exchange with Cr(III) forming a Cr(III) complex. This method gives rise to Zn(II) in solution, which may also complex with the ligand. Isolation of the desired Cr(III) complex is also made more difficult. A less complicated method is that of direct addition of Cr(II) to the aqueous mixture of Cr(III) and ligand under an inert gas.

It has been demonstrated (Reference 24) that this Cr(II) catalysis is analogous to certain Co(III) ⟶ Co(II) reactions (Reference 25), and is considered to involve bridging groups which link the two chromium atoms during electron transfer. The lability of Cr(II) and the relative inertness of Cr(III) to substitution makes this reaction extremely important in synthesis as well as studies of the influence of the nature of these bridging groups on the speed of the catalysis (Reference 24). Since o-phen is a nonbridging ligand, it is suggested that the effect on the rate of electron transfer results from the stabilization of one of the oxidation states by coordination (Reference 24). Earnshaw and Lewis (Reference 26), when studying the exchange integral between magnetic ions in the Cr(III) (o-phen) complex noted a small interaction when the bridging groups were Cl^- or OH^-; but a marked interaction when O was used as the bridging group. This was interpreted as the formation of π bonds between chromium ions and the oxygen atom bridge. This effect was also noted in the Fe(III) (o-phen) species. It can be shown that this π bond interaction helps promote the Cr(II) catalysis, as does the effect of the nonbridging ligand (Reference 24).

The catalysis reaction is seen to proceed by the following sequence (Reference 24):

$$Cr^{+2} + L \longrightarrow CrL^{+2}$$

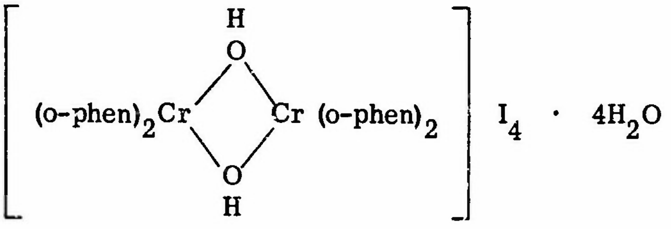


The reaction is seen to be self-supporting since Cr^{+2} is produced by the oxidation, and thus able to proceed to completion. Similar reactions (Reference 24) were found to be dependent on $\left[H^+\right]^{-1}$ thus must be run at as high as pH as possible; the olation of the $Cr(H_2O)_6^{+3}$ must also be considered.

The stabilization of the Cr(II) complex in the catalysis by coordination is of the utmost importance. Cr(II) contains 4 "d" electrons; the "d" orbitals are effectively split by a strong field ligand producing a high crystal field stabilization energy (C.F.S.E.) of 16. The resulting Cr(II) complex is thus stabilized by coordination. The rate of Cr(II) catalysis on the formation of Cr(III) complexes of various ligands shows: EDTA > $P_2O_7^{-4}$ >> $PO_4^{-3} \approx F^-$ >NCS^-

(Reference 1) which is in rough agreement with the C.F.S.E. of the ligands. This stabilization could be measured by the $Cr(III)L + e^- \rightleftharpoons Cr(II)L$ potential which is related to the ratio of the stability constants of the Cr complexes $K_{(II)}/K_{(III)}$ (Reference 27).

Herzog (Reference 28) in synthesis of the Cr(II) (o-phen), and Cr(III) $(o\text{-phen})_3$ species measured the effective magnetic moment of the complexes and compared them to the 2,2' dipyridyl analogs. The polymeric species



was measured magnetically by Earnshaw and Lewis (Reference 29).

Steric hindrance of the 1:1 complex was investigated by Sisler, et al. (Reference 30), who formed the species at -80°C. The interference was found to be intermediate between that which hinders lutidine or collidine adducts from forming. Inskeep and Bjerrum (Reference 3) in their production of the mono and bis forms, found no evidence of tris species formation, even after prolonged heating of the bis form in excess o-phenanthroline. They attributed this lack of formation to the extensive reorientation needed in the bis for the 1:3 (Cr:ligand) complex to form. The $Co\left[(o\text{-phen})_2\,Cl_2\right]Cl \cdot 3H_2O$ complex and its bromide analogs were produced by Kon (Reference 31) who studied their X-ray spectra. He determined unit cell parameters and determined the space groups of the complexes.

c. Ion Exchange Methods

After the complex is produced, either by the Cr(II) catalysis method or by heating a mixture of the reactants, there exists in solution the complex and excess starting materials which must be separated in order to isolate the desired species. Ion-exchange techniques are best suited for this type of separation. The validity of this method was proven by King and Dismukes (Reference 32). The authors showed that by carefully choosing column length and acid strength, they were able to elute a complex species without quantitative elution of uncomplexed Cr(III). This method works extremely well when a charged ligand is used in the complexation (References 1, 24, and 33), but when both excess Cr(III) and the formed complex have identical electronic charges the excess Cr(III) must be eluted first. Protonated o-phenanthroline which now also possesses a charge (+1 or +2 depending on the acid strength of the solvent) may also be eluted by acid.

d. Polarographic Methods

Following elution, the complex can be measured polarographically, i.e., the reduction of Cr(III)L to Cr(II)L. Vlcek (Reference 34) when studying a series of Co(III) $(NH_3)_5X$ complexes, correlated the activation energy with the electronic structure from absorption data, and found that a given change in electronic energy produced a much greater change in activation energy. He postulated that the polarization of the ligand X by the electric field of the electrode occurs, resulting in excitation of an electron from dxy to the d_z2 orbital, vacating the dxy orbital for electron transfer. Pecsok and Lingane (Reference 35) observed the anodic wave for the oxidation of Cr(II) ⟶ Cr(III) and found at higher pH the oxidation wave is displaced negatively. Later studies by Pecsok, et al. (References 36 and 37) found Cr(II)-EDTA and Cr(II) salicylate complexes to be powerful reductants, with $E_{1/2} = -1.48$ and -1.23v, respectively, vs Standard Calomel Electrode (S.C.E.), although quantitative measurements were difficult. Meites (Reference 38) and Kolthoff and Lingane (Reference 39) have done extensive work on half-wave potentials of chromium ions in different electrolytes, finding that complexation shifts the half-wave potentials to more negative values. Generally two waves are noted in polarographic reductions (III ⟶ II ⟶ O) although in the case of Cr(III) $(\text{dipyridyl})_3$ complex (Reference 40) three are found. This is not in agreement with Baker and Mehta (Reference 41), however, who found a two-electron transfer.

In a polarographic study of the Cd(II) (o-phen) complex, Douglas, et al. (Reference 42) found an E° value of -1.35v for the complex which was higher than those for Cd(II) complexes of dipyridyl and pyridyl. A two step reduction of the Cu(II) complex of o-phen was found by Onstatt and Laitinen (Reference 43) ($Cu^{+2} \longrightarrow Cu^{+}$ complex; $Cu^{+} \longrightarrow$ amalgam). Morinaga, et al. (Reference 44), studied the polarographic waves of Co(III) $(\text{o-phen})_3$ and found it to be two-step in Na_2SO_4. The first wave is the reduction of Co(III) ⟶ Co(II) complex, and the second is Co(II) ⟶ to Co(I) complex. Of importance is their notation that the electrode process for the reduction of Co(III) ⟶ Co(II) seems to be highly reversible.

