1961

A study of the rare-earth metal complexes

Robert Stanley Kolat
Iowa State University

Recommended Citation

Kolat, Robert Stanley, "A study of the rare-earth metal complexes " (1961). *Retrospective Theses and Dissertations*. 1970.
https://lib.dr.iastate.edu/rtd/1970

KOLAT, Robert Stanley, 1931–
A STUDY OF THE RARE–EARTH METAL
COMPLEXES.

Iowa State University of Science and Technology
Ph.D., 1961
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

A STUDY OF THE RARE-EARTH METAL COMPLEXES

by

Robert Stanley Kolat

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1961

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

I. INTRODUCTION

The group of elements having atomic numbers 57 through 71 form what is commonly known as the rare-earth or lanthanide series of the periodic table. These elements along with those of the actinide series comprise the two groups of elements which are designated as the inner transition elements. As the name implies, the elements essentially form a transition series within a transition series. In the case of the lanthanides, the group is characterized by an incomplete 5d shell along with an incomplete 4f shell. The lanthanides may be given the approximate electronic configuration $4f^{1-13}5s^25p^65d^16s^2$ (1). Strictly speaking, lanthanum, $4f^05s^25p^65d^16s^2$, and lutetium, $4f^{14}5s^25p^65d^16s^2$, would be excluded from the group. However, due to their similarity with respect to chemical properties, they are generally considered to be members of the series. A sixteenth element, yttrium, although merely a member of periodic group III A, is generally included in studies of the lanthanons. This inclusion occurs because of the lanthanide contraction which places the properties of yttrium among the heavy member lanthanons.

The term "rare earths" evolved from the difficulty in obtaining individual members of the series free from other members. The filling of the inner 4f shell changes the chemical properties of the elements only slightly, thus minimizing the effectiveness of separations by physico-chemical methods. In comparison to other elements, the rare earths are not really rare. For example, all of the lanthanons are more abundant in the earth's crust than cadmium, silver or bismuth (2).

The lanthanons have been associated with the Ames Laboratory of the Atomic Energy Commission since the development of ion-exchange separation methods (3, 4, 5, 6) at this institution. Ion-exchange methods have enabled investigators to work with macro-quantities of individually pure rare earths (99.9%). Consequently, extensive work has been carried out on the electrolytic solution, magnetic, metallic and alloying properties of the rare earths.

The unique electronic structure of the rare earths is responsible for a widespread use of these elements in theoretical investigations. As the atomic number increases from lanthanum to lutetium, the additional electrons necessary for charge balance enter 4f orbitals. Since the 4f shell is well shielded by the closed shells around it, the additional electrons contribute little if any to a change in the chemical behavior between the elements of the group. The increase in nuclear charge across the rare-earth series does result, however, in a greater electronic attraction. This attraction results in a pulling in of the electrons and causes a slight progressive decrease in atomic radius as one goes from lighter to heavier members. Thus we have at our disposal a series of chemically similar elements each varying from its neighbors by a very small size factor. The rare earths are adaptable to studies concerned with atomic and ionic radii and also, due to the presence of unpaired 4f electrons, to studies of a magnetic nature.

As mentioned earlier, the separation of rare earths is affected by ion-exchange techniques. The usual method employs an eluant solution, containing a polydentate chelating agent, which is passed over an ion-exchange bed, a portion of which is saturated with the lanthanons in the trivalent state. The differences in affinity of the chelating agent for individual lanthanon ions affords a means of separation.

One of the most efficient chelating agents applied to the method has been the ethylenediamine-N,N,N',N'-tetra-acetate anion (EDTA). In the course of experiments with the rare earths and EDTA, it was found that solid rare-earth chelates of EDTA are exceptionally interesting compounds which exhibit some unusual solubility and hydration properties. A portion of this thesis is concerned with a further study of the nature of these solid chelates.

In quest of better, more efficient chelating agents for the ion-exchange process, many polydentate chelating agents were studied. In the course of the investigations, it became apparent that the rare-earth sequence offered an excellent opportunity to study factors involved in chelate formation. Most of the studies have involved the use of strong chelating agents which are capable of occupying four or more coordination sites of a metal ion. The chemistry of the much weaker monodentate and bidentate ligands with the rare earths is relatively unknown. Consequently, the second portion of this thesis is concerned with furthering the knowledge of this chemistry. The complex formation characteristics of the acetate, methoxyacetate, thioglycolate and α-hydroxyisobutyrate anions with the rare earths have been determined and some unusual properties of these compounds are discussed.

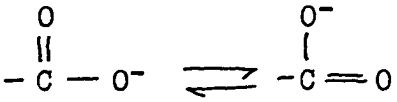
II. THE SOLID RARE-EARTH CHELATES OF ETHYLENEDIAMINETETRAACETIC ACID

A. Structural Determinations of Metal Chelates

It is well known that ethylenediaminetetraacetic acid and its derivatives and analogues form exceptionally stable chelates with a large number of metallic elements. These elements may be of the representative, transition or inner transition classes. Although numerous investigations have been made in regard to the stability constants of various chelates, little has been done concerning their structures. The majority of work has been concerned with their solution properties and little has been done on their solid properties. There are several reasons for this lag. First, the chelates are generally used in aqueous media, and a study of their structures in the solid state would not necessarily predict their structures in solution. Secondly, the complexity of the chelate molecule makes the problem of structural analysis by X-ray diffraction difficult. The problem becomes further complicated when the chelates contain ionizable hydrogen. Thus far, the major part of the structural investigations have been made using infrared spectroscopy.

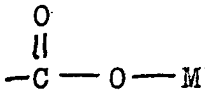
Infrared spectroscopy has received considerable attention as a tool in the determination of the structures of the complex inorganic compounds. Investigations have generally been confined to molecules containing functional organic groups, and information is obtained by measuring the effect of complexation on these groups. EDTA and its analogues form chelates by bonding to the central metal ion through nitrogen and carboxyl groups. Since participation of a carboxyl group in a bond should affect its characteristic vibration frequencies, the resonant frequency of the carboxyl group may be used in identifying chelate structures.

The basis for the use of the carboxyl group in determining structures from infrared spectra is the resonating character of the group.



$$-\overset{\overset{\displaystyle O}{\|}}{C}-O^- \rightleftharpoons -\overset{\overset{\displaystyle O^-}{|}}{C}=O$$

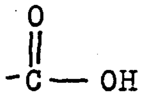
The resonance can be eliminated by removing a pair of electrons from one of the oxygen atoms. According to this view it is supposed that, if a carboxyl group is joined firmly to some group M,



$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-M$$

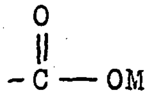
then the carboxylate resonant frequency will increase as the ionic character of the -O-M linkage increases. This increased resonance imparts enhanced single-bond character to the carbonyl oxygen due to localization of electron density in the group. This localization results in a lowering of the $-C{=}O$ stretching vibration frequency. More simply stated, it takes less energy to vibrate two atoms joined by a single bond than to vibrate the same two atoms joined by a double bond.

It is possible to have as many as three distinct types of carboxyl groups present in a molecular species.



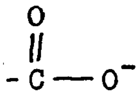
$$-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Carboxylic Acid Group



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OM$$

Complexed Carboxyl Group



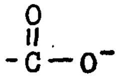
$$-\overset{\overset{\displaystyle O}{\|}}{C}-O^{-}$$

Free Carboxylate Group

The carboxylic acid group needs no clarification other than mentioning that the frequency of vibration of the carbonyl oxygen in this group is always affected by the amount of hydrogen bonding present between two such groups. The complexed carboxyl group will absorb at frequencies dependent upon the ionic character of the $-O-M$ bond. The free carboxylate group may be illustrated by an ionized carboxylic acid group. In the spectrum of a dilute solution of the sodium salt of a carboxylic acid, one observes a very strong band at 1550 cm.$^{-1}$ On addition of mineral acid to the solution this band disappears and is replaced by another strong band at approximately 1730 cm.$^{-1}$

The important infrared spectral bands associated with these carboxyl groups are tabulated in Table 1 (7).

Table 1. Characteristic vibrations of the carboxyl group[a]

Carboxylic Acid	
OH stretching vibrations (free)	3560-3500 cm.$^{-1}$ (m)
OH stretching vibrations (bonded)	2700-2500 cm.$^{-1}$ (w)
-C=O Vibrations	
saturated aliphatic acids	1725-1700 cm.$^{-1}$ (s)
acids showing internal hydrogen bonding	1670-1650 cm.$^{-1}$ (s)
-C—O Stretching or O-H deformation vibrations (coupled)	1440-1395 cm.$^{-1}$ (w) 1320-1211 cm.$^{-1}$ (s)
OH Deformation vibrations (out of plane)	950- 900 cm.$^{-1}$ (v)
 $-\overset{\overset{O}{\|}}{C}-O^-$ Vibrations	
anti-symmetric	1610-1550 cm.$^{-1}$ (s)
symmetric	1420-1300 cm.$^{-1}$ (s)

[a]s - strong
m - medium
w - weak
v - very weak.

