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METAL COMPLEXES OF ETHYLENETETRATHIOGLYCOLLIC ACID AND RELATED LIGANDS

A Thesis
submitted to the University of Warwick
for the Degree of Doctor of Philosophy

by
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CONTAINS PULLOUTS

PREFACE

The work described in this thesis was carried out during my employment as a Research Assistant in the Department of Chemistry and Metallurgy at the Lanchester College of Technology, Coventry, between November, 1965 and July, 1968. The work is original, except where otherwise indicated in the thesis, and no part of it has been submitted for a degree to any other University.

I would like to express my great appreciation to Dr. W. J. Geary, now of the Sheffield College of Technology, who supervised this work and provided very much help and encouragement. I am also grateful to Professor T. C. Waddington of the University of Warwick for a number of helpful discussions.

I would like to thank the University of Warwick for the use of the Cary Model 14 Spectrophotometer.

Finally, I would like to thank Miss Patricia Baughen for her patience and efficiency in the typing of this thesis.

ABSTRACT

The purpose of this work has been primarily the investigation of the complexes formed by ethylenetetrathioglycollic acid with Co(II), Ni(II), Cu(II) and Zn(II). This ligand has some similarities to the much-studied ethylenediaminetetraacetic acid. The complexes of ethylenetetrathioglycollic acid have been studied as the solid complexes and as the complexes formed in aqueous solution. The solid complexes as prepared have metal to ligand ratio 2 : 1 and contain bound water molecules, the number being variable but never less than two. The magnetic susceptibilities and electronic spectra of the complexes of Co(II), Ni(II) and Cu(II) have been found to be consistent with an octahedral arrangement of donor atoms about the central metal ion. The infrared spectra of the solid complexes indicated that the bonding of the carboxyl group is primarily ionic. Some preliminary studies have been done on the solid complexes of several other sulfidecarboxylic acids related to ethylenetetrathioglycollic acid.

The nature of the complexes in solution has been studied through the electronic absorption spectra and through the measurement of stability constants. The spectra of the complexes of Ni(II) and Cu(II) indicated that these complexes are octahedral. The absorption maxima occurred at slightly lower energies than those observed for the corresponding hexaquo ions, and it is suggested that ethylenetetrathioglycollic acid should be located just above water in the spectrochemical series. The spectrum of the complex of Co(II) has not been studied since the complex was found to decompose in aqueous solution above pH 4. Quantitative work has been started to determine the stability constants of the complexes formed in solution. As the first step in this direction, the acid dissociation constants of the ligand have been obtained. A least squares adjustment of potentiometric data derived from the usual pH-titration curves has given the following values: pK_{1a} 2.89, pK_{2a} 3.54, pK_{3a} 3.958, and pK_{4a} 4.572. The stability constants of the metal complexes have been sought using potentiometric and spectrophotometric techniques. A computer program has been written for the least squares adjustment of the potentiometric data, taking into account, in addition to the formation of a simple 1 : 1 complex, the formation of a binuclear complex and various protonated complexes.

As yet this program has not given a reasonable set of stability constants. From the spectrophotometric measurements the value of log β_{11} for the nickel complex was found to be 4.17, and for the copper complex 5.72. Stability constants were also found for the equilibria with the protonated ligand as in

$$B + HA \rightleftharpoons BHA$$

the value of log β'_{111} being for ~~the~~ nickel ~~being~~ 2.9 and for ~~the~~ copper 3.4. Evidence has also been found for the formation of at least one more complex, which is considerably less stable than the simple 1 : 1 complex and is probably a binuclear complex.

In general, the studies on the nickel and the copper complexes of ethylenetetrathioglycollic acid have indicated that a group of closely related, weak complexes are formed. This is in contrast to ethylenediaminetetraacetic acid which forms very stable, simple 1 : 1 complexes with these metals.

Most of the experimental data is compiled in Appendix A. The computer programs developed and used are given in Appendix B.

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Tables in Appendix A. (When tables referred to are in Appendix A this is always stated).

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LIST OF MAIN SYMBOLS AND DEFINITIONS

In general, the nomenclature is the same as that used by Rossotti and Rossotti (36). Charges are usually omitted for clarity.

A	total concentration of ligand A
A_s	optical absorbancy
a	concentration of free A
B	total concentration of central group B
b	concentration of free B
c	number of ligands in a particular complex BA_c
H	total concentration of dissociable hydrogen ions
h	concentration of free hydrogen ions
j	number of protons bound to A
J	maximum number of dissociable protons in the ligand H_JA
N	maximum value of n
$\bar{n}$	average number of ligands A bound to one central group
$\bar{n}_H$	average number of protons bound to each group A which is not bound to B
$\bar{n}_A$	average number of protons bound to A
α_c	fraction of B in the form BA_c
α_c^H	fraction A which is not bound to B in the form H_cA
μ	ionic strength
var (χ)	variance of χ = (standard deviation of $\chi)^2$
ETTA	ethylenetetrathioglycollic acid
EDTA	ethylenediaminetetraacetic acid
PDTA	thioglycollic acid derivative of terephthaldehyde, phenylene-1,6-dimethylidynetetrathioglycollic acid
BBTA	thioglycollic acid derivative of benzaldehyde, benzylbisthioglycollic acid

For the equilibrium

$$B + nA \rightleftharpoons BA_n$$

the thermodynamic, over-all stability constant is defined to be

$$^{T}\beta_n = \{BA_n\} / \{B\} \{A\}^n$$

where $\{BA_n\}$, $\{B\}$ and $\{A\}$ are the activities of BA_n, B and A respectively.

The step stability constant, $^{T}K_n$, is the activity quotient for the equilibrium

$$BA_{n-1} + A \rightleftharpoons BA_n$$

That is, $^{T}K_n = \{BA_n\} / \{BA_{n-1}\} \{A\}$

Hence, the over-all and step stability constants are related by the relation

$$^{T}\beta_n = {}^{T}K_1 \, {}^{T}K_2 \ldots\ldots {}^{T}K_n$$

It is usually possible to keep the activity coefficients of the different species in equilibrium constant by the addition of an excess of a suitable electrolyte. In this work the activity coefficients were kept constant within experimental error by making the solutions .1 M in $NaClO_4$. Perchlorate ions form complexes with metal ions only very weakly, if at all, and no consideration has been given to the formation of any perchlorate complexes. When the activity coefficients are held constant, it is possible to define the stoichiometric stability constants.

$$\beta_n = \frac{[BA_n]}{[B][A]^n} \quad \text{and} \quad K_n = \frac{[BA_n]}{[BA_{n-1}][A]}$$

where the terms in square brackets are concentrations. All stability constants referred to in this work are stoichiometric stability constants. Where stability constants reported by other authors are quoted, indication will be given of the conditions of the medium in which these constants were determined.

Stability constants referring to proton equilibria are denoted using a superscript H. Thus, for the equilibrium

$$jH + A \rightleftharpoons H_jA$$

$$\beta^H_j = \frac{[H_jA]}{[H]^j [A]} \quad \text{and} \quad K^H_j = \frac{[H_jA]}{[H_{j-1}A][H]}$$

For the formation of mixed complexes as in

$$m\,B + q\,H + p\,A \rightleftharpoons B_m\,H_q\,A_p$$

the stoichiometric stability constant is defined to be

$$\beta_{mqp} = \frac{[B_m\,H_q\,A_p]}{[B]^m\,[H]^q\,[A]^p}$$

Or, for the related equilibrium

$$m\,B + H_q\,A_p \rightleftharpoons B_m\,H_q\,A_p$$

$$\beta'_{mqp} = \frac{[B_m\,H_q\,A_p]}{[B]^m\,[H_q\,A_p]}$$

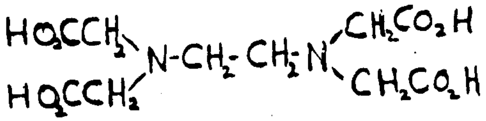
Finally, if $q = o$

$$\beta_{mp} = \frac{[B_m\,A_p]}{[B]^m\,[A]^p}$$

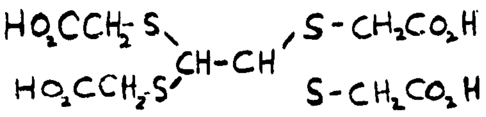
1. INTRODUCTION

1.1 The problem and the aims of the investigation

The purpose of this work was to study the metal complexes of sulfide-carboxylic acids both in aqueous solution and as the solid complexes. The aminocarboxylic acids have been the subject of very much research, and in particular ethylenediaminetetraacetic acid*(I) has proved to be one of the most remarkable ligands yet discovered (1). It has been found to form stable complexes with nearly all the metals in the periodic table, and these almost invariably have metal: ligand ratio 1 : 1. The metal complexes of EDTA have come to have many important analytical and commercial applications. In the light of the results of the researches on the metal complexes of EDTA and related aminocarboxylic acids, it was thought that the investigation of the complexes of the sulfide-carboxylic acids, in particular of ethylenetetrathioglycollic acid**(II) would be of interest.



I



II

EDTA and ETTA each has four carboxyl oxygen atoms which are potential donors to metal ions, but while EDTA has two tercovalent nitrogen atoms in addition to the carboxyl oxygens, ETTA has four bicovalent sulfurs. The difference in the stereochemistry of these atoms as well as the difference in the election donating and acceptor properties of sulfur and nitrogen would be expected to be reflected in different structures and stabilities of the metal complexes of these two compounds. As a ligand containing sulfur as a potential donor atom ETTA, unlike many other sulfur compounds, has the advantages of being fairly water soluble (about 2 x 10^{-3} M at pH 2) and of being stable in aqueous solution for at least one month.

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* Hereafter referred to as EDTA.

** Hereafter referred to as ETTA.

At the outset it was intended to study, in a series of metal complexes of related sulfide-acids, the effects of changing the ring size and the effects of changing the basicity of the sulfur through introducing different substituents, and the effects of the size of substituent groups on the stability and nature of the complexes. The investigation of ETTA itself, however, proved to be more complicated than originally anticipated, with the result that almost the entire investigation has been confined to the metal complexes of ETTA. Only a very few preliminary investigations have been carried out with some related aromatic sulfide-acids.

The metals used in the study of complexes of ETTA and the few related acids mentioned above, were Co (II), Ni (II), Cu (II) and Zn (II). In selecting metal ions that may be expected to show a strong affinity for a sulfur donor ligand, the classification of metals which has been made into class (a) and class (b) is a convenient guide (2). Class (a) metals form their most stable complexes with the first ligand atom of each group in the periodic table and class (b) with the second or subsequent ligand atoms. On this basis Ag (I) and Hg (II) would be selected as metals showing strong class (b) behavior and likely to form stable complexes with sulfur-containing ligands. However, since both of these metals were found to give complexes which were very insoluble in water and in 50 : 50 water-dioxan, they were not studied any further. The metals Co (II), Ni (II), Cu (II) and Zn (II) are usually considered in the border region of class (a) and class (b) behavior. They were found to give water soluble complexes with ETTA, and have been used throughout this work.

The nature of the complexes of ETTA in aqueous solution has been studied through the measurement of stability constants and of the near infrared and visible spectra. The two experimental techniques used in the determination of stability constants have been potentiometry and spectrophotometry. In the potentiometric method the usual pH - titration curves were obtained. These curves give the free hydrogen ion concentration in a solution containing metal ions and ligand as a function of the total dissociable hydrogen ion concentration. The basis of this method is the competitive reaction between hydrogen ions and metal ions for the ligand. In order to evaluate the stability constant of the metal complexes, the stability constants for the complexes of the hydrogen ion with the ligand, i.e. the acid dissociation constants, must be known. These were obtained from the pH - titration curve of the ligand.

The potentiometric method has a number of features which recommend it for use in the determination of stability constants in systems where the ligands are conjugate bases of weak acids. The free hydrogen ion concentration can be measured with good accuracy with currently available pH meters, the experimental set-up is simple, the amount of reagents required is less than for most other methods and ionic strength and temperature may be easily controlled. Furthermore, complex formation over a wide range of free ligand concentration can be studied. One limitation of the potentiometric method is that it depends upon the metal ions being able to compete effectively with protons for the ligand. If this condition does not apply there is little difference between the pH-titration curve for the ligand alone and the pH-titration curve for the ligand plus metal ions, and the accurate evaluation of the stability constant becomes difficult or impossible by this method. Since preliminary pH-titrations indicated the stability constants of the metal complexes were not large relative to the proton stability constants, it was decided to investigate other methods of determining the stability constants in addition to the potentiometric method. Ion exchange methods have been used to study the metal complexes of some carboxylic acids (3). Some experiments were done with the Co(II)- ETTA system at pH 7 by this technique; however, the results were anomalous, and the use of this method was not continued. The final technique used was spectrophotometry. The quantity measured is the absorbance of the solution and this depends upon both the concentration and the characteristic extinction coefficient of each absorbing species. The main approach used in the spectrophotometric studies was the measurement of absorbance as a function of pH for a solution of fixed total metal and total ligand concentrations. It was expected that the nature and concentration of the absorbing species would vary with the pH of the solution and could be related to the stability constants for the various equilibria.

Having measured the stability constants it was intended to correlate the magnitude of the constants to properties both of the central metal ion and of the ligand. The ionic charge and radius, and the ionization potential and electronegativity of the metal ion affect the stability of the metal complexes. Properties of the ligand that are factors in determining the magnitude of stability constants include the basic strength of the donor atoms, chelating properties, and steric effects.

Information concerning the metal-ligand bonding can be gained by spectrophotometric measurements as well as from stability constant measurements. The spectroscopic splitting parameter, Δ , as given by the frequency of the lowest ligand field absorption band, is related to electrostatic attractions, the effect of lone pairs on the ligand, and the metal to ligand and ligand to metal bonding (6). Since the position of sulfur ligands in the spectrochemical series, a series of ligands arranged according to Δ , is not certain at present (7), it was thought that it would be of value to try to determine the splitting parameter in complexes of ETTA.

In addition to the solution studies some investigations have been carried out on the solid complexes of ETTA and a few related ligands with Co(II), Ni(II), Cu(II), and Zn(II). It was intended to compare observations on the solid complexes with the corresponding metal complexes in solution. Elemental analyses have been carried out on the solid complexes, and measurements of the visible and IR spectra and of the magnetic susceptibility have been made in order to assist in determining the structure of the solid complexes.

1.2 General survey of work on related ligands

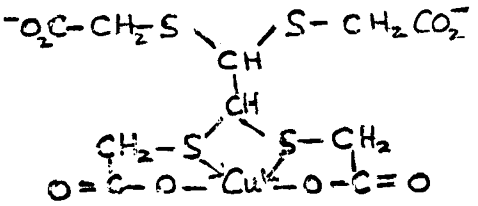
The cupric complexes of ETTA were investigated in 1961 by Saini and co-workers (19). The four acid dissociation constants and the stability constants of the copper (II) complexes were determined from potentiometric data by a method of successive approximations. The data for the cupric - ETTA system were interpreted in terms of the complexes CuH_3A^+, CuH_2A, $CuHA^-$, CuA^{2-} and Cu_2A. The stability constants reported are given in Table I.

TABLE I. Stability Constants for Cu(II) - ETTA
(μ = .1 t = 20°C)

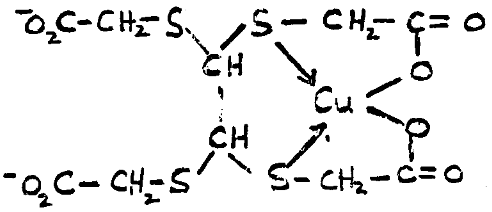
Equilibria	log of the stability constant
$Cu^{2+} + H_3A^- \rightleftharpoons CuH_3A^+$	2.64
$Cu^{2+} + H_2A^{2-} \rightleftharpoons CuH_2A$	3.24
$Cu^{2+} + HA^{3-} \rightleftharpoons CuHA^-$	4.08
$Cu^{2+} + A^{4-} \rightleftharpoons CuA^{2-}$	5.00
$Cu^{2+} + CuA^{2-} \rightleftharpoons Cu_2A$	2.33

The acid dissociation constants were reported to be $pK_1 = 3.24$, $pK_2 = 3.56$, $pK_3 = 3.99$ and $pK_4 = 4.93$.

Although no suggestions were made for the structure of the protonated complexes, the following structures were suggested for CuA^{2-}:



III

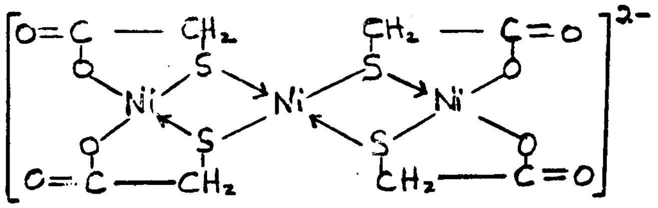


IV

It was suggested that both configurations III and IV would coexist in solution, although III, which has a 4-membered ring, would be expected to be less stable than IV, which has 5-membered rings. The authors suggested that the stability constant of CuA^{2-} is more than twice that for methylenebis (thioglycollic) acid but less than twice that of ethylenebis (thioglycollic) acid because of the presence in solution of both types of complexes, III and IV, the one containing a chelate ring like that formed by methylenebis (thioglycollic) acid, the other containing chelate rings like those formed by ethylenebis (thioglycollic) acid.

ETTA was considered as an analytical reagent for Cu(II) by Longo and co-workers (24). A spectrophotometric analysis at 365 mμ gave accuracy in copper determination of 0.3%. Iron (III) was found to be precipitated quantitatively by ETTA below pH6.

In Table II (overleaf) are compiled some stability constants for oxy-, sulfide- and aminocarboxylic acids. It is apparent that the simple acids, thioglycollic acid and glycine, form different types of complexes. Glycine forms complexes with metal to ligand ratios of 1 : 1 and 1 : 2 while thioglycollic acid forms a series of polynuclear complexes. Although in complexes of the sulfide-acids, one sulfur atom can hardly be visualized as bonding to two different metal atoms* and so leading to the formation of polynuclear complexes in the way thioglycollic acid does, the same type of 5-membered ring as is suggested for complexes of thioglycollic acid might be expected in complexes of the sulfide acids. The type of structure suggested for Ni(II)- thioglycollic acid is shown below (21):



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* This applies to the complexes in solution as distinct from solid complexes.

TABLE II. Stability constants of metal complexes of ligands related to ETTA.

Ligand	Metal	Log of the Stability const.		Ref.
$HSCH_2COOH$	H^+	K_1^H 10.203	K_2^H 3.516	21
μ = .1	Ni^{2+}	β_{12} 13.01	β_{13} 14.99	21
20°		β_{23} 22.68	β_{34} 33.27	
		β_{46} 49.85		
	Zn^{2+}	β_1 7.80	β_{12} 14.96	21
		β_{13} 17.80	β_{23} 25.20	
H_2NCH_2COOH	H^+	K_1^H 4.7796	K_2^H 2.3503	25
correc. for	Co^{2+}	K_1 5.23	K_2 4.02	28
$\mu \longrightarrow 0$	Cu^{2+}	K_1 8.62	K_2 6.97	28
25°	Ni^{2+}	K_1 5.52	K_2 4.44	28
$CH_3CH_2SCH_2COOH$	H^+	K_1^H 5.56		10
50% dioxan	Co^{2+}	K_1 3.06		10
30°	Cu^{2+}	K_1 4.55	K_2 3.60	10
$\mu = 1$ 20°	Cu^{2+}	K_1 2.56		16
$CH_3CH_2OCH_2CO_2H$	Cu^{2+}	K_1 1.79	β_2 2.87	16
μ = 1		β_3 3.20	β_4 2.8	
20°				
$S(CH_2CO_2H)_2$	H^+	K_1^H 4.35	K_2^H 3.30	23
μ = .1				
20°	Cu^{2+}	K_1 4.57		23
		$K(Cu + HA \rightleftharpoons CuHA)$	3.18	
	Ni^{2+}	K_1 4.1	K_2 2.6	15
$O(CH_2CO_2H)_2$	H^+	K_1^H 4.03	K_2^H 2.90	30
μ = .1	Co^{2+}	K_1 2.7		30
30°	Cu^{2+}	K_1 3.9		30
	Ni^{2+}	K_1 2.8		30

TABLE II (Cont'd...)

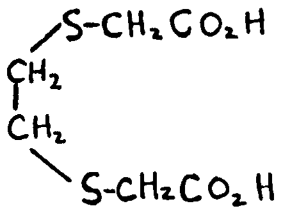
Ligand	Metal	Log of the Stability const.		Ref.
$HN(CH_2CO_2H)_2$	H^+	K_1^H 9.12	K_2^H 2.54	31
μ = .1	Co^{2+}	K_1 6.95	K_2 5.34	31
30°	Cu^{2+}	K_1 10.55	K_2 5.65	31
	Ni^{2+}	K_1 8.26	K_2 6.35	31
$(CH_2)_2$-$(SCH_2CO_2H)_2$	H^+	K_1^H 4.21	K_2^H 3.39	18
	Cu^{2+}	K_1 5.66		18
μ = .1		$K(Cu + HA \rightleftharpoons CuHA)$	3.98	18
25°	Ni^{2+}	K_1 4.5		11
$(CH_2)_2$-$(NHCH_2COOH)_2$	H^+	K_1^H 9.46	K_2^H 6.42	26
	Cu^{2+}	K_1 16.2		26
μ = .1	Ni^{2+}	K_1 13.5		26
30°				
$CH_2(SCH_2CH_2CO_2H)_2$	H^+	K_1^H 4.08	K_2^H 4.86	18
μ = .1	Cu^{2+}	K_1 2.06		18
20°		$K(Cu + HA \rightleftharpoons CuHA)$	1.38	18
$(CH_2)_2$-$(NHCH_2CH_2CO_2H)_2$	H^+	K_1^H 9.98	K_2^H 6.69	27
	Cu^{2+}	K_1 15.2		27
μ = .1	Ni^{2+}	K_1 12.2		27
20°				
EDTA	H^+	K_1^H 10.26	K_2^H 6.16	32
μ = .1		K_3^H 2.67	K_4^H 1.99	
20°	Cu^{2+}	K_1 18.79		32
		$K(Cu + HA \rightleftharpoons CuHA)$	11.54	32
	Ni^{2+}	K_1 18.62		32
ETTA*	H^+	K_1^H 4.93	K_2^H 3.99	19
μ = .1		K_3^H 3.56	K_4^H 3.24	
20°				
	Cu^{2+}	K_1 5.00		
		$K(Cu + HA \rightleftharpoons CuHA)$	4.08	19

* See also Table I for stability constants of other protonated complexes of ETTA and Cu(II).

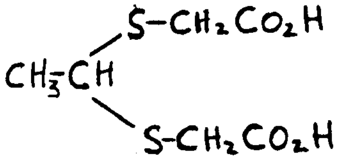
Sandell has measured the stability constants of cupric complexes of some oxy- and sulfide-carboxylic acids and from his results concluded that the sulfur atom bonds to the cupric ion in the sulfide-acids(16).The stability constants determined for cupric complexes of S-ethylthioglycollic acid and of ethoxyacetic acid reported by Sandell are given in Table II. Since the constants for the cupric complexes with the thio-derivative were generally larger than those for the oxy-derivative, this was taken to indicate that the sulfur atom was bound to the metal ion in the thio-derivative. Further evidence for the sulfur acting as a donor atom in sulfide-carboxylic acid has been reported from studies of metal complexes of a series of related imino- and sulfidedicarboxylic acids (15). A linear relationship was found between the value of the average of pK_1 plus pK_2 and log K_1 for a given metal ion. This relationship was taken as an indication of the ability of the ligand to combine with two protons compared to one metal ion. Since the log K_1 value for dithioglycollic acid fell on the same line as for the other dibasic imino-acids (presumably known to have nitrogen donation), and not below it, it was assumed that sulfur must be donating.

The last 6 entries in Table II indicate that the sulfide-carboxylic acids are considerably stronger acids than the corresponding amino-carboxylic acids, and accordingly that their metal complexes are weaker.

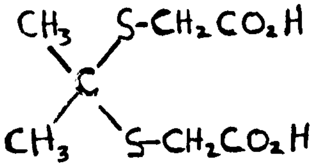
Although stability constants for a large number of sulfide-carboxylic acids have been measured, very little has been reported on the solid complexes. The Co(II), Ni(II) and Zn(II) complexes of ethylenebis (thioglycollic) acid (V), ethane - 1,1 - bis(thioglycollic) acid (VI), and isopropane -1,1 - bis(thioglycollic) acid (VII) have been prepared by Bradford (9).



V



VI



VII

The metal to ligand ratio in these complexes was found to be 1 : 1, although analytical data from elemental analysis were not sufficiently accurate to allow determination of the number of water molecules bound per complex.

The only other solid complexes related to the complexes studied in this work that have been prepared are the complexes of EDTA itself. The crystal structure of Na[Co EDTA] $4H_2O$ and of H [Ni (H_2O) HEDTA] have been determined (33,34). In the complex anion, $[\text{Co EDTA}]^-$, EDTA functions as a hexadentate ligand. A girdle of three strongly folded, quite strained rings surround the central metal ion, and at right angles to these rings and to each other are two less strained rings. In $[\text{Ni}\ (H_2O)\ \text{H EDTA}]^-$, EDTA functions as a pentadentate ligand. One of the girdle rings has opened and the equatorial co-ordination position is filled by water.

Recently, Rossotti and Sunshine have studied the structure of cupric complexes of EDTA in aqueous solution using proton relaxation techniques (35). Their results have implied that in aqueous solution cupric complexes present are $[\text{Cu}\ (\text{EDTA})\ (H_2O)]^=$ and $[\text{Cu}\ (\text{HEDTA})\ (H_2O)_2]^-$ and that in both the water is equatorial. If the co-ordination number of Cu(II) in these complexes remains six as implied by the visible spectra, then under these conditions EDTA is a pentadentate ligand and HEDTA is a tetradentate ligand.

In summary of the published work described above several conclusions may be drawn regarding complexes formed by sulfidecarboxylic acids. The sulfidecarboxylic acids are fairly strong having pK_a values ranging from about 3 to 5. The related aminocarboxylic acids have one proton for which the corresponding pK_a is about 9 to 10. Although evidence suggests that sulfur donates to the metal ion in complexes of the sulfidecarboxylic acids, the cupric complexes have log K_1 values ranging from only about 3 to 6. The corresponding cupric complexes with aminocarboxylic acids have log K_1 values ranging from about 10 to 16. The sulfidecarboxylic acids apparently also have the characteristic of forming protonated complexes in addition to the simple 1 : 1 complexes. Furthermore, there is some indication that ETTA can form a binuclear complex. Although thioglycollic acid is included in Table II it contains a thiol group as opposed to a thioether group. This leads to a great difference in the type and stability of complexes formed.

2. COMPUTATION OF STABILITY CONSTANTS

The computation of stability constants from the experimental measurements proved to be one of the greatest problems in this research. This section describes, in a general way, the approach used in the computation of the stability constants before a description is given in section 3 of the experimental results. When the methods of measurement and the results obtained in the solution studies are described, reference may be made to this section for further details of the computation of the stability constants.

2.1 Potentiometric data

2.11 Acid dissociation constants

The equations below will be written in terms of the overall constants, β_j^H but from these the acid dissociation constants may readily be calculated since $\beta_j^H = \prod K_j^H$. (Refer for nomenclature to the front of the thesis).

For equilibria of the type

$$\begin{array}{llcl} H & + A & \rightleftharpoons & HA \\ 2H & + A & \rightleftharpoons & H_2A \\ \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot \\ JH & + A & \rightleftharpoons & H_JA \end{array}$$

we can write

$$\bar{n}_H = \frac{\text{total number of protons bound to A}}{\text{total concentration of A}}$$

$$= \frac{H - h}{A}$$

$$= \frac{[HA] + 2[H_2A] + \cdots\cdots}{[A] + [HA] + [H_2A] + \cdots\cdots}$$

$$\bar{n}_H = \sum_{j=0}^{J} j[H_jA] \Big/ \sum_{j=0}^{J} [H_jA] \qquad \text{------ } 2.1$$

where J is the maximum number of protons bound to each central group A.

Putting $[H_jA] = \beta_j^H a h^j$ equation 2.1 becomes

$$\bar{m}_H = \frac{H-h}{A} = \sum_{j=0}^{J} j\beta_j^H h^j \Big/ \sum_{0}^{J} \beta_j^H h^j \qquad 2.2$$

A potentiometric titration gives h directly, and $\bar{m}_H$ or $(H-h)/A$ may be determined from the volume of alkali added to the solution of known total dissociable hydrogen ion concentration. Hence, equation 2.2 provides a relationship between the measured quantities and the stability constants β_j. Rossotti and Rossotti (36) have discussed in detail the methods of treatment of functions of this type for values of J from 1 to 3. For systems where $J > 3$ two dimensional graphical methods will not simultaneously give all the parameters. A least squares adjustment of the data, using a computer, is one way of analyzing the results of measurements on such higher order systems, especially when the number of measurements greatly exceeds the number of parameters to be determined. A least squares adjustment was used in the determination of the acid dissociations constants of ETTA.

The analysis of the problems of the application of least square adjustment to the different functions encountered in the determination of stability constants has been thoroughly treated in recent years by many workers. Sillén has given a general discussion of computer programs for studies of complex formation equilibria (38). Zimmerman (39), Rydberg (40) and Tobias (44) have discussed some of the problems in the application to particular systems. Sullivan (37) describes in detail the application of the least squares method to a simple function as given in equation 22. The principle of least squares requires the minimizing of the sum of the weighted squares of the residuals, where the residuals are the difference between the observed value of a function and its "true" value. Thus, it is required that S be minimized, by appropriate choice of the parameters, in equation 2.3

$$S = \sum_{i}^{I} w_i (F_{i\,obs} - F_{i\,true})^2 \qquad 2.3$$

where I is the total number of measurements and where w_i is the weight of the ith measurement, and is defined to be $w_i = \sigma^2/\mathrm{var}\,F_i$.

The proportionality constant , σ^2 , is arbitrary.

The criterion of least squares in arriving at the "best" set of parameters is applicable only if

(a) the correct function relating the measured quantities to the parameters is used,

and (b) the values used for w_i are a true measure of the accuracy of F_i.

The choice of the function is largely a matter of personal judgment. For the acid dissociation of ETTA it is relatively easy to decide upon the appropriate function. In some systems of metal complexes it may be more difficult. In order that the second condition, (b), above be fulfilled, the errors in the measurements should follow a Gaussian distribution. In practice this probably is never realized. However, after ensuring there are no systematic errors it is usually possible to choose weights that are a reasonable measure of the accuracy of F.

Having considered the general method of least squares adjustment and its limitations, it is now possible to discuss its particular application to the determination of the parameters, β_j^H, for a system described by the relationship in equation 2.2.

The setting up of the equations to be solved will be described first. This will be followed by a discussion of the method used to evaluate the weights, and finally by a consideration of the variance in the adjusted parameters.

The equations

Equation 2.2 can be rearranged to give, considering an acid of the type H_4A for which $J = 4$,

$$F = \sum_{j=0}^{4} (H - h - jA)\beta_j^H h^j = 0 \qquad \text{———} \; 2.4$$

It is then required to minimize

$$S = \sum_{i}^{I} w_i \Big(F_{i\,true} - \big(\sum_{j=0}^{4} (H_i - h_i - jA)\beta_j^H h_i^j \big)\Big)^2$$

with respect to the β_j^H .

Since the "true" value of F is zero and since β_0^H is defined to be 1, the error square sum can be rewritten as follows:

$$S = \sum_{i}^{I} w_i \left(H_i - h_i + \sum_{j=1}^{4} (H_i - h_i - jA)\beta_j'' h_i^j \right)^2$$

S is now differentiated with respect to each of the parameters, and the resulting equations are set equal to zero. Putting

$$F_i = \left(H_i - h_i + \sum_{j=1}^{4} (H_i - h_i - jA)\beta_j'' h_i^j \right) \quad \text{then}$$

$$\frac{\partial S}{\partial \beta_1''} = \sum_{i}^{I} w_i \, 2F_i (H_i - h_i - A) h_i = 0 \qquad \underline{\qquad\qquad} \quad 2.5$$

$$\frac{\partial S}{\partial \beta_2''} = \sum_{i}^{I} w_i \, 2F_i (H_i - h_i - 2A) h_i^2 = 0 \qquad \underline{\qquad\qquad} \quad 2.6$$

$$\frac{\partial S}{\partial \beta_3''} = \sum_{i}^{I} w_i \, 2F_i (H_i - h_i - 3A) h_i^3 = 0 \qquad \underline{\qquad\qquad} \quad 2.7$$

$$\frac{\partial S}{\partial \beta_4''} = \sum_{i}^{I} w_i \, 2F_i (H_i - h_i - 4A) h_i^4 = 0 \qquad \underline{\qquad\qquad} \quad 2.8$$

The equations 2.5 to 2.8 can conveniently be written in matrix form.

$$\begin{bmatrix} \Sigma w_i (H_i - h_i - A)^2 h_i^2 & \Sigma w_i (H_i - h_i - A)(H_i - h_i - 2A) h_i^3 & \Sigma w_i (H_i - h_i - A)(H_i - h_i - 3A) h_i^4 & \Sigma w_i (H_i - h_i - A)(H_i - h_i - 4A) h_i^5 \\ \Sigma w_i (H_i - h_i - 2A)(H_i - h_i - A) h_i^3 & \Sigma w_i (H_i - h_i - 2A)(H_i - h_i - 2A) h_i^4 & \Sigma w_i (H_i - h_i - 2A)(H_i - h_i - 3A) h_i^5 & \Sigma w_i (H_i - h_i - 2A)(H_i - h_i - 4A) h_i^6 \\ \Sigma w_i (H_i - h_i - 3A)(H_i - h_i - A) h_i^4 & \Sigma w_i (H_i - h_i - 3A)(H_i - h_i - 2A) h_i^5 & \Sigma w_i (H_i - h_i - 3A)(H_i - h_i - 3A) h_i^6 & \Sigma w_i (H_i - h_i - 3A)(H_i - h_i - 4A) h_i^7 \\ \Sigma w_i (H_i - h_i - 4A)(H_i - h_i - A) h_i^5 & \Sigma w_i (H_i - h_i - 4A)(H_i - h_i - 2A) h_i^6 & \Sigma w_i (H_i - h_i - 4A)(H_i - h_i - 3A) h_i^7 & \Sigma w_i (H_i - h_i - 4A)(H_i - h_i - 4A) h_i^8 \end{bmatrix} \begin{bmatrix} \beta_1'' \\ \beta_2'' \\ \beta_3'' \\ \beta_4'' \end{bmatrix} = \begin{bmatrix} -\Sigma w_i (H_i - h_i)(H_i - h_i - A) h_i \\ -\Sigma w_i (H_i - h_i)(H_i - h_i - 2A) h_i^2 \\ -\Sigma w_i (H_i - h_i)(H_i - h_i - 3A) h_i^3 \\ -\Sigma w_i (H_i - h_i)(H_i - h_i - 4A) h_i^4 \end{bmatrix}$$

or $\underline{W}\ \underline{B} = \underline{C}$ $\qquad \underline{\qquad\qquad}$ 2.11

and $\underline{B} = \underline{C}\,\underline{W}^{-1}$

The inversion of the matrix is done by the computer using a standard subroutine. Usually, scaling factors must be introduced to allow the computer to invert the matrix, but these are easily taken out again after the inversion.