In their work on the mechanism of the reduction of Cr(III) $(H_2O)_6$ in acid solutions, Elving and Zemel (Reference 45) postulated two possible mechanisms for electron transfer: (1) direct transfer of Cr(III) ion from the electrode at the mercury solution interface, and (2) transfer of an electron to Cr(III) from a Cr(II) ion produced at the interface. As the reduction continues, a $\left[\text{Cr(II)}\right]$ in the diffusion layer becomes so much larger that an incoming Cr(III) may be reduced by it, and thus the Cr(II) serves as an electron transfer agent between Cr(III) and the electrode.

Of utmost importance in polarography is the "reversibility" of the reduction. A provisional indication of the reversibility (one-electron change) was taken by Walsh and Earley (Reference 1) as a value of θ close to unity in:

$$\log \frac{i_d - i}{i} = 0.059\,\theta\,E, \text{ which is a form of}$$

$$E_{d.e.} = E_{1/2} - \frac{.059}{n} \log \frac{i}{i_d - i} \qquad \text{(Reference 46)}$$

It is evident that a plot of $E_{d.e.}$ vs $\log \frac{i}{i_d - i}$ should produce a straight line with slope equal to .0591/nv at 25°C. Chromic complexes can be seen to be either completely reversible or completely irreversible depending upon the ligand coordinated to the metal ion. The shift to more negative reduction potentials for ligands corresponding to increasing C.F.S.E. may be interpreted on the basis of stabilization of d^3Cr(III) relative to spin-free d^3d_γ Cr(II) (Reference 47).

e. Summary

It can be seen that this investigation must have the following steps: (a) study of the effect of increasing $[H^+]$ on the ultraviolet spectra of the ligand, and to ascertain if a Beer's Law correlation is followed; (b) synthesis of the complex $Cr(III)(o\text{-}phen)(H_2O)_4$ by two separate methods (1) mixture of metal and ligand with heating for long periods of time, and (2) use of Cr(II) catalysis; (c) separation of product from excess starting material by ion-exchange techniques; (d) identification of isolated complex by spectroscopic methods; and finally (e) use of polarographic information to ascertain if this complex is in agreement as to its reduction potential with other strong field ligand chromium complexes.

SECTION II

EXPERIMENTAL

1. REAGENTS

Throughout this investigation, double distilled water was used.

Hexaquo chromium (III) perchlorate stock solutions have been prepared by reduction of CrO_3 by formic acid in $HClO_4$ medium (Reference 48), and by recrystallizing the product from deionized water. However, a much simpler procedure is to dissolve appropriate amounts of reagent grade hydrated chromium perchlorate (Reference 49) in water. The pH of the solutions was carefully adjusted at 2.5 by the slow addition of dilute NaOH, and with constant stirring by a magnetic stirrer. Chromium concentration of these solutions was measured spectrophotometrically after alkaline peroxide oxidation to chromate. At 374 $m\mu$, ϵ is 4800 (Reference 50). All other chromium analyses were performed in this method.

Chromous perchlorate solutions could have been prepared by the electrolytic reduction of hexaquo chromium (III) perchlorate in dilute $HClO_4$ (Reference 24). However, a more direct method was to dissolve a weighed amount of electrolytically pure chromium metal in acid. A 50 ml Erlenmeyer flask containing 40 ml of 1 M $HClO_4$ was purged free of oxygen with dry helium. Chromium metal is washed with dilute HCl, rinsed with water, and dissolved in the 1 M $HClO_4$. Dry helium is passed through the solution until all the metal is dissolved (Reference 51). The flask is then quickly sealed with a soft rubber septum under helium and appropriate amounts withdrawn by a calibrated syringe. Under these conditions, it is found that the Cr(II) will not appreciably oxidize to Cr(III) within a period of two to three days. Chromium concentration was also checked spectrophotometrically after oxidation to CrO_4^-.

Solutions of o-phenanthroline (Reference 52) were prepared by weight using a Mettler Model H microchemical balance. In this study, no acid salt was formed, and the solutions of concentration of 0.005 M and above must be heated and shaken vigorously for a period of two hours to completely dissolve the ligand. The ultraviolet absorption spectrum of these solutions was then studied with respect to the change in bands with $[H^+]$. A significant difference in the spectra was seen from pH of 6.8 to 2.5; this latter value is the pH at which the Cr(III) complex was prepared catalytically.

2. INSTRUMENTATION

Visible and ultraviolet studies were made on a Cary Model 14 spectrophotometer using matched cells at room temperature. All dilutions and reference solutions were of identical pH; dilute NaOH and $HClO_4$ were used to adjust the pH. The spectrophotometer was balanced prior to each run in order to give the true spectrum of only the desired material. The infrared spectra of solids were run on a Beckman Model IR-10 infrared spectrophotometer using the KBr pellet technique with a 1-100 part dilution. All polarographic measurements were carried out at 25 ± 0.1°C using a standard H-cell and saturated calomel reference electrode with the usual circuitry. Mercury electrode drop time was 2.5 seconds in 0.1 M $NaClO_4$ at -1.00v potential. Polarograms were obtained with a Sargeant Model XV polarograph.

3. COMPLEX SYNTHESIS

The Cr(III) (o-phen) $(H_2O)_4$ complex was prepared by two separate methods. In the first procedure (Reference 3), Cr(III) $(H_2O)_6(ClO_4)_3$ was added to an o-phenanthroline salt solution at pH 2.5 using a 1:3 molar ratio of Cr(III):o-phen. The mixture was then heated on a hot plate at 100°C for 36 hours, the volume and pH of the solution being kept constant. Hydrogen ions are liberated by the reaction, which causes a decrease in rate since the reaction has an inverse $\left[H^+\right]$ dependence. After heating for the appropriate time, the scarlet solution is rapidly cooled. An orange-red precipitate is formed and filtered out leaving a deep red effluent. The precipitate is washed twice with dilute $HClO_4$, and dried over $Mg(ClO_4)_2$. Ultraviolet and microchemical analysis showed these crystals to be Cr(III) $(o\text{-phen})_2(H_2O)_2$ complex. Calculated: Cr = 7.11%; N = 7.65%. Found: Cr = 6.89%; N = 7.30%.

This complex has a visible absorption band at 510 $m\mu (\epsilon = 55)$. The deep red effluent is then placed on a 1 cm diameter column of Dowex 50W x 8(50-100 mesh). In this separation, however, both the desired complex and excess chromium are trivalent. The column is washed with 0.1 M $HClO_4$ to elute excess ligand. Then a large volume of 1.5 M $HClO_4$ is passed through the resin to elute the unreacted chromium. The feasibility of this separation has been shown by King and Dismukes (Reference 32). The washings are constantly checked for the metal ion spectrophotometrically after alkaline peroxide treatment. Only when chromium elution is complete is stronger acid used to elute the desired complex. First attempts at elution of the desired complex failed when Dowex 50X 8(100-200 mesh) was used. The large size of the complex probably prevented any elution. Throughout these washings, some red color remained at the top of the column. Washing with 6 M $HClO_4$ failed to elute it. This red species is considered to be some polymeric form of the complex. An attempt was made to concentrate the complex using the technique of Espenson and Carlyle (Reference 33); however, no complex was eluted using either 1 M barium perchlorate of 1 M cerium perchlorate.