The first work published concerning the identification of EDTA chelates by infrared spectroscopy was that of D. H. Busch and J. C. Bailar (8). They made an investigation of the structures of the Co (III) - EDTA compounds. Earlier workers (9) obtained the sodium salt of the $[Co(III)(EDTA)]^-$ chelate as a four hydrate. On drying at 150°C, the complex was completely dehydrated with no apparent change in the color or properties. Since the Co(III) ion is generally a six-coordinate metal ion, it was assumed that the EDTA acted as a hexadentate species in this compound. Schwarzenbach (10) prepared a number of Co(III)-EDTA compounds which contain a second monodentate ligand as well as the polydentate EDTA. These compounds were found to undergo exchange in aqueous solution; a water molecule could replace the monodentate ligand. As the pH of the solution was increased, a reversible color change from red to blue was observed. Schwarzenbach postulated that the EDTA molecule was pentadentate in these chelates and that the reversible color change was due to the conversion of the monoaquo complex to a monohydroxy complex. Busch and Bailar (8) claimed a proof of the existence of the penta- and hexadentate EDTA species by means of infrared spectra of the chelate molecules.

The following compounds were used in their studies.

$NaH[Co(III)(EDTA)NO_2] \cdot H_2O$

$BaH_2[Co(III)(EDTA)Br]_2 \cdot 9H_2O$

$Ba[Co(III)(EDTA)]_2 \cdot 4H_2O$

$H_4(EDTA)$

Nujol mulls were made of these compounds and studied using a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride prisms. The compounds containing the bromo and nitro groups exhibited two absorptions in the antisymmetric carbonyl region. One band in the 1630-cm.$^{-1}$ region was attributed to the presence of three coordinated carboxyl groups. A weaker band appeared in the 1730-cm.$^{-1}$ region and was attributed to an uncomplexed carboxylic acid group. These descriptions are in accord with the band assignments of Table 1. The carboxyl groups bonded to the Co(III) ion should show more free-carboxyl-group character than when bonded to hydrogen. The spectrum of the compound $Ba[Co(III)EDTA]_2 \cdot 4H_2O$ showed only one absorption of the carbonyl oxygens at 1638 cm.$^{-1}$, indicating that all four carboxyl groups are complexed in this species.

The above investigations show that the EDTA anion may act as either a penta- or a hexadentate ligand. That this anion may further behave as a bi- or tridentate ligand has been shown by further work by the above authors (11). For this work they chose the Pt(II) and Pd(II) ions, since these ions exhibit an invariable coordination number of four. It was found that the EDTA anion reacted with platinum(II) chloride, palladium(II) chloride and the corresponding tetrachloroplatinate(II) and tetrachloropalladate(II) ions in a stepwise manner. First, two chloride ions were replaced by the two nitrogen atoms of the EDTA ligand. The second step consisted of replacement of the two remaining chloride ions by two of the carboxyl-group oxygens.

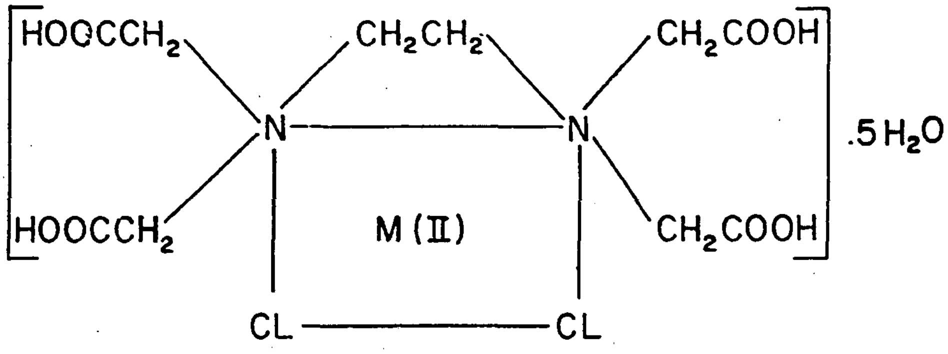
By allowing the appropriate metal compound to react with the disodium salt of EDTA in concentrated hydrochloric acid, crystals of the composition $H_4[M(II)(EDTA)Cl_2] \cdot 5H_2O$, where M(II) represents the central metal ion, were precipitated. The water of hydration was removed without any change in the compounds by drying in a vacuum, indicating that the water did not occupy any coordination positions of the metal ion.

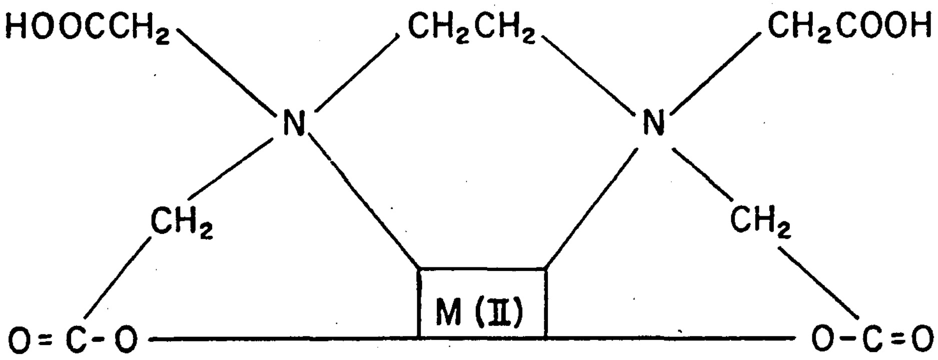
Infrared spectra of the above compounds revealed that the carbonyl oxygens absorbed only above 1700 cm.$^{-1}$, corresponding to the absorptions of free carboxylic acid groups. On the basis of these data, the structure shown in Figure 1a was assigned to these compounds.

The above bidentate chelates could be dissolved in hot water. The chloride ligands were then removed by addition of silver sulfate. When sufficient base was added to neutralize two of the acidic hydrogens a new precipitate