The value of (H - h) can be determined in one of two ways from the experimental data. It may be calculated directly from a single titration curve as in equation 2.9 below.

$$H - h = (C + 4A)\frac{V}{V + v_2} - N\frac{v_2}{V + v_2} - h \qquad \text{———————} \quad 2.9$$

where C is the initial concentration of any mineral acid added, V is the initial volume of the solution and v_2 is the volume of alkali of normality N added to correspond to a free hydrogen ion concentration, h. It is difficult to determine the difference (H - h) accurately in the most acidic solutions since under these conditions $C \simeq H \simeq h$. A more accurate way of finding the difference (H - h) has been described by Irving and Rossotti (41). In Figure I consider first curve (1). It is possible to write for any given value of pH that

$$h' = \frac{C'V}{V + v_1} - N\frac{v_1}{V + v_1} + [OH]'$$

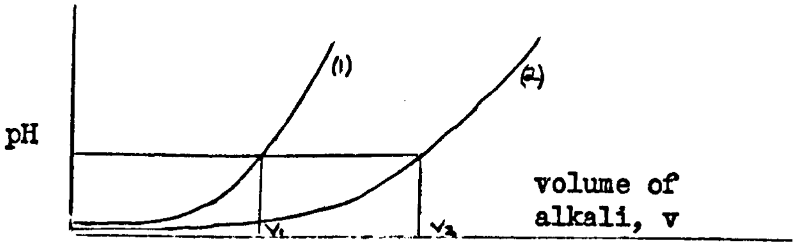


Figure I. (1) Mineral acid alone
(2) Mineral acid plus ligand

where v_1 is the volume of base of normality N required to make the free hydrogen ion concentration equal to h'. The term in [OH] appears because of hydrolysis, and is usually negligible compared to the other terms. Considering curve (2), resulting from the titration of the solution containing mineral acid plus ligand, for any value of h where $v = v_2$ it is possible to write

$$h'' = (C'' + JA)\frac{V}{V + v_2} - N\frac{v_2}{V + v_2} + [OH]'' - \bar{n}_H A\frac{V}{V + v_2}$$

If the solutions are prepared such that C" = C' = C, and if points on the titration curves are chosen so that

$$h' = h''$$

then

$$(C + JA)\frac{V}{V+v_2} - \frac{v_2 N}{V+v_2} - \bar{n}_H A \frac{V}{V+v_2} = C\frac{V}{V+v_1} - \frac{v_1 N}{V+v_1}$$

This can be rearranged to give

$$\bar{n}_H A = \left(JA + \frac{(v_1 - v_2)(N+C)}{V+v_1} \right)$$

and

$$\bar{n}_H A = H - h$$

The original equation relating the stability constants and the measured quantities, equation 2.4, could have been written directly in terms of $\bar{n}_H$ and h to give

$$F' = \sum (\bar{n}_H - j)\beta_j^H h^j = 0$$

The computer program was written on the basis of F as in equation 2.4 and either method of evaluating (H - h) can readily be used.

<u>The weights</u>

Having set up the equations to be solved, the choice of weights must be considered. As previously stated in this section, the weight, w, of a function, F, is defined to be inversely proprtional to the variance of the function. That is,

$$W = \sigma^2 / \mathrm{var}\ F$$

where σ^2 is a proportionality factor. The expression commonly used for the propagation of variance in F where F is a function of h and H is

$$\mathrm{var}\ F = \left(\frac{\partial F}{\partial h}\right)^2 \mathrm{var}\ h + \left(\frac{\partial F}{\partial H}\right)^2 \mathrm{var}\ H$$
$$+ 2\left(\frac{\partial F}{\partial h}\frac{\partial F}{\partial H}\ \mathrm{covariance}(h, H)\right) \quad \text{—— 2.10}$$

If the variables h and H are statisically independent the last term in equation 2.10 is zero. Statistical independence relates to independence in the fluctuations in the measured values of h and H, not to the relationship between their true values. To evaluate (var F) it is necessary to first evaluate the derivatives $\partial F/\partial h$ and $\partial F/\partial H$ and to know (var h) and (var H). Reasonable estimates of (var h) and (var H) may be made from the results of replicate experiments. To evaluate the derivatives requires a knowledge of the stability constants. One of two approaches may be used. In one method, the first solution of equations 2.5 to 2.8 is done using initial estimates of the values from rough graphical analysis or reported values to evaluate the weights. The new β_j^H values obtained from the solution of the equations is then used to evaluate new weights. This process is repeated until convergence to a satisfactory limit is reached. Alternatively, in the first cycle, equations 2.5 to 2.8 are solved using equal weights. The resulting β_j^H values are then used to evaluate the new weights and the process is repeated until satisfactory convergence as before. The latter method was used in the program in which the acid dissociation constants of ETTA were determined.

In the treatment of the acid dissociation constants it was assumed as a first trial that all the error could be carried in the variance of h. The variance in h was estimated from four replicate experiments.

The weight of F was then taken to be

$$w = \frac{1}{\text{var}\, h\ (\partial F/\partial h)^2}$$

It was concluded that this was a sufficiently accurate method of evaluating the weights when it was found that the experimental $\bar{n}_H, h$ points lay almost exactly, throughout the entire range of measurements, on the $\bar{n}_H, h$ curve calculated from the refined constants. Convergence to a satisfactory limit was taken to be when two successive refinements gave β_j^H values differing by 1 part in 10^5, or less.

<u>The variance in the adjusted parameters</u>

It can be shown (42) that the reciprocal of the weights of the parameters are found on the diagonal of the inverse of the matrix W, in equation 2.11.

$$\text{var}\, \beta_j^H = W_{jj}^{-1}\sigma^2$$

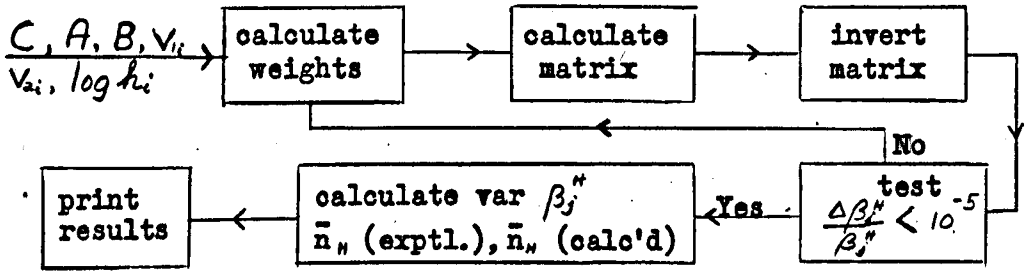
where the W_{jj}^{-1} are the elements on the diagonal of the inverse of $\underline{W}$ and where σ^2 is a proportionality constant.

An estimate of σ^2 may be made (43) by putting

$$\sigma^2 = \frac{S_{min}}{k-1}$$

where k is the number of degrees of freedom, that is, the number of measurements minus the number of parameters determined minus one (since β_0 fixed at 1), and where S min is the value of S, equation 2.3, when the β_j^H values are the final, refined values.

The entire process used in the least squares method of obtaining the desired stability constants is summarized below.



2.12 Metal stability constants

The potentiometric data resulting from the titration of solutions containing metal ions and ligand were treated by a least square adjustment in a very similar way to the method of analysis described in the preceding section, 2.11, for the acid dissociation constants. Only a brief discussion will be given here of the extensions to the systems containing metal ions.

In the problem of determining acid dissociation constants, the main species present in solution are known with reasonable certainty. However, in systems containing metal ions it is sometimes much more difficult to make a judgment concerning the main species present and hence concerning the parameters that should be introduced in the analyses of the data. For systems of ETTA and metal ions it was decided that the system was not likely to contain in appreciable concentrations other complexes than the following five: BH_3A, BH_2A, BHA, BA and B_2A. Saini (19) reported stability constants for each of these complexes when the metal was Cu(II). In the discussion which follows, consideration is given to each of the above possible complexes. For simpler systems appropriate terms may be omitted (or if other complexes are believed to exist appropriate terms may be added). When the stability constants are sought for a system containing protonated complexes, in addition to complexes which are not protonated, it is convenient to consider $\bar{n}_A$, the average number of protons bound to each A group.

$$\bar{m}_A = \frac{H-h}{A} = \Big([BHA] + 2[BH_2A] + 3[BH_3A] + [HA] + 2[H_2A] + 3[H_3A] + 4[H_4A] - h\Big) \Big/ \Big([BA] + [BHA] + [BH_2A] + [BH_3A] + [B_2A] + [A] + [HA] + [H_2A] + [H_3A] + [H_4A]\Big)$$

$$= \frac{\sum_{q=0}^{3} q b h^q \beta_{1q1} + \sum_{0}^{4} j h^j \beta_j^H}{\sum_{q=0}^{3} b h^q \beta_{1q1} + \sum h^j \beta_j^H + \beta_{21} b^2} \qquad \text{———— } 2.12$$

Equation 2.12 gives on rearrangement

$$F = \sum_{q=0}^{3} (H-h-qA) b h^q \beta_{1q1} + (H-h) b^2 \beta_{21} + \sum_{j=0}^{4} (H-h-jA) h^j \beta_j^H = 0$$

As before, the error square sum

$$S = \sum_i \omega_i F_i^2$$

is minimized with respect to each of the parameters.

The free metal concentration is found through solution of the two simultaneous equations for mole balance of the metal and of the ligand.

$$f = B - [BH_3A] - [BH_2A] - [BHA] - [BA] - [B_2A] - [B]$$

$$= B - b - \beta_{131} b h^3 a - \beta_{121} b h^2 a - \beta_{111} b h a - \beta_{11} b a - \beta_{21} b^2 a \qquad \text{———— } 2.13$$

$$y = A - [BH_3A] - [BH_2A] - [BHA] - [BA] - [B_2A] - [A] - [HA] - [H_2A] - [H_3A] - [H_4A]$$

$$= A - \beta_{131} b h^3 a - \beta_{121} b h^2 a - \beta_{111} b h a - \beta_{11} b a - \beta_{21} b^2 a - \sum_{j=0}^{4} \beta_j^H h^j a \qquad \text{———— } 2.14$$

Equations 2.13 and 2.14 are solved for a and b using a Newton-Raphson iteration. Initial estimates of the stability constants are used in the first evaluation of a and b. Thereafter the last values of the stability constants obtained from minimizing the error square sum with respect to each of the constants are used.

The weights are evaluated from

$$\omega = \sigma^2 / \mathrm{var}\, F$$

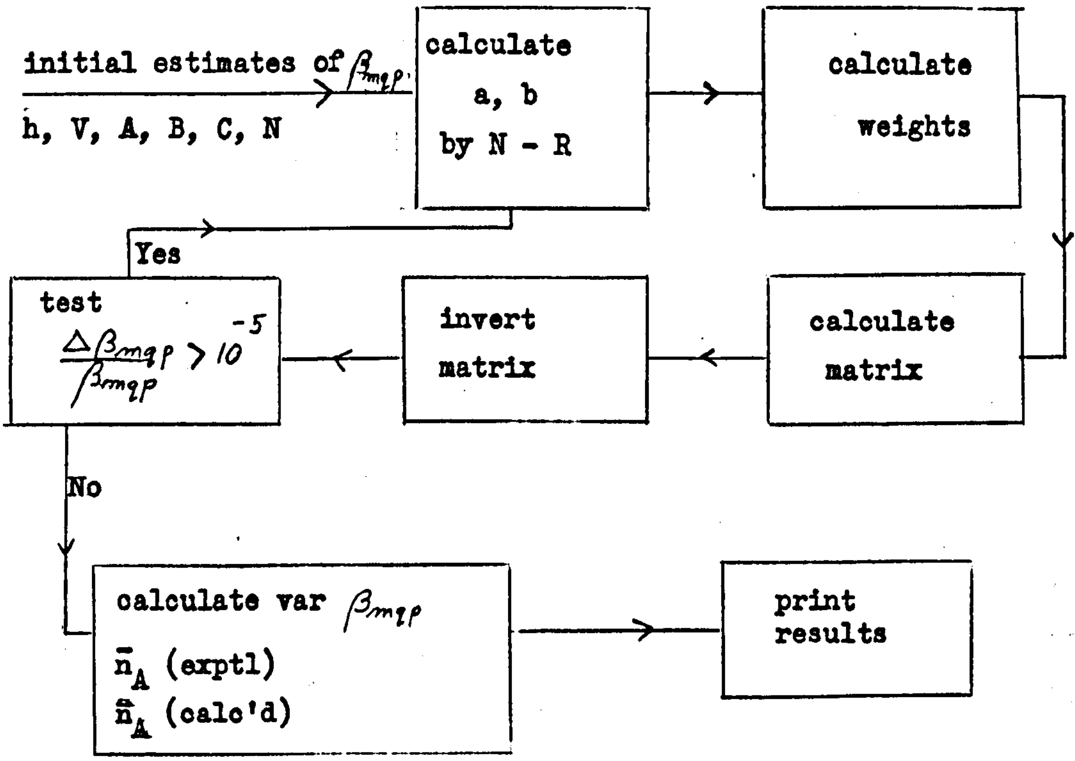
as before. The experimental quantities that determine F are C, A, B, h, and also N (normality of base) and v since $H = C + 4A - Nv/V$. From replicate experiments it was found that the variances in v, and in h, particularly, were greater than the estimated variances in the other quantities. On this basis it was decided in the first attempts, at least, to allow the error in F to be carried by var(h) and var(v).

Hence,

$$\mathrm{var}\, F = \left(\frac{\partial F}{\partial v}\right) \mathrm{var}\ v \;+\; \left(\frac{\partial F}{\partial h}\right) \mathrm{var}\ h$$

The derivatives were evaluated in the first instance using estimated stability constants, and thereafter using the constants obtained from the minimization of S.

The plan of the program used was as illustrated below.



The particular application of this method in determining the stability constants for complexes of ETTA will be considered in section 3.

2.2 Spectrophotometry

Spectrophotometry was used in the study of the metal-ligand systems. It was not used to determine the acid dissociation constants since these could be obtained reasonably simply and accurately from the potentiometric titrations. Hence, the discussion in this section applies to systems of metal complexes in which the acid dissociation constants of the ligand are known.

In the analysis of spectral data of systems of complexes, not only are the stability constants parameters of the system, but also the extinction coefficients of the different species present are parameters which must be determined. Usually at least two of the extinction coefficients, namely, those for the hydrated metal ion and the uncomplexed ligand, may be determined independently. The first thought in treating spectrophotometric data might be to apply a least squares adjustment using a computer as has been done successfully with potentiometric data. Conrow and Johnson (45) have written a program for calculating stability constants and extinction coefficients according to the least squares method for a system of the type

$$xX + yY \rightleftharpoons Z$$

where the absorption per unit path length is given by

$$\frac{A_s}{l} = \epsilon_x(X) + \epsilon_y(Y) + \epsilon_z(Z)$$

and ϵ_x, ϵ_Y and ϵ_z are the extinction coefficients of the species X, Y, and Z and (X), (Y) and (Z) are, respectively, their equilibrium concentrations. When this program was tested on synthetic data it was found that the calculated parameters were inordinately sensitive to variations in the input data. Although in certain favourable cases convergence to satisfactory values of the parameters was obtained, in other cases there were large differences between the calculated parameters and those used to generate the data. The authors also reported "an impossibly large and erratic temperature dependence". In view of the accuracy expected in the present work in the measurement of A_s and of the concentration variables, it was decided to use graphical methods and successive approximations rather than to resort to computer techniques.

On the basis of Saini's work (19) on Cu(II) - ETTA, it was expected that a series of protonated complexes as well as mononuclear and binuclear complexes would be present in solutions of ETTA and metal ions. It was intended to divide the experimental results into parts, such that each part could be approximately described by one or two of the stability constants. Preliminary values for the stability constants could then be evaluated graphically in the different parts. Subsequently, these values could be successively refined. In treating data characterized by three or fewer parameters, curve-fitting methods, elimination methods or linear plots may be used. Linear plots, in which the stability constants are determined from appropriate slopes and intercepts, are convenient when the range over which the free ligand concentration varies is not great (i.e. not several orders of magnitude), and were used in analyzing the spectrophotometric data in this work. When the results of the absorbance measurements are described in section 3, specific mention will be made of the way in which the results were divided into sections and of the particular plots used in the evaluation of the stability constants.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The results of the investigation of the solid complexes will be described and discussed in section 3.1 and the work on the complexes in solution will follow in section 3.2.

3.1 The solid complexes

3.11 Preparation of the ligands

The method used in the preparation of the thioglycollic acid derivatives was that described by Ritter and Lover (47). In this method the appropriate aldehyde or ketone is mixed with the thio-acid, and HCl is bubbled into the reaction mixture for about five minutes. The thio-derivative separates almost immediately, and in good yield. The thioglycollic acid used in the preparations below was G.P. grade, supplied by B.D.H. Limited. All C, H, and S microanalyses were carried out by Weiler and Strauss, Oxford Microanalytical Laboratories. The melting points recorded were taken on a Gallenkamp melting point apparatus.

a. ETTA

Thioglycollic acid (35 mls) and 50% W/W glyoxal (12 mls) were mixed together, and dry HCl bubbled through the mixture for about five minutes. The mixture became hot, and then set solid. The product was recrystallised four times from water and dried under vacuum at 100°C. The yield of purified, white, crystalline product was 20 g, or about 60% based on the thioglycollic acid.

Observed m.p. 192-3° (Reported 189° (47); 203-4° (19)).

Observed gram-equivalent weight 97.6 (phenolphthalein end point)

Calculated g.e.w. for $C_{10}H_{14}O_8S_4$ as a tetrabasic acid 97.6.

	Observed	Calculated for $C_{10}H_{14}O_8S_4$
% C	30.76, 31.14 (av. 30.95)	30.74
% H	3.62, 3.96 (av. 3.79)	3.62
% S	33.60	32.85

The product obtained sometimes had an equivalent weight corresponding to the formula $C_{10}H_{14}O_8S_4 . 4H_2O$, probably depending upon the exact conditions of recrystallisation. Only very rigorous drying conditions would convert this product into one corresponding to the anhydrous formula.

b. Thioglycollic acid derivative of terephthaldehyde

(Phenylene - 1, 6 - dimethylidyne (tetrathioglycollic acid). Hereafter referred to as PDTA).

Terephthaldehyde (14 g) was mixed with thioglycollic acid (36 mls) and HCl bubbled into the mixture for five minutes, or until the mixture set solid. After four recrystallisations from water, and drying at 109°, a white product was obtained. The product softens at 195°, and decomposes at 198-9°.

Observed g.e.w. 115 (phenolphthalein end point)

Calculated g.e.w. for $C_{16} H_{18} O_8 S_4$ as a tetrabasic acid 117

	Observed	Calculated for $C_{16} H_{18} O_8 S_4$
% C	40.59	41.19
% H	4.07	3.89
% S	27.54	27.48

c. Thioglycollic acid derivative of benzaldehyde

(Benzylbis (thioglycollic acid). Hereafter referred to as BBTA).

Benzaldehyde (22 mls), purified by fractional distillation under reduced pressure, was mixed with thioglycollic acid (31 mls) and HCl bubbled into the mixture for about ten minutes. The mixture became hot and set solid. The white product was recrystallised three times from water-ethanol, and dried at 60° for 24 hours. The product melted at 103-4°.

Observed g.e.w. 140 (phenolphthalein end point)

Calculated g.e.w. for $C_{11} H_{12} O_4 S_2$ as a dibasic acid 136.

	Observed	Calculated for $C_{11} H_{12} O_4 S_2$
% C	49.31	48.49
% H	4.43	4.44
% S	23.45	23.55

d. Thioglycollic acid derivative of acetophenone

(Methylphenylmethylidynebis (thioglycollic acid)).

Acetophenone (14 mls) was mixed with thioglycollic acid (17 mls), HCl was bubbled into the reaction mixture, and when the mixture set solid the product was recrystallised three times from water-ethanol and dried at 30°. The product melted at 135-6°. (Reported 135° (47)).

Observed g.e.w. 144 (phenolphthalein end point)

Calculated g.e w. for $C_{12}H_{14}O_4S_2$ as a disbasic acid 143.

	Observed	Calculated for $C_{12}H_{14}O_4S_2$
% C	49.08, 50.24 (av. 49.66)	50.31
% H	4.81, 4.79 (av. 4.80)	4.93
% S	22.88	22.40

e. Attempted syntheses of thioglycollic derivatives of some heterocyclic compounds

When thioglycollic acid was mixed with each of 2 - benzoylpyridine, 2 - acetylpyridine, quinoline - 2 - aldehyde and di - 2 - pyridylglyoxal, and HCl bubbled into the mixture, the thioglycollic acid derivative was not obtained. The reaction mixture became in each example a malodorous "glass", and all attempts to separate crystalline products were unsuccessful. When a portion of the reaction mixture was mixed with a solution of nickel acetate, no precipitate formed. No further attempts were made to prepare the thioglycollic acid derivatives of heterocylic compounds. Ritter and Lover (47) reported that the formation of the thio-derivatives was inhibited by the presence of a nitro group ortho to the carbonyl bearing carbon. It may be that the ring nitrogen, α- to the carbonyl carbon in the four compounds mentioned above had a similar effect to a nitro group in inhibiting the formation of the derivatives.

3.12 Preparation of the complexes, thermogravimetric analyses and magnetic susceptibilities

The metal complexes described below were prepared by mixing a solution of the ligand, 2g, or .005 moles, in about 15 mls of aqueous ethanol with a filtered solution of G.P. grade metal acetate, 2.5 g, or .01 moles, dissolved in the minimum volume of ethanol. A few drops of acetic acid were added to the solution of metal acetate. As soon as the solutions were mixed, a copious amount of finely divided precipitate formed. The solution from which the precipitate separated was about pH 4.5. The solution was filtered, and the collected precipitate either boiled with ethanol, the solution filtered and the precipitate washed well with hot alcohol, or the precipitate was Soxhlet extracted, using ethanol, for four hours. The product was then dried at 40° for at least six hours.

Unless ethanol was added, no precipitate would form in a solution containing the ETTA and the metal acetate made up from pure water. In an aqueous ethanollic solution containing ETTA and the metal chloride, rather than the acetate, a precipitate did not form unless the pH of the solution was raised by addition of alkali from the initial value of pH 2 to pH 4.5.

In the complexes prepared, Co was determined by electrodeposition, and Cu either by electrodeposition or volumetrically using EDTA and PAN indicator. Nickel was determined gravimetrically as the dimethylglyoximate, and zinc volumetrically using EDTA and Eriochrome Black T indicator. In the Co analyses it was found necessary to fuse the complexes with $KHSO_4$ before deposition of the Co in order to destroy completely any organic matter. In the Cu, Ni and Zn analyses decomposition of the complex was effected by boiling the complex in 1 : 3 HNO_3 - HCl

a. Co(II) - ETTA* complex. Dried to constant weight at 43°. Color: pale mauve. Soluble in water; insoluble in chloroform, ethanol or nitrobenzene.

	Observed	Calculated for	
		$Co_2 C_{10} H_{10} O_8 S_4 .4H_2O$	$Co_2 C_{10} H_{10} O_8 S_4 .2H_2O$
% Co	20.6 (variation in 3 replicate experiments ± .1)	20.45	21.82
% C	21.88	20.82	22.21
% H	3.29	3.15	2.61
% S	19.47	22.25	23.74

The observed elemental analyses were found to agree better with the calculated values for $Co_2 C_{10} H_{10} O_8 S_4 .4H_2O$, considering the expected accuracy in the analyses for the different elements, than with the values for any other formulae which were thought to be reasonable possibilities. The precision in the Co analysis was about 1%, as indicated, and the analytical method used in the determination is known to give accurate results under the experimental conditions existing in the analysis of the complex (49). It was found that duplicate C and S analyses could differ by as much as 5%, and duplicate H analyses by as much as 10%. The complex as prepared was taken to be $Co_2C_{10}H_{10} O_8 S_4 .4H_2O$.

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* Sometimes ETTA is used to refer to the anion, A^{4-}, and sometimes to the undissociated acid, H_4A. The context will make clear which is meant.

When the complex was dried to constant weight at 83°, the color of the complex changed from pale mauve to purple, and the complex became hygroscopic. The weight loss observed was 6.93%. Conversion of $Co_2C_{10}H_{10}O_8S_4.4H_2O$ to $Co_2C_{10}H_{10}O_8S_4.2H_2O$ corresponds to a weight loss of 6.25%. The observed % Co in the complex dried at 83° was 21.4.

b. Ni(II) - ETTA complex. Dried to constant weight at 43°. Color: pale blue-green. Soluble in water; insoluble in chloroform, ethanol or nitrobenzene.

	Observed	Calculated for $Ni_2C_{10}H_{10}O_8S_4.8H_2O$	Calculated for $Ni_2C_{10}H_{10}O_8S_4.6H_2O$
% Ni	18.2 (variation in 5 replicate experiments ± .1)	18.12	19.19
% C	20.0 (average of 19.47, 20.53)	18.52	19.61
% H	3.56 (average of 3.60, 3.52)	4.03	3.62
% S	19.95 (average of 20.25, 19.65)	19.79	20.96

Again, as for the Co - ETTA complex, considering the accuracy and precision of the analyses for the different elements, the observed values agree better with the formula $Ni_2C_{10}H_{10}O_8S_4.8H_2O$ than with any other formulae thought to be reasonable possibilities. The formula of the complex as prepared was taken to be $Ni_2C_{10}H_{10}O_8S_4.8H_2O$.

When the complex was dried to constant weight at 83°, its color became pale green. The weight loss observed was 7.0%. The calculated weight loss for $Ni_2C_{10}H_{10}O_8S_4.8H_2O$ losing three molecules of water is 8.35%. The nickel content in the dried product was 19.7; the calculated nickel content of the pentahydrate is 19.8%. The complex was dried at a still higher temperature, 119°, and the observed weight loss relative to the product dried at 43° was 17.0%. The removal of six molecules of water from $Ni_2C_{10}H_{10}O_8S_4.8H_2O$ would give a weight loss of 16.7%. Both the product of drying at 83° and at 119° were hygroscopic. Finally, the complex was heated to 152°. A continuous weight loss was observed, and the complex, normally odourless, began to smell of sulfur.

c. Cu(II) - ETTA complex. Dried at 40°. Color: green. Soluble in water; insoluble in ethanol or chloroform.

	Observed	Calculated for $Cu_2 C_{10} H_{10} O_8 S_4 \cdot 2H_2O$
% Cu	23.8 (EDTA) 23.6 (Electrodeposition)	23.13
% C	21.62	21.84
% H	2.85	2.57
% S	23.08	23.34

When the complex was heated to 83° it continued very gradually to lose weight.

d. Zn(II) - ETTA complex. Dried at 40°. Color: white. Soluble in water; insoluble in ethanol.

	Observed	Calculated for $Zn_2 C_{10} H_{10} O_8 S_4 \cdot 2H_2O$
% Zn	23.2	23.6
% C	21.66	21.69
% H	3.25	2.55
% S	20.00	23.18

e. Co(II) - PDTA complex. Dried at 50°. Color: pink.

	Observed	Calculated for $Co_2 C_{16} H_{14} O_8 S_4 \cdot 8H_2O$
% Co	16.6	16.28
% C	26.8	26.5
% H	3.84	4.17
% S	17.5	17.7

f. Ni(II) - PDTA complex. Dried at 50°. Color: pale blue-green.

	Observed	Calculated for $Ni_2 C_{16} H_{14} O_8 S_4 \cdot 8H_2O$
% Ni	16.5	16.22
% C	28.2	26.5
% H	3.67	4.17
% S	15.9	17.7

g. Cu(II) - PDTA

When solutions of PDTA and of cupric acetate were mixed, the solution became violet in color, and gradually a dark brown precipitate formed. No further investigations were carried out on the reaction mixture.

h. Ni(II) - BBTA complex. Dried at 40°. Color: pale green. Insoluble in water or ethanol.

	Observed	Calculated for $NiC_{11}H_{10}O_4S_2 \cdot H_2O$
% Ni	16.9	16.92
% C	39.04	38.06
% H	2.99	3.49
% S	14.06	18.48

i. Co(II) - BBTA complex. Dried at 40°. Color: purple. Insoluble in water or ethanol.

	Observed	Calculated for $CoC_{11}H_{10}O_4S_2$
% Co	17.95	17.92
% C	40.71	40.12
% H	3.29	3.06
% S	14.83	19.48

j. Cu(II) - BBTA complex

The reaction of BBTA and cupric acetate in aqueous ethanol gave a cream-colored precipitate and the reaction mixture smelled of benzaldehyde. The copper content of the precipitate was about 40%. No further investigations were carried out on the reaction products.

k. Ni(II) and Zn(II) - methylphenylmethylidene (bisthioglycollic acid)

The reaction products of nickel acetate and zinc acetate with methylphenylmethylidene (bisthioglycollic acid) were high in metal content (40%) and low in carbon (12%). Studies on these products were not continued.

Thermogravimetric analyses

The complexes listed in Table III were heated on a Stanton Thermogravimetric Balance, in air and at a rate of 4.5°C/min. or less. With the present programing device on the balance it was not possible to hold the temperature constant below 130°. When the first sharp weight loss occurred, the products smelled strongly of sulfur, and it was inferred that the complex completely decomposed at this temperature. At temperatures lower than this a gradual weight loss was observed.

Table III - Thermogravimetric results

Sample	Temperature of sharp decomposition	Other weight losses
Ni_2 ETTA $.8H_2O$	260	13% lost gradually 60 to 230°
Cu_2 ETTA $.2H_2O$	160	9% lost gradually 40° to 160°
Zn_2 ETTA $.2H_2O$	235	8% lost gradually 40° to 108°
Co_2 PDTA $.8H_2O$	270	15% lost gradually 100 to 270°
Ni_2 PDTA $.8H_2O$	260	20% lost gradually 90 to 260°
Co BBTA	300	-
Ni BBTA $.H_2O$	310	-

The complexes of BBTA appear to be the most stable thermally. The complexes of ETTA and PDTA show a gradual weight loss of 8 to 20%, depending upon the particular complex, before sharp decomposition occurs at about 250°. The Cu(II) - ETTA complex decomposes at a temperature about 90° lower than the Ni and Zn complexes with ETTA.

Magnetic susceptibilities

Magnetic susceptibility measurements were made using a Newport Instruments Gouy Balance. The balance was calibrated with $Hg[Co(CNS)_4]$ (48), and measurements were made at room temperature only. The magnetic susceptibilities and the calculated effective magnetic moments of the complexes are tabulated in Table IV.

Table IV - Magnetic susceptibility measurements

Temperature 20 ± 2°C.

Sample	Gm susceptibility $\times 10^6$	Effective magnetic moment (Bohr magnetons)
ETTA	-.54	-
Co_2 ETTA $.4H_2O$	36.1	4.87
Ni_2 ETTA $.8H_2O$	13.5	3.27
Cu_2 ETTA $.2H_2O$	4.47	1.77
Zn_2 ETTA $.2H_2O$	diamagnetic	-
Ni_2 PDTA $.8H_2O$	13.78	3.50
Co_2 PDTA $.8H_2O$	31.69	5.23
Co BBTA	30.29	4.83

3.13 Visible and near infrared spectra

The diffuse reflectance spectra of the solid complexes between 4000 and 25,000 cm^{-1} (2500 to 400 mμ) were recorded using a Beckman DK - 2A spectrophotometer and a Unicam SP 800 spectrophotometer. MgO was used as reference. The principal absorption maxima are recorded in Table V. The complete spectra are given in Figures II to VI between 5000 - 20,000 cm^{-1}.

Table V - Principal absorption maxima in the diffuse reflectance spectra of metal complexes of ETTA, and of Ni(II) - PDTA and of Co(II) - BBTA between 4000 and 25,000 cm^{-1}.

Co_2ETTA $.4H_2O$	Ni_2 ETTA $.8H_2O$	Cu_2 ETTA $.2H_2O$	Ni_2 PDTA $.8H_2O$	Co BBTA
4140	4095	4115	4150	4170
4330	4310	4330	4330	4350
5140	5130	5140	5160	5240
	5700			
8080	8760		8160	7780
		13,300		
			12,900	
	15,150		14,700	
				16,500
				18,450
				19,400
20,000				20,400
	25,000		24,700	

The spectra of the Co and Ni complexes dried at 83°, and probably of simplest formula Co_2 ETTA $.2H_2O$ and Ni_2 ETTA $.5H_2O$, are included in Figures II and III respectively for comparison with Co_2 ETTA $.4H_2O$ and Ni_2 ETTA $.8H_2O$

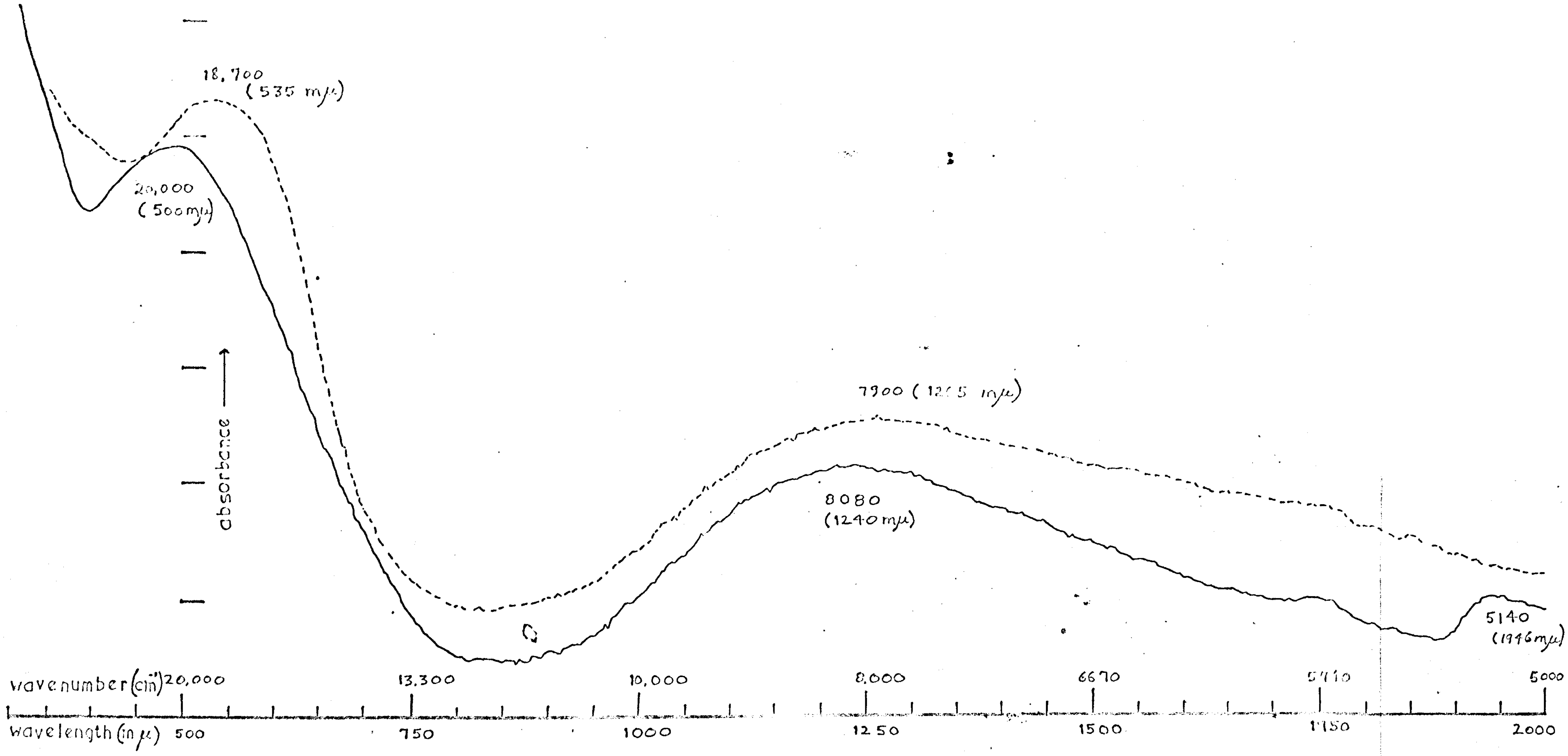

Figure II. Diffuse reflectance spectra of $Co_2ETTA.4H_2O$ and $Co_2ETTA.2H_2O$ (the product of drying at 83°C.