After elution, the red solution was brought up to a pH of 2.5 by the slow addition of Na_2CO_3 with constant stirring. Analysis for Cr(III) was performed spectrophotometrically after alkaline-peroxide oxidation as chromate. Since the ultraviolet band intensity of the o-phenanthroline changes when bonded to the metal, no Beer's Law relationship could be performed. However, o-phenanthroline could be analyzed after destruction of the complex (alkaline-peroxide oxidation). Using this method $\left[Cr\right]$ was found to be 0.0012; and $\left[o\text{-phen}\right]$ = 0.0013 M. In this way, a 1:1 molar ratio of chromium to o-phenanthroline was established. Also, the ultraviolet spectrum of the ligand gave a very definite shift toward the visible, a shift of almost equal wavelength which was seen in the Zn(o-phen) complex (Reference 5).

The second method used in the synthesis was that of Cr(II) catalysis. A 5:1 molar ratio of Cr(III) stock solution to o-phenanthroline was placed in a 50 ml Erlenmeyer flask sealed by a soft rubber septum under these conditions: pH 2.5, $\mu = 1.0$ ($NaClO_4$), temperature at 25 ± 1°C. At first a metal hypodermic syringe needle was used for purging the solution free of oxygen, but it was found that the o-phenanthroline reacted readily with the iron of the needle to form the $Fe(o\text{-phen})_3^{+3}$ complex. This necessitated the use of a glass capillary which was immersed directly into the solution and dry helium bubbled freely for at least 10 minutes. The system was vented by another glass capillary. Reaction was then initiated by the addition of Cr(II) by means of a calibrated syringe being careful not to immerse the syringe needle into the solution. A molar ratio of 30:1 Cr(III):Cr(II) was found to be the most favorable.

The mixture was allowed to stand for at least 20 minutes under helium to insure completion. Oxygen was then bubbled through the flask to convert the unreacted Cr(II) to Cr(III). The contents of the flask were placed in an ion-exchange column of similar construction and treated as previously stated. Again the $\left[\mathrm{Cr(III)}\right]$ and $\left[\text{o-phen}\right]$ were measured spectrophotometrically after destruction of the complex. For example, using 0.004 M o-phen and 0.0020 M Cr(III) stock solution, and an appropriate amount of Cr(II), it was found after separation that $\left[\mathrm{Cr(III)}\right] = 0.00027\mathrm{M}$; $\left[\text{o-phen}\right] = 0.00029$ M. Thus the 1:1 $\left[\mathrm{Cr}\right] : \left[\text{o-phen}\right]$ composition is confirmed.

An attempt was also made to produce the tris form of the complex. Chromium metal was dissolved as before, in 1 M $HClO_4$, under dry helium, but with a fivefold excess of o-phenanthroline present in the solution. A dark amber solution formed as the metal dissolved, and upon air oxidation and cooling, dark red crystals precipitated. These were filtered and washed with dilute $HClO_4$, dried, and analyzed for nitrogen using a Coleman Nitrogen Analyzer.

Calculated for $Cr(C_{12}H_8N_2)_3(ClO_4)_3$, Nitrogen = 9.47%. Found: Nitrogen = 7.55%.

This result matches the nitrogen content for the $Cr(\text{o-phen})_2(H_2O)_2(ClO_4)_3$ complex.

SECTION III

RESULTS AND DISCUSSION

1. o-PHENANTHROLINE ULTRAVIOLET SPECTRA

Figure 1 shows the ultraviolet spectra of o-phenanthroline at pH 2.5 (with $HClO_4$) compared with that of the ligand dissolved in water (pH 6.5). These spectra closely match the reported values (Reference 53) where:

Solvent/pH	λ (maximum) m	log ϵ
H_2O	227	5.3
	263	5.21
5.8	224	4.5
	266	4.5
dil HCl	218	4.5
	270	4.5
	275 (shoulder)	4.5

It can be seen that the 263 mμ peak (in H_2O) is continuously shifted at lower pH values to the reported 270 mμ value when dilute HCl is used as the solvent. This band, attributed to $\pi \longrightarrow \pi^*$ transitions of the ring structure, exhibits this shift due to the addition of hydrogen ion to the free electron pair of the nitrogen atoms of the compound. Bliznynkov and Reznikov (Reference 54), studying the solvent effects on the spectra of pyridine and related derivatives, experienced similar shifts when EtOH: HCl (1:1) solutions were used. The spectral data received using the Cary Model 14, showed another absorption band at 205 mμ which has not been previously reported. This band is present in both acid and neutral solutions.

2. Cr(III) (o-PHEN) MADE BY HEATING

The visible absorption spectra of a Cr(III) o-phenanthroline mixture as it is heated at 100°C is given in Figure 2. Samples were removed, cooled to room temperature, and spectra recorded. After a short period of time, an absorption at 530 mμ is visible and on prolonged heating, this band broadens and increases in intensity into the 520 mμ region.

The monocomplex was then isolated from excess reagents by filtration and ion-exchange techniques. Figure 3 shows the visible absorption spectrum after separation, using matched 5 cm cells at pH 2.5. It shows a maximum absorption at 515 mμ, with shoulders at about 430 and 390 mμ, going off scale at 370 mμ (ϵ at 515 mμ = 60). The absorption shift of 580 mμ for hexaquo chromium (III) to the 515 mμ level for the mono-o-phenanthroline complex gives