Fig. 1a. The bidentate EDTA molecule

Fig. 1b. The tetradentate EDTA molecule


HOOCCH2
CH2CH2
CH2COOH
N
N
.5H2O
HOOCCH2
M (II)
CH2COOH
CL
CL

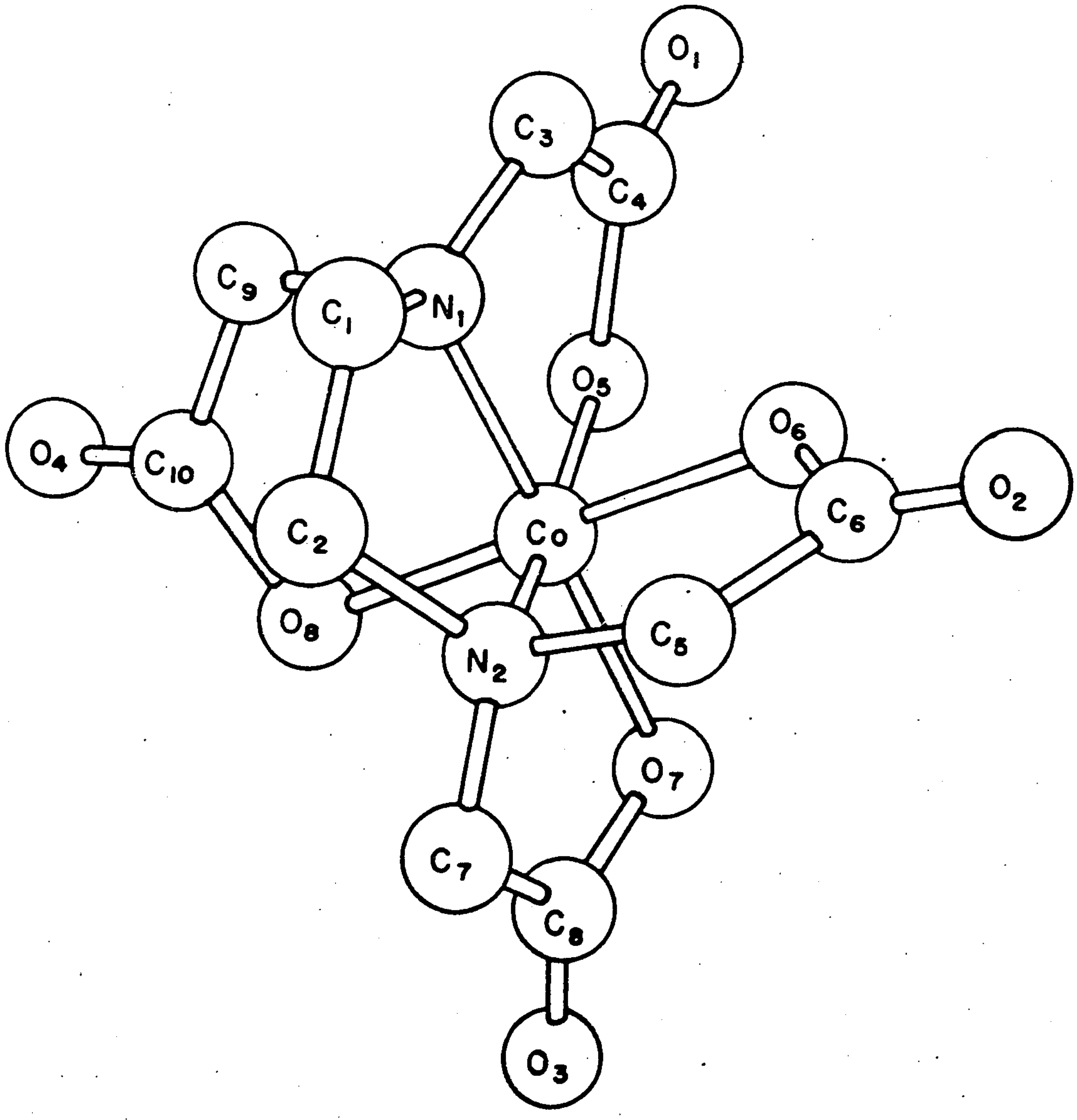

HOOCCH2
CH2CH2
CH2COOH
N
N
CH2
CH2
M (II)
O=C-O
O-C=O

was formed. The empirical formula of the precipitate corresponded to the compound $H_2[M(II)(EDTA)]$. Determination of the equivalent weight of the precipitate verified that this was the correct formula.

The infrared spectra of the $H_2[M(II)(EDTA)]$ compounds displayed two strong absorptions in the carbonyl region. One occurred at 1730 $cm.^{-1}$ and the other at 1635 $cm.^{-1}$ Both bands were of similar intensities. The two bands were interpreted to signify that two of the carboxyl groups of the EDTA anion had coordinated while the remaining two were bonded to acidic hydrogens. Therefore, it was concluded that the EDTA anion can exist as a bi-, tetra-, penta- or hexadentate species. The proposed structure of the tetradentate species is shown in Figure 1b.

The existence of a hexadentate EDTA molecule has been questioned by Pecsok (12). It was suggested that the formation of five five-membered rings would present too great a strain for the polydentate ligand. Weakliem and Hoard (13) made complete X-ray diffraction studies of $NH_4[Co(III)(EDTA)] \cdot 2H_2O$ and $Rb[Co(III)(EDTA)] \cdot 2H_2O$. These workers showed that the cobalt atom is bonded octahedrally to the two nitrogen atoms and the four oxygen atoms of the EDTA molecule. The molecular model in true perspective is shown in Figure 2. If the plane defined by

Fig. 2. The $[Co(III)(EDTA)]^-$ anion in true perspective


O$_1$
C$_3$
C$_4$
C$_9$
C$_1$
N$_1$
O$_5$
O$_6$
O$_4$
C$_{10}$
C$_6$
O$_2$
C$_2$
Co
O$_8$
N$_2$
C$_5$
O$_7$
C$_7$
C$_8$
O$_3$

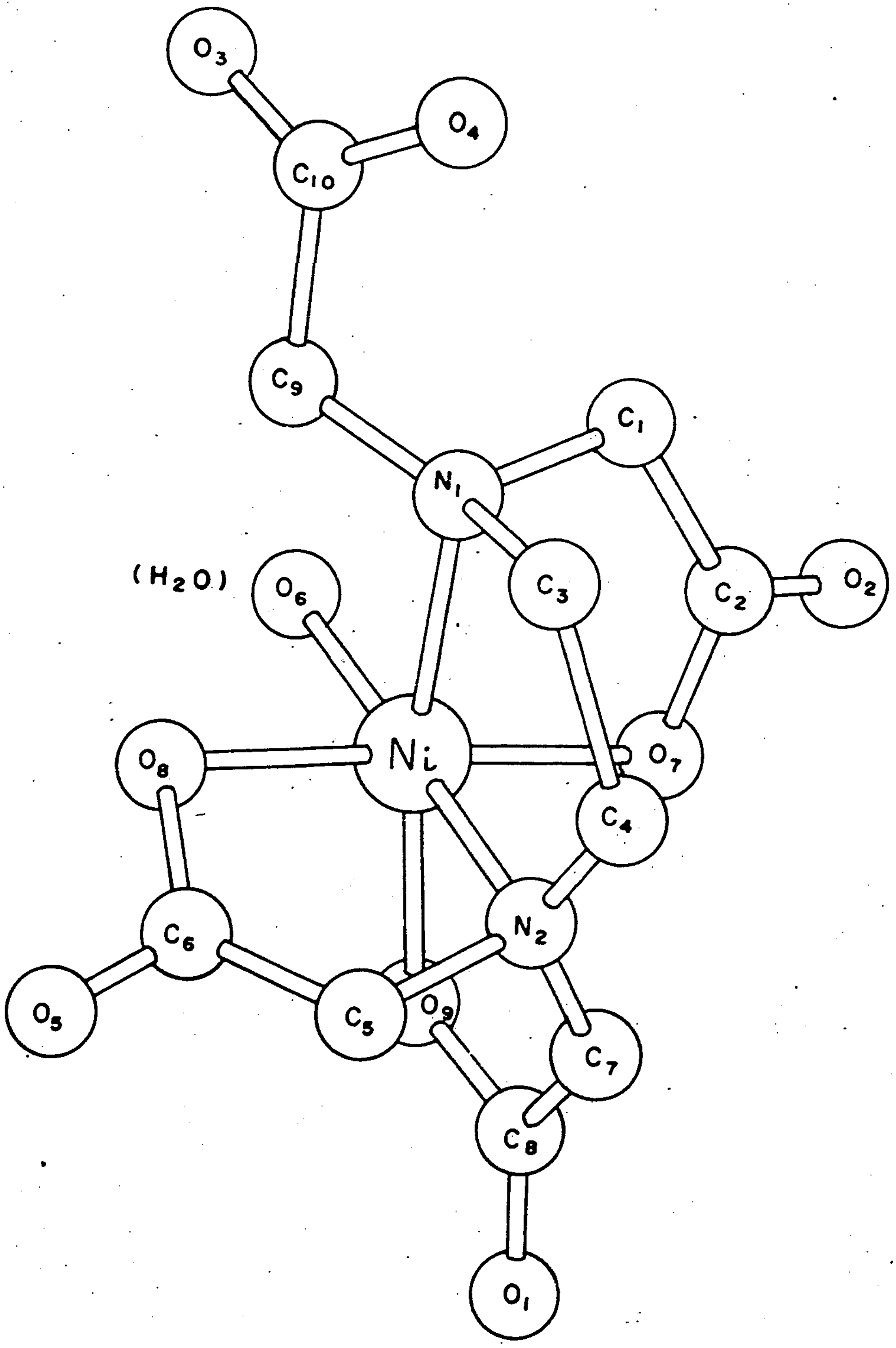
the two nitrogen atoms and the central atom is designated by NNM, a line in NNM which bisects the angles N_1CoN_2 and O_5CoO_7 and passes through the midpoint of C_1C_2 serves as a quasi-two-fold axis for the molecule. Three of the five chelate rings form a girdle about the cobalt atom with bonds from N_1, N_2, O_5 and O_7. The other two rings are formed by O_6 and O_8 bonds. A consideration of bond angles and distances show that the two glycinic rings formed by O_5 and O_7, the girdle rings, are considerably more strained than those formed by O_6 and O_8.