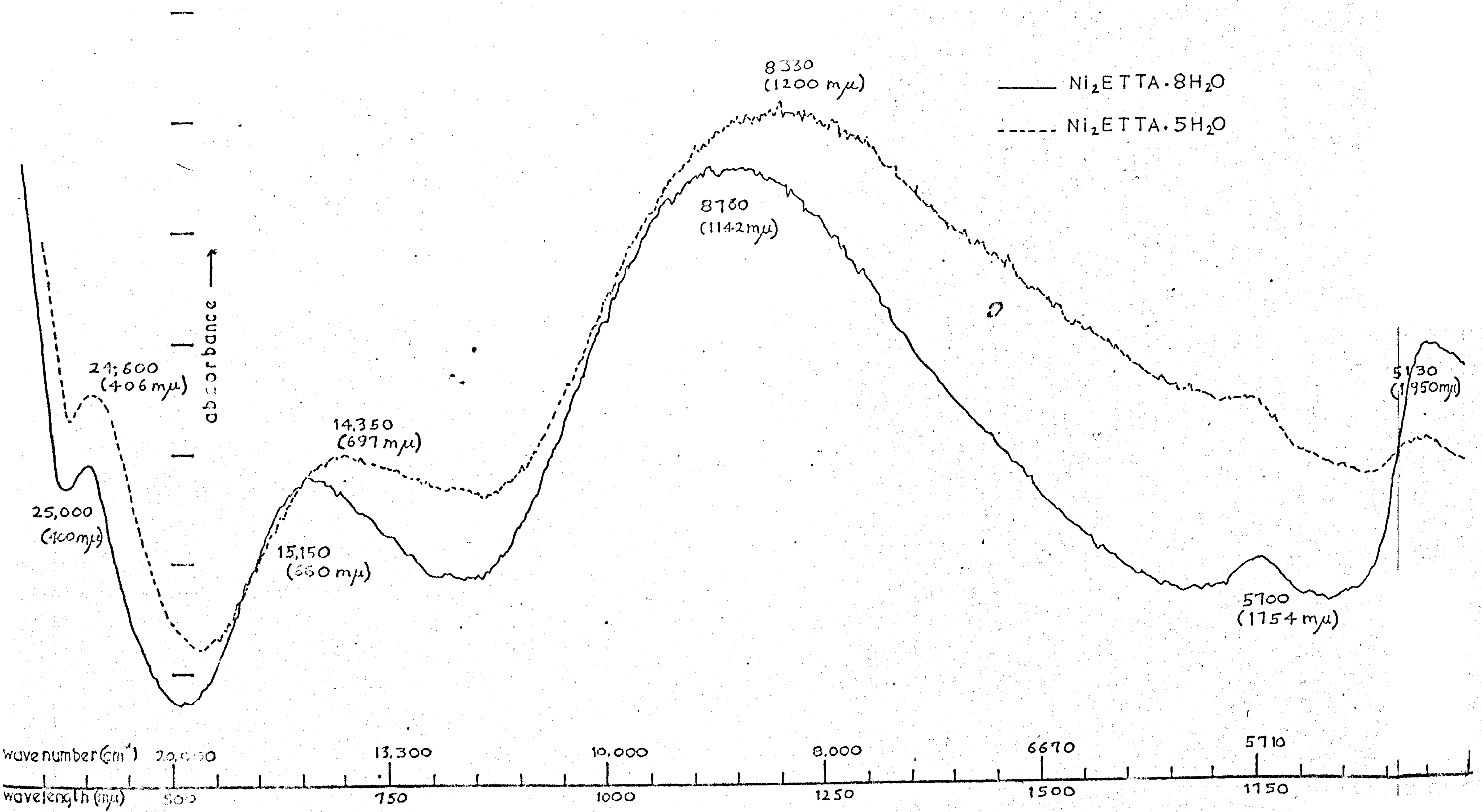

Figure III. Diffuse reflectance spectra of $Ni_2ETTA.8H_2O$ and $Ni_2ETTA.5H_2O$ (the product of drying at 83 °C).

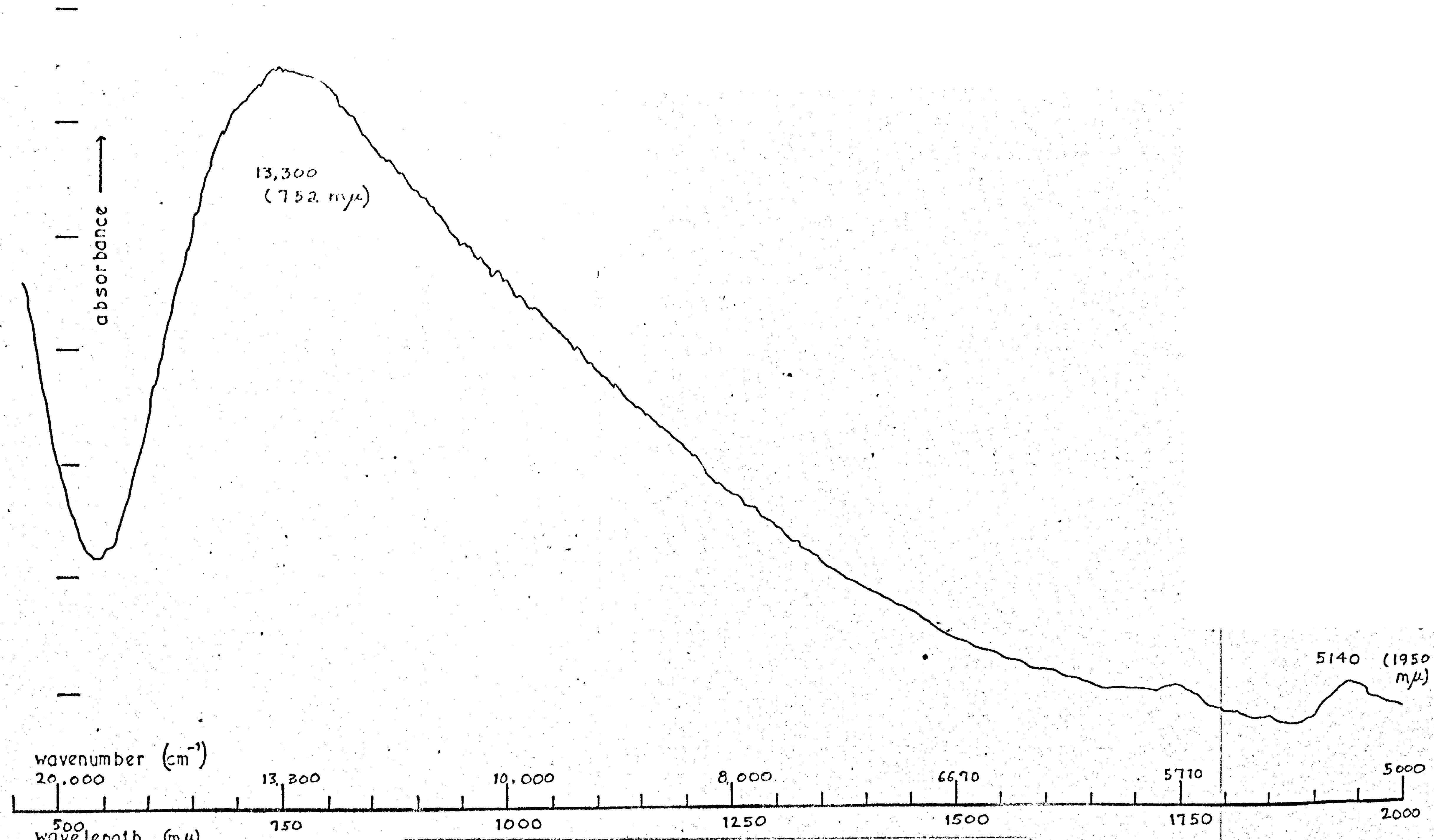

Figure IV. Diffuse reflectance spectrum of $Cu_2ETTA.2H_2O$.

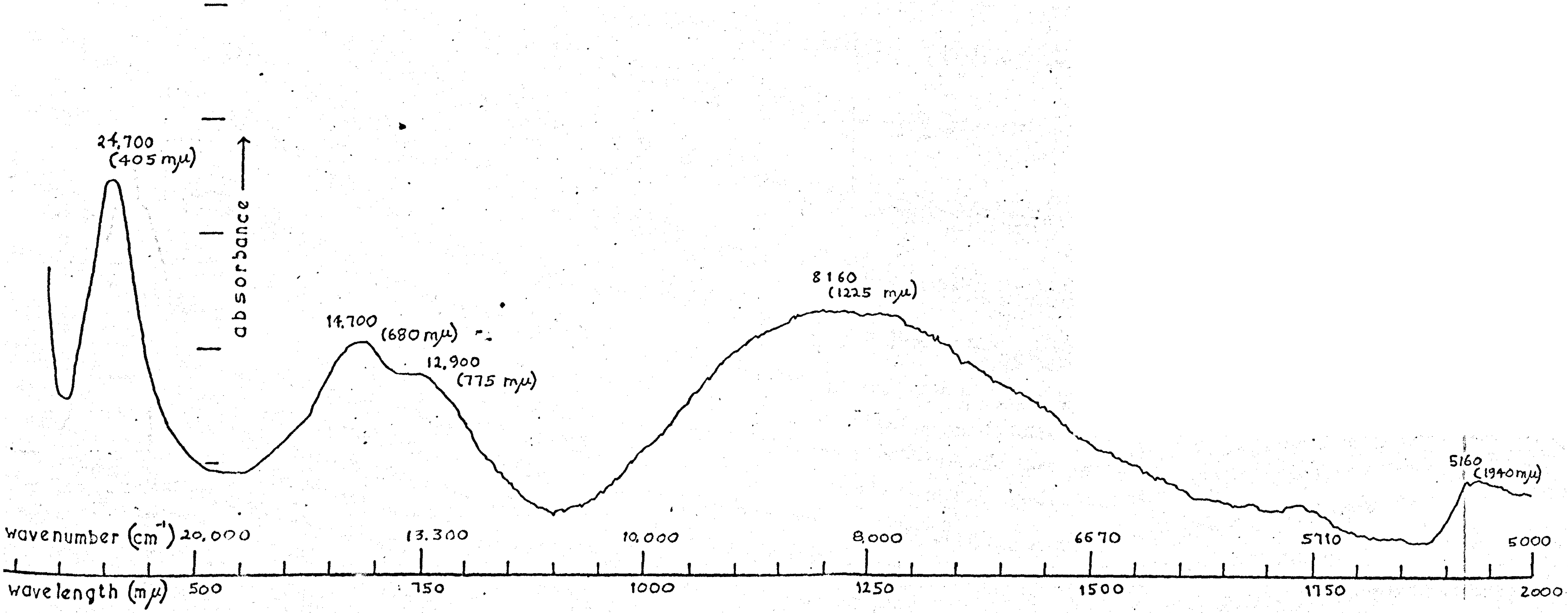

Figure V. Diffuse reflectance spectrum of $Ni_2PDTA.8H_2O$.

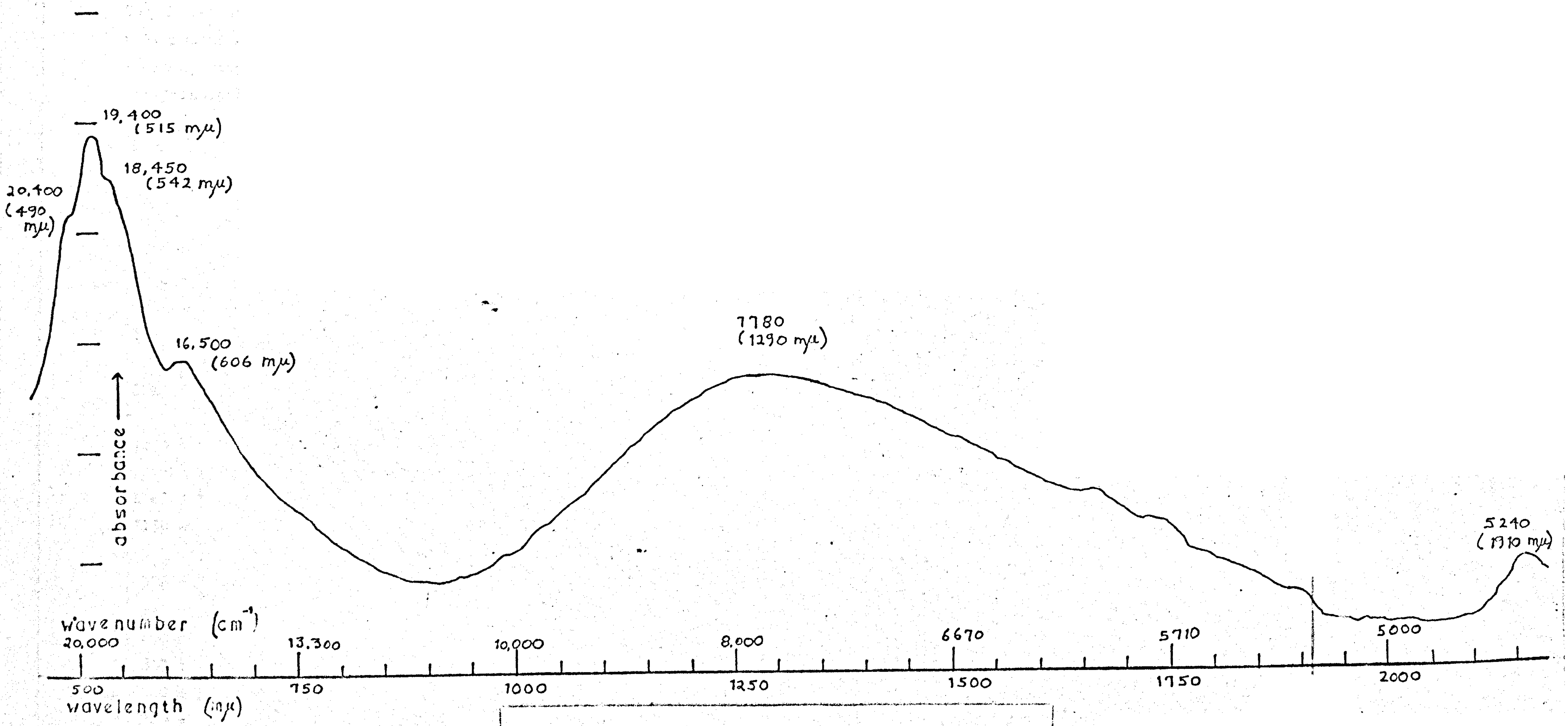

Figure VI. Diffuse reflectance spectrum of Co_2BBTA.

3.14 Infrared spectra

The infrared spectra of ETTA and its complexes with Co(II), Ni(II), Cu(II) and Zn(II) were taken between 650 and 4500 cm^{-1}. Samples were prepared as Nujol mulls and the spectra recorded on a Unicam SP 200 spectrophotometer. The complete spectra are given in Figures VII to XI. The principal bands are listed in Table VI.

Table VI - Principal infrared absorption bands of ETTA and metal complexes of ETTA between 650 and 4500 cm^{-1}.

ETTA	Co_2ETTA .4H_2O	Ni_2 ETTA .8H_2O	Cu_2 ETTA .2H_2O	Zn_2ETTA .2H_2O
	3250 s*	3300 s	3300 m*	3200 s
3000 s				
1810 s				
1690 s			1690 w*	1690 w
	1570 s	1580 s	1570 s	1570 s
1410 s				
	1380 s	1380 s	1400 s	1400 s
1280 s				
	1220 m	1220 m	1220 w	1220 m
1180 s				
1130 s	1140 w	1150 w		1150 w
				1040 w
920 m	930 w	930 w		940 w
910 m	900 w	900 m	900 w	900 w
880 m				
830 m				
800 m				
780 w	780 w	770 w	780 w	780 m

* s - strong, m - medium, w - weak.

In Figure IX the spectrum of the Ni complex dried at 119° and apparently corresponding to the formula Ni_2 ETTA .2H_2O is included for comparison with the spectrum of Ni_2 ETTA .8H_2O. The spectra are not significantly different except that the intensity of the absorption at 3300 cm^{-1} is reduced in the product dried at 119°.

3.2 Discussion of the solid complexes

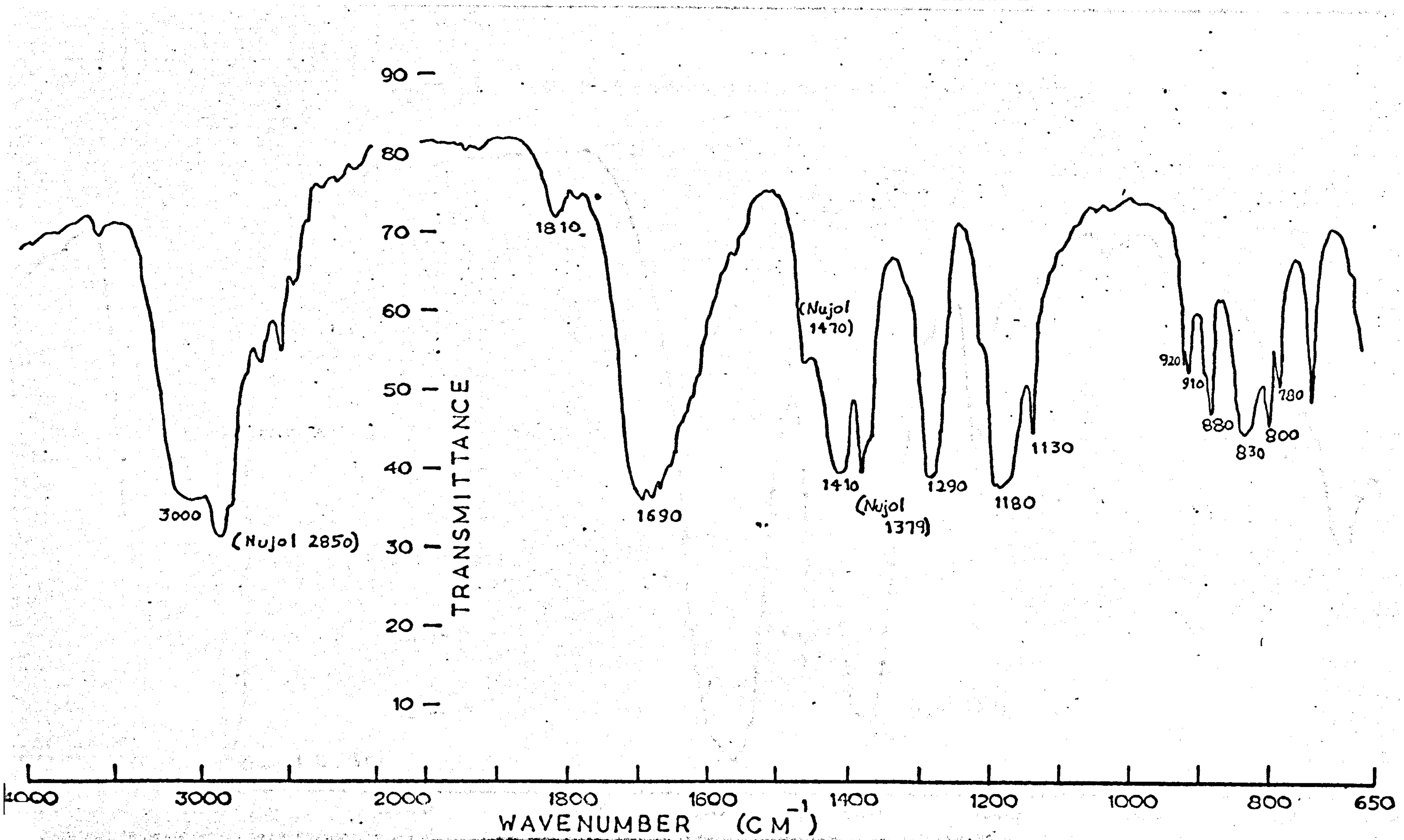

Figure VII. Infrared spectrum of ETTA. (Nujol mull.)

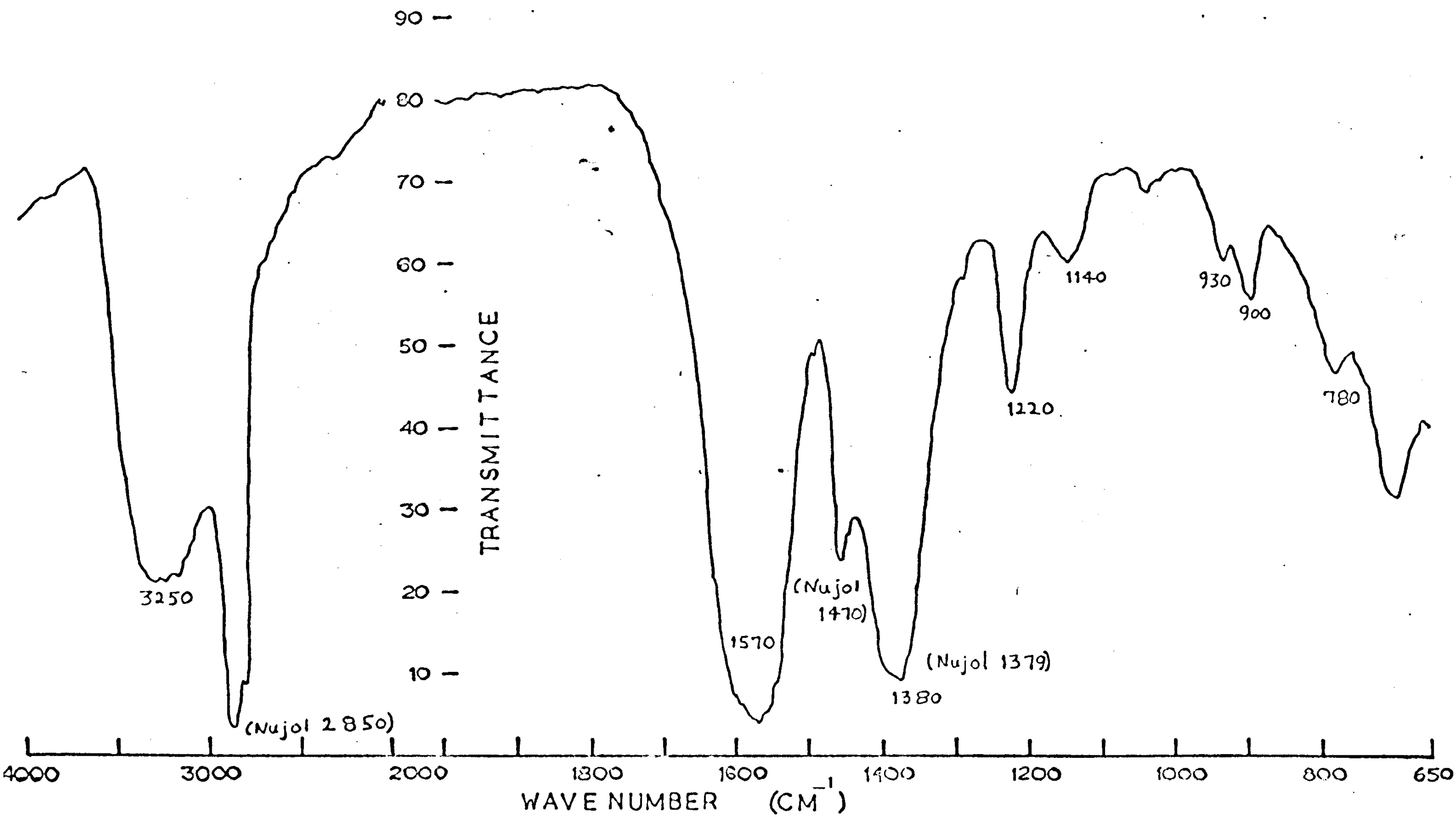

Figure VIII. Infrared spectrum of $Co_2ETTA.4H_2O$. (Nujol mull.)

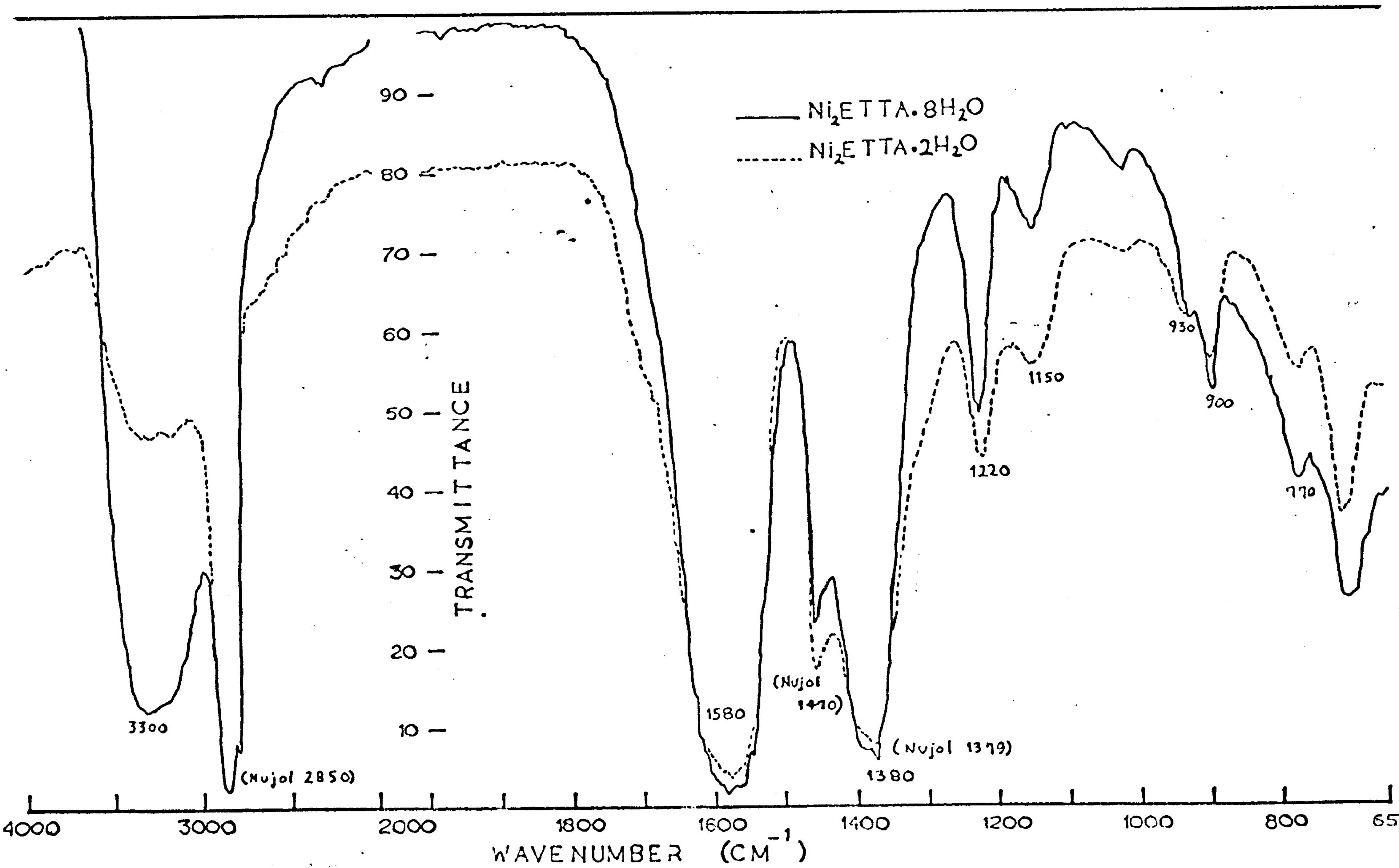

Figure IX. Infrared spectra of $Ni_2ETTA.8H_2O$ and $Ni_2ETTA.2H_2O$. (Nujol mulls.)

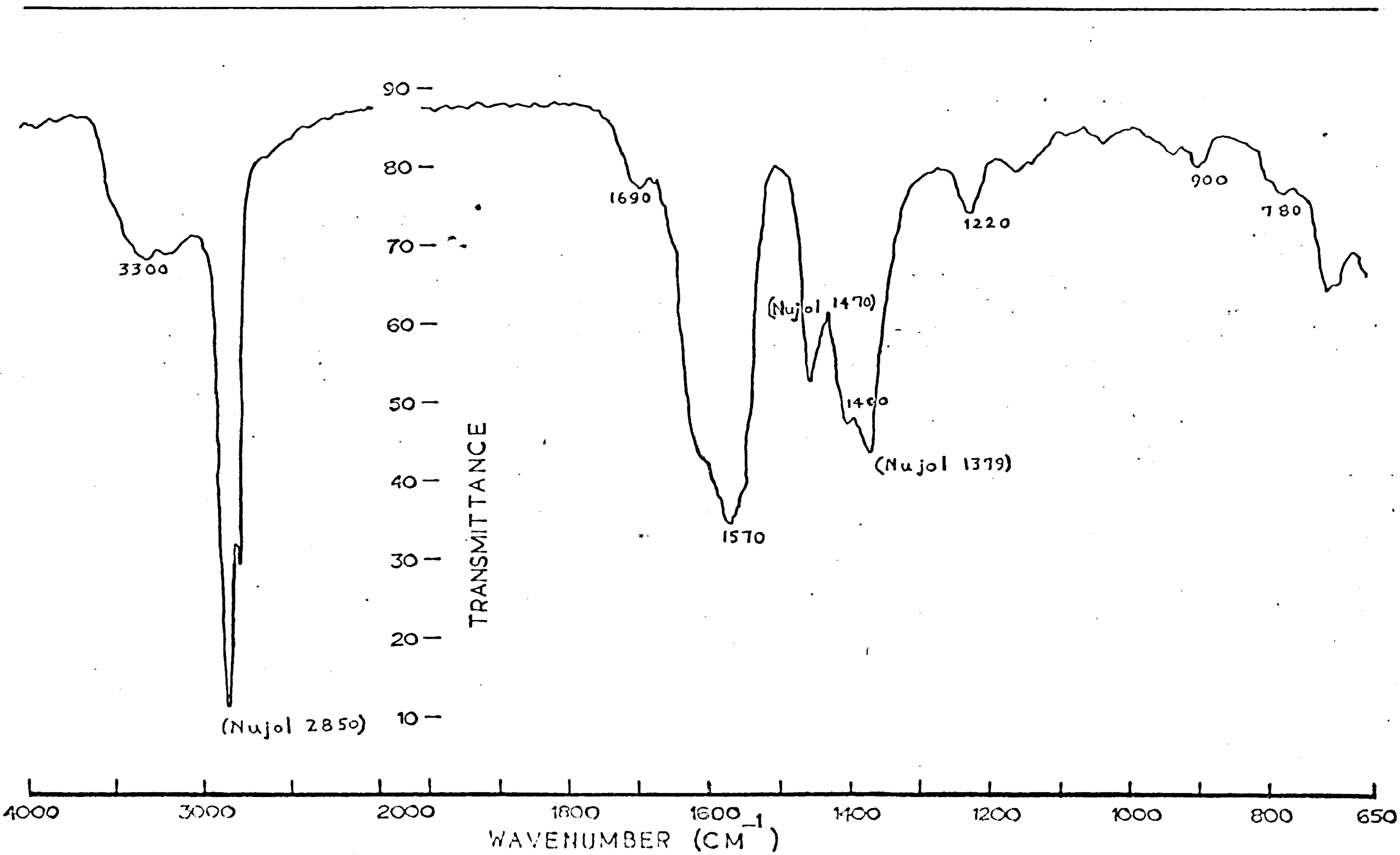

Figure X. Infrared spectrum of Cu$_2$ETTA.2H$_2$O. (Nujol mull.)

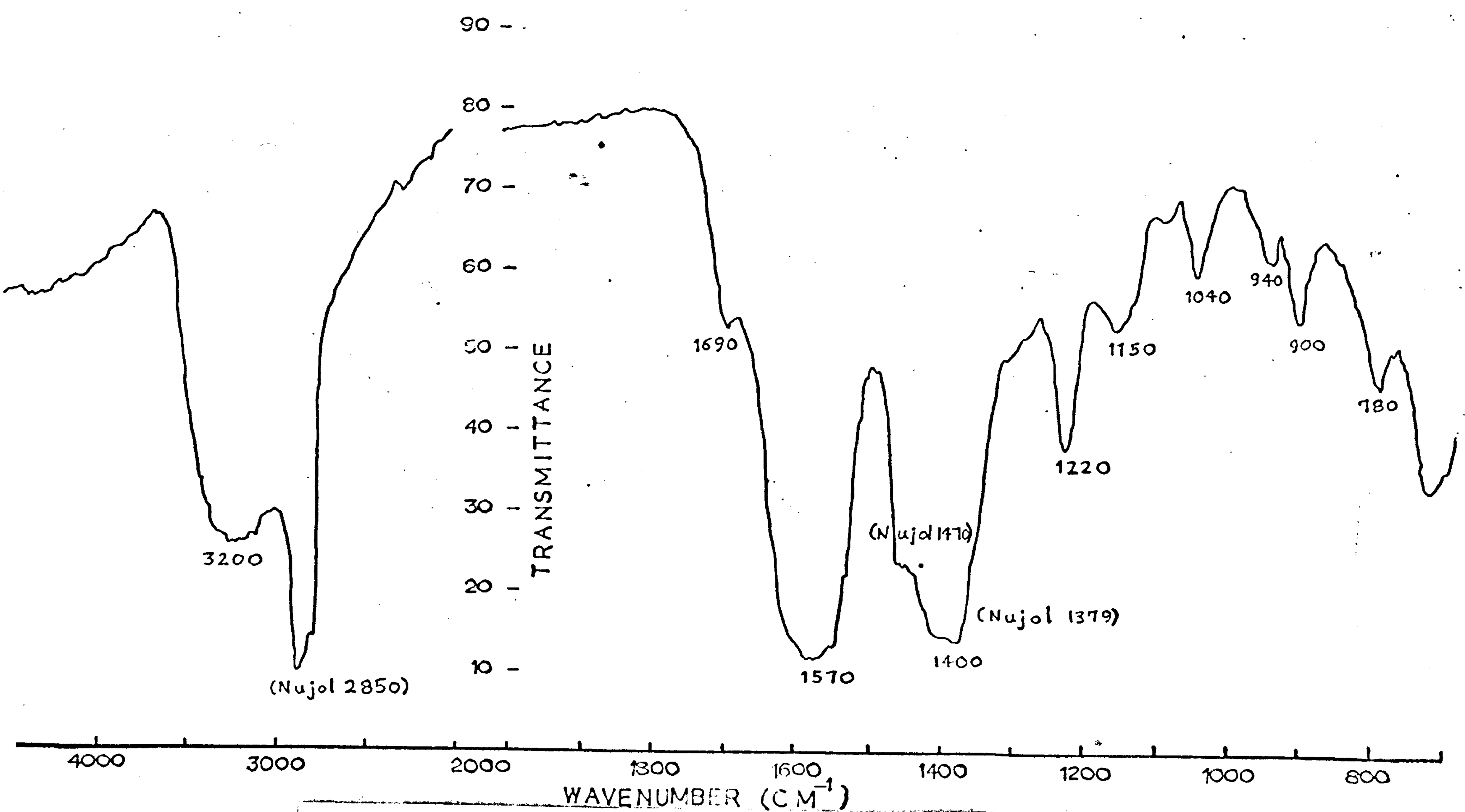

Figure XI. Infrared spectrum of $Zn_2ETTA.2H_2O$. (Nujol mull.)

3.21 Complexes of ETTA

a. Co_2 ETTA $.4H_2O$

Complexes of Co(II) are usually octahedral or tetrahedral, although a few examples of square complexes and of ones in which there is 5 - coordination are known. The magnetic moment and the visible and near infrared spectra are useful in determining the structure of a particular Co(II) complex. The magnetic moments observed for the different stereochemistries will be considered first. All known square planar complexes of Co(II) have a single unpaired electron, and magnetic moments close to the spin-only value of 1.73 B.M. Five coordinate complexes of Co(II) may be either high spin (3 unpaired electrons) or low spin (1 unpaired electron). High spin five coordinate complexes are of fairly recent characterisation (50, 51, 52, 53) and have been found to have magnetic moments in the range 4.4 to 5.5 B.M. (54), orbital contribution to the moment raising it above the spin-only value of 3.89 B.M. for three unpaired electrons. Tetrahedral complexes always have three unpaired electrons as do all cobalt complexes known definitely to be octahedral. The former have magnetic moments in the range 4.1 to 4.9 B.M. and the latter in the range 4.7 to 5.2 B.M.* Since by far the greater number of high spin Co(II) complexes have been found to be either octahedral or tetrahedral, a Co(II) complex observed to be high spin is usually expected to have one of the structures mentioned rather than to be five coordinate.