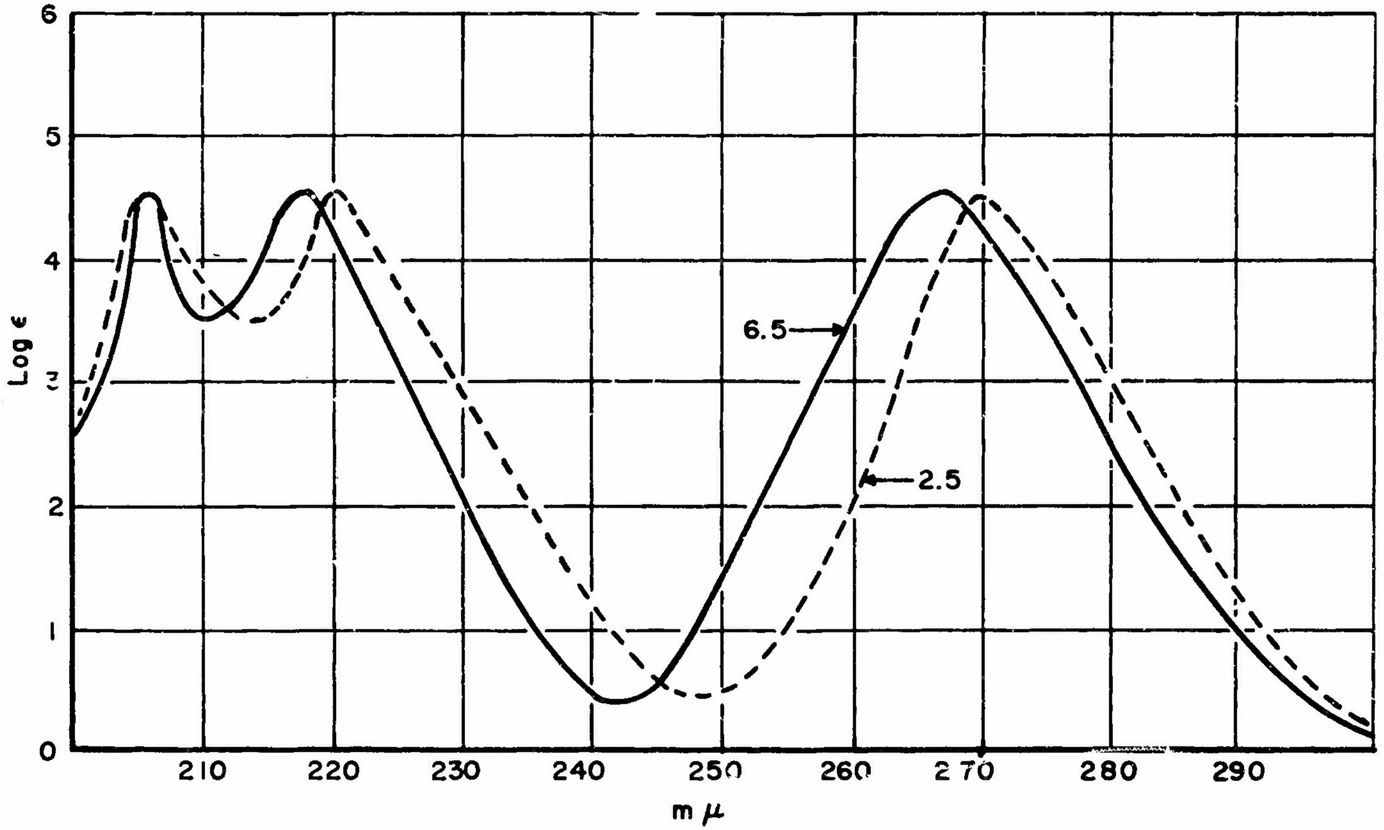


Figure 1. Ultraviolet Spectra of o-Phenanthroline at pH of 2.5 Compared With That at pH 6.5 (1 cm Cell)

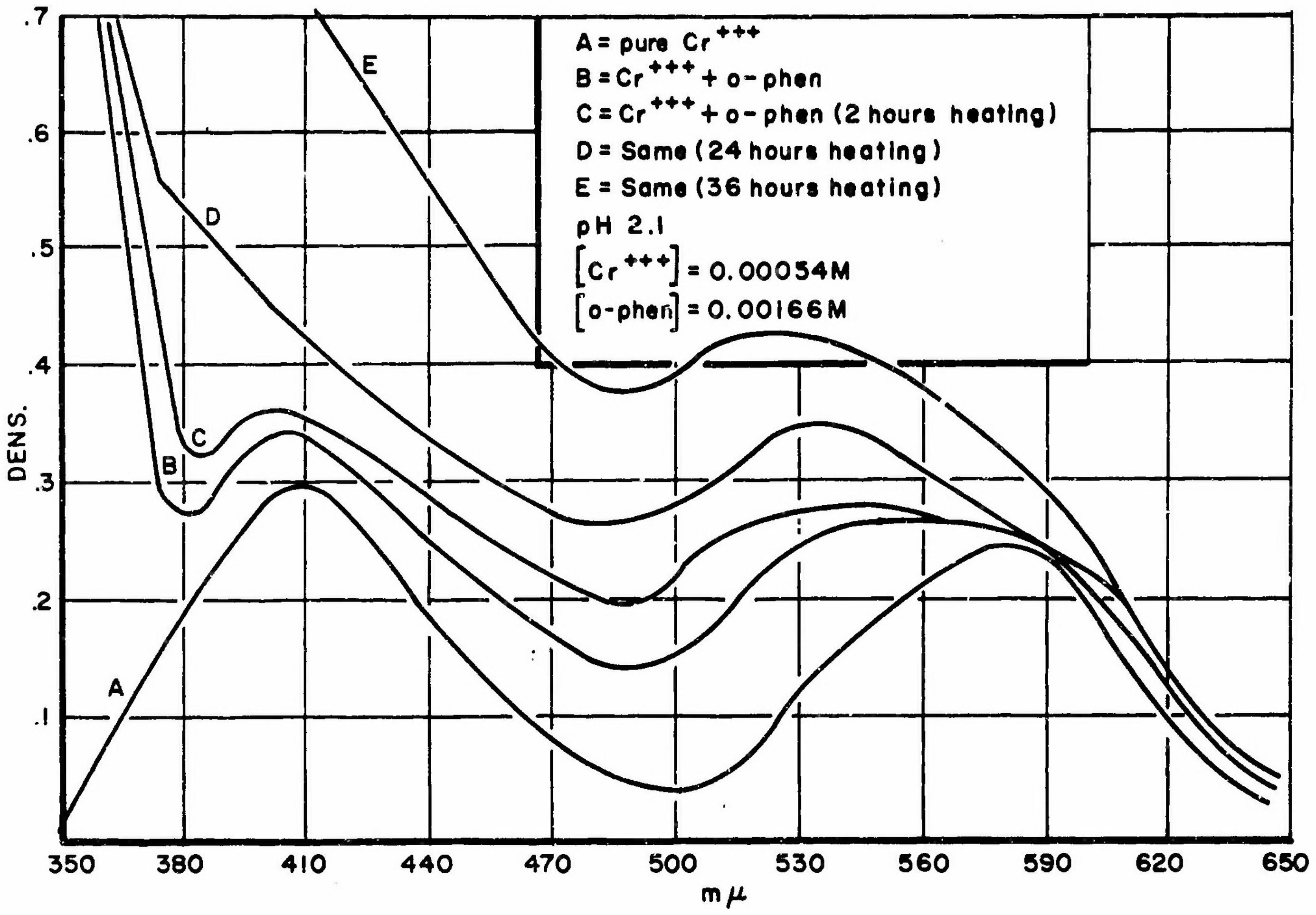


Figure 2. Visible Absorption Spectra of a Cr(III) o-Phenanthroline Mixture Heated at 100°C