An example in which interpretations of the infrared spectrum of a chelate have led to an incorrect structural assignment is offered by the work done on the divalent copper compounds of EDTA. S. Kirschner (14) prepared and examined the compounds $K_2[Cu(II)(EDTA)]$ and $H_2[Cu(II)(EDTA)]$. He attempted to show that the divalent copper ion could exhibit coordination numbers of four and six. The infrared spectrum of the $K_2[Cu(II)(EDTA)]$ compound showed strong absorption at 1615 $cm.^{-1}$ This band was attributed to four carboxyl groups all attached to the central copper ion. Since two acidic hydrogens are present in the $H_2[Cu(II)(EDTA)]$ compound, it was assumed that two carboxyl groups were thus blocked from coordination. The infrared spectrum of this compound showed two carbonyl absorptions in the antisymmetric region, one corresponding to carboxylic acid groups and the other to complexed carboxyl groups.

Smith and Hoard (15) have done a complete X-ray diffraction study of the $H_2[Ni(II)(EDTA)] \cdot H_2O$ and the isomorphous $H_2[Cu(II)(EDTA)] \cdot H_2O$ compounds. The model found for the nickel compound is shown in true perspective in Figure 3. Since the evidence of isomorphism for the nickel and copper compounds is so great, the same model is proposed for the copper compound also. It was stated earlier that the presence of acidic hydrogens in EDTA chelates prevent the coordination of carboxyl groups to the metal ion. However, Smith and Hoard found that, even though the nickel compound contains two acidic hydrogens, only one carboxyl group is prevented from joining to the central ion. In the structural analysis of the hexadentate $[Co(III)(EDTA)]^-$, it was shown that the two girdled glycinic rings are the most strained. In the nickel compound, it is one of these rings which is broken to bond with the acidic hydrogen. However, the three remaining carboxyl groups remain joined to the central atom. It is inferred from packing relations that the remaining acidic hydrogen atom is bound to one of the carbonyl oxygens of a complexed carboxyl group.

This brief summary does not include all of the published information concerning the studies of solid chelates. Only several of the more important papers are discussed here. It is noteworthy, however, that only two chelate anions of EDTA

Fig. 3. The H_2 [Ni(II)(EDTA)] molecule in true perspective


O3
O4
C10
C9
C1
N1
(H2O)
O6
C3
C2
O2
O8
Ni
O7
C4
N2
C6
O5
C5
O9
C7
C8
O1

(13, 15) have been identified in regard to their structure by means of a complete X-ray analysis. Thus, in the main, chelate structural proposals are presently made on the basis of intelligent speculation rather than exact information.

B. The Solid Rare-Earth Chelates

The ability of EDTA to form exceptionally stable chelates with the trivalent rare-earth ions (abbreviated Ln) is well known. Most of the published information on the rare-earth chelates has been concerned with their properties in aqueous solutions. Studies of the solid compounds have been limited to several fragmentary investigations of rare-earth EDTA chelates. Brintzinger and his co-workers (9, 16) reported the preparation of the compounds $H[La(EDTA)]$, $H[Nd(EDTA)]$ and $Y[Y(EDTA)]_3$. Moeller and his co-workers (17) reported on the nature of the solid acid chelates $H[Ln(EDTA)]$ and their sodium salts. They examined several of the lighter rare-earth chelates using infrared spectroscopy, differential thermal analysis, X-ray diffraction and light rotation measurements in an attempt to characterize these compounds. These workers have concluded that the lighter rare-earth acid chelates $H[Ln(EDTA)]$ contain a pentadentate EDTA molecule. Since the compounds studied all contained one mole of tightly bound water it was assumed that a hexacoordinated rare-earth ion satisfies its sixth coordination position with water. The present manuscript is an extension of Moeller's work to include the entire series of rare-earth compounds.

C. Experimental

Preparation of the acids H[Ln(EDTA)]

The rare-earth oxides used in the preparation of these compounds were supplied by the rare-earth separation group at the Ames Laboratory of the Atomic Energy Commission. All of the oxides were of 99.9% or greater purity as determined by emission spectroscopy. Each rare-earth oxide was dissolved in hydrochloric acid and the excess acid removed by evaporation to incipient dryness. The rare-earth chloride obtained was used to saturate a cation-exchange column. The exchange column was then eluted with a 5 g. per liter solution of the tri-ammonium salt of EDTA acid (Geigy Chem. Co.). A dilute solution of eluant was necessary to prevent the precipitation of the slightly soluble H[Ln(EDTA)] chelate in the interstices of the resin bed. The eluate collected from the column contained the nearly pure H[Ln(EDTA)] which was precipitated by concentrating the eluate solution by means of evaporation. The molecular weights of the acidic chelate compounds were determined by direct ignition of the chelates to the corresponding rare-earth oxides. Molecular weights were calculated on the basis of one mole of rare-earth metal complexed by one mole of EDTA.

Preparation of $K[Ln(EDTA)]$ and $NH_4[Ln(EDTA)]$

These compounds were obtained either by direct neutralization of the chelate acids or by direct reaction in water of rare-earth oxide, EDTA acid and the proper hydroxide in the mole ratio of 0.5:1:1 (18). The ammonium salts were crystallized directly from water. The potassium salts were crystallized by first concentrating their solutions by evaporation and then adding acetone and stirring. The molecular weights of the ammonium salts were determined by direct ignition to the rare-earth oxides, but this method was not applicable to the potassium salts. Attempts to analyze the rare-earth content by oxalate precipitation of the rare earth also failed due to potassium-ion interference. The molecular weights of the potassium salts were determined by first decomposing the chelates with a nitric acid-perchloric acid mixture and evaporating to dryness. After treating the residue with concentrated nitric acid and evaporating to dryness several times, the resulting rare-earth salt was dissolved in water and buffered to pH 4.6 with acetic acid-sodium acetate buffer. After adding several drops of a 0.04-molar solution of $Na_2[Hg(EDTA)]$, the solution was titrated potentiometrically with standard EDTA solution using a mercury electrode (19).

Determination of acid ionization constants

The ionization constants of the acids $H[Ln(EDTA)]$ were determined at 20°C by titration of the acids with standardized carbonate-free potassium hydroxide prepared by the method of Powell and Hiller (20). The ionic strength of the solutions was kept at 0.015 using potassium nitrate. Hydrogen ion concentrations were determined by pH measurements made with a Beckman Model G pH meter. The measurements were taken at pH's high enough to permit the dissociation of the chelate to be neglected in calculating the ionization constants.

Infrared spectra

Infrared spectra of the acids $H[Ln(EDTA)]$ were recorded using a Perkin-Elmer Model 13 spectrophotometer equipped with calcium fluoride prisms. The solid chelates were pressed into discs using potassium bromide as a diluent. Approximately 1 mg. of chelate was used in each disc.

X-ray powder patterns

Diffraction patterns were obtained using a Norelco Debye-Scherrer type camera with a 57.3 mm. radius. Copper K_α radiation was used.

D. Discussion of Results

When precipitated from water and dried in air, the chelates H$[Ln(EDTA)]$ do not appear to correspond to hydrates of definite composition. The amount of water present was found to be a function of the humidity of the air as well as the temperature. When these chelates were dried at 110°C for 24 hours, it was found that the group consists of two types. Those containing cerium, praseodymium, neodymium and samarium retained one mole of water per mole of chelate; those containing the heavier rare earths became anhydrous. Thermobalance studies made on the light-rare-earth chelates revealed that the water is strongly associated and is not released until the chelate itself decomposes. It is reasonable to assume that this tightly-bound water occupies one of the coordination positions of the central rare-earth ion. This is in accord with previous work performed with the neodymium and samarium compounds (17). Thus it appears that the acid chelates of cerium, praseodymium, neodymium and samarium contain a pentadentate EDTA molecule in the solid state. An explanation of the nature of the EDTA molecule in the anhydrous group of rare-earth chelates is not arrived at so easily. If we assume that the presence of an acidic hydrogen blocks one of the carboxyl groups from coordination, then it is difficult to explain why the central rare-earth ion does not satisfy its sixth coordination position with water. On the other hand, if we assume that EDTA satisfies all six coordination positions of the lanthanon ion we are left with a free acidic hydrogen atom in the molecule. Information relative to this problem is obtained from the infrared spectra of the chelate compounds.

The infrared spectra of H [Sm(EDTA)] and H [Eu(EDTA)] are shown in Figures 4 and 5. The absorption bands of all the compounds up to and including H [Ho(EDTA)] are listed in Table 2. The spectra of the erbium, thulium, ytterbium and lutetium compounds have also been recorded and their spectra are similar to that of the holmium compound. However, the bands of these spectra become quite difficult to measure accurately and have been omitted from the table. Table 2 contains only those bands obtained using calcium fluoride prisms in the infrared spectrophotometer. These prisms were chosen to give better resolution in the absorption region associated with the carboxyl group. The spectra shown in Figures 4 and 5 were obtained using sodium chloride prisms.