Co_2 ETTA $.4H_2O$ was found to have a magnetic moment of 4.87 B.M., which would be consistent with either an octahedral or tetrahedral structure of the complex as discussed above. In addition to the magnetic moment, the spectrum of Co_2 ETTA $.4H_2O$ may also be considered. It is found to be very similar to the spectra observed for octahedral complexes of Co(II). The main features of the spectrum of Co^{2+} in an octahedral field may be understood by considering the partial energy level diagram in Figure XII.**

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* F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 1st ed., Interscience Publishers, 1962, p.725.

** Cotton and Wilkinson, op.cit., p.724

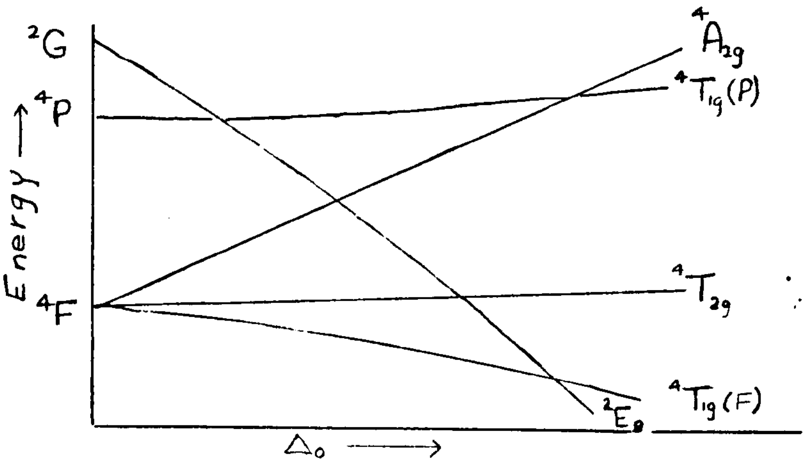

Figure XII Partial energy level diagram for a d^7 ion in an octahedral field (Qualitative only)

Three Russell-Saunders states of the field-free ion, ^4F, ^4P, ^2G, are located at the extreme left of the figure, and the splitting of these states is shown with increasing field strength. The different states in the ligand field are given their usual symbols. On the basis of this splitting of the energy levels of the field-free ion, three spin-allowed ($\Delta S = 0$), d - d transitions would be expected. These occur in octahedral complexes of Co^{2+} in the following ranges.*

$T_{2g}(F) \longleftarrow {}^4T_1(F)$	8 - 9,000 cm^{-1}
$^4A_{2g}(F) \longleftarrow$	16 - 18,000 cm^{-1}
$^4T_1(P) \longleftarrow$	20 - 21,100 cm^{-1}

The transitions are weak, having molar extinction coefficients of approximately 10 or less. The weak absorption in the 16 - 18,000 cm^{-1} range accounts for the pale pink color of octahedral Co(II) complexes. Tetrahedral Co(II) complexes, on the other hand, have a very intense absorption in the red part of the spectrum, at about 14,000 cm^{-1}. The molar extinction coefficient for this absorption is about 500, and tetrahedral complexes are usually an intense blue. Co_2 ETTA $.4H_2O$ was observed to be pale pink, and to show in its diffuse reflectance spectrum a weak absorption at 8080 cm^{-1} and a second weak absorption at 20,000 cm^{-1}. The spectrum is shown in Figure II. It was not possible to observe any d - d transitions above about 20,000 cm^{-1} because

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* T. M. Dunn in Modern Coordination Chemistry, J. Lewis and R. G. Wilkins (eds.), 1st ed., Interscience Publishers, 1960, p.290.

of the very intense absorption above this energy due presumably to charge transfer. In diffuse reflectance spectra, usually there is more band broadening and the spectra show less fine structure than do single crystal or solution spectra. However, the spectrum of Co_2 ETTA $.4H_2O$ corresponded in intensity and general position of observable bands to those of octahedral complexes of Co(II). The two observable bands in the ETTA complex occur at energies fairly close to those assigned in the spectrum of $Co(H_2O)^{2+}$ to $^4T_{2g}(F) \leftarrow {}^4T_1(F)$ at 8000 cm^{-1} and to $^4A_{2g} \longleftarrow {}^4T_1(F)$ at 19,600 cm^{-1}*. In $Co(H_2O)_6^{2+}$ another absorption maximum at 21,600 cm^{-1} is observed, and is assigned to $^4T_1(P) \longleftarrow {}^4T_1(F)$.

The spectrum of the complex which is apparently Co_2 ETTA $.2H_2O$ does not differ basically from that of the tetrahydrate. The bands in the dihydrate are shifted slightly towards lower energies compared to the tetrahydrate, i.e. from 8080 to 7900 cm^{-1} and from 20,000 to 18,700 cm^{-1}. From this it is inferred that the field about the Co^{2+} ion is charged only slightly in the dihydrate and remains approximately octahedral.

An absorption maximum at 5140 cm^{-1} was observed in the diffuse reflectance spectrum of Co_2 ETTA $.4H_2O$; however, this absorption disappeared when the complex was dried to the dihydrate. An absorption maximum at 5140 cm^{-1} was observed also in the spectra of Ni_2 ETTA $.8H_2O$ and Cu_2 ETTA $.2H_2O$, as shown in Figures III and IV. The absorption was greatly reduced in the nickel complex when it was dried to the pentahydrate. Since drying removed or reduced this absorption it was thought probable that the absorption was related to the vibrational spectrum of the bound water in these complexes.

If Co_2 ETTA $.4H_2O$ and Co_2 ETTA $.2H_2O$ are octahedral as implied by their spectra then it is almost certain that each ETTA group can provide eight or ten donor atoms in order to satisfy the coordination number of the Co^{2+} ions. For the tetrahydrate it is possible to visualize that each ETTA group could provide 2 S atoms and 2 O atoms to each of two different Co^{2+} ions, and the remaining two coordination sites on each Co^{2+} ion could be filled by the water molecules. Molecular models indicate there are a number of sterically possible structures for the complex, but the elucidation of the actual structure must await X-ray crystal analysis.

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* B. N. Figgis, *Introduction to Ligand Fields*, Interscience Publishers, (1966), p.233.

If two coordination sites on each Co^{2+} are filled by water molecules then when water is removed to form the dihydrate, the coordination sites previously filled by water molecules would presumably be filled by interactions between neighbouring groups in the crystal lattice. The hygroscopic behaviour of the dihydrate would imply that the tetrahydrate is the more stable form.

b. Ni_2 ETTA $.8H_2O$

Ni(II) complexes are usually one of octahedral, tetrahedral or planar structure, and in any one of these the Ni^{2+} ion may have two unpaired electrons. In some planar complexes of Ni(II), the Ni^{2+} is diamagnetic. A planar structure is probably very seldom strictly obtained since neighbouring molecules in the crystal lattice in solids or solvent molecules in solution may convert the otherwise planar structure into a distorted octahedral structure. It is generally considered that octahedral complexes of Ni(II) should have magnetic moments up to roughly 10% greater than the spin-only value of 2.83 B.M., and that tetrahedral complexes should have moments in the range 3.2 to 4.2 B.M. Many Ni(II) complexes once thought to be tetrahedral are now known to be octahedral, and true tetrahedral complexes are believed to be of very rare occurrence. Five coordinate complexes of Ni(II) are known (50), but again these are very uncommon compared to octahedral complexes. High spin five coordinate complexes have magnetic moments of the order of 3.2 B.M. (54).

The magnetic moment of Ni_2 ETTA $.8H_2O$ was found to be 3.27 B.M., which is consistent with the octahedral structure implied by the diffuse reflectance spectrum of the complex. The main features of the spectra of octahedral complexes of Ni(II) may be understood by considering Figure XIII*.

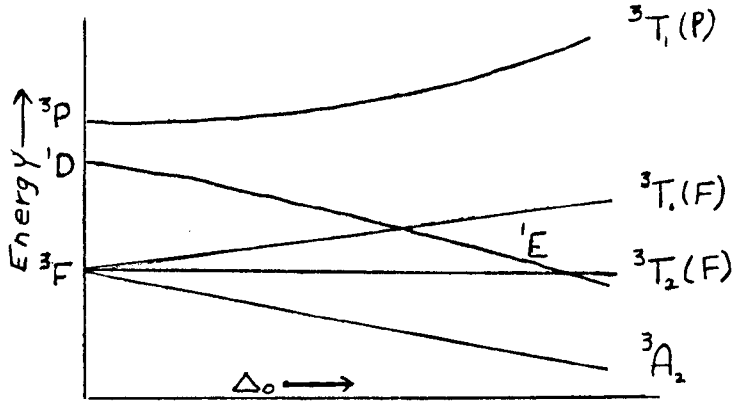

Figure XIII Partial energy level diagram for a d^8 ion in an octahedral field. (Qualitative only).

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* Cotton and Wilkinson, op.cit., p. 577.

Three spin-allowed transitions are expected, and in octahedral Ni(II) complexes these have been assigned as follows:*

${}^3T_{2g}(F) \longleftarrow {}^3A_{2g}$	8600 cm^{-1}
${}^3T_{1g}(F) \longleftarrow$	14000 cm^{-1}
${}^3T_{1g}(P) \longleftarrow$	25000 cm^{-1}

The transitions are weak, having molar extinction coefficients of about 10 or less. The spectra of tetrahedral Ni(II) complexes, on the other hand, show an absorption at about 15,000 cm^{-1} of very high intensity, the molar extinction coefficient being about 200. The spectra of five coordinate Ni(II) complexes, although showing considerable variation from complex to complex usually have a more complex pattern (50, 54) than that observed for octahedral complexes.

The diffuse reflectance spectrum of Ni_2 ETTA $.8H_2O$ has absorption maxima at 8760 cm^{-1}, at 15,150 cm^{-1} and at 25,000 cm^{-1}, as shown in Figure III. The position of these bands is very similar to the position of corresponding bands in the spectrum of $Ni(H_2O)_6^{2+}$, i.e. at 8,700 cm^{-1}, 14,500 cm^{-1} and 25,300 cm^{-1}**. The spectrum of the complex dried at 83°, Ni_2 ETTA $.5H_2O$, did not differ basically from that of the octahydrate, although the absorption maxima were altered in position slightly, from 8760 in Ni_2 ETTA $.8H_2O$ to 8330 cm^{-1} in the pentahydrate, from 15,150 to 14,350 cm^{-1} and from 25,000 to 24,600 cm^{-1}. From this it is inferred that not all of the eight water molecules in the octahydrate are necessary in order that six coordination sites will be filled on each Ni^{2+} ion. The nickel complex could be converted to the dihydrate without decomposing the complex completely, but removing more water than this apparently did destroy the complex, as described in section 3.12. If the dihydrate is octahedral, as the octahydrate and pentahydrate apparently are, this would imply that an ETTA molecule can fill up to ten coordination sites on two different Ni^{2+} ions.

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* T. Dunn in Lewis and Wilkins (eds.), op.cit., p.288.

** Figgis, op.cit., p.220.

c. Cu_2 ETTA $.2H_2O$

The observed magnetic moment of Cu_2 ETTA $.2H_2O$ was 1.77 B.M. This is equal within experimental error to the spin-only value of 1.75 B.M., and indicates the presence of Cu(II) in the complex. It appears that the copper complex of ETTA does not show the quenching of the spin moment observed for a number of copper (II) complexes of dicarboxylic acids of the type $HOOC-(CH_2)_n - COOH$, for which the magnetic moment is in the order of 1.4 B.M. (59). The lowering of the moment is believed due to metal-metal bonding in complexes of these acids.

Complexes of Cu(II) usually show distorted octahedral symmetry, or in the limit of this distortion, a square planar arrangement. Some five coordinate complexes of Cu(II) have been reported (50). The interpretation of the electronic spectrum is complicated. There is a very broad absorption band in the region 11,100 to 16,600 cm^{-1}, but this is believed to be made up of overlapping bands. The diffuse reflectance spectrum of Cu_2 ETTA $.2H_2O$, as given in Figure IV, shows a single absorption maximum at 13,300 cm^{-1}, and a very intense band, presumably due to charge transfer, absorbing strongly by about 22,000 cm^{-1}. This absorption may explain the yellow-green color of the complex, as opposed to the usual blue or blue-green color of complexes of Cu(II). The absorption maximum at 13,300 cm^{-1} is fairly close to the value observed for the corresponding band in Cu $(H_2O)_6^{2+}$, i.e. at 12,500 cm^{-1}.*

Since Cu_2 ETTA $.2H_2O$ was not found to be measurably hygroscopic, unlike the dihydrates of the Ni(II) and Co(II) complexes, it appears that the cupric ion can satisfy its coordination number more readily using the donor atoms available from ETTA than can the cobalt and nickel ions. Like the Ni(II) complex, the Cu(II) complex completely decomposed when the dihydrate was heated. If Cu_2 ETTA $.2H_2O$ has an octahedral structure as expected, then the decomposition when the bound water is removed would suggest that the ETTA group can fill up to ten coordination sites on two different Cu^{2+} ions.

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* Figgis, op.cit., p.218

d. Zn_2 ETTA .$2H_2O$

Since Zn(II) is a d^{10} ion, it is diamagnetic and has no spectrum due to d- d transitions, in contrast to Co(II), Ni(II) and Cu(II). Although the zinc complex of ETTA has the same stoichiometry as the Cu(II) complex, it is thermally much more stable, suggesting the nature of the zinc complex is different from that of the copper complex.

e. The infrared spectra

The carboxyl stretching frequency in a carboxylic acid would be expected to change when -COOH is replaced, by -COOM, where M represents a metal ion. As the O-M bond becomes more ionic, the carboxylate resonance would be expected to increase, the single bond character of the carboxyl group to increase, and the stretching frequency to decrease. The carboxyl stretching bands are usually very strong and easily identified in the spectra of carboxylic acids and of metal complexes of carboxylic acids. In saturated aliphatic acids the strong band in the region 1700 - 1725 cm^{-1} is assigned to carboxyl stretching (57). Morris and Busch have discussed O-M bonding in Co(III) complexes of EDTA (55). For EDTA itself the carboxyl stretching frequency is found at 1745 cm^{-1}. In Na_4 EDTA .$0.5H_2O$ the carboxyl stretching frequency was observed at 1605 cm^{-1} and this was taken to be the value characteristic of ionic bonding for metal complexes of EDTA. In $Na_2[\text{Co EDTA } NO_2].H_2O$ two absorptions were observed in the carboxyl stretching frequency region, one at 1650 cm^{-1} and the second at 1604 cm^{-1}. The absorption at 1650 cm^{-1} was associated with more covalent O-M bonding, and the absorption at 1604 cm^{-1} with an ionic metal ion-carboxylate linkage. It was pointed out that the resolution of the spectra of metal carboxylates may not always be sufficiently good to show both types of carboxylate groups when both are present in a given complex. In the infrared spectra of the complexes of Co(II), Ni(II), Cu(II), and Zn(II), with EDTA, Sawyer and Paulsen found a single absorption in the carboxyl stretching frequency region, at 1605 cm^{-1}, and concluded that the carboxylate bonds in these complexes were primarily ionic.

From Table VI and Figures VIII to XI it can be seen that the metal complexes of ETTA have an absorption at 1570 cm^{-1} which can almost certainly be attributed to carboxyl stretching vibration. The carboxyl stretching frequency in the pure acid is assigned to the absorption at 1690 cm^{-1}. See Figure VII. The carboxyl stretching frequency has shifted about 80 cm^{-1} towards lower frequencies in the complexes, and is in the region 1550 - 1610 cm^{-1} where ionic carboxylates have been found in other complexes as described. Although the complexes with Co(II) and Ni(II) have a single band in the carboxyl stretching frequency region, under the present resolution, the complexes with Cu(II) and Zn(II) have a second, weaker absorption at 1690 cm^{-1}. This would seem to suggest the presence of a -COOH group in these complexes. However, if this were so, the resulting complex would have to have metal : ligand ration 3 : 2 to balance the electrical charge, and this is inconsistent with the elemental analysis. No explanation can be offered for this absorption at the present time.

All four complexes showed a broad absorption in the region 3250 to 3300 cm^{-1}. This absorption is assigned to vibrational modes of the bound water in the complex. In general water trapped in the crystal lattice or coordinated to the metal ion absorbs in this region (58).

3.22 Other complexes

Some work was begun on metal complexes of ligands related to ETTA. The Co(II) and Ni(II) complexes of PDTA $(HO_2C-CH_2-S)_2CH$-⌬-$CH(S-CH_2CO_2H)_2$ showed metal : ligand ratio 2 : 1, and from the metal and carbon analyses it was inferred that the complexes had eight molecules of water bound per formula unit. The diffuse reflectance spectrum of the Ni(II) complex was obtained, and is shown in Figure V. The spectrum is similar to that observed for known octahedral complexes of Ni(II), with a band at 8160 cm^{-1}, one at 14,700 cm^{-1} and a sharper absorption at 24,700 cm^{-1}. The second band shows some splitting with a shoulder at 12,900 cm^{-1}. The splitting of the second band is observed in the spectrum $Ni(H_2O)_6^{2+}$ and it has been suggested that this is due to mixing of close triplet and singlet states*. The Cu(II) complex of PDTA could not be prepared, at least by the method used in preparing the Co(II) and Ni(II) complexes. The changing of $>CH-CH<$ as in ETTA for $>CH$-⌬-$CH<$ as in PDTA, is apparently sufficient to cause the ligand to be oxidized in the presence of Cu(II).

The Co(II) and Ni(II) complexes of BBTA $(HO_2CCH_2S)_2CH$-⌬, although prepared under the same conditions as the complexes of ETTA, did not contain as much bound water as did the latter. The complexes had metal : ligand ratio 1 : 1, and the nickel complex had one molecule of water per formula unit while the cobalt complex was anhydrous.

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* Cotton and Wilkinson, op.cit., p.736.

The complexes were insoluble in water, unlike the corresponding complexes of ETTA and PDTA, and this suggests that the complexes of BBTA have structures different in some respects from the structures of complexes of ETTA and PDTA. The diffuse reflectance spectrum of the cobalt complex only was taken, and is shown in Figure VI. The absorption maxima are listed in Table V. The absorption is in the regions expected for Co(II) in an octahedral complex, that is at about 8000 cm^{-1} and about 20,000 cm^{-1}. If the complex is at least approximately octahedral, some of the six coordination sites on the Co^{2+} ions must be filled by interactions between adjacent units.

Even Ni(II) and Zn(II) complexes of methylphenylmethylidynebis-(thioglycollic acid), HO_2CCH_2S C (CH_3)-⌬, could not be prepared by the method used to prepare the other complexes described. This implies that when -C -S$)_2$-CH -⌬ is changed to -C -S$)_2$-C(CH_3) -⌬, the nature of the ligand is changed sufficiently that the latter ligand decomposes in the presence of metal ions.

3.23 Summary

$Co_2ETTA.4H_2O$ was found to have a magnetic moment and an electronic spectrum consistent with an octahedral structure of the complex. When $Co_2ETTA .4H_2O$ was heated to form the dihydrate the spectrum of the complex remained essentially the same. In an octahedral complex of simplest formula, $Co_2ETTA .2H_2O$, a total of 10 coordination sites would have to be filled by donation from the ETTA molecule. $Ni_2ETTA .8H_2O$ was also found to have a magnetic moment and an electronic spectrum consistent with an octahedral structure. The spectrum of the pentahydrate implied that it has the same type of structure as the octahydrate. Although the electronic spectrum of the complex corresponding to $Ni_2ETTA .2H_2O$ was not taken, if it is octahedral as expected on the basis that it has nearly the same color as the octahydrate and the pentahydrate, then the ETTA group again would be required to fill a total of 10 coordination sites.

The cupric complex with ETTA is expected to have a tetragonally distorted octahedral structure as is usual for Cu(II) complexes. The stoichiometry of the cupric complex, $Cu_2ETTA .2H_2O$, suggested, as for the Ni(II) and Co(II) complexes, that the ETTA group can fill a total of 10 coordination sites. Since both $Cu_2ETTA .2H_2O$ and $Ni_2ETTA .2H_2O$ decomposed on further removal of water, it appears that 10 is the maximum number of coordination sites that can be filled by one ETTA group. In the complexes of ETTA with Co(II), Ni(II) and Cu(II) the position of the absorption bands in the electronic spectrum corresponded closely to those for the corresponding hexaquo ions.

The zinc complex, $Zn_2ETTA.2H_2O$, has the same stoichiometry as the copper complex, but the observation that it is thermally much more stable suggests that the nature of the bonding in the copper and zinc complexes is different.

The infrared spectra of the Co(II), Ni(II), Cu(II) and Zn(II) complexes of ETTA indicated that the metal-carboxylate bonding is primarily ionic. In this respect the complexes of these metals with ETTA are similar to the corresponding complexes with EDTA.

Only the Ni(II) and Co(II) complexes of PDTA were prepared, but these appeared to be similar to the complexes of ETTA. Both complexes contained 8 molecules of water per formula unit, and were found to be soluble in water. The electronic spectrum of the nickel complex implied an octahedral structure, the energy of the first transition being close to that observed for the first transition in the nickel complex of ETTA.

The Ni(II) complex with BBTA had only one bound molecule of water, the Co(II) had no bound water, and both complexes were insoluble in water. These observations suggest that the basic structure of these complexes is different from that of ETTA and PDTA. The electronic spectrum of the Co(II) complex of BBTA indicated an octahedral structure, in which case some of the coordination sites on the Co^{2+} ion must be filled by interactions between neighbouring groups in the crystal lattice.

When the ligand $(HO_2C-CH_2-S)_2-C(CH_3)-\emptyset$ was mixed with Ni(II) or Zn(II), decomposition of the ligand occurred, implying that when H- is replaced by CH_3- in going from $(HO_2C-CH_2-S)_2-CH\emptyset$ to $(HO_2C-CH_2-S)_2-C(CH_3)\emptyset$ the nature of the ligand and the complexes it can form are critically changed.

Although sulfidecarboxylic acids form weak complexes in solution, as shown in Table I in section 1, the solid complexes form readily and indicate by their stoichiometry and spectra that sulfur donation to the metal ions is important in these compounds.

EDTA has been reported to form complexes of the stoichiometry Ni_2EDTA, $Co_2EDTA.3H_2O$ and Zn_2EDTA when a solution of the ligand is mixed with a solution of the metal carbonate (67, 68). However, very little more is known about these complexes than that they can be prepared.

The structural investigations on the Co(II), Ni(II) and Cu(II) complexes of EDTA to date have been done on complexes containing one transition metal ion bound per EDTA group as in $Na_2[CoEDTA].4H_2O$, $H[Ni(H_2O)HEDTA]$, and $H[Cu(H_2O)HEDTA]$. These complexes were prepared in a basically different way to that used in the preparation of the 2 : 1 complexes. The X-ray crystal analysis of the 1 : 1 complexes has shown that in $H[Cu(H_2O)HEDTA]$ and in $H[Ni(H_2O)HEDTA]$ the ligand is pentadentate while in $Na_2[CoEDTA].4H_2O$ it is hexadentate. It would be of interest in future work to prepare complexes of ETTA by the methods used to prepare the 1 : 1 complexes of EDTA, and hence to determine the number of transition metal ions bound per ETTA in the complexes formed under these conditions.

3.3 The complexes in solution

3.31 Experimental methods

3.311 Potentiometric measurements

Potentiometric titrations were carried out by adding NaOH from an Agla micrometer syringe to a solution containing the ligand, mineral acid and metal perchlorate, or in the determination of the acid dissociation constants to a solution containing the ligand and mineral acid only. The solution being titrated was maintained at $25 \pm 0.1^\circ C$ in a thermostatted water bath. To keep activity coefficients constant, the titrated solution was made 0.1 M in $NaClO_4$. The pH measurements were made using a Pye-Ingold combined glass-calomel electrode and a Dynacap pH-meter which gave a precision of ± .0025 pH units. The total volume of the solution was 50 mls in most of the experiments, and the solution was stirred using a magnetic stirer. A 250 ml conical flask with four necks was convenient to contain the solution and provide openings for the combined glass-calomel electrode, the thermometer, the Agla syringe and in the fourth neck a rubber bung fitted with two openings to allow purified nitrogen to be blown over the surface of the solution during the titration, thus preventing CO_2 from being absorbed by the solution. Equilibrium was reached rapidly in all systems, a constant pH reading being obtained after not longer than five minutes after each addition of alkali.

The pH meter was calibrated initially between pH 4 and 10.8 using a solution of pH 4.010 prepared from buffer tablets, N.B.S. Formula, and two solutions, one of pH 9.90 and the other of pH 10.80, prepared from borax and sodium hydroxide (60). The calibration curve, shown in Figure XIV, was found to be linear over the range of interest and in subsequent work the meter was simply calibrated with the solution of pH 4.010. The calibration of the pH meter held with no measurable drift for at least 24 hours.

The reagents used in the titrations were as follows. The $NaClO_4$, G.P. grade from B.D.H. Limited, was recrystallised from water and dried at 120°. The dried product showed no signs of melting below 230°, and was taken to be the anhydrous salt since the monohydrate melts at 130°. A solution which was .1M in the $NaClO_4$ showed no turbidity when tested with $AgNO_3$ indicating that the chloride ion concentration was negligibly low.

The NaOH solution, approximately 1N, was prepared from AR pellets, provided by B.D.H. Limited. To remove carbonate, the pellets were first dissolved in sufficient water to give a 50% solution, which was then allowed to stand until the carbonate precipitated. The solution was filtered, CO_2 being excluded, and finally diluted with freshly boiled distilled water until it was about 1 N. The 1 N solution was standardised against AR potassium hydrogen phthalate and stored in a polythene bottle, provision being made for filling the microsyringe without contamination by CO_2.

The perchlorates of Co(II), Ni(II), Cu(II) and Zn(II) were prepared using the ion exchange method described by Serjeant (61). In this method a column of cation ion exchange resin is treated with a solution of the metal sulfate or chloride, and after eluting the excess metal salt solution with water, the metal ions on the resin are displaced by passing $Ba(ClO_4)_2$ through the column. The nickel and copper perchlorate solutions were standardised by electrodeposition of the metal, and the cobalt and zinc solutions by titration against standard EDTA, all to a precision of better than 0.5%.

The perchloric acid used was B.D.H. AR grade and the approximately .3N solution was standardised against NaOH.

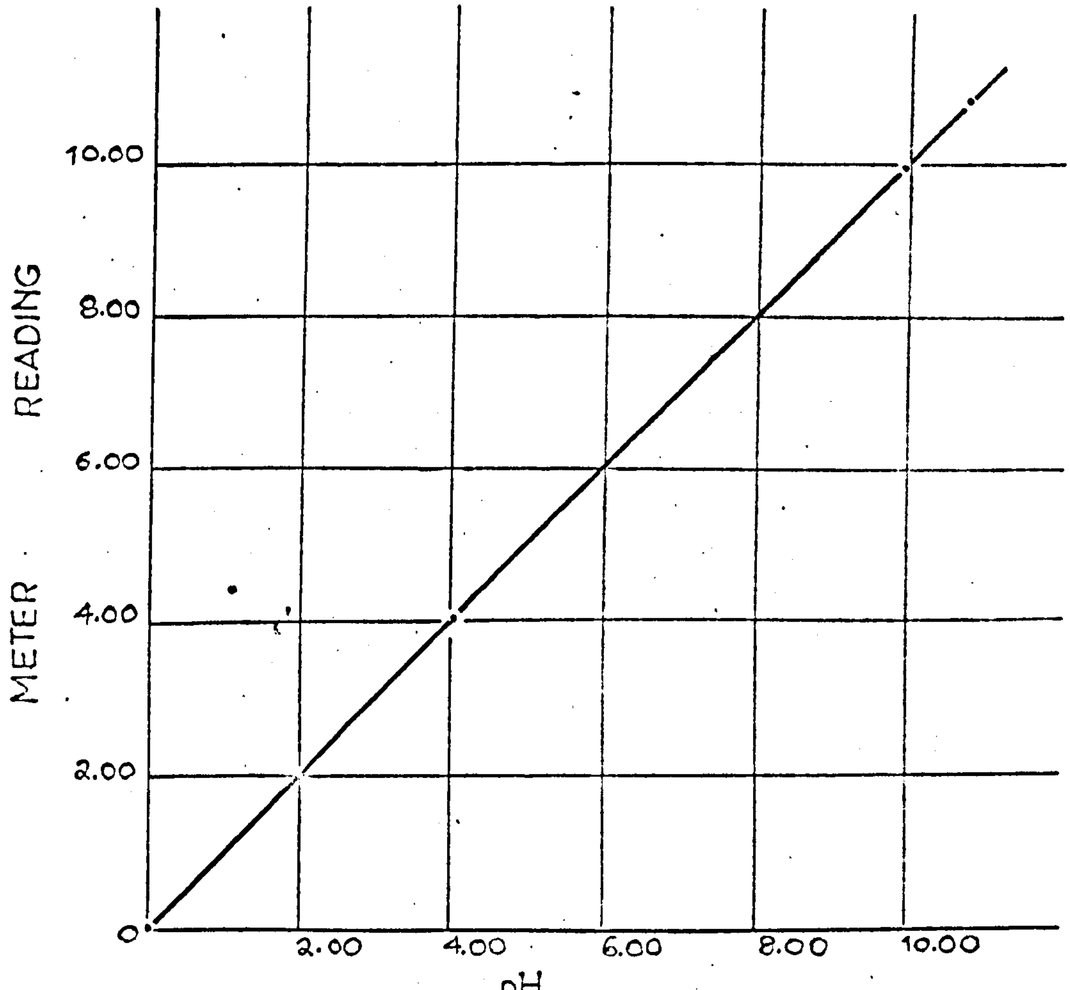


Figure XIV. Calibration of the pH meter.

Solutions of ETTA were made by dissolving the pure acid, prepared and purified as described in section 3.11, in the appropriate volume of water. It was found that although microorganisms tended to grow in solutions of the acid, the concentration of an approximately .002 M solution remained constant, as determined by titration of the solution against standard NaOH, for at least one month. It was noted towards the end of this work that a convenient way to prevent the appearance of the microorganisms was to add $NaClO_4$ to the solution as soon as it was prepared.

All the volumetric glassware used in the experiments was of 'A' grade standard.

3.312 Spectrophotometric measurements

Some of the spectrophotometric measurements were made using a Cary Model 14 Spectrophotometer, and the remainder using a Unicam SP 500. A thermostatted 10 cm cell was used in all the experiments, the temperature inside the cell being maintained at 25 ± .2°C. In the experiments in which it was desired to obtain the absorbance of a solution containing fixed total concentrations of ligand and metal ions as a function of pH, accurately measured increments of 1 N NaOH were added to the solution in the 10 cm cell from the Agla microsyringe and the absorbance measured after each addition. The pH of the solution in the cell was not measured directly, except initially and at the end of the titration, but was found from the "calibration curve" prepared from the results of doing a pH-titration on an equivalent volume of solution to that in the cell. It was found that the measured pH of the solution in the cell at the final and initial points was always within 1% of the value read from the calibration curve. Different spectrophotometric titrations were stopped at different values of pH, and hence the final values provided a means of checking the applicability of the calibration curve throughout its range. Using the calibration curve, the absorbance of a single solution could easily be measured over the pH range of interest. The method described proved considerably simpler than a batch technique, and did not require the addition of a buffer which might have complexed some of the metal ions or led to mixed complex formation. The volume of the solution in the cell, the knowledge of which was required to prepare the calibration curve, was obtained by finding the weight of solution in the cell, and using the measured density of the solution to calculate the volume.

3.32 Determination of the acid dissociation constants

The titration curves for a solution containing $HClO_4$, 8.685 x 10^{-3} M, and for a second solution containing the same concentration of $HClO_4$ and ETTA, 1.934 x 10^{-3} M, are shown in Figure XV. The actual values of the pH measurements and the volumes of alkali added are given in Tables I and II, Appendix A. Triplicate titrations were carried out for each solution, and the average pH taken for a given volume of alkali added. These curves were used to calculate the four, overall proton stability constants

$$\beta_j^H = \frac{[H_jA]}{h^j\,a}$$

(where j takes the values 0,1, 2, 3 and 4 and where β_0^H is defined to be 1)

by the least squares adjustment of the data as described in section 2.11. The program used is given under Program I in Appendix B, where the symbolism used in the program and some details of the operation of the program are given. For convenience, the program is written in terms of the overall constants. These are simply related to the acid dissociation constants since

$$\beta_j^H = K_1^H K_2^H \dots K_i^H \dots K_j^H$$

where $K_i^H = [H_iA] / h \times [H_{i-1}A]$

The acid dissociation constants, pK_{1a}, pK_{2a}, etc., are given by $pK_{1a} = -\log K_4^H$, $pK_{2a} = -\log K_3^H$, $pK_{3a} = -\log K_2^H$ and $pK_{4a} = -\log K_1^H$.

The least squares refinement was done over 28 points covering the pH range 2.350 to 5.915. As was indicated in section 2.11 in calculating the weights in the error square sum, it was assumed that all the error could be carried in the pH measurement, and from the fit of the calculated proton formation curve to the experimental curve this was taken to be a reasonable assumption. The program was allowed to continue the refinement of the constants until two successive sets of constants differed by less than one part in 10^5. Five cycles were found to be sufficient to give this degree of refinement. The stability constants obtained, and their respective standard deviations, as given from the least squares adjustment, are listed in Table VII.

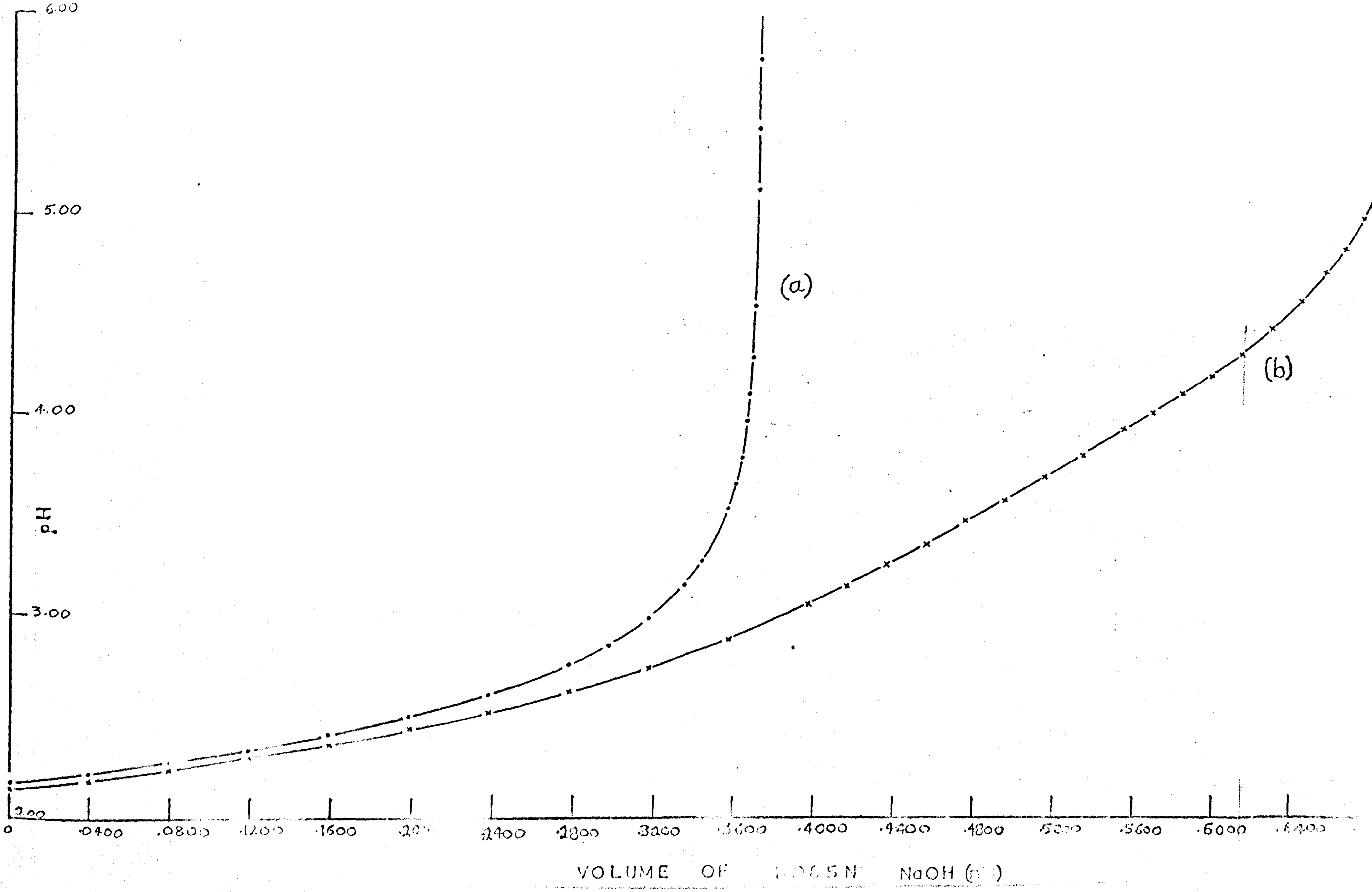


Figure [illegible]. Potentiometric titration (a) of $HClO_4$ and (b) of $HClO_4$ and ETTA. Concentration of $HClO_4$ 8.685×10^{-3} M; concentration of ETTA 1.934×10^{-3} M.