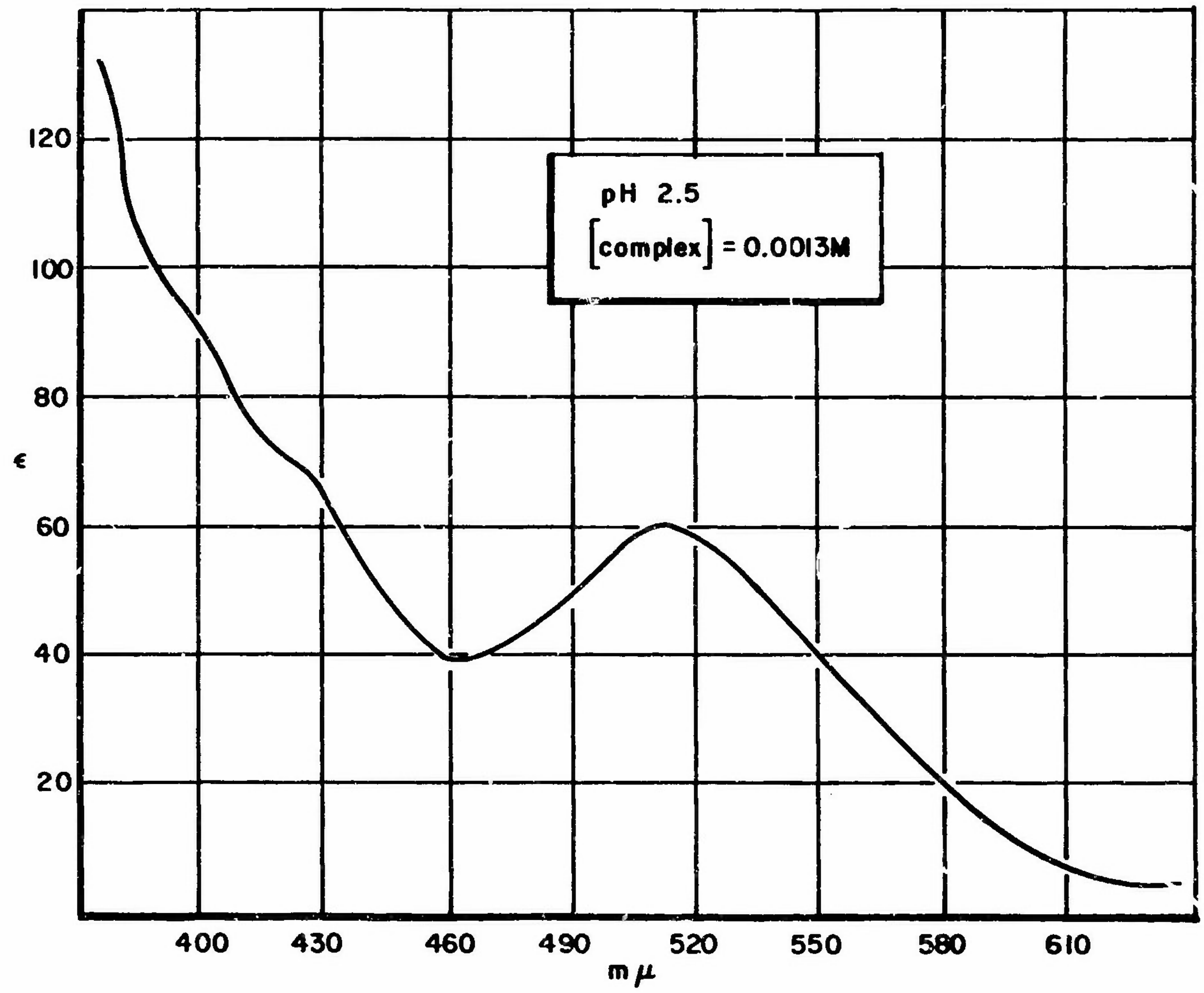


Figure 3. Visible Absorption Spectra of Thermally Prepared Complex After Separation (5 cm Cell)

a good indication as to the magnitude of the "d" orbital splitting by the ligand. Using these absorption maxima, the 10 Dq energy can be calculated:

Complex	λ (maximum) Å	Dq
Cr(III) $(H_2O)_6$	5800	17,300 cm^{-1} (1)
Cr(III) (o-phen) $(H_2O)_4$	5150	19,400 cm^{-1} (2)

The difference between (2) and (1) is 2100 cm^{-1} or corresponding to an increase in the 10 Dq value for the mono-o-phen complex compared with the hexaquo complex of 210 cm^{-1} or 600 cal/mole (Reference 55). Due to solvent ion interaction, the absorption is not as sharp as the atomic spectra of gaseous ions. The wavelength of maximum absorption, however, does coincide with the value which would be obtained in the absence of these interactions (Reference 56).

The isolated complex was then run in the ultraviolet region, the resultant spectra compared with that of the pure ligand, all at pH 2.5 as shown in Figure 4. It can be seen that the 218 mμ ligand peak is shifted to 223 mμ, and the 270 mμ band shifted to 275 mμ. Of interest is the absorption intensity change of the 270 mμ peak. The intensity of this $\pi \longrightarrow \pi^*$ transition in the ring structure of o-phenanthroline is probably due to the increased stability given the ligand when bonded to the heavy metal ion. The 218 mμ band also shows this decrease in intensity. Other o-phenanthroline complexes, showing the ligand shifts are (Reference 53):

Complex	Solvent/pH	λ(maximum) m	log ϵ
Fe(III) (o-phen) $(H_2O)_4$	H_2O	274	4.73
Zn(II) (o-phen)	4.5	270	3.99
Cd(II) (o-phen)	5.84	227	4.5
		267	4.8

3. Cr(III) (o-PHEN) MADE BY Cr(II) CATALYSIS

Using the complex synthesized by the Cr(II) catalysis method, similar spectra were reproduced in all cases. Figure 5 shows the visible spectra of Cr(III) o-phen mixture after Cr(II) addition. The 525 to 530 m μ absorption band is clearly visible, as in the presence of excess chromium (III). In these runs, only small amounts of reactants were used. The reaction is extremely rapid, going from violet to cherry-red as soon as the Cr(II) is added. After column separation, the visible and ultraviolet spectra of the monocomplex produced by both methods are similar.

4. PORTION OF INFRARED SPECTRA OF Cr(III) $(o\text{-}PHEN)_2$

Figure 6 shows a selected portion of the infrared spectra of the bis complex produced by the heating method. The 3700 to 3100 cm^{-1} region shows a slight shift in the N-H stretching vibrations, however, complicated by the presence of -OH bands in the pure ligand. This N-H shift could correspond to a N-metal stretch (Reference 57), but cannot be taken as definite N-Cr bond formation.