The carbonyl stretching frequency in a normal -COOH group occurs in the 1700-cm.$^{-1}$ region of the spectrum. Table 2 shows that the acid chelates of cerium, praseodymium, neodymium and samarium have an absorption band in the 1670-cm.$^{-1}$ region which is attributed to a highly associated -COOH group in the chelate molecule. The -COOH groups in

Fig. 4. The infrared spectrum of the H [Sm (EDTA)] • H_2O molecule

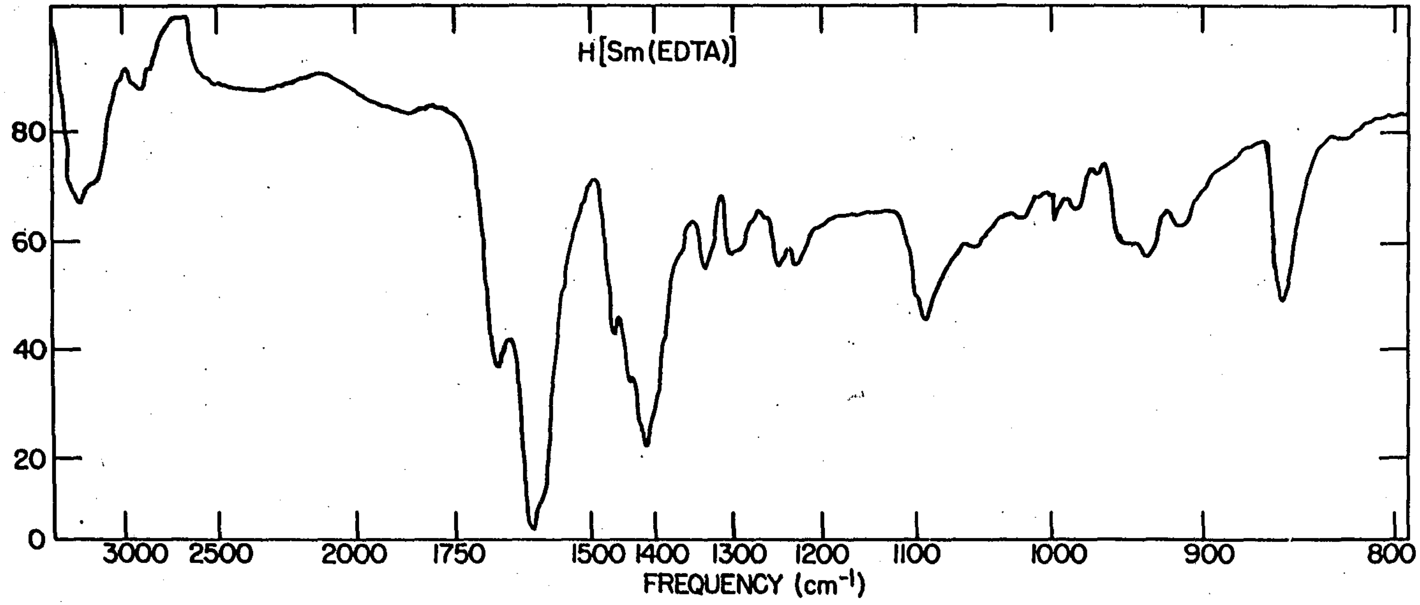

H[Sm(EDTA)]
80
60
40
20
0
3000
2500
2000
1750
1500
1400
1300
1200
1100
1000
900
800
FREQUENCY (cm^{-1})

Fig. 5. The infrared spectrum of the $\mathrm{H\,[Eu\,(EDTA)]}$ molecule

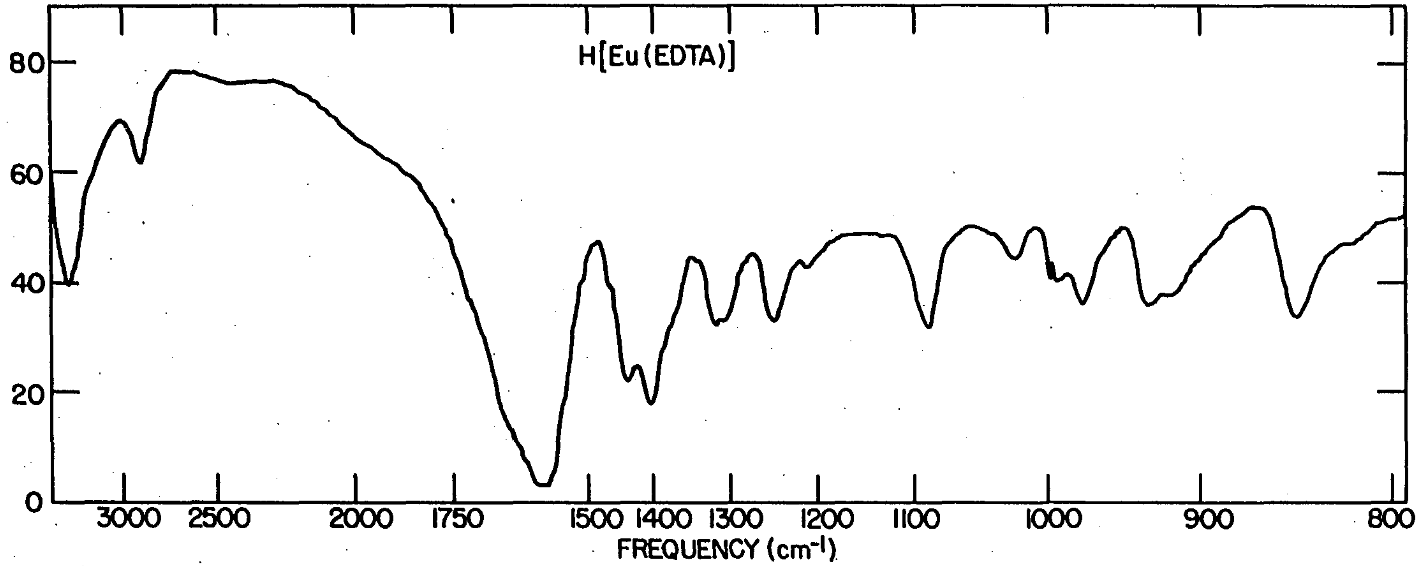

H[Eu(EDTA)]
80
60
40
20
0
3000
2500
2000
1750
1500
1400
1300
1200
1100
1000
900
800
FREQUENCY (cm-1)

Table 2. Principal absorption bands[a] of the compounds H [Ln(EDTA)]

H[Ln(EDTA)]	-CH	-COOH	$-COO^-$(antisym.)
Ce	2849 2910 2962	1667	1600
Pr	2848 2911 2960	1669	1600
Nd	2849 2908 2966	1670	1600
Sm	2849 2911 2961	1670	1600
Eu	2934 2992	----	1600
Gd	2931 2990	----	1600
Tb	2933 2990	----	1600
Dy	2933 2995	----	1600
Ho	2933 2994	----	1600

[a] Absorptions are reported in $cm.^{-1}$

Table 2 (Continued)

H[Ln(EDTA)]	$-COO^-$(sym.)	$-COO^-$(sym.)	$-COO^-$(sym.)
Ce	1416	1439	1460
Pr	1417	1439	1459
Nd	1418	1440	1459
Sm	1422	1440	1460
Eu	1408	1443	----
Gd	1416	1445	----
Tb	1411	1445	----
Dy	1414	1446	----
Ho	1417	1445	----

the free H_4(EDTA) absorb at 1690 cm.$^{-1}$ It is certain that the free acid contains associated groups, so that it would seem that the acid group in the light-rare-earth chelates is more highly associated than in the free acid. Since all except one carboxylic acid group is removed from the molecule on chelation the degree of association would be expected to decrease. This has been found to be true in other chelates. For example the -COOH group in H_2 [Cu(EDTA)]$\cdot$ H_2O absorbs at a frequency of 1718 cm.$^{-1}$ (14). It may be possible that the lowering of the frequency observed in the light-rare-earth chelates is due to interactions occurring between adjacent molecules in the crystal. Another possibility is that internal hydrogen bonding takes place between the acid group and the carbonyl oxygen of an adjacent associated carboxyl group. It is interesting to note that Flett (21) has found that the majority of acids absorbing below 1680 cm.$^{-1}$ exhibit internal hydrogen bonding. At any rate it seems reasonable to say that the acid chelates of cerium, praseodymium, neodymium and samarium have one carboxyl group which is prevented from coordinating by the presence of the acidic hydrogen. Consequently, the EDTA anion in these chelates is pentadentate and a molecule of water occupies the sixth coordination point of the rare-earth ion. This configuration is in accord with the thermobalance studies noted above and also with previous work done on several of these compounds (17).