Table VII. Proton stability constants and acid dissociation constants for ETTA in water. $\mu = .1$ (NaClO$_4$), $t = 25^\circ$C.

Refined stability constant				Acid dissociation constants			
$\log \beta_1$	4.572	±	.010	pK_1	2.89	±	.16
$\log \beta_2$	8.530	±	.049	pK_2	3.54	±	.11
$\log \beta_3$	12.07	±	.072	pK_3	3.958	±	.059
$\log \beta_4$	14.96	±	.088	pK_4	4.572	±	.010

The experimental formation curve, ($\bar{n}_H$, log a) and the curve calculated from the refined constants is shown in Figure XVI. The values used in plotting these graphs are given in Table III, Appendix A. The $\bar{n}_H$ values calculated from the stability constants plus or minus their calculated standard deviations gave values within less than ~.5% of the values calculated from the stability constants given by the refinement except for $\bar{n}_H$ values less than 2.8 when the values differed by as much as ~2%. Within the accuracy with which the formation curve in Figure XVI was plotted, the curves calculated from the β_j and the ($\beta_j \pm \sigma_{\beta_j}$) values were the same. The distribution of the acid in the various protonated forms and in the completely dissociated form as a function of pH was calculated from the proton stability constants obtained and is shown in Figure XVII. The values used in the plotting of these curves are given in Table IV, Appendix A, and were conveniently calculated using Program II, Appendix B. This is a general program for calculating the relative concentration of the various species in equilibrium, as a function of pH, for a solution containing the polybasic acid, H_JA, from a knowledge of the proton stability constants. The program calculates, in addition to $\alpha_0^H, \alpha_1^H \ldots \alpha_J^H$ the value of the sum $\alpha_0^H + \alpha_1^H + \ldots \alpha_c^H$ for each of the possible values of C, 0 to (J - 1), as a function of pH, although these latter curves have not been plotted for ETTA.

3.33 Discussion of the acid dissociation~~s~~ constants

At the outset, some consideration should be given to the expected accuracy of the calculated dissociation constants. In Table VII the standard deviations as calculated from the least squares adjustment of the data depend indirectly on a reasonable estimation of the accuracy in the original experimental measurements. In a least squares adjustment if there are no systematic errors and the weights in the experimental

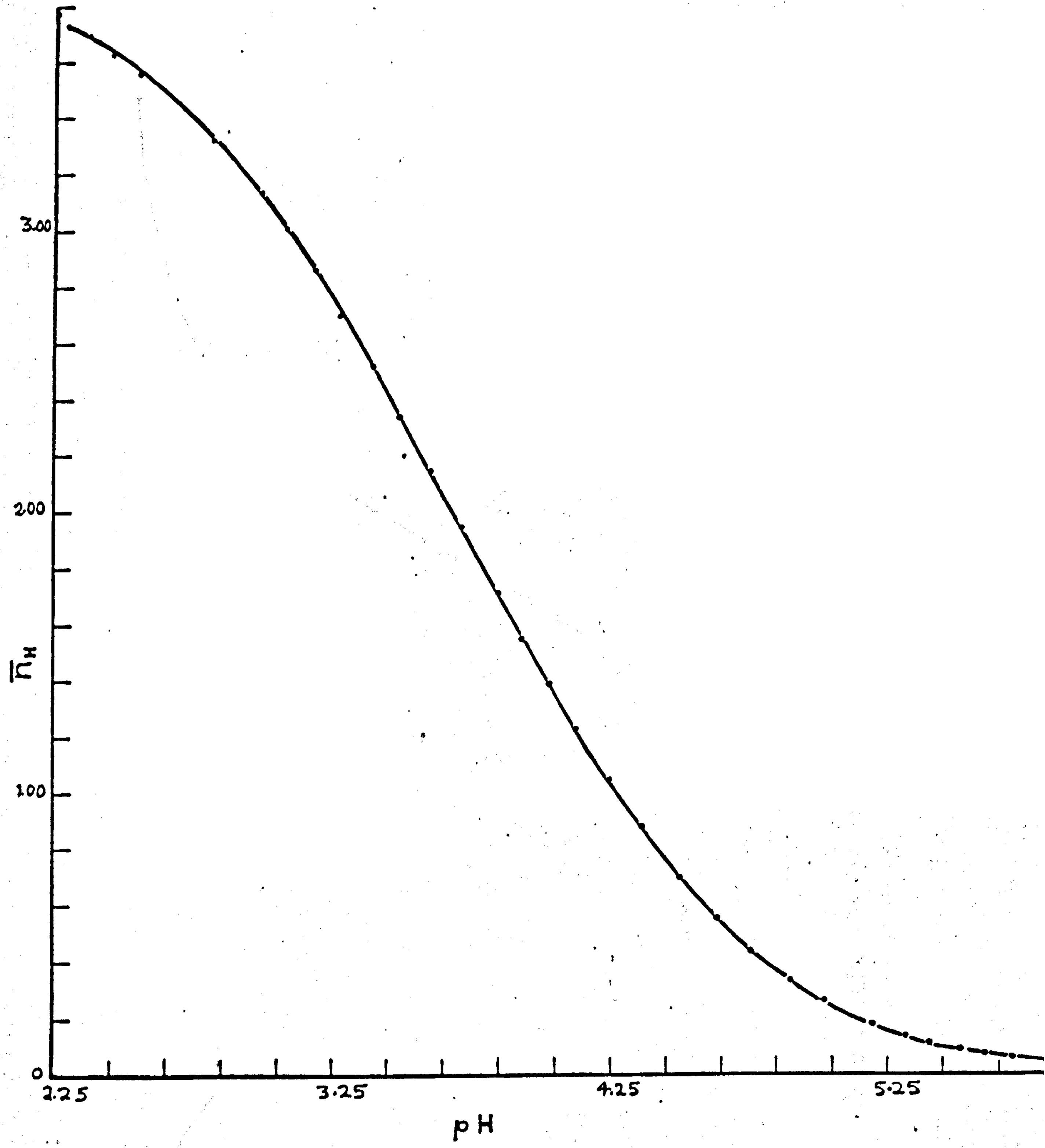


Figure XVI. The formation curve for ETTA. (.... – experimental $\bar{n}_H$; ——— -calculated $\bar{n}_H$ from refined β_j^H.)

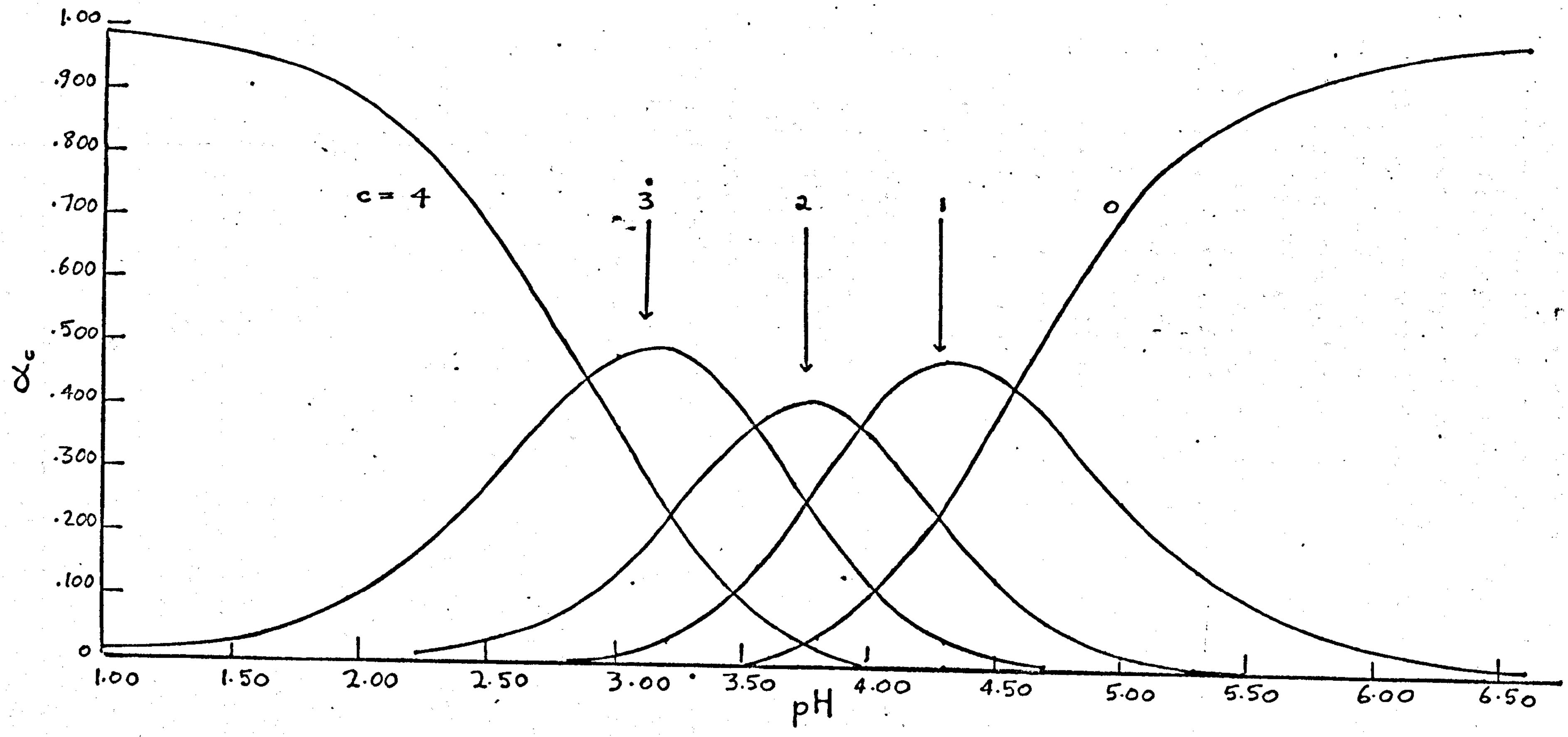


Figure XVII. The distribution of the various protonated forms of ETTA as a function of pH.

variables have been estimated accurately, as is believed to be true in the present studies, then the calculated standard deviations are a reasonable indication of the accuracy of the adjusted parameters. As shown in Table VII, the accuracy with which the dissociations constants are known increases towards pK_{4a}. This is expected since the first pK_a values are determined largely by the measurements in the most acidic solutions where it is more difficult to measure accurately the smaller difference between the titration curves of the mineral acid and of the mineral acid plus ligand. While the values obtained in this work for pK_{2a} and pK_{3a} agree within the experimental error with those obtained by Saini (19), the values for pK_1 and pK_4 appear to be significantly different. Saini's values were calculated by a method of successive approximations, and he shows a calculated pH-titration curve agreeing well with the experimental curve over the range pH 3.25 to 5.00. The present measurements extended over pH 2.34 to 5.91 and hence would be expected to permit more accurate evaluation of pK_{1a} and pK_{4a}.

The relative magnitudes of the acid dissociation constants of acids related to ETTA, and also the relative magnitudes of pK_{1a}, pK_{2a}, pK_{3a} and pK_{4a} for ETTA are useful in understanding the structure of ETTA and its various ionised forms. An important factor determining the strength of a carboxylic acid is the electronic effect of substituents attached to the carboxyl group. Electron - withdrawing substituents increase the ease of loss of a proton, and hence make the acid stronger, while electron-donating substituents have the opposite effect. The effect of a substituent is reduced the further away along the carbon chain the substituent is located, and when sufficiently far away it would be expected to have a negligible effect. The acid dissociation constants of a number of sulfide-carboxylic acids related to ETTA are given in Table VIII.

Table VIII Dissociation constants of sulfide-carboxylic acids. $\mu = .1$ Ref.18 - 25°C Ref.12 - 18°C

Acid	pK_{1a}	pK_{2a}	Ref.
$CH_2-(SCH_2CO_2H)_2$	3.37	4.19	18
	3.156	4.280	12
$(CH_2)_2-(SCH_2CO_2H)_2$	3.39	4.21	18
	3.208	4.298	12
$(CH_2)_3-(SCH_2CO_2H)_2$	3.44	4.25	18
	3.261	4.331	12

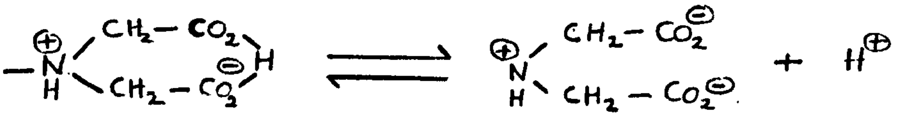
Table VIII (Cont'd...)

Acid	pK_{1a}	pK_{2a}	Ref.
$(CH_2)_4-(SCH_2CO_2H)_2$	3.254	4.384	12
$(CH_2)_5-(SCH_2CO_2H)_2$	3.301	4.377	12
$(CH_2)_4-(CH_2CH_2CO_2H)_2$	4.304	5.386	12

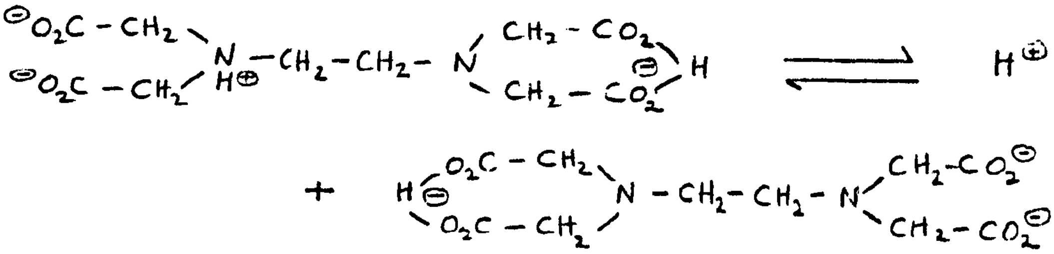
It can be seen by comparing the pK_{1a} values for $(CH_2)_4-(SCH_2CO_2H)_2$ and $(CH_2)_4 - CH_2CH_2CO_2H$, 3.254 and 4.304 respectively, that the presence of the S atom in place of the $-CH_2-$ group increases the ease of the loss of a proton about 10 times, and hence has a definite effect on the strength of the O - H bond in this type of acid. In comparing the pK_{1a} values of all the sulfide-carboxylic acids given in Table VII from Ref.(12) it can be seen that these values increase very slightly, with increasing number of methylene groups between the two $-SCH_2CO_2H$ groups, going from a pK_{1a} value of 3.16 in $CH_2(SCH_2CO_2H)$ to 3.30 in $(CH_2)_5-(SCH_2CO_2H)_2$. This implies that the presence of the second $-SCH_2CO_2H$ group affects the ionisation of the first when the groups are separated by one methylene group but that the effect decreases as the $-SCH_2CO_2H$ groups become further apart. On this basis it would be expected that the pK_{1a} value for ETTA would be close to the same as for the bifunctional acids, since in ETTA each $-SCH_2CO_2H$ group is separated by $CH\lessdot$ or $(CH\lessdot)_2$, but slightly less since any one $-SCH_2CO_2H$ group in ETTA could be considered to be influenced by three other $-SCH_2CO_2H$ groups rather than just one other as in the bifunctional acids. The value of pK_{1a} observed for ETTA was 2.89 ± .16, which is slightly below the value of 3.2 to 3.3 reported for $CH_2-(SCH_2CO_2H)_2$ and seems reasonable on the basis of the effect of the $-SCH_2CO_2H$ groups just discussed.

Once one proton is lost from an acid of the type $(CH_2)-(SCH_2CO_2H)_2$, the second ionisation would be expected to be more difficult due to the remaining negative charge. From Table VIII it is apparent that pK_{2a} is certainly larger than pK_{1a}. It is also true for ETTA, that the second proton is lost much less readily than the first. The values of pK_{2a} and pK_{3a} for ETTA are very close to each other being 3.54 ± .11 and 3.96 ± .06 respectively.

ETTA, as expected, does not behave in the ionisation process like EDTA which shows a very great difference between the second and third pK_a values, pK_{2a} being for EDTA 2.67 and pK_{3a}, 6.16(4). In EDTA the presence of nitrogen atoms greatly affect the acidity, since the nitrogen atoms can strongly bind protons. It has been suggested (5) that in the second ionisation (pK_{2a}) probably an important process is



while in the third step (pK_{3a}) the following ionisation is believed to be important



For ETTA, in which sulfur replaces nitrogen, a straightforward dissociation from each of the four carboxyl groups in turn would be expected, the dissociation becoming gradually less favoured as the $-COO^-$ groups replace -COOH. If in H_4ETTA, the presence of three other $-SCH_2CO_2H$ groups can be considered to increase the acidity of the first proton, lowering pK_{1a} relative to the bifunctional acids, then by the same reasoning it would be expected that three $-S-CH_2CO_2^-$ groups would raise the pK_{4a} value above the pK_{2a} value for the bifunctional acids. The value of pK_{4a} observed for ETTA of 4.57 ± .01 is, in fact, slightly above the values of 4.2 to 4.4 reported for the bifunctional acids. For the acids listed in Table VIII, the difference (pK_{2a} - pK_{1a}) is about 1.1 while for ETTA (pK_{4a} - pK_{1a}) is about 1.7.

To go on to consider the relative values of the successive dissociation constants of ETTA, it is possible to predict these ratios on a statistical basis. The statistical probabilities of gaining and losing protons, depend upon the number of coordination sites available and the number already filled, and hence for the equilibrium.

$$H_n A \rightleftharpoons H + H_{n-1} A$$

it is possible to write that

$$K_{na} \propto \frac{n}{N-(n-1)}$$

where N is the total number of coordination sites.

In the same way for

$$H_{n+1}A \rightleftharpoons H + H_nA$$

it is possible to write

$$K_{(n+1)a} \propto \frac{n+1}{N-n}$$

Hence,

$$\frac{K_{na}}{K_{(n+1)a}} = \frac{n(N-n)}{(n+1)(N-n+1)}$$

For a tetrafunctional acid the following ratios of the acid dissociations constant would be predicted

$$\frac{K_{1a}}{K_{2a}} = .375 \quad \frac{K_{2a}}{K_{3a}} = .444 \quad \frac{K_{3a}}{K_{4a}} = .375$$

The ratios calculated from the measured values of the dissociation constants for ETTA are less than these, being the following:

$$\frac{K_{1a}}{K_{2a}} = .224 \quad \frac{K_{2a}}{K_{3a}} = .383 \quad \frac{K_{3a}}{K_{4a}} = .243$$

The observed ratios compared to the statistically predicted values indicate that the loss of one proton affects the ease of loss of subsequent protons. However, the values of the ratios observed for ETTA are close to those observed for other acids where the effect between groups in the molecule is about as small as it ever is observed to be. For the dicarboxylic acids, $(CH_2)_n\ CO_2H$ the predicted ratio is .250, but it is found that when $n = 1$ this ratio is about .001, gradually increasing until for $n = 8$ the ratio is about .1.

In conclusion, it may be said that all four dissociable protons in ETTA are fairly acidic, the four pK_a values ranging from 2.89 for pK_{1a} to 4.572 for pK_{4a}, and that these are of the order observed for the bifunctional sulfidecarboxylic acids which have pK_a values in the range 3.2 to 4.4. Since the stability constants of complexes formed between the conjugate base of an acid and metal ions are at least roughly proportional to the pK_a values of the parent acid it would be expected that ETTA with its lower overall pK_a values would form less stable complexes than those of EDTA where pK_{3a} is 6.16 and pK_{4a} is 10.23. This was verified in the investigation of the metal stability constants of complexes with ETTA.

3.34 Potentiometric work on the complexes

The curves for the potentiometric titration of ETTA in the presence of each of Co(II), Ni(II), Cu(II) and Zn(II) are shown in Figure XVIII. The curve for the titration of the same concentration of ETTA with no metal ions present is included in Figure XVIII to show the magnitude of the change in the titration curve of the acid when it is titrated in the presence of the metal ions mentioned. The concentration of ETTA in the titrated solution was 1.546×10^{-3} M in each of the examples, and the metal ion concentration was about 1.7×10^{-3} M, and thus in each solution the metal to ligand ratio was 1.1 to 1. The exact concentration of metal ions for each titration is given in Figure XVIII. Each titration curve shown is the result of at least two titrations in which the same increments of alkali were added, and the average value taken of the corresponding pH readings. The latter were always within 0.5% of each other below pH 4.6. In addition to these titrations, a titration was performed for nickel in which the metal to ligand ratio was .5 to 1. The data for all these titrations are given in Tables V to X, Appendix A. To ensure that the stability constants determined for a system of metal complexes are reliable, measurements should be made in solutions of different total metal to total ligand ratios. The metal complexes of ETTA have been studied for only one metal to ligand ratio, except for the additional nickel solution mentioned, since it was decided to concentrate on developing a computer program to give the stability constants from one set of data before accumulating more data.

Formation curves, which are plots of $\bar{n}$, the average ligand number versus log a, the logarithm of the free ligand concentration are often calculated from potentiometric data to gain some insight into the stoichiometry of the complexes formed in solution and to be used in the calculation of the stability constants. In the absence of protonated or hydroxo complexes, $\bar{n}$ is calculated in the following way.

$$\bar{n} = \frac{\text{total concentration of A bound to B}}{\text{total concentration of B}}$$

$$= \frac{\text{total concentration of A} - \text{concentration of A not bound to B}}{\text{total concentration of B}} \qquad \ldots\ 3.1$$

and since $$\bar{n}_H = \frac{\text{total concentration of protons bound to "uncomplexed" A}}{\text{concentration of A not bound to B}}$$

or $$\bar{n}_H = \frac{[HA] + 2[H_2A] + 3[H_3A] + 4[H_4A]}{\text{concentration of A not bound to B}} \qquad \ldots\ 3.2$$

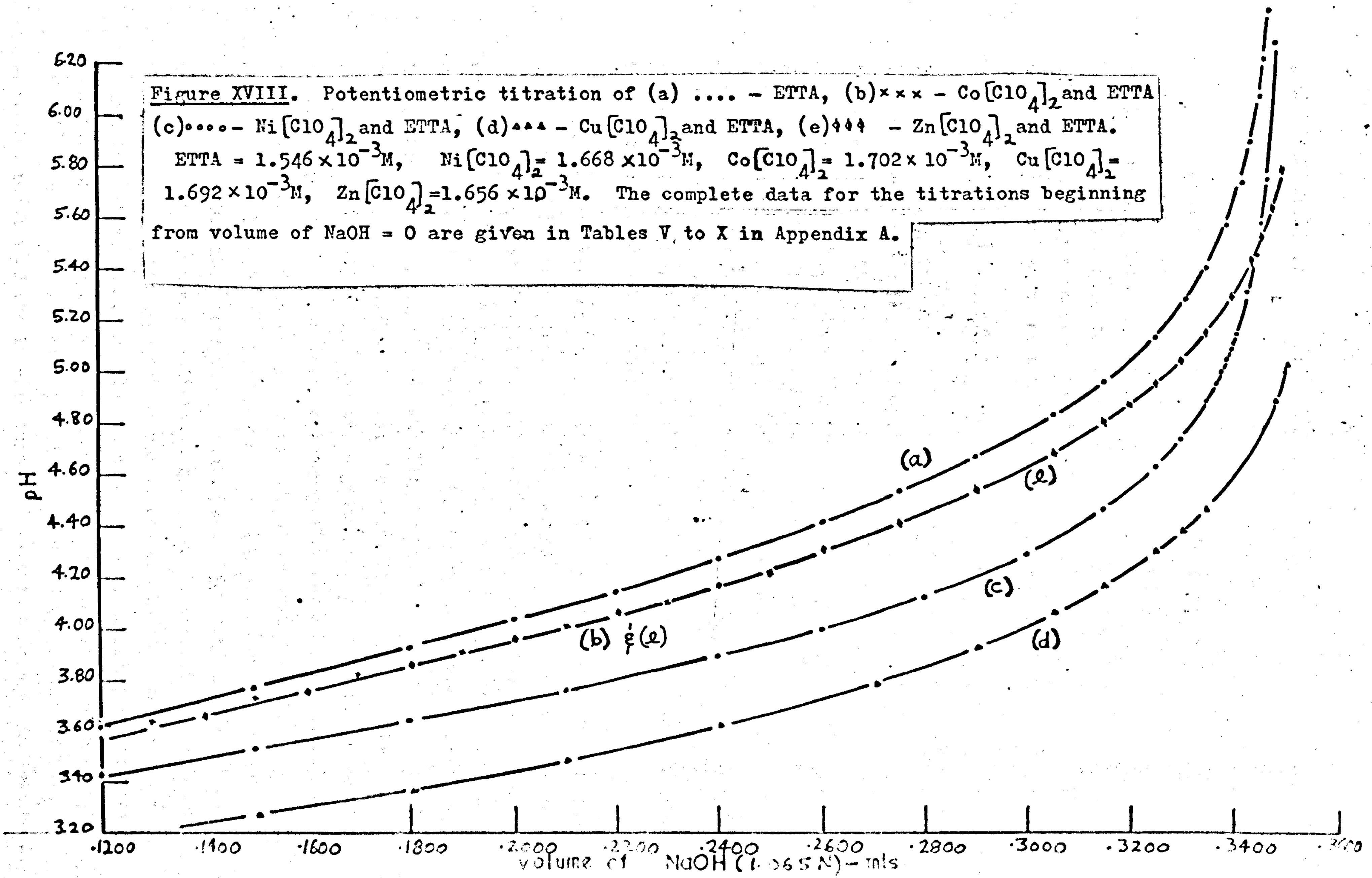


Figure XVIII. Potentiometric titration of (a) .... – ETTA, (b)××× – Co$[ClO_4]_2$ and ETTA (c)∘∘∘∘– Ni$[ClO_4]_2$ and ETTA, (d)▴▴▴ – Cu$[ClO_4]_2$ and ETTA, (e)ⴲⴲⴲ – Zn$[ClO_4]_2$ and ETTA. ETTA = 1.546×10^{-3}M, Ni$[ClO_4]_2$ = 1.668×10^{-3}M, Co$[ClO_4]_2$ = 1.702×10^{-3}M, Cu$[ClO_4]_2$ = 1.692×10^{-3}M, Zn$[ClO_4]_2$ = 1.656×10^{-3}M. The complete data for the titrations beginning from volume of NaOH = 0 are given in Tables V to X in Appendix A.

$$= \frac{\text{total concetration of dissociable proton - concentration of free protons}}{\text{concentration of A not bound to B}} \quad \ldots\ldots 3.3$$

If protonated metal complexes are not formed then it is correct to put the numerator of equation 3.2 equal to the numerator of equation 3.3, the latter being determinable from the experimental data. Since $\bar{n}_H$ is known from the separate titration of the acid, the denominator of equation 3.3, and hence $\bar{n}$, can be evaluated from equation 3.1. However, if protonated complexes do form then the numerator of equation 3.3 becomes equal to

$$[HA] + \ldots + 4[H_4A] + [BHA] + 2[BH_2A] + \text{etc.}$$

and it is not possible to calculate $\bar{n}$ in the usual way. In work already published on other sulfidecarboxylic acids (18, 23) and on the cupric complexes of ETTA itself (19), it has been found necessary to introduce protonated species to adequately explain the observed data. Also, in the present work from the results of spectrophotometric measurements which will be described in section 3.36, there is indication of protonated complexes. Since the $\bar{n}$ values which were calculated from the potentiometric data assuming no protonated complexes were very peculiar they were suspected to be of little value, and the corresponding formation curves have not been included in this thesis.

In the titration of the solution containing copper ions it was found that above pH 5, the pH reading tended to decrease with time. When a solution of initial pH 5.4 was allowed to stand for 16 hours a fluffy brown solid was deposited, and it was concluded that the copper complex decomposes when the pH is raised above 5. In the solutions containing Co^{2+}, the pH readings increased smoothly up to pH 6, and were constant at this value for at least 15 minutes. However, it was noticed that the solution which was pale pink at the beginning of the titration when the pH was 3.1, become increasingly a brown-yellow color as the titration proceeded. It was found in later spectrophotometric work that the absorbance at 19,600 cm^{-1} (510 mμ) decreased about 1% every 5 minutes even at pH 3.9. The color change could be explained by the oxidation of Co^{2+} to Co^{3+} under these conditions. Although the titration curve above pH 4.0 was smooth and appeared normal it was concluded that potentiometric data above pH 4.0 should not be used in determining the stability constants of the complexes of Co(II) with ETTA. The apparent oxidation of Co^{2+} in solutions containing ETTA provides an explanation of the anomalous results of the ion-exchange measurements mentioned in section 1.

The ion-exchange experiments were done at pH 7 before the later spectrophotometric measurements showed that solutions of Co^{2+} and ETTA should not be taken above pH 4. It may be possible that the Co(II) - ETTA system could be studied above pH 4 in solutions from which all dissolved oxygen had been removed.

Solutions of Ni^{2+} and ETTA appeared to be stable with respect to decomposition at pH values as high as 6 (and possibly higher) since the absorbance of a solution made up at this pH stayed constant for at least two days, and also the pH stayed constant at 6 if the solution was excluded from atmospheric CO_2.

3.35 Discussion of the application of the least squares adjustment to the potentiometric data

The usual Gaussian least squares analysis as applied to a system containing complexes of the type expected in solutions of metal ions and ETTA has been discussed in detail in section 2. The program used is given as Program III in Appendix B where a few notes are given on the symbolism used in the program and on the format of the program. However, although work is still in progress, this program has not yet given a good set of refined constants. To the present the program has been tried only on the data from the titration of the Cu(II) - ETTA system. As can be seen from the titration curves shown in Figure XVIII, Cu^{2+} forms complexes with ETTA more strongly than any of the other metals, and for this reason it was selected as the one from which it was most likely to be possible to obtain the stability constants.

Program III as written could easily be made to perform a least squares refinement for systems characterised by the following combinations of complexes: BA, B_2A; BA, BHA, B_2A; BA, BHA, BH_2A, B_2A; and BA, BHA, BH_2A, BH_3A, B_2A. All but the first set, which does not contain a protonated complex have been used in trying to analyse the potentiometric data. The program has given the following values for the different sets of parameters to date.

(BA)	β_{11}	5.7×10^4	β_{11}	2.6×10^5	β_{11}	7.8×10^4
(BHA)	β_{111}	neg.	β_{111}	neg.	β_{111}	neg.
(BH_2A)			β_{121}	4.2×10^{12}	β_{121}	1.5×10^{12}
(BH_3A)					β_{131}	neg.
(B_2A)	β_{211}	3.3×10^8	β_{21}	neg.	β_{21}	neg.

These were the results obtained after only two cycles had been done by the computer. The program failed at this stage because the negative values obtained for one or more of the parameters which were then put back into the Newton-Raphson iteration for finding the new free metal and free ligand concentrations, made it impossible for the iterative procedure to converge. In the future development of Program III it is intended to prevent this from happening by arbitrarily fixing the maximum change permissible in two successive values of a given parameter at 50% of the first value.

In addition to this suggestion to avoid "overshooting", a number of other suggestions may be made for improvements to Program III to overcome difficulties which sometimes arise in performing a least squares adjustment. It has been suggested by some authors that if a stability constant is sought for an unimportant species this may be manifested by a negative stability constant being obtained for this species (62). Another related possibility that has been suggested for failure to obtain convergence is poor initial estimates of the parameters (21). How close the initial estimates must be to the true values seems to be variable from system to system. The initial estimates used in seeking to analyse the data from the Cu(II) - ETTA system were the values reported by Saini (19). It is possible that improved initial estimates would assist the refinement procedure. Another aspect of the program which may require improvement is the method of evaluating the weights. In section 2 it was stated that as a first trial the weights would be calculated assuming all the error could be carried in the measurements of the pH and the volume of alkali added (which is related to the error in the analytical hydrogen ion concentration at any point in the titration). It is recommended that consideration also be given to errors in the total metal, total ligand and total initial analytical hydrogen ion concentration. Finally, difficulty may be encountered in obtaining the desired parameters if the parameters are not well defined by the data (64), and this is believed to be important in the present investigation. Perrin and Sayce (21) have also pointed out that when several species coexist over the same pH range, the values obtained for the stability constants are very sensitive to the accuracy of the input data. In their studies on nickel complexes of thioglycollic acid, the variances in the parameters obtained were comparable using either of the two sets of complexes, $Ni\ A_2^{2-}$, $Ni\ A_3^{4-}$, $Ni_2\ A_3^{2-}$, $Ni_3\ A_4^{2-}$ or $Ni\ A$, $Ni\ A_2^{2-}$, $Ni\ A_3^{4-}$ and $Ni_4\ A_6^{4-}$. To be able to determine accurately the stability constants of all the important species which it is thought probable do exist over the rather short pH range 2.5 to 5 in metal-ETTA systems, it may be necessary to improve the accuracy of the experimental measurements. It is also possible that the formation of an important species is being overlooked, but this is not believed to be very probable.

The method of least squares adjustment which has been discussed to the present is the common linear Gaussian method in which the normal equations resulting from the minimization of the error square sum contain the desired parameters as the "unknowns", and the parameters are solved for directly. It is also possible to set up the normal equations in terms of corrections to the initial estimates of the parameters, i.e. the unknowns are $\Delta \beta_{11}$, $\Delta \beta_{111}$, etc. In each successive cycle the corrections to the immediately preceding set of parameters become smaller until the corrections become negligibly small. This method has been used successfully by other workers in systems containing protonated complexes (44, 64) and it is possible that it would be a more fruitful approach to use in the present investigation.

As far as is known, no results from a least squares analysis of potentiometric data have as yet been published for a system similar to that believed to be true for complexes of ETTA. For the latter two or possibly three protonated forms in addition to a binuclear complex and a simple 1 : 1 complex, all relatively weakly formed, may coexist over the same short pH range.

In conclusion, it is believed that it is worthwhile to pursue the potentiometric technique and the least squares treatment of the data. This method seems, when all limitations are considered, to be as likely as most other methods to give all the stability constants characteristic of the system.

3.36 Results of the spectrophotometric studies

The spectrophotometric studies have been concerned almost exclusively with the nickel and copper complexes of ETTA. As stated earlier, the Co(II) complex was found to give increasing absorbance readings at 19,600 cm^{-1} even when the pH was no higher than 3.9, the solution changing color from pink to yellow-brown. A spectrum was taken rapidly of a solution of cobalt and ETTA at approximately pH 4 between 11,800 and 25,00 cm^{-1}. One weak, broad band was found in this region with a maximum at 19,600 cm^{-1}. The spectrum of the nickel complex over the range 8,850 to 27,800 cm^{-1} is shown in Figure XIX. The molar extinction coefficients, ϵ_1, have been measured as described later in this section, at three of the four observed maxima and were found to be as follows:

9220 - 9,390 cm^{-1}	19.8 ± 2.0
12,400 cm^{-1}	< 8
15,400 cm^{-1}	8.00
25,500 cm^{-1}	(18.4) (ϵ_1 determined at 25,600)

For the copper - ETTA system in aqueous solution at pH 3.10 the spectrum between 11,000 and 25,000 cm^{-1} is shown in Figure XX. The spectrum shows the usual broad band in the red part of the spectrum for copper complexes. The absorption maximum for this band occurs at 12,600 to 12,800 cm^{-1}. The molar extinction coefficient was determined at 12,400 cm^{-1} in the quantitative work described below and found to be 47.0. A very intense absorption occurs above 25,000 cm^{-1}, presumably due to charge transfer. This band is shifted to lower energies in the copper complex compared to the corresponding band in the nickel complex.