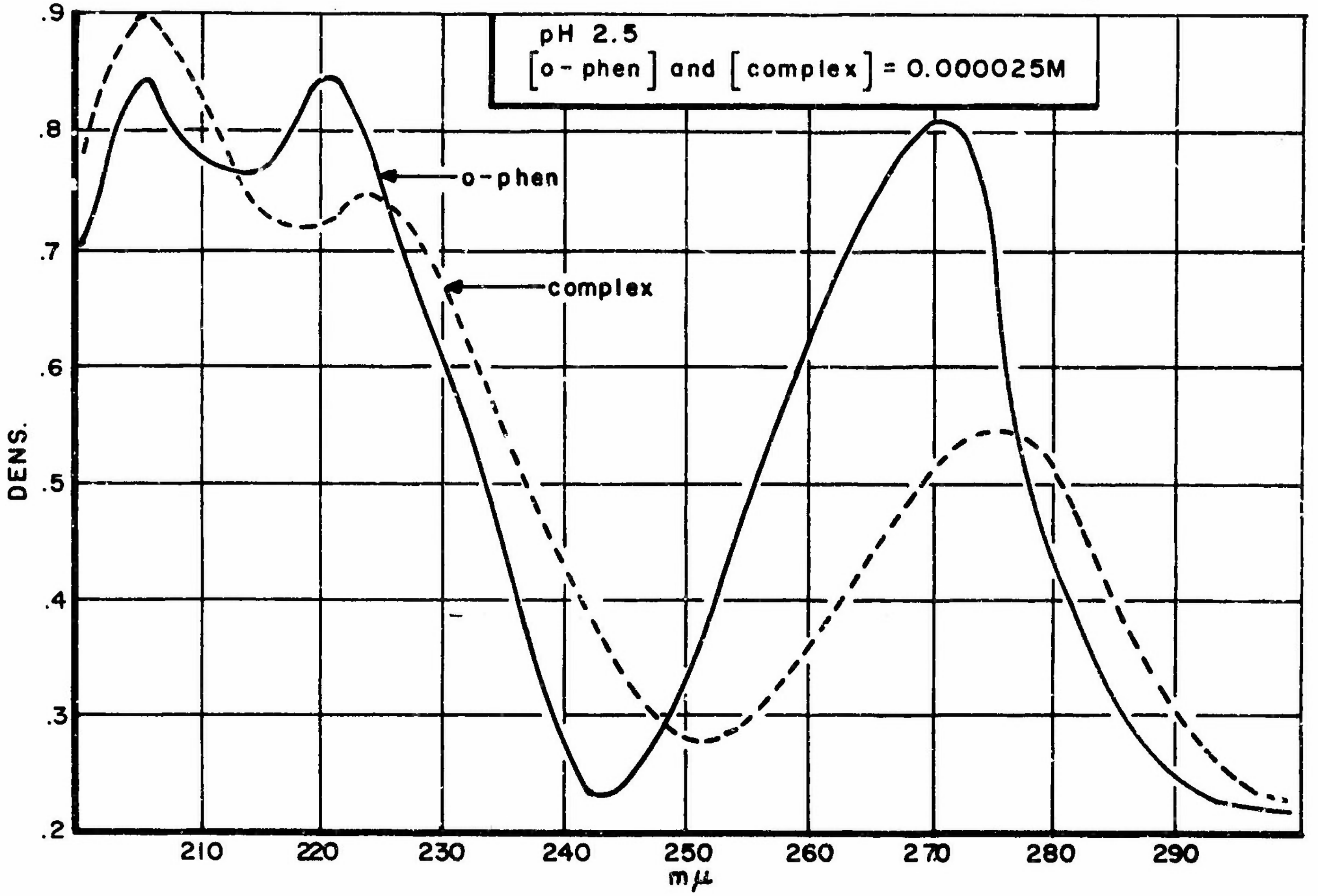


Figure 4. Ultraviolet Absorption Spectra of Complex After Separation Compared With Pure Ligand (1 cm Cell)

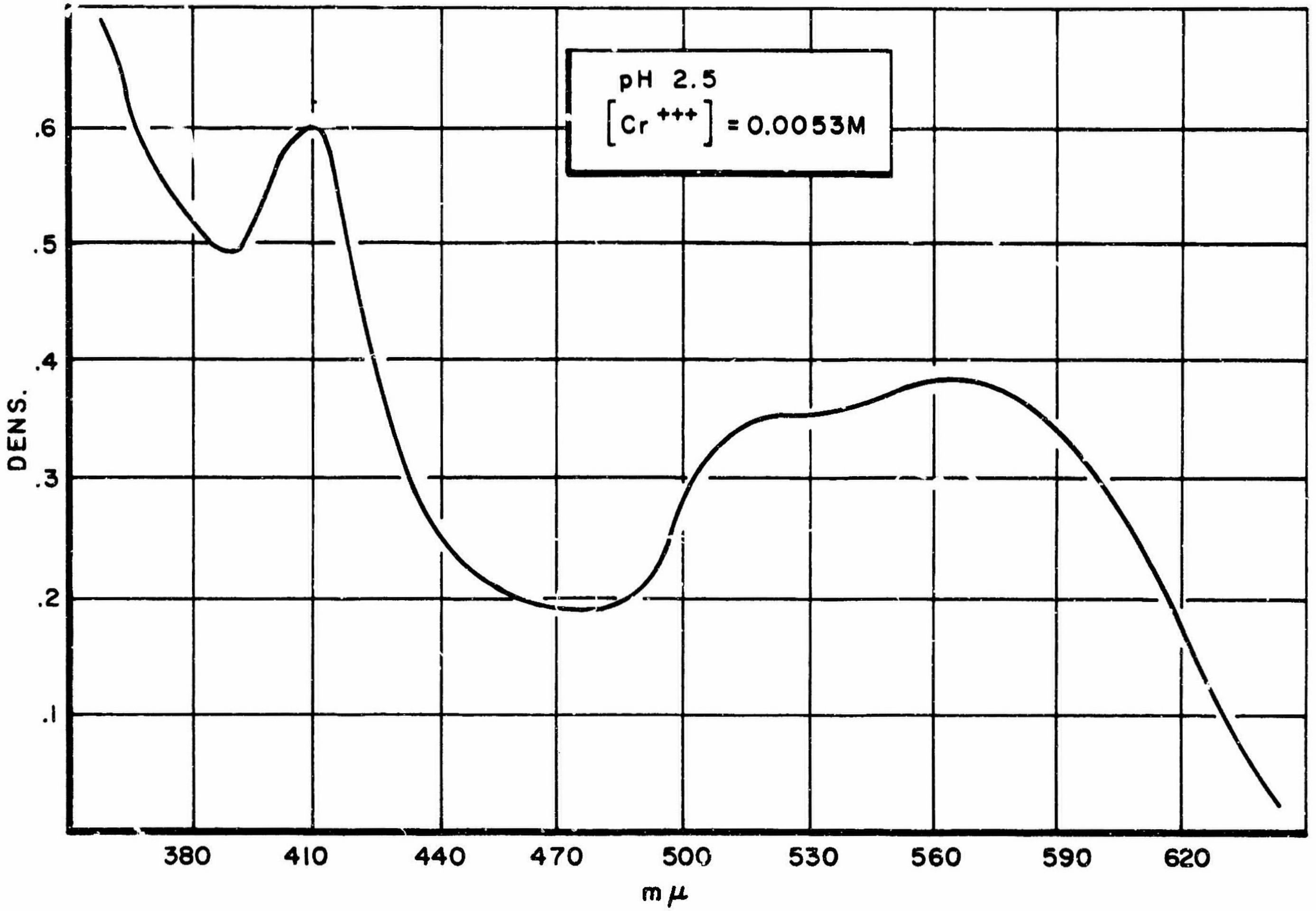


Figure 5. Visible Absorption Spectra of Cr(III) o-Phenanthroline Mixture After Cr(II) Addition (1 cm Cell)