It will be noted from Figure 5 and Table 2 that the band observed in the light-rare-earth chelates at 1670 cm.$^{-1}$ is completely absent in the heavier rare-earth chelates. All attempts to resolve a band in this region failed. An examination of Figure 5 shows that the very broad band in the 1600-cm.$^{-1}$ region extends well into the 1670-cm.$^{-1}$ region. However, the presence of a band at 1670-cm.$^{-1}$ would still be detected if it were present. It should be mentioned, perhaps, that a comparison of the spectrum of Figure 5 with those obtained by Sawyer and McKinnie (22) shows that the two are similar even though these workers investigated only the sodium salts of EDTA metal chelates. If the interpretation of the infrared spectra of these heavy-rare-earth chelates is correct then it must be concluded that there is no -COOH group present in these chelate molecules. Again assuming a hexa-coordinated central rare-earth ion, the EDTA molecule in these anhydrous rare-earth acid chelates would be hexadentate. That this type of structure is not only possible but may be quite common in acid chelates has been shown by Smith and Hoard (15). These workers have made a complete X-ray analysis of the solid dihydrogen ethylenediaminetetraacetatoaquonickel(II) chelate ($H_2[Ni(EDTA)] \cdot H_2O$). In this compound they found the EDTA to be pentadentate even though two acidic hydrogens are present in the molecule. One of the hydrogens is attached to a carboxyl group which is thus blocked from coordination. However the remaining three carboxyl groups coordinate with the central Ni(II) ion. Smith and Hoard have inferred from packing relations that one of the uncomplexed oxygens of a complexed carboxyl group carries the free hydrogen. The same structure has been assigned to the chelate $H_2[Cu(EDTA)] \cdot H_2O$ from the isomorphism of this chelate with the nickel chelate. Unfortunately a comparison of the infrared spectra of these compounds with the heavy-rare-earth chelates cannot be made, since the divalent metal compounds have a -COOH group present. Apparently the heavy-rare-earth chelates of EDTA are also examples wherein hydrogen does not prevent a carboxyl group from bonding to the central atom.

The anti-symmetric carbonyl vibrations of the complexed carboxyl groups are listed at 1600 cm.$^{-1}$ in Table 2. All are extremely broad and very intense. Therefore, measurements of this band could not be made with any degree of accuracy. There is no doubt that several different absorptions are occurring in this region, but they cannot be resolved. On the basis of resonance theory, the resonance occurring in a carboxyl group will increase as the bond between the carboxyl group and a metal ion becomes more ionic. An increase in resonance imparts greater single bond character to the carbonyl oxygen and leads to a lowering of its absorption frequency. The low frequency of absorption observed for these groups is an indication that considerable resonance is present in the carboxyl group. Therefore, the ligand-metal bonding appears to be primarily ionic. Sawyer has reported that the symmetric vibrations of complexed carboxyl groups occur in the 1350-1450 cm.$^{-1}$ region (23). The bands in this region are listed in Table 2 and have been assigned to the symmetric stretching vibrations. It should be emphasized, however, that there is no justification for assuming that these are the only bands due to the symmetric vibrations. Evidence for a change in structure in the series of rare-earth chelates is also observed in this region. The monohydrated members exhibit three absorption bands while the anhydrous members show only two bands. The bands in this region are quite sharp. This suggests a possibility that infrared investigations of complexed carboxyl groups may be studied more fruitfully in this region than in the anti-symmetric region provided proper identification of bands can be made.

The -CH stretching vibration occurs in the 2800-3100 $cm.^{-1}$ region (7). Further evidence for a change in structure in the rare-earth chelates is noted here. The light monohydrated species have three bands in this region. Those at frequencies of 2910 and 2960 $cm.^{-1}$ are doublets. The heavier members exhibit only two absorption bands at 2930 and 2990 $cm.^{-1}$ It is possible that one of the three bands associated with the light members is due to an -OH vibration of the -COOH group. Flett (21) has reported the presence of a band in the 2800-3000 $cm.^{-1}$ region for a number of carboxylic acids. Associated with this band is a much weaker band which should exist between 2500 and 2700 $cm.^{-1}$ Such a band is not observed in the chelate spectra. However, it has been pointed out that this band may be absent in high molecular weight acids such as these chelates.

Metal-EDTA chelates consist of a central metal ion that is essentially completely engulfed by the organic chelating agent. Therefore, relations between adjoining molecules in the crystal should be dependent on the configuration of the EDTA molecule surrounding the metal ion. For a series of chelates of similar metal ions such as the rare-earths one might suspect that, if the EDTA molecule is similar in all of the compounds, the solids should have isomorphous structures. The changes in structure of the H $[\text{Ln(EDTA)}]$ chelates noted above should be accompanied by corresponding changes in the packing of molecules in the chelate crystals. This would suggest that the crystalline solids should exhibit two series of isomorphous compounds. The chelates from cerium to samarium should be mutually isomorphous but not isomorphous with the chelates from europium through lutetium. X-ray diffraction patterns of the entire series of compounds have been recorded and the above is shown to be true. Table 3 lists the d-spacings in angstroms calculated for several of the lines of the neodymium, samarium, europium and gadolinium chelates. The patterns of the cerium and praseodymium compounds are similar to those of neodymium and samarium while the patterns of the heavy members are similar to those of europium and gadolinium. Many more lines than those listed are observed in the patterns but only a few are used for illustration.

It was noted above that relationships between adjoining molecules in the crystal should be dependent upon the

Table 3. Observed d-spacings of the compounds $H[Ln(EDTA)]$

Compound	d-spacings
$H[Nd(EDTA)] \cdot H_2O$	5.89 vs[a]
	4.91 w
	4.38 vvw
	3.94 s
$H[Sm(EDTA)] \cdot H_2O$	5.83 vs
	4.88 w
	4.35 vvw
	3.93 s
$H[Eu(EDTA)]$	5.70 s
	4.68 vs
	4.18 vvw
	3.82 w
$H[Gd(EDTA)]$	5.62 s
	4.60 vs
	4.16 vvw
	3.79 w

[a] vs - very strong
s - strong
w - weak
vvw - very very weak

configuration of the EDTA anion surrounding the central ion. If the EDTA anion is capable of adjusting to the size of the metal ion it surrounds, then the distance between planes in the crystal should be dependent upon the size of the metal ion. It is interesting to observe the lanthanide contraction in the rare-earth chelates of EDTA. Table 4 lists the calculated d-spacings in angstroms for an arbitrary line of the diffraction patterns.

It can be seen at this point that molecular weight, thermal decomposition, infrared absorption and X-ray diffraction studies all show that there is a change in the structure of the solid chelates $H[Ln(EDTA)]$. Infrared studies suggest that the change corresponds to a change in the EDTA anion from a pentadentate to a hexadentate configuration. Whether or not such a change occurs in solution is another problem. First of all, the solid compounds were studied after they had been dried at 110°C. Secondly, the change in environment from solid to solution may well be accompanied by a change in the nature of the molecule. There is little doubt that EDTA chelates are stabilized by hydrogen bonding in solution. Four carbonyl oxygens available for hydrogen bonding should certainly influence the properties of the molecule in solution. Effects due to hydrogen bonding would seem highly likely in view of the strain present in a hexadentate EDTA chelate (12).

Table 4. Lanthanide contraction in rare-earth - EDTA chelates

Series I	d-spacing	Series II	d-spacing
H [Ce(EDTA)] · H_2O	5.96	H [Eu(EDTA)]	5.70
H [Pr(EDTA)] · H_2O	5.92	H [Gd(EDTA)]	5.62
H [Nd(EDTA)] · H_2O	5.89	H [Tb(EDTA)]	5.59
H [Sm(EDTA)] · H_2O	5.83	H [Dy(EDTA)]	5.59
		H [Ho(EDTA)]	5.56
		H [Er(EDTA)]	5.49
		H [Tm(EDTA)]	5.49
		H [Yb(EDTA)]	5.47
		H [Lu(EDTA)]	5.43

The apparent change in solid rare-earth chelates suggests a displacement of an acidic hydrogen atom from one site in the molecule to another. Hence, if this change persists in solution, one might expect a significant change in the magnitude of the acid dissociation constant where the change in the structure occurs. The acid dissociation constants have been determined roughly by a potentiometric method and their values are listed in Table 5.