Having found that the nickel and copper complexes absorbed strongly at the energies indicated, quantitative measurements were begun from which the stability constants of the complexes could be determined. The results obtained for the nickel solutions will be discussed first.

The method of continuous variations was initially used to provide some information regarding the stoichiometry of the main complexes in solution. If one complex, of stoichiometry BA_n, forms in solution then it can be shown that the difference, ΔA_s, betwen the measured value of the absorbance and the value calculated assuming no complex formation is proportional to the concentration of the complex.

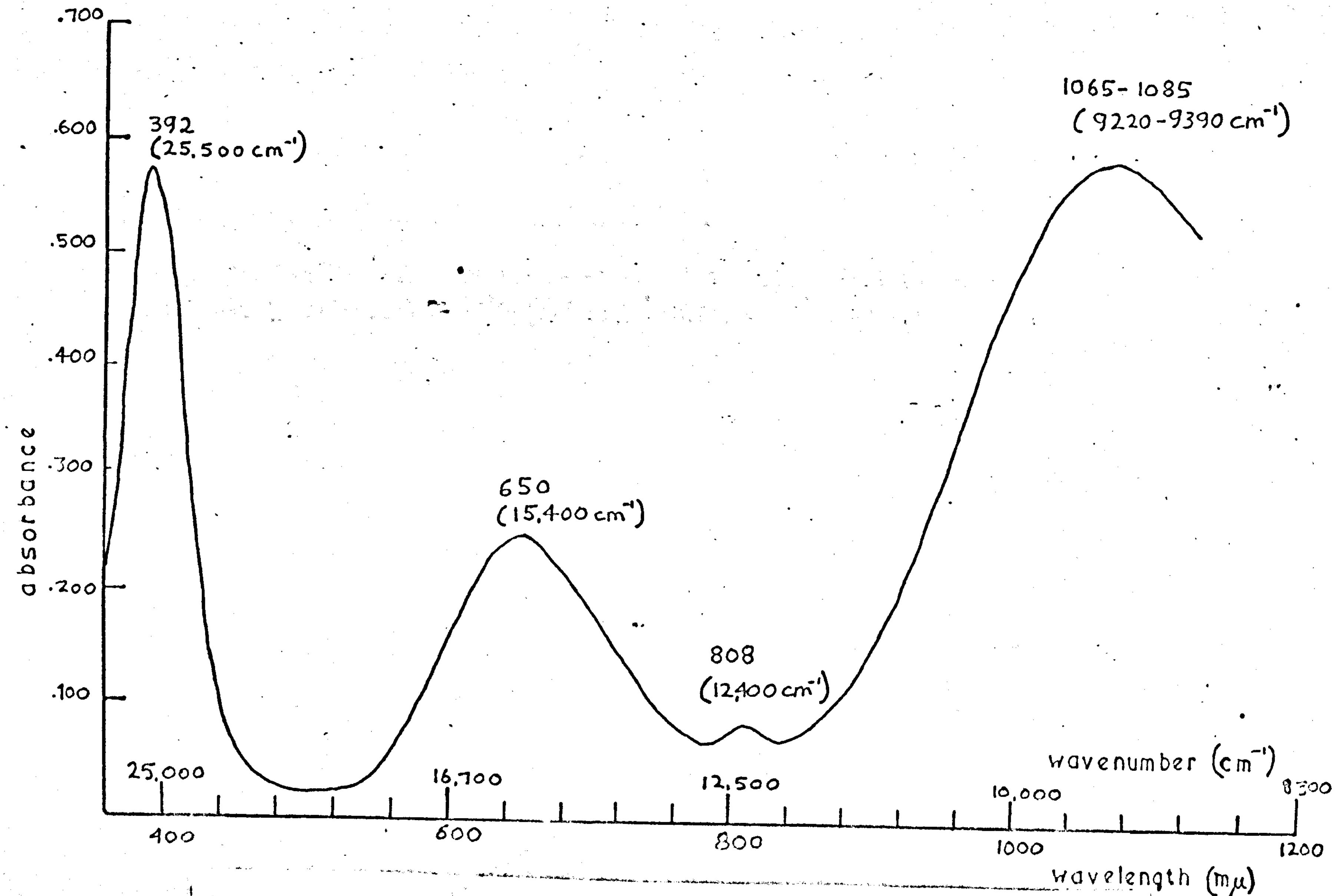


Figure XIX. The spectrum of the complex of ETTA with Ni(II) in aqueous solution. [ETTA]$=7.989\times10^{-3}$M; [Ni$(ClO_4)_2$]$=7.989\times10^{-3}$M. pH 5.

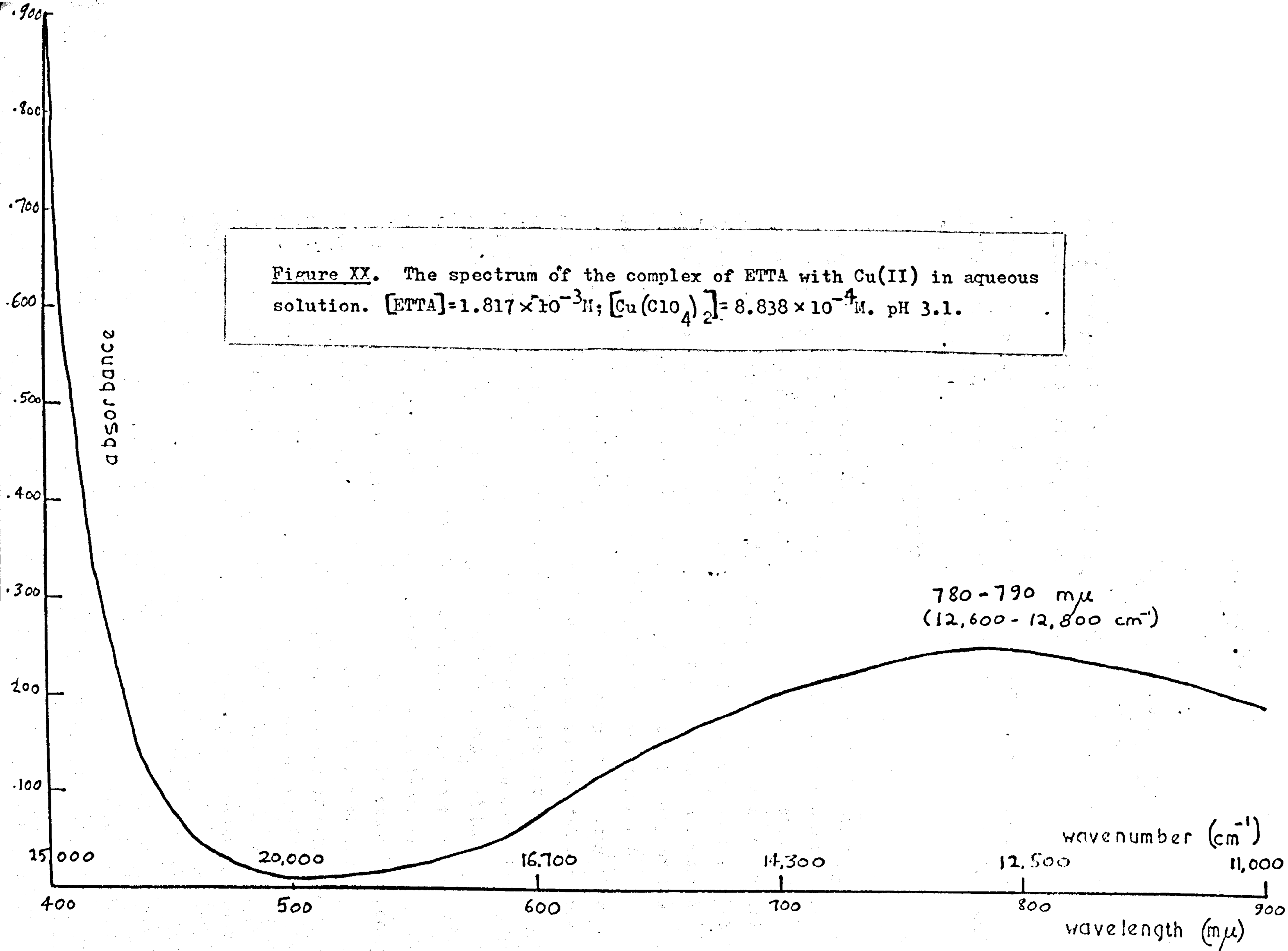


Figure XX. The spectrum of the complex of ETTA with Cu(II) in aqueous solution. $[ETTA] = 1.817 \times 10^{-3}$ M; $[Cu(ClO_4)_2] = 8.838 \times 10^{-4}$ M. pH 3.1.

$$A = 1(\epsilon_a a + \epsilon_o b + \epsilon_1 [BA_n])$$

or, substituting

$$a = A - n[BA_n] \quad \text{and} \quad b = B - [BA_n]$$

then,

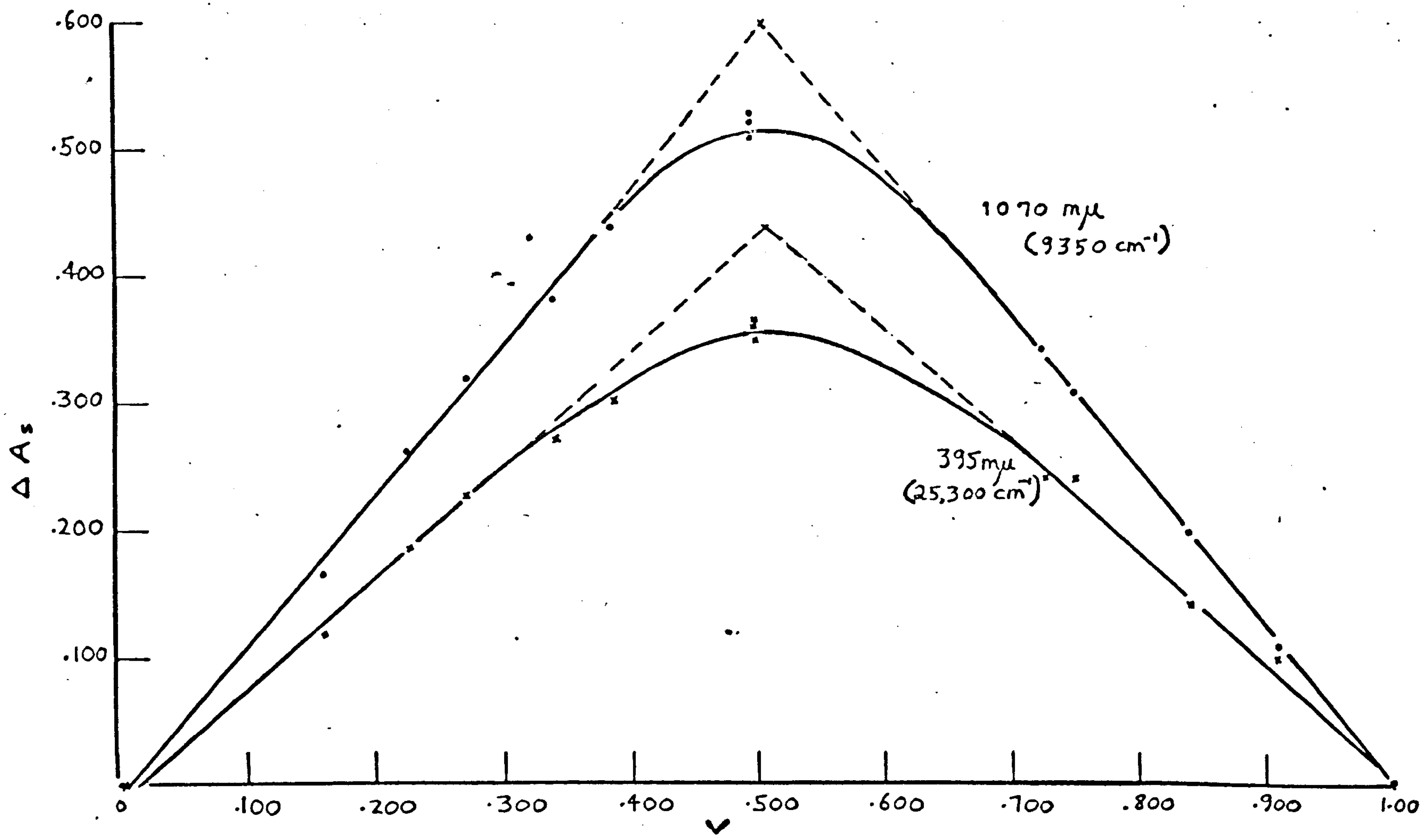
$$A_s - 1\epsilon_o B - 1\epsilon_a A = \Delta A_s = 1(\epsilon_1 - \epsilon_o - n\epsilon_a)[BA_n]$$

where 1 the path length and ϵ_o, ϵ_a and ϵ_1 are the molar exinction coefficients of B, A and BA_n respectively.

It is also possible to show, assuming the only complex formed is BA_n, that when v volumes of A are mixed with (1-v) volumes of B, A and B being equimolar,

$$n = \frac{v_{max}}{1 - v_{max}}$$

where v_{max} is the volume where BA_n is at a maximum. The value of v_{max} can be found by plotting ΔA_s versus v. The method of continuous variations has not been used in this work for the calculation of stability constants since there were indications that more than one complex formed in solution. However, the plot shown in Figure XXI of ΔA_s versus v at 9350 cm^{-1} and at 25,300 cm^{-1} for the nickel - ETTA system was prepared for the purpose of obtaining an indication of the stoichiometry of the main complex(es) formed in solution. The pH of the solutions was approximately 5. The curve obtained was fairly sharp, suggesting that the main complex is well-formed. Since the maximum in the plot occurred at v = .5 it was inferred that an important species present has the metal to ligand ratio 1 : 1. It was also noticed that the curve in Figure XXI was nearly symmetrical. If the values of ΔA_s had been higher on the left hand side of the maximum point, where there was an excess of metal ions, this would have suggested the existence of a binuclear complex, weakly formed, but still in appreciable concentration relative to the mononuclear complex. It was concluded from the above measurements that to a first approximation when the ratio of metal to ligand concentration was 1 : 1 or less, and the pH of the solutions in the vicinity of 5, only the formation of mononuclear species need be considered in analysing spectrophotometric data to determine stability constants.



<u>Figure XXI.</u> The continuous variations method applied to Ni-ETTA. Abscissa is v volumes of 7989×10^{-3} M ETTA mixed with (1-v) volumes of 7.989×10^{-3} M $Ni[ClO_4]_2$. pH ~ 5.

Many methods have been used in the spectrophotometric determination of stability constants (8), the different methods having different limitations. The method finally used in this work in the determination of stability constants will now be described. It was assumed that the various mononuclear complexes believed likely to form, i.e. NiA , NiHA and possibly NiH_2A, would have the same extinction coefficients. This is true for certain complexes of EDTA. For example, CoEDTA$^-$ and CoHEDTA have the same extinction coefficient at wavelengths greater than 370 mμ (28). It is then possible to write

$$\frac{A_s}{l} = \epsilon_o b + \epsilon_a a + \epsilon_1([NiA] + [NiHA] + [NiH_2A])$$

The absorbance of the ligand was found to be negligible between 9350 and 25,300 cm^{-1}, and ϵ_a was put equal to zero.

Then

$$\frac{\Delta A_s}{l} = \Delta\epsilon([NiA] + [NiHA] + [NiH_2A]) \qquad \ldots\ldots 3.3$$

where $\Delta\epsilon = \epsilon_1 - \epsilon_o$

The value of ϵ_1 was found from solutions containing an excess of ligand over metal. In these solutions complex formation was forced to completion, as accurately as could be measured, and the value of ϵ_1 was put equal to the slope of the plot of (A_s/l) versus B. Once ϵ_1 was found it was possible to calculate using equation 3.3 the sum of the concentrations of the complexes formed in solutions of metal to ligand ratio 1 : 1 where the nickel was not fully complexed. Having found this sum, the free ligand concentration was calculated by putting

$$a = \alpha_o^H \; (A - \Delta A_s/l\Delta\epsilon)$$

where $\alpha_o^H = \dfrac{a}{a + [HA] + [H_2A] + [H_3A] + [H_4A]}$

and is known from the acid dissociation constants previously determined.

Also, the free metal concentration was calculated by simply putting

$$b = B - \Delta A_s/l\Delta\epsilon$$

The absorbance of a solution containing metal to ligand concentration approximately 1 : 1 was then measured as a function of pH over the range pH 3.4 to 5. The lower pH limit was imposed by the solubility of the ligand, which decreased with decreasing pH. The lowest concentration of ligand which would, in solutions containing metal ions, give an accurately measurable absorbance due to complex formation was used. The experimental technique used in these measurements was described in section 3.312.

Having obtained a series of absorbance readings as a function of pH, which could be related to a and b as described, it was decided to divide the data into two parts which could approximately be described considering only one or two of the complexes, to then find the stability constants of these complexes from the slopes and intercepts of the appropriate plots, and to subsequently refine the separately determined values.

Considering the measurements taken at the highest pH values, it was found that the results could not be explained by assuming the formation of only NiA. The formation of both NiA and NiHA was then considered. The fraction of the total metal concentration in the uncomplexed form is given by

$$\alpha_o = \frac{b}{b + [BA] + [BHA]}$$

where $[BA] = \beta_{11}\,ba$ and $[BHA] = \beta'_{111}\,b\,[HA]$

Hence

$$\alpha_o b + \alpha_o \beta_{11} ba + \alpha_o \beta'_{111} b\,[HA] = b$$

or

$$\frac{1 - \alpha_o}{\alpha_o} = \beta_{11} a + \beta'_{111}\,[HA]$$

Dividing through by $[HA]$ gives

$$\frac{1 - \alpha_o}{\alpha_o [HA]} = \beta_{11} \frac{a}{[HA]} + \beta'_{111}$$

or

$$\frac{1 - \alpha_o}{\alpha_o \alpha_1^H (A - \Delta A_s / l\Delta\epsilon)} = \beta_{11} \frac{\alpha_o^H}{\alpha_1^H} + \beta'_{111} \qquad \ldots\ 3.4$$

Plotting the left hand side of equation 3.4 versus α_o^H / α_1^H should give a stright line over the range for which the system can be described by considering the formation of only NiA and NiHA. The line will have a slope equal to β_{11} and intercept equal to β'_{111}.

The absorbance as a function of pH for a solution containing 4.353×10^{-3} M $Ni(ClO_4)_2$ and 5.227×10^{-3} M ETTA, and which was .1M in Na ClO_4 to control activity coefficients, is shown in Figure XXIV. Absorbance measurements were taken at 15,400 cm^{-1} (650 mμ) and at 25,600 cm^{-1} (390 mμ). The curves shown are the result of duplicate determinations. All data is given in Table XI, Appendix A. The absorption maximum at 9350 cm^{-1} (1070 mμ) would have been the best place at which to take the absorbance measurements since the absorption of free metal is lower at this wavelength while the complex has a higher extinction coefficient than at either of the wavelengths at which the measurements were actually taken. However, at the time these experiments were done only the SP 500 spectrophotometer was available on which the wavelength range extends only to 1000 mμ.

The molar extinction coefficient, α_1, of the Ni-ETTA complex and the extinction coefficient, α_0, of the hydrated metal ion, also required in the calculations were determined from the slopes of the lines shown in Figures XXII and XXIII, respectively. The data used in the plot of Figure XXII are given in Table IX below.

Table IX Determination of ϵ_1 for Ni(II)-ETTA in water at 25,600cm^{-1}(390 mμ) and 15,400cm^{-1}(650 mμ)

Ni ClO_4 moles/l	ETTA / Ni ClO_4	Absorbance	
		25,600cm^{-1}	15,400cm^{-1}
3.037×10^{-3}	5.9	.544	.240
4.837×10^{-3}	3.7	.885	.394
6.474×10^{-3}	2.6	1.170	.517
7.255×10^{-3}	2.2	1.293	.576

Since the points for each of the solutions given in Table IX fell on the same straight line, this was taken to support the assumption that the concentration of a binuclear species could be neglected compared to the mononuclear species, even in solutions where the ligand was not present in great excess.

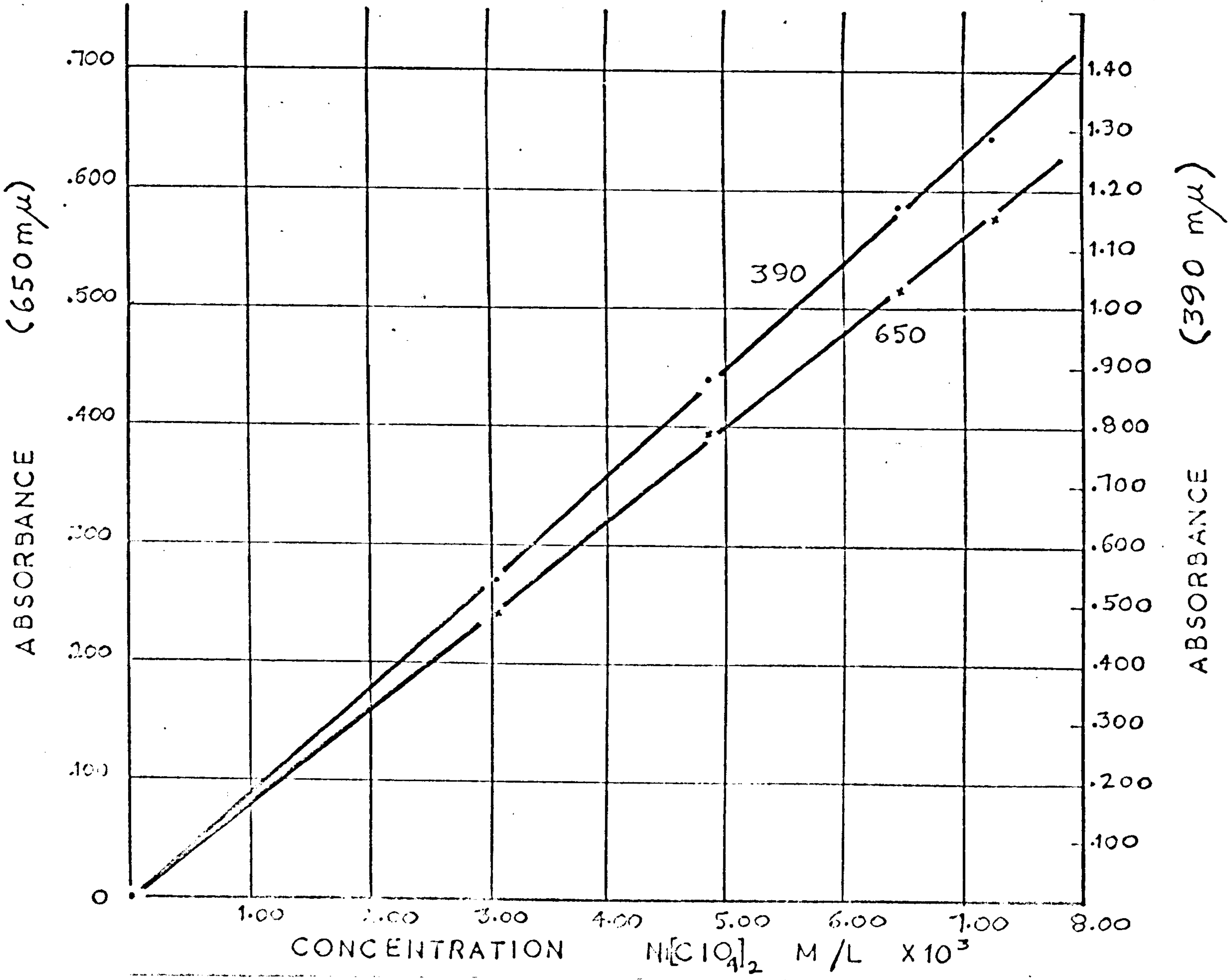


Figure XXII. Determination of the extinction coefficient of Ni-ETTA.

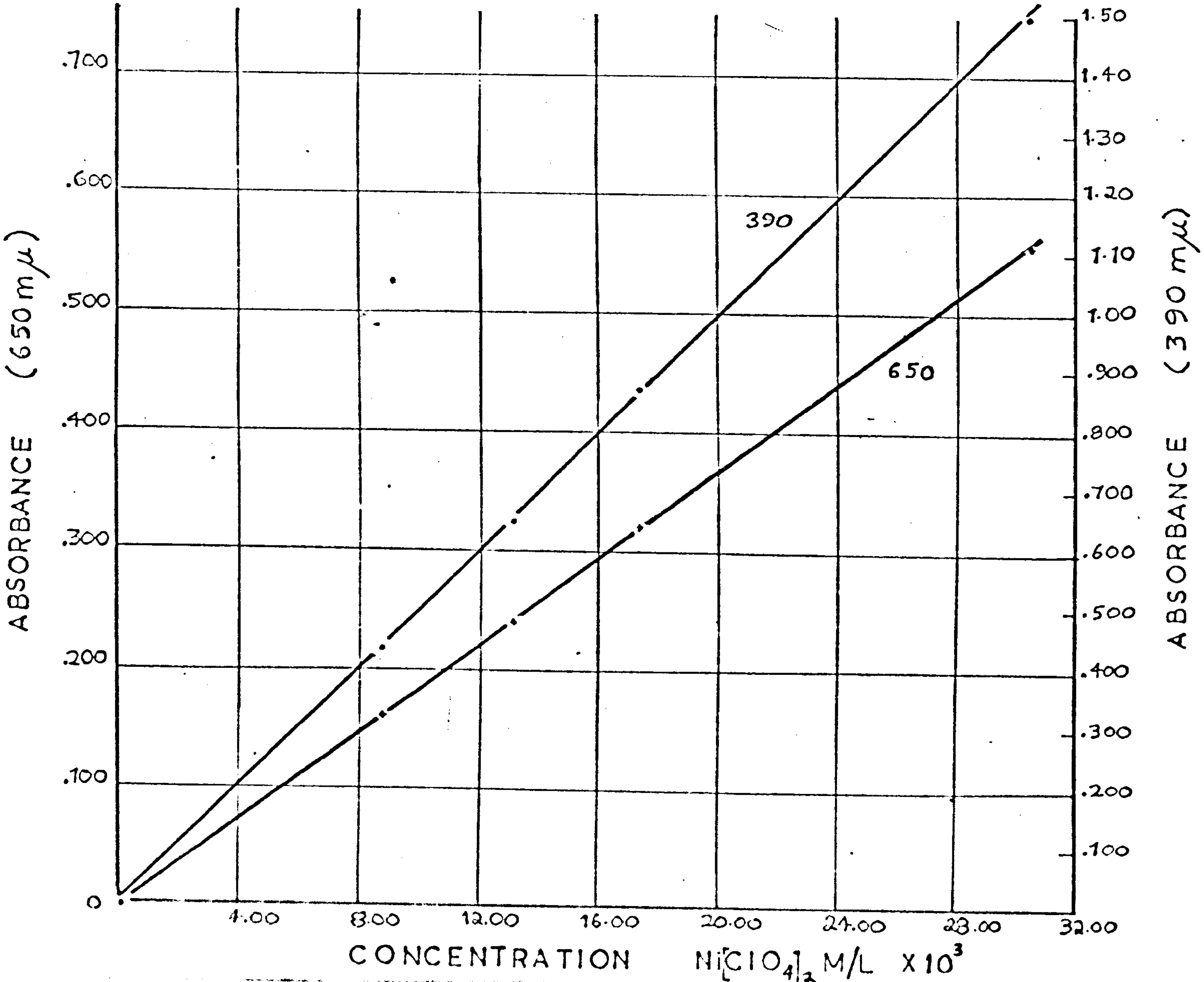


Figure XXIII. Determination of the extinction coeffient of $Ni(H_2O)^{2+}$

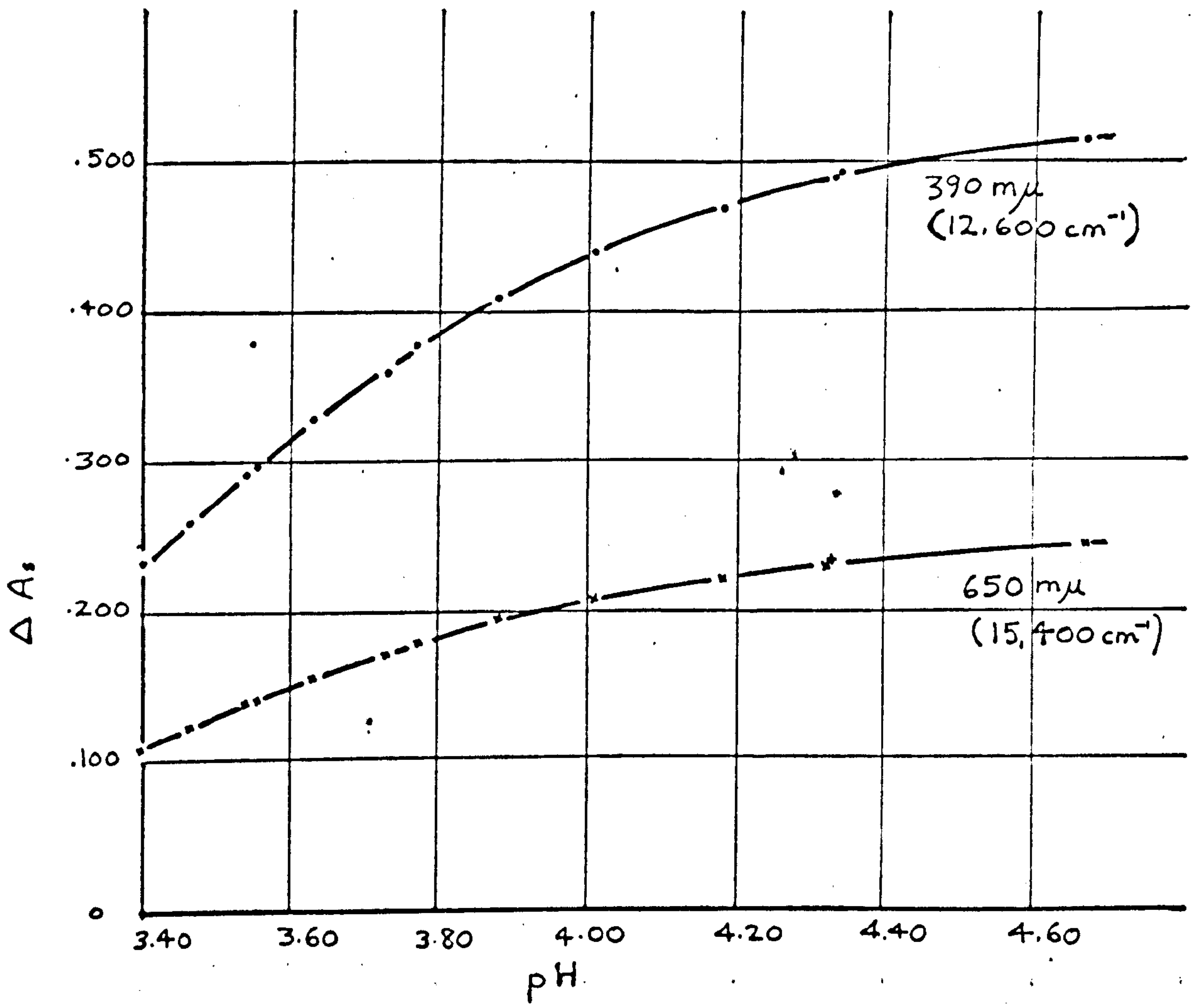


Figure XXIV. The absorbance of Ni-ETTA as a function of pH.

The results of the absorbance measurements as a function of pH were plotted according to equation 3.4, and are shown in Figure XXV. The data for this plot are given in Table XII, Appendix A. From Figure XXV it can be seen that over the pH range 3.7 to 4.4 the data are consistent with the formation of only the two complexes NiA and NiHA. Although the pH range over which a linear plot was obtained was rather short, the value of α_o^H increases by 10-fold, and α_1^H approximately doubles while α_2^H halves, as indicated in Figure XVII. The linearity of the graph at each wavelength over the pH range 3.7 to 4.4 suggests that the stability constant for the formation of NiH_2A must be considerably less than for NiHA since over this pH range α_2^H is comparable in magnitude to α_1^H. The stability constants determined were as follows, where the errors are estimated from the variations permissible in the slopes and intercepts while still obtaining a reasonable fit to all the points:

25,600cm^{-1}(390 mμ) $\beta_{11} = (1.44 \pm .04)\ 10^4$
15,400cm^{-1}(650 mμ) $\beta_{11} = (1.53 \pm .06)\ 10^4$
average $\beta_{11} = (1.48 \pm .06)\ 10^4$

25,600cm^{-1} $\beta'_{111} = (7.5 \pm 2.0)\ 10^2$
15,400cm^{-1} $\beta'_{111} = (7.8 \pm 2.0)\ 10^2$
average $\beta'_{111} = (7.6 \pm 2.0)\ 10^2$

Attempts were made to explain the data below pH 3.7, where the approximation of considering only NiA and NiHA is no longer valid by considering the formation of NiH_2A in addition to the other two complexes. This was done by putting

$$\alpha_o = \frac{b}{b + \beta'_{111}\, b\,[HA] + \beta'_{121}\, b\,[H_2A] + \beta_{11}\, b\,[A]}$$

which can be rearranged to give

$$\frac{1-\alpha_o}{\alpha_o\,[H_2A]} - \beta_{11}\frac{[A]}{[H_2A]} = \beta'_{111}\frac{[HA]}{[H_2A]} + \beta'_{121}\frac{[H_2A]}{[H_2A]}$$

or, $$\frac{1-\alpha_o}{\alpha_o\alpha_2^H\,(A - \Delta As/l\Delta\epsilon)} - \beta_{11}\frac{\alpha_o^H}{\alpha_2^H} = \beta'_{111}\frac{\alpha_1^H}{\alpha_2^H} + \beta'_{121} \qquad \ldots.\ 3.5$$

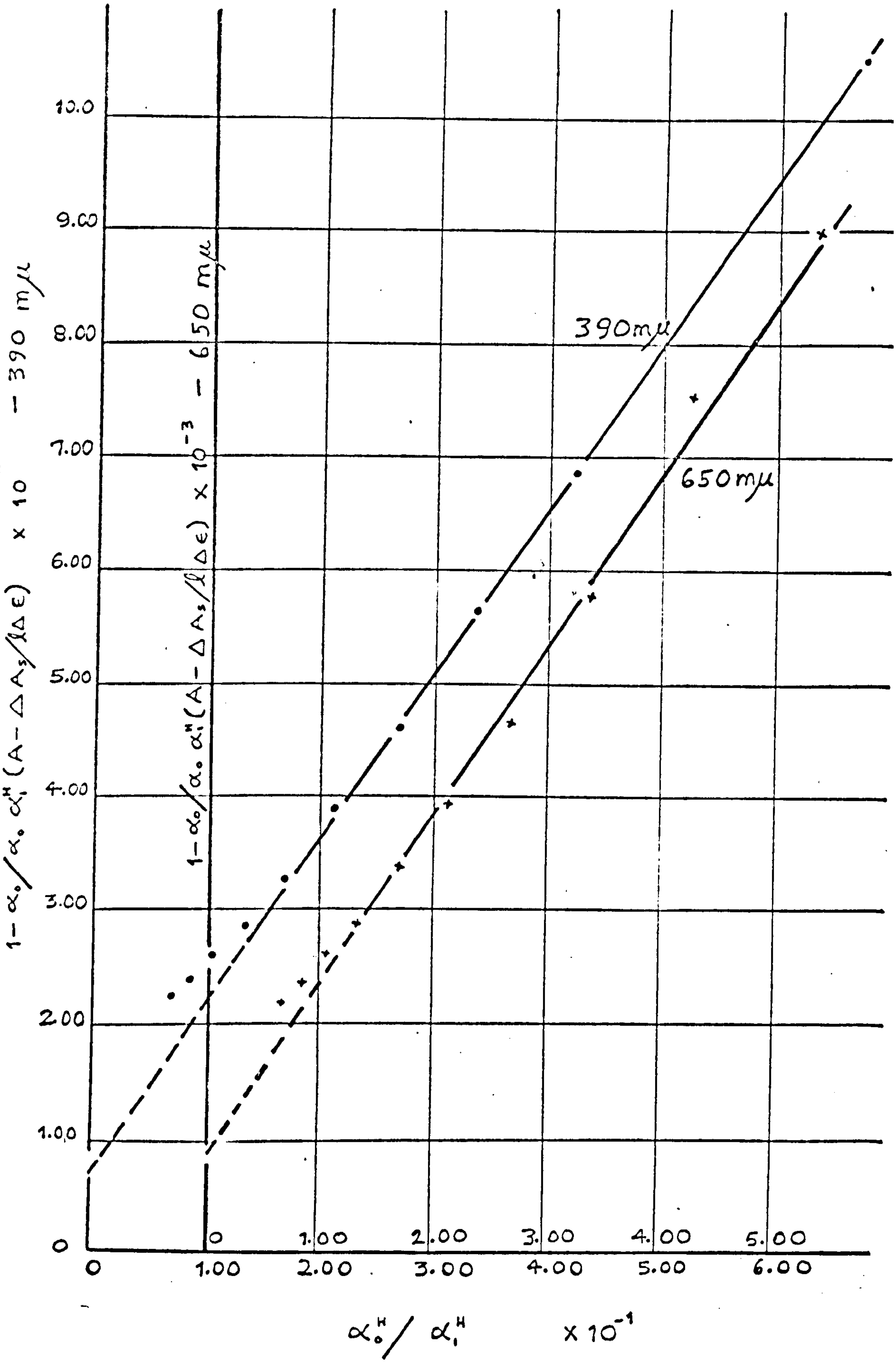


Figure XXV. Determination of β_{11} and β'_{111} for Ni-ETTA.