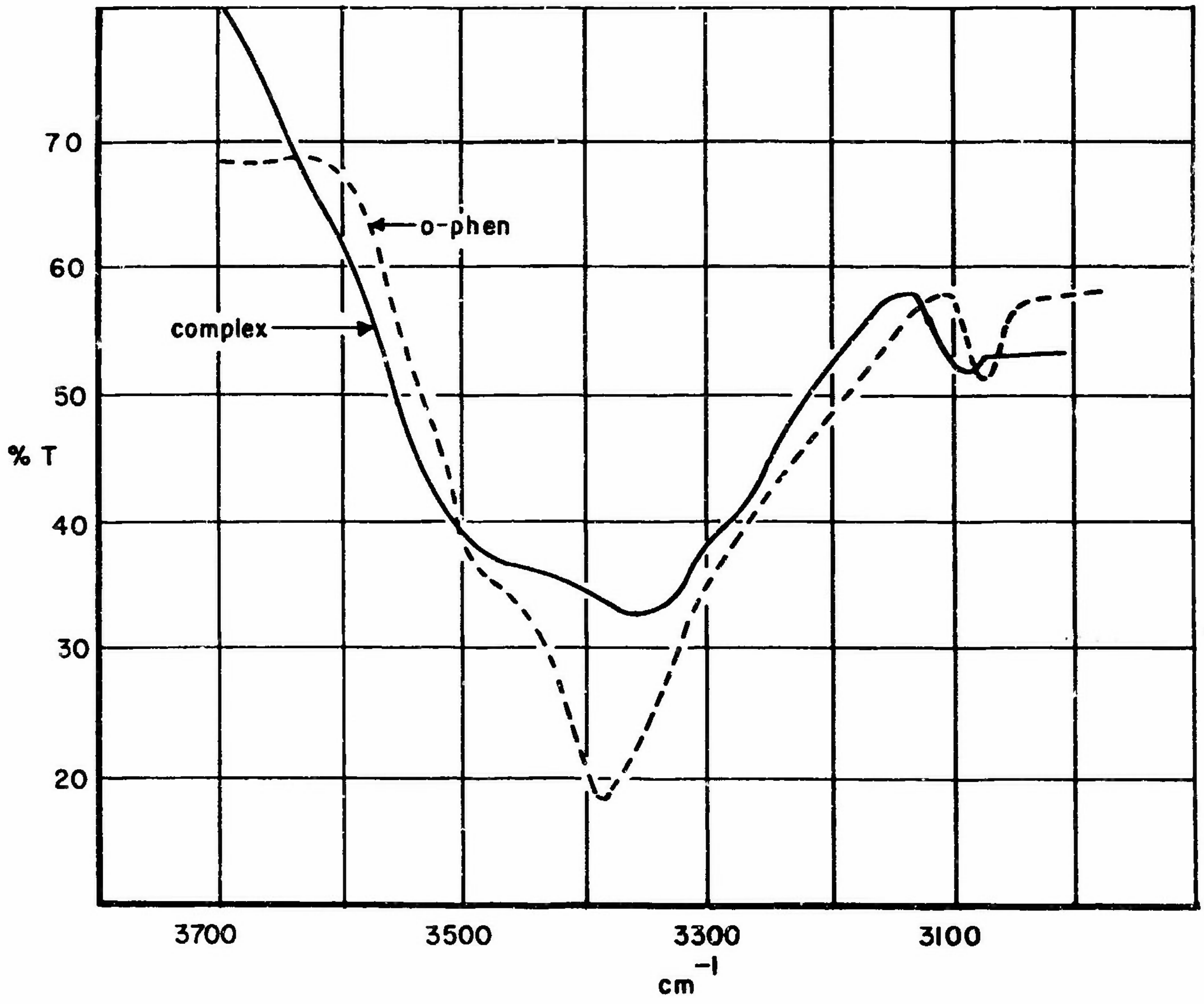


Figure 6. Portion of Infrared Spectra of bis Cr(III) o-Phenanthroline Perchlorate

5. POLAROGRAPHIC ANALYSIS OF COMPLEX PRODUCED BY HEATING AND CATALYSIS

Isolated complex solutions were subjected to polarographic reductions. The efficiency of the ion-exchange technique for the separation of the uncomplexed Cr(III) was noted as the polarogram showed little, if any, excess Cr(III) except that for the occurrence of normal equilibrium. Figure 7 shows a polarogram of a 1.0 ± 0.2 mM monocomplex at pH 3.70. The small wave at about -0.81v is the occurrence of unreacted Cr(III) or normal equilibrium (Reference 1). The large reduction at about -1.1v is the reduction of the Cr(III) complex. The conditions used for these determinations were: 25° ± 0.1°C, N_2 atmosphere, 0.1 M $NaClO_4$, 0.002% gelatin with no buffers. 1.0 ± 0.2m M solutions of Cr(III) $(H_2O)_6$ were reduced prior to reduction of the mono-o-phenanthroline complex in media of varying pH, with results that closely follow those of Walsh and Earley (Reference 1).

Figure 8, a Tomes plot ($E_{d.e.}$ vs $\log i/i_d-i$) of the complex produced by both methods shows some diversion from reversibility ($\theta = 1.19$ for both plots). The difference in $\epsilon_{1/2}$ values for the plots ($E_{d.e.}$ where plot passes through $\log i/i_d-i = 0$) are due to the pH differences in the solutions. The complex produced by catalysis being reduced at pH 3.70, that of the complex produced by heating being run at 2.5. This follows the finding of Pecsok and Lingane (Reference 35). These $E_{1/2}$ values are -1.14v and -1.11v vs S.C.E. for the catalytically prepared and the thermally prepared complex, respectively.