The constants of the cerium and praseodymium acid

Table 5. Ionization constants of the compounds H[Ln(EDTA)]

H [Ln(EDTA)]	pK_{ion}	H [Ln(EDTA)]	pK_{ion}
Nd	2.5	Dy	2.8
Sm	2.6	Ho	2.7
Eu	2.6	Er	2.8
Gd	2.7	Tm	2.6
Tb	2.6	Yb	2.7

chelates have been omitted due to the low solubility of these compounds. The determination of the constants was hindered by the strength of the acids and the necessity of measuring small hydrogen-ion concentrations so that dissociation of the chelates could be neglected. For this reason the pK_{ion} values are reported only to the first decimal place. Variations in the constants were noted as the pH was varied, but the deviations were similar in all cases. No serious errors should be introduced in comparing these pK_{ion} values as long as the comparison is made at the same degree of neutralization. It is evident from Table 5 that little change in the ionization constant of the acid chelate occurs across the series of rare-earths. This would seem to indicate that the anion $[Ln(EDTA)]^-$ in solution is similar throughout the series.

Studies of the ionic salts of the Ln(EDTA) - anion should be more indicative of its nature in solution than a study of the solid acids. The presence of an acidic hydrogen in the EDTA chelates does not permit an a priori assumption of a carboxyl group blocked from coordination (15). Nevertheless, the presence of an acidic hydrogen certainly constitutes a driving force tending to change the coordination number of the EDTA anion. This has been shown to be the case for the Co(III)-EDTA chelates (24). Thus, it may be that ionic salts of [Ln(EDTA)] - are similar in structure even though their acids are not.

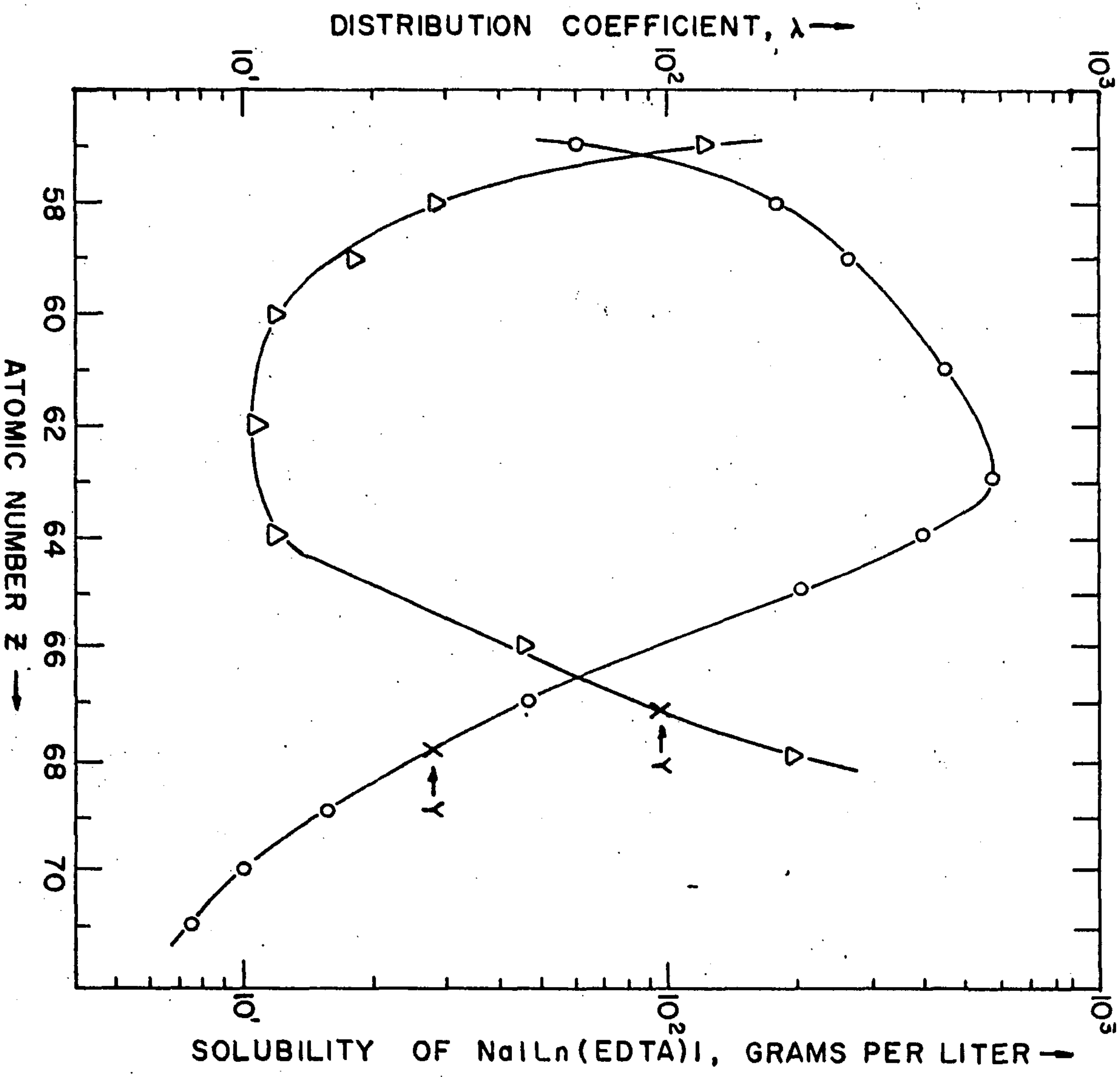
Brunisholz (25) has reported on the hydrates of the ammonium and potassium salts of rare-earth chelates of EDTA. These compounds crystallize directly from water with eight moles of water per mole of chelate. The author of this manuscript has found that salts having the form K [Ln(EDTA)] • H_2O can be obtained by neutralization of the acids, concentration of the resulting solution by evaporation and addition of acetone with stirring. The resulting precipitate, dried at 110°C for 24 hours, yields the monohydrate. No change in hydration is noted across the rare-earth series. Thermal decomposition studies of these salts revealed that the water is not removed before decomposition of the compound occurs. Since we are dealing with ionic salts, the postulation of a pentadentate EDTA species based on these results is weak. The fact that all chelates are monohydrate is of greater significance than the fact that they cannot be completely dried. It may be that the molecule of water serves as a bridge between the chelate anion and the potassium cation rather than being in the coordination sphere of the rare-earth ion. More definite information could be obtained from X-ray diffraction patterns of these salts; however, all of the diffraction patterns obtained at this laboratory had very dark backgrounds and the lines were impossible to characterize. Other workers (26) have had similar difficulties with several rare-earth chelates crystallized from alcohol. An attempt was made to obtain patterns from the ionic salts which were first crystallized from water and then dried at 110°C. for 24 hours. The ammonium salts were chosen for this purpose. The powder patterns obtained after drying, however, were not much better than those obtained with the potassium salts. Comparison of the patterns of the dried neodymium and gadolinium compounds showed that the two are probably isomorphous. The patterns were such that it did not appear worthwhile to run the entire series. It is interesting to note that the octa-hydrated sodium salts of praseodymium, neodymium, samarium and gadolinium are isomorphous (17).

In measuring stability constants, one might expect that the stability of the rare-earth chelates should increase as one goes from the lighter to the heavier members of the series due to the decrease in the ionic radii. This trend is usually followed by the rare-earths. However, it is frequently noted that the gadolinium constant is lower than that of either europium or terbium. This anomaly to the trend has been observed in the EDTA series (27). In order to account for this break, it has been proposed that, due to the decreasing size of the lanthanon ions, there is a change in the EDTA ligand from a hexa- to a pentadentate configuration. The above studies indicate that such a change does not occur. There is other experimental evidence which also suggests that the chelate anion does not undergo the transformation.

Marsh (28) has measured the solubilities of a number of the alkali salts of the rare-earth-EDTA anions. The data obtained for the sodium salts are shown in Figure 6. It is seen that the solubility decreases to a minimum in the neodymium-samarium-europium region and then rises again with the heavier members. Moeller (29) has pointed out that these salts are probably isomorphous. If there were a sharp break in the configuration of the anion on passing into solution, one would expect a corresponding break in the solubility curve. As seen in Figure 6, the solubility versus atomic number curve is smooth.