Since the value of β_{11} was known fairly accurately from the measurements at the higher pH values, the left hand side of question 3.5 could be plotted against α_1^H / α_2^H giving β'_{111} and β'_{121} as the slope and intercept respectively. However, the points in this plot were scattered, and the graph ambiguous and not considered to be useful. Furthermore, as discussed in more detail in section 3.37, it is possible that the ~~in~~formation of a binuclear species may be important relative to the concentration of mononuclear complexes at lower pH values where the concentration of free metal is higher.

The results of the measurements on the copper complexes of ETTA were treated in a similar way to that described for the nickel complexes. The copper complexes were expected to follow the same general pattern as the nickel complexes. Saini has reported a symmetrical plot obtained by the method of continuous variations for copper complexes of ETTA at pH 4.5 with a maximum at v = .5. This suggests that for the measurements in the higher pH range, it would be a reasonable initial approximation to consider the formation of only mononuclear species. As for the complexes with nickel, it was assumed that the extinction coefficients of CuA and any protonated forms would be essentially the same, and that it was therefore possible to put

$$\frac{A_s}{1} = \epsilon_0 b + \epsilon_1 \times ([CuA] + [CuHA] + [CuH_2A] + \ldots\ldots) + \epsilon_a a$$

The absorbance measurements were made at 12,400 cm^{-1} (805 mμ) where ϵ_a = .., and the results of the measurements between pH 2.2 and 4.2 are shown in Figure XXVI. The data is tabulated in Table XIII, Appendix A. Since ϵ_1 was larger for the copper complexes than for the nickel complexes lower concentrations of reagents were possible, down to 1.7 x 10^{-3}M, and hence the measurements could be extended to lower pH values. The plots used to determine the extinction coefficients of the hydrated metal ion, and of the copper complex with ETTA are shown in Figure XXVII, and the data for the latter are given in Table X.

Table X. Determination of ϵ_1 for Cu(II) - ETTA in water at 12,400 cm^{-1} (805 mμ)

$[Cu(ClO_4)_2]$ (moles/l)	$[ETTA]/[Cu(ClO_4)_2]$	Absorbance
.8828 x 10^{-3}	22	.386
1.199 x 10^{-3}	17	.542
1.589 x 10^{-3}	11	.747
1.690 x 10^{-3}	1	.826

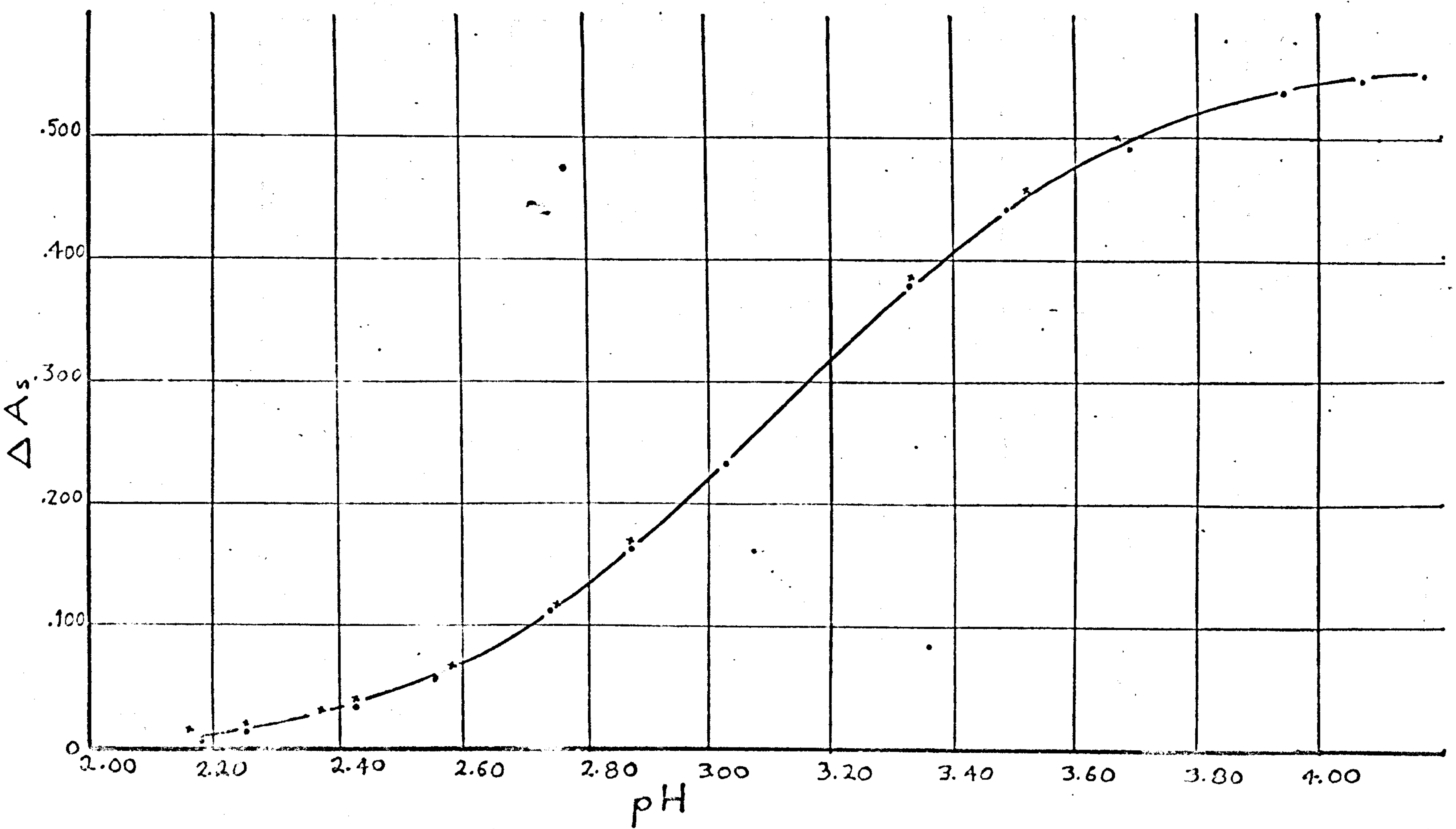


Figure XXVI. The absorbance of Cu-ETTA as a function of pH. Absorbance measured at 805 mμ (12,400 cm^{-1}). (.... -run 1 ; ×××× -run 2).

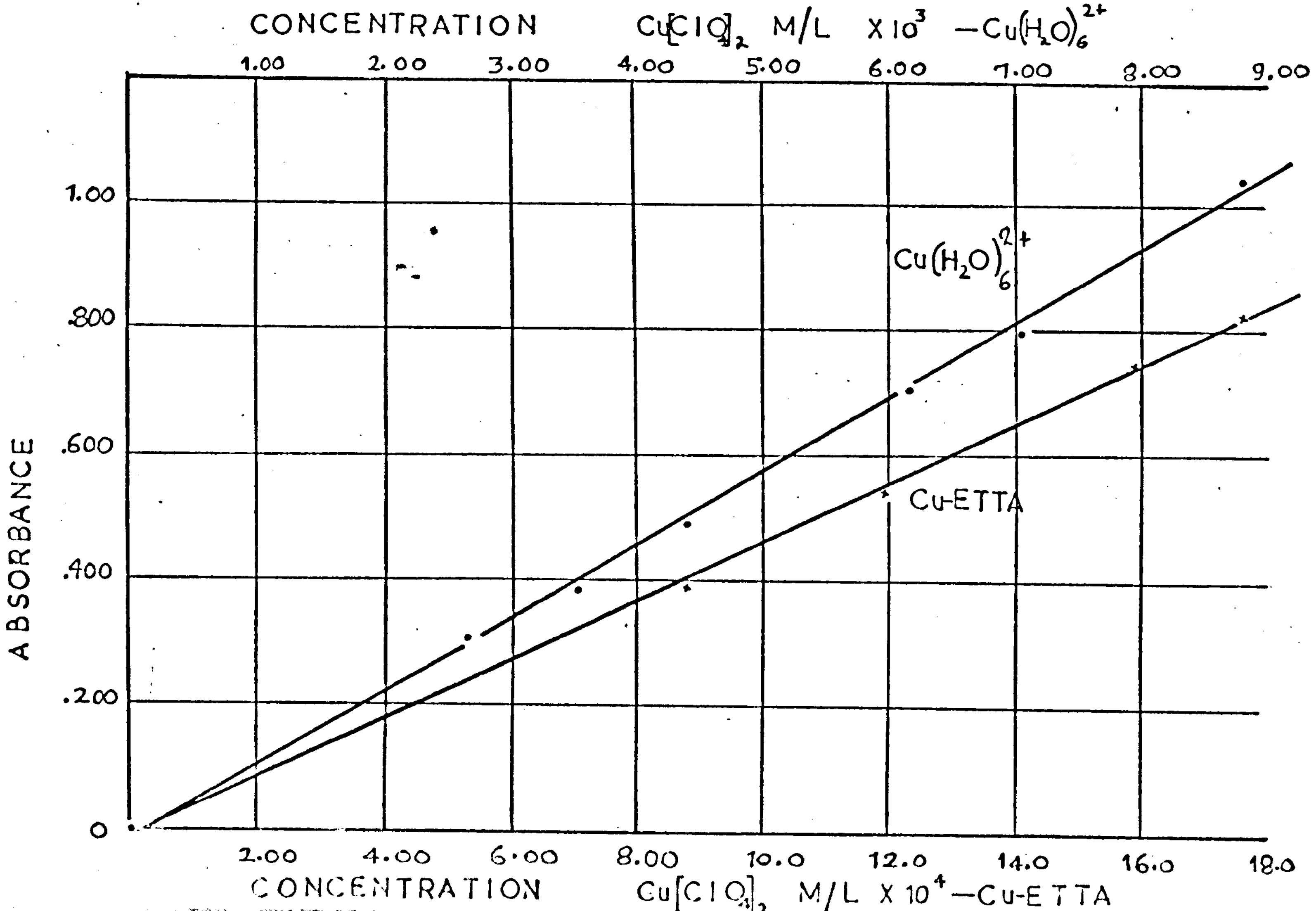


Figure XXVII. Determination of the extinction coeffients of Cu-ETTA and of $Cu(H_2O)_6^{2+}$ at 805 mμ(12,400 cm^{-1}).

The experimental points listed in Table X lay on the same straight line. This supports the assumption that the concentration of any binuclear species can be neglected compared to mononuclear species. The extinction coefficient of the binuclear species would be expected to be considerably greater than for the mononuclear species, and hence one would expect to see an increased absorbance for the lower ligand to metal ratios where the formation of the binuclear species would be favoured.

The results of the absorbance measurements as a function of pH were plotted according to equation 3.4, as shown in Figure XXVIII. The corresponding data are given in Table XIV, Appendix A. The results are consistent with the formation of only the two complexes CuA and CuHA over the pH range 3.4 to 4.0; however, in this range α_0^H varies from .005996 to .1065, while α_1^H varies from .8910 to 3.975 and hence the formation of CuA and CuHA has been measured over a considerable range of $[A]$ and $[HA]$.

From the slope,

$$\beta_{11} = (5.23 \pm .10)\,10^5$$

and from the intercept

$$\beta'_{111} = (3.4 \pm 2.0)\,10^3$$

The results below pH 3.4 could not be explained by considering only CuH_2A in addition to CuHA and CuA, using equation 3.5. Below pH 3.4 it may be necessary to consider the formation of a binuclear species as discussed in section 3.37.

3.37 Discussion of the spectrophotometric studies

The results will be discussed in the following order: firstly, the position and intensity of the absorption maxima in the spectra of the nickel and copper complexes of ETTA, and, secondly, the results of the measurements of the stability constants.

The absorption maxima and molar extinction coefficients observed for the nickel complex are compared in Table XI with assignments that have been made for Ni-EDTA and for $Ni(H_2O)_6^{2+}$.

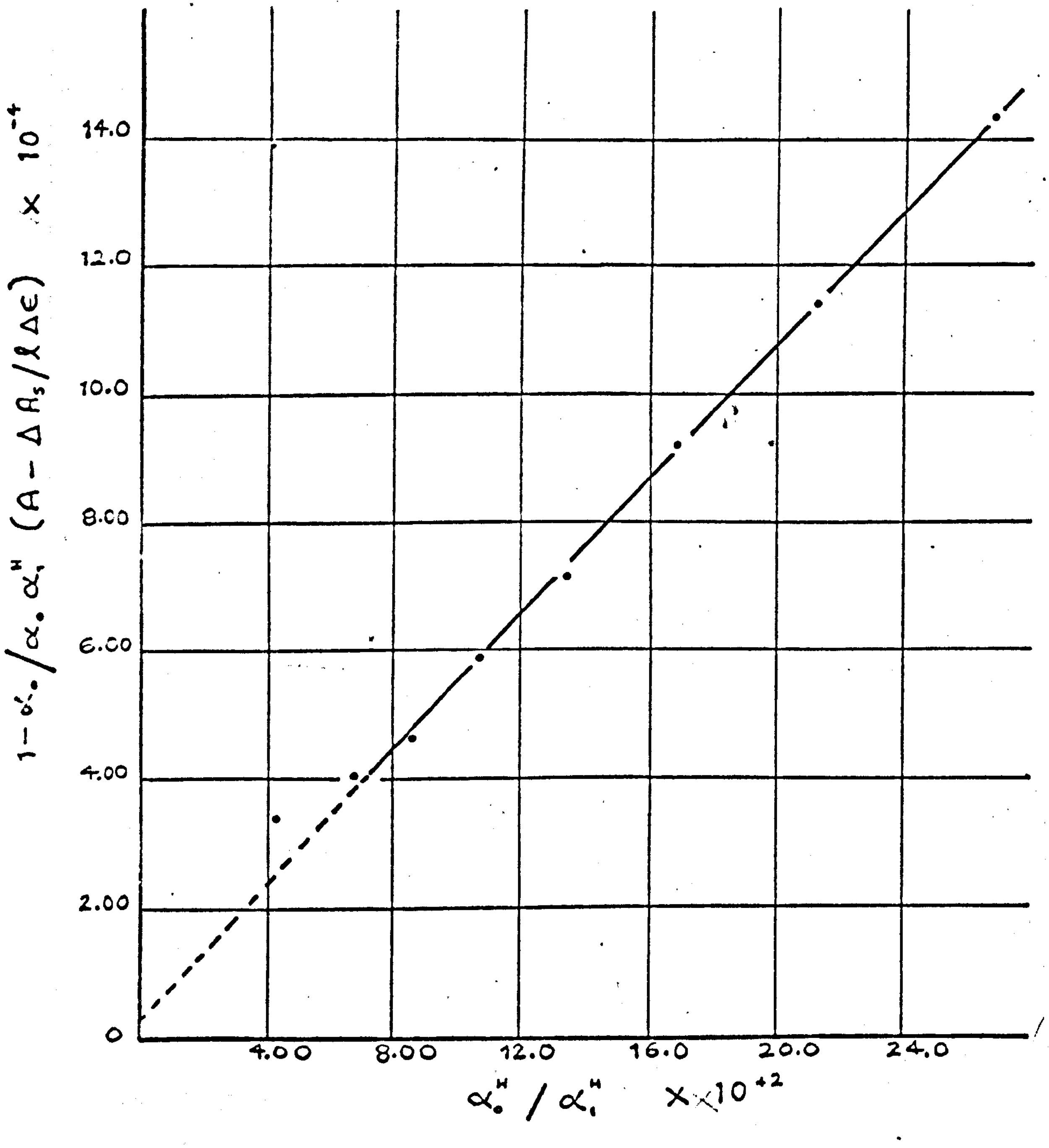


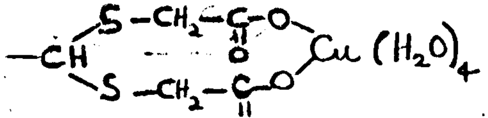
Figure XXVIII. Determination of β_{11} and β'_{111} for Cu-ETTA.

Table XI Comparison of spectrum of Ni(II)-ETTA with related compounds. Energies in cm^{-1}.

Ni-ETTA		Ni-EDTA (Ref. 63)			$Ni(H_2O)_6^{2+}$ (Ref. 14)		
	ϵ		ϵ	Assignm't		ϵ	Assignm't
		8700	16.7				
9220-9390	20	10,300	32	$^3T_{2g} \leftarrow {}^3A_{2g}$	8700	2.0	$^3T_{2g} \leftarrow {}^3A_{2g}$
12,400	<8	12,700	5		13,500)	1.7	$^3T_{1g} \leftarrow$
15,400	8.0	16,900	8.3		15,400)		
25,500	18	26,300	12.3	$^3T_{1g} \leftarrow$	25,500	5.2	$^3T_{1g} \leftarrow$

The spectrum of Ni-ETTA has the same general pattern as other known octahedral complexes. The main features of a d^8 ion in an octahedral field were discussed in section 3.21 where it was shown that three spin allowed transitions would be expected. The first electronic absorption for Ni-ETTA, was observed at 9220 - 9390 cm^{-1}, and it is suggested that this corresponds to the transition $^3T_{2g}(F) \longleftarrow A_{2g}$. This being so, the empirical splitting energy, Δ, is intermediate between that observed for Ni-EDTA and $Ni(H_2O)_6^{2+}$, being rather closer to the value observed for the latter. The extinction coefficients observed for Ni-ETTA are closer in magnitude to those of Ni-EDTA than to those of $Ni(H_2O)_6^{2+}$. It would be expected that the ligand field is more nearly symmetrical in $Ni(H_2O)_6^{2+}$ than in Ni-ETTA or Ni-EDTA and hence that d ⟷ d transitions would occur with a lower intensity.

For the Cu-ETTA complex a single broad band is observed at 12,600 to 12,800 cm^{-1} with a molar extinction of 47. In the hexaquo ion the absorption maximum is at approximately 12,500 cm^{-1} with a molar extinction of 12. As for the nickel complex, the observed splitting energy, Δ, is close to that observed for water, and would imply that the ligand ETTA, which very probably bonds through S and O, can be placed near or slightly above H_2O in the spectrochemical series. The observation that the extinction coefficient is so large compared to water could be explained by a greater distortion in the symmetry of the ligand field in Cu-ETTA than in the $Cu(H_2O)_6^{2+}$ ion. This would suggest that the ETTA complex is not simply



but rather involves some bonding between the sulfur and the Cu^{2+} ion.

The stability constants determined for the complexes of ETTA with Ni(II) and Cu(II) are also useful in understanding the nature of these complexes in aqueous solution. The stability constants determined are listed in Table XII.

Table XII. Stability constants of complexes of ETTA. Values in parentheses reported by Ref. 19
$\log \beta'_{111}$ corresponds to $B + HL \rightleftharpoons BHL$

	Ni(II) - ETTA	Cu(II) - ETTA	
$\log \beta_{11}$	4.17 ± .03	5.72 ± .02	(5.00)
$\log \beta'_{111}$	2.88 ± .26	3.53 ± .60	(4.08)

It should be stressed that these constants were determined from the results of measurements in the rather narrow range, pH 3.5 to 4.5. The results obtained are believed to show that the complexes BA and BHA are the main complexes formed in this range when B/A is approximately 1.

In order for the results to be adequately explained within the limits of error by considering only the formation of BA and BHA in the pH range 3.4 to 5, an approximate upper limit can be estimated for the stability of other complexes which might be considered likely to form. For the formation of a binuclear complex, B_2A, according to the equilibrium

$$BA + B \rightleftharpoons B_2A$$

the stability constant, β'_{21}, may be written

$$\beta'_{21} = \frac{[B_2A]}{[BA][B]}$$

or

$$\frac{[B_2A]}{[BA]} = \beta'_{21}[B]$$

Hence, B_2A can be neglected relative to BA when $[B]$, the concentration of free metal, is sufficiently small. For the purposes of estimating the maximum size of β'_{21} for which $[B_2A]/[BA]$ would be about 1/100, one may take as an upper limit to $[B]$ the total analytical concentration of metal ions. In the experiments on the nickel and copper complexes of ETTA, the total metal concentration was about 10^{-3}M, hence, if $[B_2A]/[BA] \sim 1/100$

$$\beta'_{21} \lesssim \frac{1}{100 \times 10^{-3}} = 10$$

The value reported by Saini for log β'_{21} for the copper system is 2.33. However, the results of the present work have differed appreciably from the previously reported values, and there is not necessarily any reason to think the results would be in exact agreement for β'_{21}. For the relative values of β_{11} and β'_{21} to be about 10^3: 1 or 10^4 : 1 seems not unreasonable. For example, the relative values of β_{11} and β'_{21} reported by Schwarzenbach in studies of the β - dimercaptosuccinic acid complexes of zinc may be compared (69). The value reported for log β_{11} was 15.82 while the value of log β'_{21} was found to be 3.85.

The results of the spectrophotometric measurements also indicate that if a complex of the type BH_2A forms, it must be considerably less stable than the complex BHA. Defining β'_{111} and β'_{121} as

$$\beta'_{111} = \frac{[BHA]}{[B][HA]} \quad \text{and} \quad \beta'_{121} = \frac{[BH_2A]}{[B][H_2A]}$$

it is then possible to write

$$\frac{[BH_2A]}{[B][HA]} = \frac{\beta'_{121}\,[B]\,[H_2A]}{\beta'_{111}\,[B]\,[HA]} = \frac{\beta'_{121}\,\alpha_2^H}{\beta'_{111}\,\alpha_1^H}$$

In the pH ranges 3.4 to 4.0, as can be seen from Figure XVII, α_1^H varies from .08910 to .3975 while α_2^H varies from .3220 to .3609, and hence in this range HA and H_2A are in comparable concentrations. Unless $\beta'_{121} < \beta'_{111}$ the plots shown in Figures XXV and XXVIII would not have been expected to be linear, since these are calculated on the assumption that only BA and BHA are present in appreciable concentrations. On the basis of the present evidence, it is suggested that

$$\beta'_{121} \lesssim \frac{1}{100}\,\beta'_{111}$$

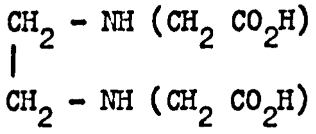
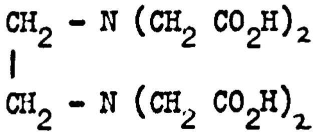
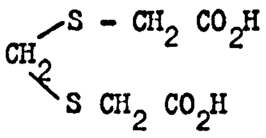
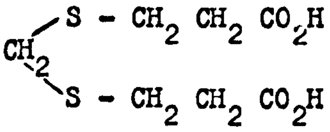
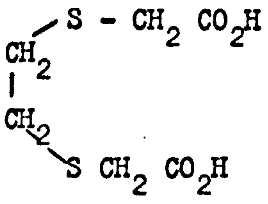
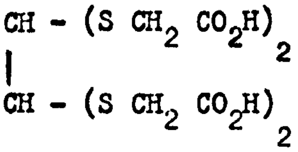
Below about pH 3.4, as pointed out in section 3.36, the measurements could not be explained by considering only BH_2A in addition to BA and BHA. It is possible that in the lower pH range, where the concentration of free metal is higher, the concentration of the binuclear species, B_2A, becomes appreciable relative to the concentration of other complexes. It is very laborious by hand computation to determine the stability constants where three or possibly four complexes coexist, the extinction coefficient for one of the species being unknown as well, by successive refinement. Furthermore, to determine the extinction coefficient of a possible binuclear species separately would require very accurate absorbance measurements since the measurements would have to be made in solutions containing a large excess of metal ions, the absorbance of B_2A being found as a small difference between two large numbers. The stability constant for B_2A could possibly be found through measurements above pH 3.4 by using higher total metal to total ligand concentrations. For such solutions, B_2A, BA and BHA would contribute to the absorbance, but β_{11} and β'_{111} having been previously determined, the extinction coefficient and stability constant for B_2A could be determined by a process of successive refinements. However, the computations would again be very laborious to do by hand, but could be done readily using a computer.

The stability constants determined may be discussed in terms of the relative stability expected for the Ni(II) and Cu(II) complexes, and also may be considered in relation to complexes of other similar ligands. Considering first the effect of changing the central metal ion, it has been found that a general order of stability holds for the divalent metals of the first transition series from Mn^{2+} to Zn^{2+} with ligands in which the donor atoms are N,O or S or any combination of these donor atoms (70). The general order of stability is $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. The copper complex of ETTA, $CuETTA^{=}$, was found to be about 35 times as stable as the nickel complex, $NiETTA^{=}$. Although the stability constants for the monoprotonated complexes were not determined accurately, it is apparent that the copper complex is more stable than the nickel. The potentiometric titration curves suggested that the complexes with Zn(II) and Co(II) are of comparable stability, but are appreciably less stable than the complexes with nickel.

In considering ETTA as a ligand, a number of generalisations have been found to be valid for chelate ligands such as ETTA, which are bonded to the same metal ion at more than one coordination site.

Chelated compounds are usually more stable than closely related non-chelated structures. However, in the context of the present systems it is difficult to conceive of a non-chelating ligand that could be used in this kind of a comparison to a sulfidecarboxylic acid.

The stability of a metal chelate is also related to the size and number of rings formed by the chelating ligand. It has been confirmed that in solution 5-membered rings are usually more stable than 6-membered rings (73). Four-membered rings are regarded as strained though they are believed to exist in many polynuclear complexes. For large membered rings the stability of the complexes approaches that of the corresponding bis-complexes. The increase in stability accompanying increased number of chelate rings is illustrated by comparing log K_1 for the cupric complexes of the ligands listed below. The maximum number of possible rings is listed for all the complexes. The complex $CuEDTA^{=}$ has recently been shown to actually contain only 4 rings in aqueous solution (35), and not the maximum number possible, i.e. 5. (For precise experimental conditions see the references given).

	log K_1	Maximum number of possible rings	Ref.
 $\begin{array}{l} CH_2-NH(CH_2CO_2H) \\ \vert \\ CH_2-NH(CH_2CO_2H) \end{array}$	16.2	3 5-membered	(20)
 $\begin{array}{l} CH_2-N(CH_2CO_2H)_2 \\ \vert \\ CH_2-N(CH_2CO_2H)_2 \end{array}$	18.79	(5) 5-membered	(32)
	3.17	2 5-membered	(18)
	2.06	2 6-membered 1 4-membered	(18)
	5.66	3 5-membered	(18)
 $\begin{array}{l} CH-(SCH_2CO_2H)_2 \\ \vert \\ CH-(SCH_2CO_2H)_2 \end{array}$	5.72 5.00	5 5-membered	(This work) (19)

While in going from ethylenediaminediacetic acid to EDTA an increase in stability of about 800 fold is observed, there is no significant increase observed in going from ethylenebisthioglycollic acid to ETTA. This would suggest that the number of chelate rings is not increased in ETTA relative to ethylenebisthioglycollic acid.

That at least one carboxyl group is free would seem to be borne out by the relative stabilities of the simple 1 : 1 complex and the protonated complex when these are compared to the stabilities of the corresponding complexes formed with EDTA. For the equilibrium

$$Ni^{2+} + HEDTA^{-} \rightleftharpoons Ni\,HEDTA$$

log β'_{111} is 11.56 while log β_{11} for the reaction between the metal ion and the completely dissociated acid is 18.67 (32).

The corresponding log β'_{111} and log β_{11} values for the complexes with copper are 12.03 and 18.79. Thus, for the nickel complex with EDTA the stability of the complex $NiEDTA^{=}$ is about 10^{7} times as stable as $NiHEDTA^{-}$ while for ETTA, the complex $NiETTA^{=}$ is only about 10 times as stable as $NiHETTA^{-}$. The complexes with copper show the same behavior, $CuEDTA^{=}$ being approximated 10^{6} times as stable as $CuHEDTA^{=}$ while CuETTA is only about 100 times as stable as $CuHETTA^{-}$. As mentioned before, the NMR studies of Rossotti and Sunshine on aqueous solutions containing $CuEDTA^{=}$ and $CuHEDTA^{-}$ have indicated that in the former EDTA is pentadentate forming 4 rings while in the latter it is tetradentate forming 3 chelate rings (35). This may suggest that the decrease in stability is related to there being one less chelate ring in $CuEDTA^{=}$ than in $CuHEDTA^{-}$. The logarithm of the stability constant for $CuHEDTA^{-}$ of 12.03 is somewhat below the log K_1 value of 16.2 observed for ethylenediaminediacetic acid which presumably forms three chelate rings. If the difference in stability of $CuEDTA^{=}$ and $CuHEDTA^{-}$ can be correctly associated with a difference in the number of chelate rings, this would lead to the implication that the small difference in stability between the protonated and simple 1 : 1 complexes of ETTA is not one of the breaking of a chelate ring which is very important in the stability of the complex, but more probably corresponds to the simple protonation of a free carboxyl group.

The much lower stability of the complexes of ETTA with Co(II), Ni(II), Cu(II) and Zn(II) compared to the corresponding complexes of EDTA, and of the bifunctional sulfidecarboxylic acids compared to related aminocarboxylates as described in section 1.2, must be related to the nature of the donor atoms $-N<$ and $-S-$. Nitrogen is a much stronger base towards protons than is $-S-$. Taking the values of the appropriate pK_{na}, as an indication of the ability to form σ-bonds, the ligands containing $-N<$ would be expected to form more stable complexes than those formed by ligands containing $-S-$. Although sulfur has d-orbitals available and conceivably could form π-bonds in addition to σ-bonds under appropriate conditions, the stability of the complexes of the sulfidecarboxylic acids remain much below that of the aminocarboxylates. It is possible that the arrangement of the donor atoms about the central metal ion is never suitable to permit the formation of strong π-bonds. Other differences between nitrogen and sulfur that could lead to differences in the stability of complexes of ligands containing these atoms are the larger size of the sulfur atom and also its greater number of non-bonding pairs. When the sulfur atom in sulfidecarboxylic acids is complexed to a metal ion, it is presumably tercovalent and pyramidal. In complexes of the aminocarboxylates, on the other hand, the nitrogen is tetracovalent and tetrahedral. This difference in the stereochemistry of the donor atoms may be sufficient to make the "wrapping around" of the $-SCH_2CHO_2^-$ groups and of $-SCH_2CH_2S-$ in ETTA less effective than that found in EDTA for $-\underset{|}{N}-CH_2CO_2^-$ and $>NCH_2CH_2N<$.

In comparing ETTA with thioglycollic acid, it is apparent that the stability and nature of the complexes formed is considerably different. Thioglycollic acid has been found to form a series of polynuclear complexes of high stability in aqueous solution with Ni(II) and Zn(II) (21). All the stability constants reported for the various complexes formed are listed in Table I, however, the value of log β_{12} for the nickel complex of 13.01 and of log β_{11} for the zinc complex of 7.80 may be taken as an indication of the order of stability of the complexes formed by thioglycollic acid. In contrast, the complexes of the sulfidecarboxylic acids even with copper have log K_1 values less than about 5.5.

The difference in stability of these complexes is related to differences in the coordinating ability of the thioether group and the mercaptide ion. Thiols would be expected to form more stable complexes than the thioethers on the basis of the relative proton basicity of the two groups. The mercaptide ion has a strong proton basicity while the thioether structure has practically none. It has been suggested that the differences in stability of complexes containing RS^- and R-S-R are related basically to the fact that RS^- is the more polarisable, although R-S-R is a better π-electron acceptor (71). It would be expected that thiols could form polynuclear complexes more readily than thioethers, since with the former, a polynuclear complex can be formed when the sulfur is bound to 3 other atoms (including the R - group), while in the latter it would be required for the sulfur to be bound to 4 other atoms (including the two R - groups).

It has been suggested that the coordinating ability of thioethers is enhanced in molecules containing other coordinating groups (7). For example, for the complex of $NH_2-CH_2\ CH_2-SCH_2\ CH_2-NH_2$ with Cu(II), log K_1 is 9.07 while for the complex with $NH_2-CH_2\ CH_2\ NH\ CH_2\ CH_2-NH_2$ log K_1 is 16.0 (20). Ligands containing two thioether groups form complexes of comparable stability to ligands containing only one thioether group (7). In the sulfidecarboxylates, however, the presence of the carboxyl group as a second coordinating agent does not lead to sufficiently enhanced stability to make the sulfidecarboxylates approach the stability of the corresponding aminocarboxylates.

3.38 Summary

ETTA has been found to form very weak complexes compared to the corresponding complexes with EDTA. Quantitative work has been carried out for the complexes with Ni(II) and Cu(II) and the logarithm of the stability constants for the 1 : 1 complexes with these metals have been found to be 4.17 ± .03 and 5.72 ± .02 respectively. These may be compared with the values for the corresponding complexes with EDTA, 18.6 and 18.8 respectively (20). The results of the present work indicate that the stability of the complex of ETTA with copper (II) is nearly the same as the corresponding complex with ethylenebisthioglycollic acid, for which the log K_1 value is reported to be 5.66 (18). ETTA has been found to form monoprotonated complexes, the logarithm of the stability constants for the formation of these complexes being only about two units lower than for the simple 1 : 1 complexes. The value of log β'_{111} for the nickel complex was found to be 2.88 ± .26 and for the copper 3.53 ± .60. There is also indication of another complex species being formed, having a lower stability constant than those for the complexes mentioned and this is believed to probably be a binuclear complex.

Thus it is apparent that while EDTA forms a single complex with metal ions of stability overwhelmingly greater than any other, ETTA forms a group of weaker, closely related complexes.

The complexes of ETTA with Co(II) were found to be unstable with respect to decomposition above pH 4, and the complexes of Cu(II) above about pH 5. The nickel complex was found to be stable in solutions having pH as high as 7.

A few comparisons may be made between the complexes formed in solution with ETTA and the corresponding solid complexes. Since the solid complexes formed in good yield from aqueous-ethanollic solutions, and were found to be thermally stable to at least 100°C (except for the copper complex which slowly decomposed at 83°C) these complexes may be considered stable from a preparative point of view. However, it has been shown that the stability of the complexes in aqueous solution, as measured by the concentration of the complex relative to the concentration of the species that combine to form it, is not great by comparison to the normally accepted order of magnitude for stable complexes, i.e. 10^9 or greater.

The electronic spectra of the solid complexes and the complexes in solution of nickel and copper, the two metals for which both spectra were taken, are similar, as indicated below (energies in cm^{-1}).