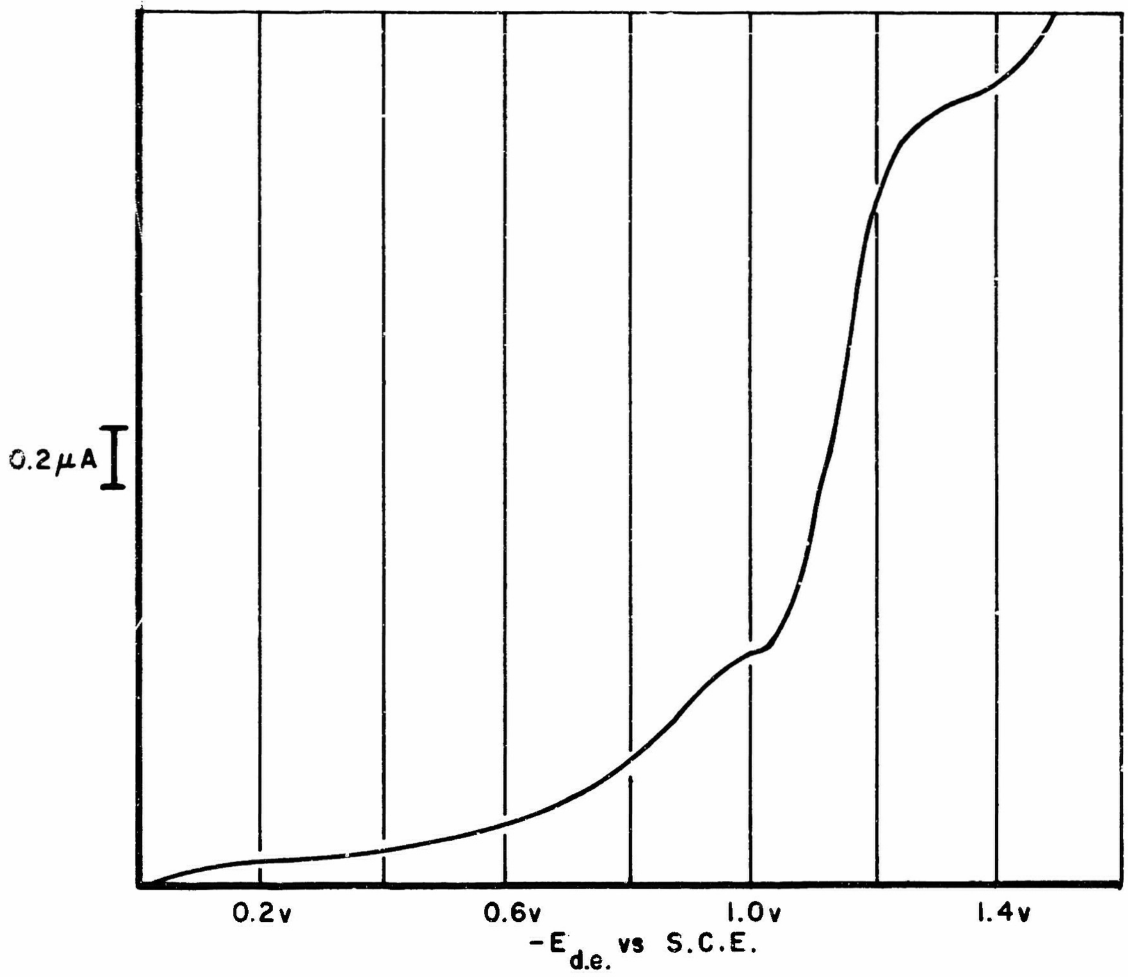


Figure 7. Polarogram of a 1.0 ± 0.2 mM Monocomplex at pH 3.70

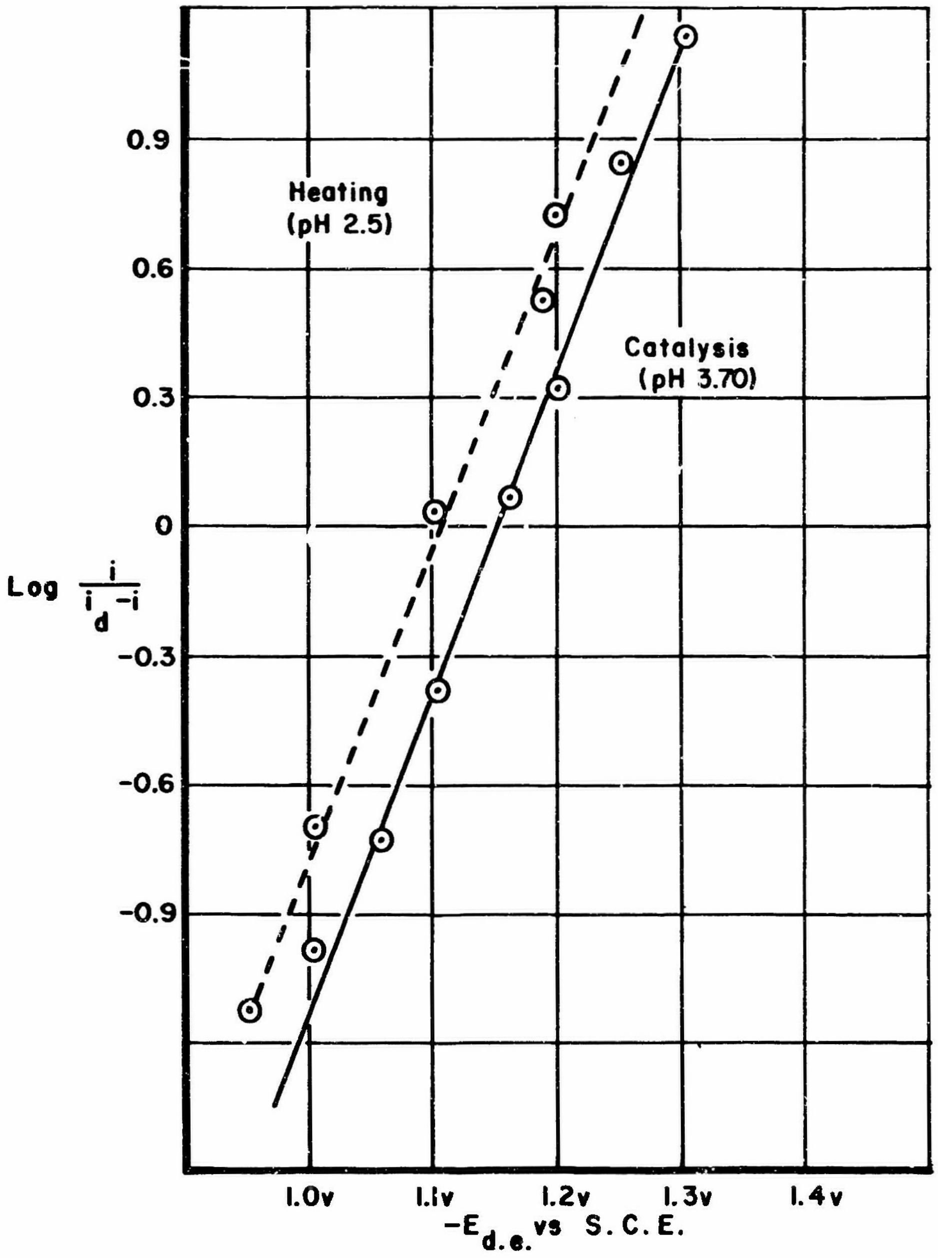


Figure 8. Tomes Plot of the Complex Produced by Heating and Catalysis

SECTION IV

CONCLUSION

The results of this investigation suggest that there is a relationship, although complex, between those factors which favor Cr(III) complex synthesis by Cr(II) catalysis, and those which favor reduction of the Cr(III) complex at negative potentials, similar to those findings of Walsh and Earley (Reference 1).

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13. ABSTRACT

The mono-o-phenanthroline chromium (III) perchlorate complex is prepared by two separate methods, (1) direct addition of the base to the metal ion in acid solution and heating, and (2) the use of Cr(II) to catalyze the reaction. The desired complex is then isolated by ion-exchange methods, and determined by spectrophotometric and elemental microanalytical procedures. Polarographic information is also given.

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