$Ni(ETTA)^{=}$ aq.	9220 - 9390	12,400	15,400	25,500
$Ni_2ETTA.8H_2O$	8760		15,150	25,000
$Cu(ETTA)^{=}$ aq.		12,600 - 12,800		
$Cu_2ETTA.2H_2O$		13,300		

Thus the spectra suggest that for the nickel complexes both the solid complex and the complex in solution have an octahedral structure, and for the copper complexes that both forms probably have the usual tetragonally distorted octahedral structure. The magnitude of the splitting parameter appears largely unchanged for the complexes in solution compared to the solids. The slight shift in the absorption maxima in going from the solid complexes to the complexes in solution, to higher energies in the nickel complexes and to lower energies in the copper complexes, suggests that there are some differences of structure between the solid complexes and those formed in solution.

3.4 Suggestions for further work

Considering first the solid complexes, as has already been mentioned, it would be of interest to try to prepare 1 : 1 complexes of ETTA. If these could be prepared, an X-ray crystal analysis to elucidate their structure would be of value. For the solids it would also be valuable to study the paramagnetic susceptibility as a function of temperature.

Further work needs to be carried out on the complexes in solution to determine accurately the stability constants of all the complexes of measurable stability formed by ETTA with metal ions. It is believed that this may be achieved by refinements to the present program for determining the stability constants from potentiometric data. Work is continuing on this at present. It will be necessary to extend the potentiometric data, and perhaps to improve its accuracy.

The spectrophotometric measurements also need to be extended and amplified in order to find accurately all the stability constants of interest. It is suggested that the spectrophotometric data at least in its final stages should be refined by a least squares adjustment.

Having measured accurately all the stability constants of interest it would then be valuable to measure the enthalpy changes for the formation of the different complexes. Since ΔG, the free energy change, may be evaluated directly from the stability constant using the relationship

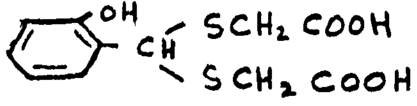
$$-\Delta G = RT \ln K$$

it would then be possible to separate ΔG into its heat and entropy terms since

$$\Delta G = \Delta H - T\Delta S$$

It may then be possible to come to a better understanding of the factors that are important in the complex formation and hence in the nature of the metal-ligand bonds formed.

In continuing to study S, O donor ligands it has been found in some preliminary measurements that the ligand which is the thioglycollic acid derivative of solicylaldehyde, i.e.



forms much more stable complexes with nickel (II) and cobalt (II), than do the ligands containing only the sulfidecarboxylic acid group.

The logarithm of the stability constant for the nickel complex of the salicylaldehyde derivative has been found to be about 6.0 and for the cobalt about 5.7. It is suggested that this ligand and various substituted derivatives of it could be studied to investigate further the nature of the coordination of the thioether group.

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APPENDIX A

EXPERIMENTAL DATA

Table I. Potentiometric titration of $HClO_4$ (8.685×10^{-3}M). Total volume of solution 46.00 mls. μ = .1 ($NaClO_4$). t = 25.0 ± .1°C.

pH	mls 1.065 N NaOH
2.165	0
2.215	.0400
2.325	.1200
2.400	.1600
2.490	.2000
2.600	.2400
2.750	.2800
2.845	.3000
2.975	.3200
3.145	.3380
3.260	.3470
3.395	.3550
3.515	.3600
3.640	.3640
3.765	.3670
3.950	.3700
4.085	.3716
4.270	.3730
4.530	.3740
5.120	.3744
5.430	.3746
5.770	.3748
6.590	.3750

Table II. Potentiometric titration of ETTA (1.934×10^{-3}M) in the presence of $HClO_4$ (8.685×10^{-3}M). Total volume of solution 46.00 mls. $\mu = .1$ ($NaClO_4$). t = 25.0 ± .1°C.

pH	mls 1.065 N Na OH	pH	mls 1.065 N Na OH
2.140	0	3.905	.5600
2.185	.0400	3.990	.5750
2.230	.0800	4.090	.5900
2.290	.1200	4.190	.6050
2.350	.1600	4.305	.6200
2.430	.2000	4.430	.6350
2.510	.2400	4.565	.6500
2.610	.2800	4.700	.6620
2.725	.3200	4.820	.6720
2.870	.3600	4.975	.6810
3.045	.4000	5.090	.6870
3.135	.4200	5.260	.6940
3.240	.4400	5.380	.6970
3.335	.4600	5.465	.6990
3.450	.4800	5.570	.7010
3.550	.5000	5.665	.7024
3.665	.5200	5.770	.7038
3.775	.5400	5.915	.7052

Table III. Experimental $\bar{n}_H$ values, and $\bar{n}_H$ values calculated from the refined constants. $pK_{1a} = 2.89 \pm .16$, $pK_{2a} = 3.54 \pm .11$, $pK_{3a} = 3.958 \pm .059$, $pK_{4a} = 4.572 \pm .010$. $t = 25.0 \pm .1^\circ C$. $\mu = .1\ (NaClO_4)$.

pH	$\bar{n}_H$ exptl.	$\bar{n}_H$ calc'd using β_j^H	$\bar{n}_H$ calc'd using $\beta_j^H + \sigma_{\beta_j}$	$\bar{n}_H$ calc'd using $\beta_j^H - \sigma_{\beta_j}$
2.350	3.723	3.750	3.754	3.746
2.430	3.717	3.707	3.711	3.703
2.510	3.646	3.658	3.663	3.653
2.610	3.574	3.587	3.593	3.581
2.725	3.610	3.492	3.499	3.485
2.870	3.341	3.351	3.359	3.341
3.045	3.149	3.146	3.156	3.133
3.135	3.018	3.026	3.038	3.012
3.240	2.874	2.874	2.888	2.858
3.335	2.706	2.726	2.741	2.709
3.450	2.533	2.535	2.552	2.516
3.550	2.343	2.360	2.379	2.339
3.665	2.146	2.151	2.171	2.128
3.775	1.935	1.947	1.968	1.923
3.905	1.720	1.706	1.728	1.683
3.990	1.555	1.553	1.573	1.530
4.090	1.388	1.378	1.398	1.357
4.190	1.218	1.213	1.230	1.194
4.305	1.048	1.035	1.051	1.019
4.430	.8755	.8608	.8736	.8477
4.565	.6983	.6947	.7047	.6845
4.700	.5546	.5521	.5598	.5444
4.820	.4373	.4448	.4507	.4388
4.975	.3296	.3314	.3355	.3272
5.090	.2578	.2638	.2670	.2606
5.260	.1764	.1860	.1881	.1838
5.380	.1405	.1442	.1458	.1426
5.465	.1165	.1201	.1214	.1188
5.570	.09499	.09552	.09655	.09450
5.665	.07823	.07748	.07830	.07666
5.770	.06135	.06388	.06199	.06071
5.915	.04712	.04433	.04478	.04387

Table IV. The distribution of ETTA in its various ionised forms as a function of pH. $pK_{1a} = 2.89$, $pK_{2a} = 3.54$, $pK_{3a} = 3.958$, $pK_{4a} = 4.572$. $\mu = .1$ ($NaClO_4$). t = 25.0 ± .1°C.

pH	α_0^H	α_1^H	α_2^H	α_3^H	α_4^H
2.00	1×10^{-7}	3.613×10^{-5}	3.278×10^{-3}	.1140	.8827
2.20	5.7×10^{-7}	1.342×10^{-4}	7.687×10^{-3}	.1686	.8236
2.40	3.24×10^{-6}	4.810×10^{-4}	.01738	.2405	.7416
2.60	1.748×10^{-5}	1.639×10^{-3}	.03737	.3263	.6347
2.80	8.808×10^{-5}	5.210×10^{-3}	.07497	.4129	.5068
3.00	4.054×10^{-4}	.01513	.1374	.4774	.3697
3.10	8.349×10^{-4}	.02475	.1785	.4928	.3031
3.20	1.667×10^{-3}	.03926	.2249	.4932	.2410
3.30	3.219×10^{-3}	.06022	.2740	.4773	.1853
3.40	5.996×10^{-3}	.08910	.3220	.4455	.1374
3.50	.01075	.1269	.3642	.4002	.09802
3.60	.01850	.1735	.3956	.3453	.06718
3.70	.03055	.2275	.4121	.2857	.04416
3.80	.04833	.2859	.4114	.2266	.02782
4.00	.1065	.3975	.3609	.1254	9.010×10^{-3}
4.20	.1994	.4697	.2690	.05899	2.883×10^{-3}
4.40	.3226	.4794	.1733	.02397	7.391×10^{-4}
4.80	.5947	.3518	.05062	2.788×10^{-3}	3.423×10^{-5}
5.00	.7101	.2650	.02406	8.362×10^{-4}	6.48×10^{-6}
5.20	.8004	.1885	.01080	2.368×10^{-4}	1.16×10^{-6}
5.40	.8665	.1288	4.654×10^{-3}	6.439×10^{-5}	2×10^{-7}
5.60	.9125	.08555	1.951×10^{-3}	1.703×10^{-5}	-
6.00	.9637	.03597	3.265×10^{-4}	1.13×10^{-6}	-
7.00	.9963	3.719×10^{-3}	3.38×10^{-6}	-	-

Table V. Potentiometric titration of ETTA (1.546×10^{-5} M). Total vol. of sol'n 60.00 mls. $\mu = .1$ ($NaClO_4$). $t = 25.0 \pm .1^{\circ}C$.

pH	mls 1.065 N Na OH
3.065	0
3.190	.0300
3.325	.0600
3.460	.0900
3.610	.1200
3.760	.1500
3.920	.1800
4.035	.2000
4.140	.2200
4.275	.2400
4.415	.2600
4.535	.2750
4.670	.2900
4.835	.3050
4.970	.3150
5.145	.3250
5.290	.3310
5.410	.3350
5.580	.3390
5.745	.3420
5.905	.3440
6.085	.3456
6.225	.3464
6.415	.3472
6.570	.3476
6.685	.3478
6.850	.3480
7.075	.3482

Table VI. Potentiometric titration of ETTA (1.546×10^{-3} M) in the presence of $Co(ClO_4)_2$ (1.702×10^{-3} M). Total vol. of sol'n 60.00 mls. $\mu = .1$($NaClO_4$). $t = 25.0 \pm .1^{\circ}C$.

pH	mls 1.065 N Na OH
3.075	0
3.200	.0300
3.285	.0500
3.365	.0700
3.450	.0900
3.545	.1100
3.630	.1300
3.725	.1500
3.815	.1700
3.905	.1900
4.010	.2100
4.105	.2300
4.225	.2500

Table VII. Potentiometric titration of ETTA (1.546×10^{-3} M) in the presence of $Ni(ClO_4)_2$ (1.668×10^{-3} M) Total vol. of sol'n 60.00 mls.
$\mu = .1$ ($NaClO_4$) t = 25.0 ± .1°C.

pH	mls 1.065 N NaOH
3.020	0
3.120	.0300
3.220	.0600
3.330	.0900
3.420	.1202
3.525	.1500
3.635	.1800
3.755	.2100
3.895	.2400
4.000	.2600
4.125	.2800
4.295	.3000
4.470	.3150
4.635	.3250
4.745	.3300
4.890	.3350
4.960	.3370
5.005	.3380
5.050	.3390
5.095	.3400
5.150	.3410
5.210	.3420
5.315	.3430
5.365	.3440
5.460	.3450
5.585	.3460
5.755	.3470
6.290	.3490

Table VIII. Potentiometric titration of ETTA (1.546×10^{-3} M) in the presence of $Cu(ClO_4)_2$ (1.692×10^{-3} M) Total vol. of sol'n 60.00 mls.
$\mu = .1$ ($NaClO_4$) t = 25.0 ± .1°C.

pH	mls 1.065 N NaOH
2.875	0
2.940	.0300
3.020	.0600
3.090	.0900
3.175	.1200
3.270	.1500
3.370	.1800
3.490	.2100
3.625	.2400
3.790	.2700
3.930	.2900
4.065	.3050
4.170	.3150
4.305	.3250
4.385	.3300
4.465	.3350
4.560	.3390
4.670	.3430
4.735	.3450
4.815	.3470
4.880	.3484
4.950	.3496
5.005	.3506
5.025	.3510
5.050	.3514
5.100	.3520
5.180	.3530
5.275	.3540

Table IX. Potentiometric titration of ETTA (1.546×10^{-3} M) in the presence of $Zn(ClO_4)_2$ (1.65×10^{-3} M). Total vol. of sol'n 60.00 mls. $\mu = .1$ ($NaClO_4$)
t = 25.0 ± .1°C.

pH	mls 1.065 N Na OH
3.050	0
3.170	.0300
3.300	.0600
3.390	.0800
3.470	.1000
3.570	.1200
3.665	.1400
3.755	.1600
3.865	.1800
3.965	.2000
4.065	.2200
4.170	.2400
4.310	.2600
4.410	.2750
4.535	.2900
4.685	.3050
4.805	.3150
4.870	.3200
4.950	.3250
5.045	.3300
5.150	.3350
5.290	.3400
5.430	.3440
5.520	.3460
5.630	.3480
5.775	.3500
5.870	.3510
5.980	.3526

Table X. Potentiometric titration of ETTA (1.687×10^{-3} M) in the presence of $Ni(ClO_4)_2$ (0.8708×10^{-3} M). Total vol. of sol'n 60.00 mls. $\mu = .1$ ($NaClO_4$)
t = 25.0 ± .1°C.

pH	mls 1.065 N Na OH
3.010	0
3.110	.0300
3.230	.0600
3.330	.0900
3.435	.1200
3.550	.1500
3.665	.1800
3.790	.2100
3.930	.2400
4.030	.2600
4.140	.2800
4.280	.3000
4.410	.3150
4.500	.3250
4.610	.3350
4.750	.3450
4.830	.3500
4.920	.3550
5.035	.3600
5.170	.3650
5.275	.3680
5.405	.3710
5.470	.3724
5.565	.3738
5.670	.3752
5.805	.3764
5.900	.3772

Table XI. Absorbance of a solution of ETTA ($5.227 \times 10^{-3}M$) and $Ni(ClO_4)_2$ ($4.353 \times 10^{-3}M$) as a function of pH. $\Delta A_s = A_s - 1\epsilon_o [Ni(ClO_4)_2]$. At 25,600 cm^{-1}, $\epsilon_o = 4.93$ and hence the constant subtracted was $10 \times 4.93 \times 4.353 \times 10^{-3} = .215$. Similarly at 15,400 cm^{-1} (650 mμ), where $\epsilon_o = 1.83$, the constant subtracted was $10 \times 1.83 \times 4.353 \times 10^{-3} = .080$. $\mu = .1$ ($NaClO_4$). t = 25.0 ± .1°C. The values of ΔA_s are the average for two separate experiments.

pH	15,400 ΔA_s	25,600 cm^{-1} ΔA_s
3.400	.231	.108
3.465	.259	.124
3.540	.291	.138
3.555	.297	.140
3.630	.328	.155
3.720	.359	.171
3.770	.378	.179
3.880	.409	.195
4.010	.441	.209
4.180	.470	.223
4.330	.491	.232
4.335	.495	.234
4.670	.517	.245

Table XII. Data for the plot of $(1 - \alpha_o)/\alpha_o \alpha_1^H (A - \Delta As/1\Delta\epsilon)$ as a function of α_o^H/α_1^H for Ni(II) - ETTA. At 25,600 cm^{-1} (390 mμ), $\Delta\epsilon = 13.02$, and at 15,400 cm^{-1} (650 mμ) $\Delta\epsilon = 6.17$. In this Table $\alpha_o = (B - \Delta As/1\Delta\epsilon)/B$ and $y = (1 - \alpha_o)/\alpha_o \alpha_1^H (A - \Delta A_s/1\Delta\epsilon)$.

pH	α_o^H	α_1^H	$\frac{\alpha_o^H}{\alpha_1^H} \times 10^2$	25,600 cm^{-1} ΔA_s	 α_o	 $y \times 10^3$	15,400 cm^{-1} ΔAs	 α_o	 $y \times 10^{-3}$
3.40	5.996×10^{-3}	8.910×10^{-2}	6.73	.231	.5925	2.24	.108	.5980	2.17
3.50	1.075×10^{-3}	.1269	8.47	.275	.5148	2.38	.130	.5160	2.37
3.60	1.850×10^{-2}	.1735	10.7	.315	.4443	2.57	.150	.4415	2.61
3.70	3.055×10^{-2}	.2275	13.4	.352	.3788	2.86	.167	.3781	2.87
3.80	4.833×10^{-2}	.2859	16.9	.385	.3207	3.26	.184	.3150	3.39
3.90	7.327×10^{-2}	.3443	21.3	.415	.2679	3.89	.197	.2665	3.93
4.00	.1065	.3975	26.8	.438	.2272	4.59	.208	.2256	4.65
4.10	.1486	.4406	33.7	.458	.1918	5.60	.218	.1884	5.77
4.30	.2580	.4827	53.4	-	-	-	.232	.1362	8.96
4.40	.3226	.4794	67.3	.497	.1231	10.5	-	-	-

Table XIII. Absorbance of a solution of ETTA (1.690×10^{-3}M) and $Cu(ClO_4)_2$ (1.766×10^{-3}M) as a function of pH. All measurements taken at 12,400 cm^{-1} (805 mμ). $\Delta A_s = A_s - 1\,\epsilon_o\,[Cu(ClO_4)_2]$. Since $\epsilon_o = 11.9$ at 12,400 cm^{-1}, the constant subtracted from all A_s readings was $10 \times 11.9 \times 1.766 \times 10^{-3} = .210$. $\mu = .1$ ($NaClO_4$). $t = 25.0 \pm .1$°C.

Run 1		Run 2	
pH	ΔA_s	pH	ΔA_s
2.175	.014	2.155	.014
2.425	.033	2.250	.018
2.555	.056	2.370	.030
2.740	.114	2.425	.038
2.870	.164	2.580	.066
3.025	.234	2.750	.116
3.330	.378	2.870	.168
3.490	.444	3.330	.386
3.690	.492	3.520	.456
		3.670	.500
3.940	.538	3.925	.546
4.070	.546		
4.170	.550		

Table XIV. Data for the plot of $(1-\alpha_o)/\alpha_o\,\alpha_1^H\,(A - \Delta A_s/l\Delta\epsilon)$ as a function of α_o^H/α_1^H for Cu(II) - ETTA. At 12,400 cm^{-1} (805 mμ) $\Delta\epsilon = 35.1$. In this Table $\alpha_o = (B - \Delta A_s/l\Delta\epsilon)/B$ and $y = (1-\alpha_o)/\alpha_o\alpha_1^H\,(A - \Delta A_s/l\Delta\epsilon)$.

pH	$\alpha_o^H \times 10^2$	α_1^H	$\frac{\alpha_o^H}{\alpha_1^H} \times 10^2$	ΔA_s	α_o	$y \times 10^{-4}$
3.00	.04054	.01513	2.68	.223	.6404	3.52
3.20	.1667	.03926	4.25	.318	.4870	3.42
3.40	.5996	.08910	6.73	.407	.3431	4.05
3.50	1.075	.1269	8.47	.443	.2854	4.61
3.60	1.850	.1735	10.7	.476	.2322	5.71
3.70	3.055	.2275	13.4	.502	.1903	7.19
3.80	4.833	.2859	16.9	.522	.1580	9.18
3.90	7.327	.3443	21.3	.536	.1353	11.4
4.00	10.65	.3975	26.8	.547	.1178	14.3

APPENDIX B

COMPUTER PROGRAMS

All programs have been written in Elliott Algol, and were performed on a Elliott 803 computer.

<u>Program I</u>

Calculation of proton stability constants (or acid dissociation constants) for an acid of the type H_JA.

Notes on the use of the program:

1. Of the integer declarations, I is the number of readings and J the number of dissociable protons. For ETTA, J = 4.

2. Of the real declarations, the following represent experimental variables and constants:

   vone - volume of base used to reach a particular pH in the titration of the mineral acid alone.

   N - normality of the base.

   E - concentration of mineral acid.

   V - volume of initial solution.

   A - total concentration of ligand.

3. Of the arrays the following were used to hold sets of experimental values:

   v, logh - the volume of base (v) required in the titration of the mineral acid and ligand to reach a particular value of - pH (logh).

   d - arbitrarily selected scaling factors.

4. Other variables were used to do the work in the program.

5. - procedure calc W calculates the elements of the maxtrices in the equation which is solved for the stability constants.
   - procedure calc w calculates the weights.
   - the program requires a matrix package.
6. For more description of the program see section 2.11.

Program I. Calculation of proton stability constants (or acid dissociation constants) for acids of the type H_JA.

```
begin integer i,j,K,m,I,J;
     real vone,N,E,V,A,S,phi;
     read I,N,E,V,A,J;
     begin real b,deltaU,P,Q;
          array w,y,h,v,p,logh,q[1:I],W[1:J,1:J],B,C,D[1:J,1:1],d[1:J];
          switch ss:=recycle,again,repeat;
          procedure calcW;
          begin for i:=1 step 1 until J do
               begin C[i,1]:=0;
                    for j:=1 step 1 until J do
                    W[i,j]:=0;
               end;
               for i:=1 step 1 until I do
               for j:=1 step 1 until J do
               begin C[j,1]:=C[j,1]-(w[i]*y[i]*(y[i]-j*A)*h[i]↑j)*d[j];
                    for K:=j step 1 until J do
                    begin b:=(w[i]*(y[i]-j*A)*(y[i]-K*A)*h[i]↑(j+K))*d[K]*d[j];
                         W[j,K]:=W[j,K]+b;
                    end;
               end;
               for i:=1 step 1 until (J-1) do
               for j:=i+1 step 1 until J do
               W[j,i]:=W[i,j];
          end calcW;

          procedure calcw:
          begin for i:=1 step 1 until I do
               begin deltaU:=0;
                    for j:=1 step 1 until J do
                    deltaU:=delta U + D[j,1]*((E-N*v[i]/(V+v[i])+A)*j*h[i]↑(j-1)
                         -h[i]↑j*(j+1)-j↑2*A*h[i]↑(j-1));
                    w[i]:=1/((1-deltaU)*2.30258*h[i]*(.001*logh[i]+.0182))↑2;
                    print scaled(6),w[i];
               end:
          end calcw;

          for i:=1 step 1 until I do
          begin read logh[i],vone,v[i];
               h[i]:=2.71828↑(2.30258*logh[i]);
               y[i]:=4*A+(vone-v[i])*(N+E)/(V+vone);
               w[i]:=10↑10;
          end;
          for i:= 1 step 1 until J do read d[i];
          m:=0;
again:    calcW;
          for i:=1 step 1 until J do
          begin print ££1??;
               for j:=1 step 1 until J do
               print scaled(6),W[i,j];
          end;
          mxquot(D,W,C);
          for i:= 1 step 1 until J do D[i,1]:=D[i,1]*d[i];
          calcw:
          m:=m+1;
```

```
            if m=1 then goto recycle:
            for i:=1 step 1 until J do
            if abs((B[i,1]-D[i,1])/B[i,1])>.0001 then goto recycle;
            calcw;
            calcW;
            for i:=1 step 1 until J do
            begin  B[i,1]:=D[i,1];
            end;
            invmx(W);
            for i:= 1 step 1 until J do W[i,i]:=W[i,i]*d[i]↑2;
            S:=0;
            for i:=1 step 1 until I do
            begin p[i]:=0;
                  for j:= 1 step 1 until J do p[i]:=p[i]+(y[i]-j*A)*B[j,1]*h[i]↑j;
                  S:=S+w[i]*(y[i]+p[i])↑2;
            end:
            print S,££l2??;
            for i:=1 step 1 until J do
            begin phi:=W[i,i]*S/(I-5);
                  print £phi?,sameline,scaled(6),phi,££s2??,ln(B[i,1])/2.30258;
            end;
            print ££l2??;
            for i:= 1 step 1 until I do print scaled(4),y[i]/A;
            print ££l2??;
            for i:= 1 step 1 until I do
            begin y[i]:=0; p[i]:=0; q[i]:=0;
                  for j:= 1 step 1 until J do
                  begin p[i]:=p[i]+j*B[j,1]*h[i]↑j;
                        q[i]:=q[i]+B[j,1]*h[i]↑j;
                  end:
                  y[i]:=(p[i])/(1+q[i]); print scaled(4),ln(h[i])/2.30258,sameline,
                                                ££s2??,y[i];

            end;
            K:=1;
repeat:     for i:=1 step 1 until J do
            begin B[i,1]:=B[i,1]+(sqrt(W[i,i]*S/(I-5)))*(if K=1 then 1 else -2);
                  print scaled(4),B[i,1];
            end;
            K:=K+1;
            for i:=1 step 1 until I do
            begin y[i]:=0;  p[i]:=0;  q[i]:=0;
                  for j:=1 step 1 until J do
                  begin p[i]:=p[i]+j*B[j,1]*h[i]↑j;
                        q[i]:=q[i]+B[j,1]*h[i]↑j;
                  end;
                  y[i]:=p[i]/(1+q[i]);
                  print scaled(4),y[i];
            end;
            if K=2 then goto repeat;
            stop;
recycle:    for i:=1 step 1 until J do
            begin B[i,1]:=D[i,1];
                  print ££l??,scaled(4),B[i,1];
            end;
            print ££l2??;
            if m>10 then wait;
            goto again;
      end;
end;
end;
```

Program II

Calculation of the distribution of a polybasic acid in the various protonated forms as a function of pH.

Notes on the use of the program:

1. Of the integar declarations I represents the number of values of pH at which it is desired to calculate the values of α_0, α_1, etc. and J represents the number of dissociable protons.

2. The real variable log B is used to read in the logarithm of the proton stability constants.

3. The array logh is used to hold the values of the pH at which the distribution is to be calculated.

4. Other variables are used to do the work in the program.

Program II. Calculation of the distribution of a polybasic acid in its various protonated forms as a function of pH.

```
D.Malcolm/Calculation of distribution;

begin integer I,J,K,i,j;
      real logB:
      read I,J,K;
      begin array h,logh,d[1:I],B[0:J],a,t[1:I,0:K];
            for j:=0 step 1 until J do
            begin
                  read logB;
                  B[j]:=exp(2.30258*logB);
            end;
            for i:=1 step 1 until I do
            begin
                  d[i]:=0;
                  read logh[i]:
                  h[i]:=exp(2.30258*logh[i]);
                  for j:=0 step 1 until J do
                  d[i]:=d[i]+B[j]*h[i]↑j;
                  for K:=0 step 1 until (J-1) do
                  begin
                        a[i,K]:=(B[K]*h[i]↑K)/d[i];
                        if K=0 then t[i,K]:=a[i,K]
                        else
                        t[i,K]:=t[i,K-1]+a[i,K];
                        print i,K,sameline,££s2??,t[i,K],££s2??,logh[i],££s2??,a[i,K];
                  end;
                  print ££s24??,J-t[i,K];
            end;
      end;
end;
```

Program III

Calculation of the stability constants of metal complexes. This program can be used for any of the following combinations of complexes: BA, B_2A; BA, BHA, B_2A; BA, BHA, BH_2A, B_2A, etc. up to BA, BHA,.....BH_tA, B_2A.

Notes on the use of the program:

1. Of the integer declarations t represents the maximum number of protons in the metal complexes, and I the number of measurements.

2. The following real declarations are used to represent experimental variables and constants:

   N - normality of the base.

   E - concentration of mineral acid.

   V - total volume of initial solution.

   M - total concentration of metal.

   l - a constant scaling factor, arbitrarily chosen.

   var v - variance in the volume measurements.
   var h - standard deviation in the pH measurements, and used to calculate the variance in the free hydrogen ion concentration.

3. Arrays are used to hold the following sets of numbers:

   gamma - the acid dissociation constants, gamma[0,0] being 1.

   logh, v - the sets of experimental measurements of volume of alkali added and the corresponding pH.

   B - the initial estimates of the parameters.

   S, R - arbitrarily chosen scaling factors.

4. Other variables are used to do the work in the program.

5.
- procedure calc W calculates the elements of the matrices in the equation which is solved for the stability constants.
- procedure calc w calculates the weights.
- procedure calc b (L) is a Newton-Raphson iteration for finding the free metal ion and free ligand concentration from the mole balance equations.
- procedure calc sum is used in the calculation of $\bar{n}_A$ as a function of pH from the refined constants.
- the program requires a matrix package.

6. More description of this program is given in section 2.12.

Program III. Calculation of the stability constants of metal complexes.

```
begin integer i,j,k,I,m,p,q,n,mm,t;
     real N,E,V,A,M,s,l,ksum,kksum,ga,gb,d,Fv,Fh,beta,alpha,
           Fvv,Fhh,varv,varh,g,f,fa,fb,c;
     switch sss:=finish;
     read I,N,E,V,A,M,l,varv,varh,t;
     begin array w,y,h,v,logh,sum,a,b[1:I],gamma[0:4],sigma[0:4],W[0:t,0:t],
           B,C,D[0:t,1:1],S[0:t],R[0:t];
           switch ss:=again,finish,here;
           procedure calcW;
           begin for k:=1 step 1 until I do
                 begin ksum:=0;
                       for j:=0 step 1 until 4 do
                       ksum:=ksum+(y[k]-j*A)*h[k]↑j*gamma[j];
                       sum[k]:=ksum;
                 end;
                 for i:=0 step 1 until t do
                 for j:=0 step 1 until i do
                 begin p:=if i=t then 1 else i;
                       q:=if j=t then 1 else j;
                       d:=0;  c:=0;
                       for k:=1 step 1 until I do
                       begin if j=0 then
                            c:=c-(w[k]*(y[k]-p*A)*sum[k]*b[k]*h[k]↑p)*
                                  (if i=t then b[k] else 1.0);
                            d:=d+(w[k]*(y[k]-q*A)*(y[k]-p*A)*b[k]*b[k]*
                                  h[k]↑(p+q))*(if i=t or j=t then b[k] else 1.0);
                       end;
                       if j=0 then C[i,1]:=c*R[i];
                       W[i,j]:=d*R[i]*S[j];
                       if i≠j then W[j,i]:=W[i,j];
                 end;
          end calcW;
          procedure calcw;
          begin for k:=1 step 1 until I do
                begin Fv:=0;  Fvv:=0;  Fh:=0;  Fhh:=0;
                      for j:=0 step 1 until (t-1) do
                      begin Fv:=Fv-N/V*b[k]*h[k]↑j*B[j,1];
                            Fh:=Fh+B[j,1]*b[k]*(-h[k]↑j+j*(y[k]-j*A)*h[k]↑(j-1));
                      end;
                      for j:=0 step 1 until 4 do
                      begin Fhh:=Fhh+gamma[j]*(-h[k]↑j+j*(y[k]-j*A)*h[k]↑(j-1));
                            Fvv:=Fvv+(-N/V)*h[k]↑j*gamma[j];
                      end;
                      w[k]:=1/((Fv+Fvv-N/V*b[k]*b[k]*B[t,1])↑2*varv+
                            (Fh+Fhh-b[k]*b[k]*B[t,1])↑2*(varh*2.30258*logh[k]*h[k])↑2
                      print scaled(6),w[k];                                     /
                end;
         end calcw;
         procedure calcb(L);
         label L;
         begin switch ss:=recycle;
               for k:=1 step 1 until I do
               begin ksum:=0;  n:=0;  a[k]:=A;  b[k]:=M;  kksum:=0;
                     for i:=0 step 1 until 4 do
                     ksum:=ksum+h[k]↑i*gamma[i];
                     for i:=0 step 1 until (t-1) do
                     kksum:=kksum+h[k]↑i*B[i,1];
```

```
    recycle:    f:=A-a[k]*b[k]*kksum-a[k]*b[k]*b[k]*B[t,1]-ksum*a[k];
                g:=M-b[k]*a[k]*kksum-2*b[k]*b[k]*a[k]*B[t,1]-b[k];
                fa:=-b[k]*kksum-b[k]*b[k]*B[t,1]-ksum;
                fb:=-a[k]*kksum-2*a[k]*b[k]*B[t,1];
                ga:=-b[k]*kksum-2*b[k]*b[k]*B[t,1];
                gb:=-a[k]*kksum-4*a[k]*b[k]*B[t,1]-1;
                n:=n+1;
                if n>30 then goto L;
                beta:=(g*fa-ga*f)/(ga*fb-gb*fa);
                alpha:=(-beta*fb-f)/fa;
                if alpha≤0.95*A then a[k]:=a[k]+alpha else a[k]:=0.1*A;
                if beta≤0.95*M then b[k]:=b[k]+beta else b[k]:=0.1*M;
                print n,sameline,k,scaled(6),a[k],££s2??,b[k];
                if abs((M-b[k]*a[k]*kksum-2*b[k]*b[k]*a[k]*B[t,1]-b[k])/M)
                    >0.00001 or abs((A-a[k]*b[k]*kksum-a[k]*b[k]*b[k]*
                    B[t,1]-ksum*a[k])/A)>0.00001 then goto recycle;
        end;
    end calcb;
    procedure calcsum;
    begin for k:=1 step 1 until I do
        ksum:=0;
        kksum:=0;
        for i:=0 step 1 until (t-1) do
        begin ksum:=ksum+i*b[k]*h[k]↑i*D[i,1];
            kksum:=kksum+b[k]*h[k]↑i*D[i,1];
        end;
        g:=0;
        f:=0;
        for i:=0 step 1 until 4 do
        begin g:=g+i*h[k]↑i*gamma[i];
            f:=f+h[k]↑i*gamma[i];
        end;
        sum[k]:=(ksum+g)/(kksum+f+b[k]*b[k]*B[t,1]);
        print sum[k];
    end calcsum;
    for i:=1 step 1 until I do
    begin read logh[i],v[i];
        h[i]:=2.71828↑(2.30258*logh[i]);
        y[i]:=(E+4*A)/(V+v[i])*V-N*v[i]/(V+v[i])-h[i];
    end;
    for i:=0 step 1 until t do
    begin read B[i,1];
        B[i,1]:=2.71828↑(2.30258*B[i,1]);
    end;
    for i:=0 step 1 until t do
    begin read S[i];
        read R[i];
    end;

    for i:=0 step 1 until 4 do
    begin read gamma[i];
        gamma[i]:=2.71828↑(2.30258*gamma[i]);
    end;
    m:=0;
    mm:=0;
again:calcb(finish);
    calcw;
    calcW;
    m:=m+1;
```

```
            for i:=0 step 1 until t do
            begin print ££1??;
                  for j:=0 step 1 until t do
                  print scaled(6),W[i,j];
            end;
            mxquot(D,W,C);
            for i:=0 step 1 until t do D[i,1]:=D[i,1]*S[i];
            for i:=0 step 1 until t do
            begin if abs((B[i,1]-D[i,1])/B[i,1])>0.0001 then
                  begin for i:=0 step 1 until t do
                        begin B[i,1]:=D[i,1];
                              print ££1??,scaled(4),B[i,1];
                        end;
                        print ££12??;
                        if m>10 then goto finish;
                        goto again;
                  end;
                  B[i,1]:=D[i,1];
                  print scaled(4),B[i,1];
            end;
            invmx(W);
            for i:=0 step 1 until t do W[i,i]:=W[i,i]*S[i]*R[i]*1;
            s:=0;
            for k:=1 step 1 until I do
            begin ksum:=0;  kksum:=0;
                  for i:=0 step 1 until (t-1) do
                  ksum:=ksum+(y[k]-i*A)*h[k]↑i*B[i,1];
                  for i:=0 step 1 until t do
                  kksum:=kksum+(y[k]-i*A)*h[k]*gamma[k];
                  s:=s+w[k]*(ksum*b[k]+y[k]*b[k]*b[k]*B[t,1]+kksum)↑2;
            end;
            print s,££12??;
            for i:=0 step 1 until t do
            begin sigma[i]:=sqrt(s*W[i,i]/(I-1));
                  print £sigma=?,sameline,sigma[i];
            end;
            print ££12??;
            for i:=0 step 1 until t do
            D[i,1]:=B[i,1]-sigma[i];
            calcsum;
            for i:=0 step 1 until t do
            D[i,1]:=B[i,1]+sigma[i];
            calcsum;
            for i:=0 step 1 until t do
here:       D[i,1]:=B[i,1];
            calcsum;
            for i:=1 step 1 until I do
            begin print y[i]/A,sameline,logh[i],scaled(6),w[i],v[i],
                        (sum[i]*A+h[i]-E-4*A)/(-N/V);
                  print A,sameline,M,N,V,E;
            end;
     end;
finish:
end;
end;
```