Fig. 6. ○ - Distribution coefficients of the $[\mathrm{Ln\ (EDTA)}]^-$ species on an anion exchange column

△ - Solubilities of the rare-earth salts $\mathrm{Na}\,[\mathrm{Ln\ (EDTA)}]$


DISTRIBUTION COEFFICIENT, λ →
10^1
10^2
10^3
58
60
62
64
66
68
70
ATOMIC NUMBER Z →
← Y
← Y
10^1
10^2
10^3
SOLUBILITY OF NaILn(EDTA)I, GRAMS PER LITER →

Minczewski and Dybczynski (30) have performed some extremely interesting experiments with the rare-earth-EDTA chelates. They saturated an anion-exchange column with the $H_2Y^=$ ion. They then passed solutions containing $[Ln(EDTA)]^-$ ions through the columns and measured the weight distribution coefficients of these chelate anions. Their results are shown in Figure 6. The distribution coefficient, λ , is defined as the amount of substance per gram of the dry ion-exchange resin divided by the amount of the substance per milliliter of the solution. It is seen in Figure 6 that this curve is exactly opposite to the solution curve. The distribution coefficient, λ , may be taken as a measure of the stability of a chemical species in one medium (resin phase) relative to its stability in another medium (solution phase) just as the solubility may be taken as a measure of the stability of a solid as compared to its stability in solution. This the results of the solubility and distrition coefficient studies may be interpreted as meaning that the intermediate atomic number rare-earth-EDTA chelates have less solution stability than those of the lighter and heavier members.

Minczewski and Dybczynski (30) have interpreted the data in the following manner. If the lighter chelates are pentadentate, a free hydrophylic carboxyl group is available for hydration which can stabilize the chelate anion in solution. As the central ion decreases in size, the attraction for the free carboxyl group becomes greater reaching a maximum at europium. This increase in attraction results in a decrease in hydration of the free carboxyl group until at europium the EDTA assumes a hexadentate configuration. With the heavier members, the continued decrease in size of the rare-earth ion results in new steric hindrances which causes the carboxyl group to become free for hydration again.

Experimental evidence does not support this theory too well. The postulation of affecting greatly the hydration of a carboxyl group not complexed by the central ion is certainly questionable. Also the existence of new steric hindrances operating toward preventing the hexadentate structure in the heavy members is not borne out by a comparison of the ionic radii of the trivalentrare-earth ions with trivalent cobalt. The $[Co(III)(EDTA)]^-$ anion exists in the solid state as the hexadentate structure (13). The Co(III) ion has a crystal radius of 0.63 angstroms while the Lu(III) ion has a radius of 0.93 angstroms (31). Therefore no steric difficulties should come into play.

Hydrogen bonding, however, should play an important role in determining the stability of the EDTA chelate anions in solution. Even with the hexadentate structure there are still four carbonyl oxygens available for bonding with water molecules. It is possible that these bonds could be bridged across two carbonyl oxygens of complexed carboxyl groups. This type of bonding could account for the observed behavior of the rare-earth chelate anions.

III. THE MATHEMATICAL DETERMINATION OF STEPWISE FORMATION CONSTANTS

The determination of equilibrium constants has taken up a large percentage of the time spent by the research chemist in the present century. One need only browse through the chemistry book shelves to realize what an integral part of modern-day chemistry the equilibrium constant has become. The quantitative expressions for chemical equilibria came into being in 1864 when Guldberg and Waage formulated the law of mass action. Now, nearly a century later, interest in these expressions has not yet reached its culmination. Rather, like the proverbial bean stalk, it just grows and grows.

The determination of stepwise formation constants has the unique position of being one of the few fields of classical chemistry which require mathematics beyond algebra. These determinations have even penetrated into the computer rooms normally reserved for the quantum theoretician. There are many methods presently devised for calculating stepwise formation constants (32). Only two of these will be described in this section. The first, Bjerrum's half-$\bar{n}$ method (33), gives a quick estimation of the stability constant. The second, that of Fronaeus (34), will be the method used in this manuscript for the calculation of the stepwise formation constants of the rare-earths with several low-molecular-weight organic ligands.

The following equilibria correspond to a series of consecutive reactions involving a central group M and a ligand A

$$\begin{aligned} M + A &\rightleftharpoons MA\ ; \\ MA + A &\rightleftharpoons MA_2 ; \\ \cdots\cdots &\cdots\ ; \\ \cdots\cdots &\cdots\ ; \\ MA_{N-1} + A &\rightleftharpoons MA_N . \end{aligned}$$

Assuming that the activities of the individual species taking part in the above reactions can be expressed by their concentrations, we have the following expressions for the mass action constants of the above system

$$\begin{aligned} b_1 &= \frac{[MA]}{[M]\,[A]}\ ; \\ b_2 &= \frac{[MA_2]}{[MA]\ [A]}\ ; \\ &\cdots\cdots\cdots\ ; \\ &\cdots\cdots\cdots\ ; \\ b_N &= \frac{[MA_N]}{[MA_{N-1}]\,[A]}\ . \end{aligned} \qquad (1)$$

The average ligand number, $\bar{n}$, is defined by Bjerrum (33) as the average number of ligands bound to M. The total concentration of ligand bound to M is given by

$$[MA] + 2[MA_2] + 3[MA_3] + \dots\dots + N[MA_N] .$$

The total concentration of M present in the system is given by

$$[M] + [MA] + [MA_2] + [MA_3] + \dots\dots\dots + [MA_N] .$$

The ligand number, $\bar{n}$, is then

$$\bar{n} = \frac{[MA] + 2[MA_2] + \dots\dots + N[MA_N]}{[M] + [MA] + [MA_2] + \dots\dots + [MA_N]}, \qquad (2)$$

which, using equation 1, becomes

$$\bar{n} = \frac{b_1[A] + 2b_1b_2[A]^2 + \dots\dots + Nb_1b_2 \dots b_N[A]^N}{1 + b_1[A] + b_1b_2[A]^2 + \dots\dots + b_1b_2 \dots b_N[A]^N}.$$

The individual b_n's are the step stability constants for each individual reaction occurring in the system. We can define overall complexity constants in the following manner

$$\begin{aligned} \beta_1 &= b_1 ; \\ \beta_2 &= b_1b_2 ; \\ &\dots\dots ; \\ &\dots\dots ; \\ \beta_N &= b_1b_2 \dots b_N. \end{aligned} \qquad (3)$$

The expression for $\bar{n}$ becomes

$$\bar{n} = \frac{\beta_1 [A] + 2\beta_2 [A]^2 + \ldots + N\beta_N [A]^N}{1 + \beta_1 [A] + \beta_2 [A]^2 + \ldots + \beta_N [A]^N}$$

$$= \frac{\sum_{n=0}^{N} n\beta_n [A]^n}{\sum_{n=0}^{N} \beta_n [A]^n} \qquad (4)$$

where β_0 is understood to be equal to unity.

Bjerrum's half-$\bar{n}$ method is now devised in the following manner. The step stability constant of some species, MA_t $(0 < t \leq N)$, may be obtained from Equation 4

$$\log b_t = -\log[A] + \log \frac{\sum_{n=0}^{t-1} (\bar{n}-n) \beta_n [A]^n}{\sum_{n=t}^{N} (n-\bar{n}) \beta_n b_t^{-1} [A]^{n-1}} \,. \qquad (5)$$

When $\bar{n}$ is equal to t - 1/2, $[A]$ equals $[A]_{t-1/2}$, and Equation 5 becomes

$$\log b_t = -\log [A]_{t-1/2} + \log F \qquad (6)$$

where

$$F = \frac{\sum_{n=0}^{t-1} (t-1/2-n)\beta_n \ [A]^n_{t-1/2}}{\sum_{n=t}^{N} (n-t+1/2)\beta_n \ b_t^{-1} \ [A]^{n-1}_{t-1/2}} . \qquad (7)$$

If the nature of the equilibrium system is such that, at $\bar{n}$ equal to t - 1/2, the only species present in the system are MA_{t-1} and MA_t, then the function F reduces to

$$F = \frac{1/2\ \beta_{t-1}\ [A]^{t-1}_{t-1/2}}{1/2\ \beta_t\ b_t^{-1}\ [A]^{t-1}_{t-1/2}} = 1. \qquad (8)$$

In this case

$$b_t = \left(\frac{1}{[A]}\right)_{t-1/2} . \qquad (9)$$

In the extrapolation method of Fronaeus, use is made of the polynomial which serves as the denominator of Equation 4

$$X = \sum_{n=0}^{N} \beta_n\ [A]^n . \qquad (10)$$

Let C_M and C_A represent the total concentrations of M and A present in the system. These quantities can be expressed as functions of [A] and [M], the free ligand and free metal present in the system,

$$C_M = [M] \cdot X,$$
$$C_A = [A] + [M] \cdot X' \cdot [A], \qquad (11)$$

where X' is understood to mean the derivative of X with respect to [A]. The ligand number, $\bar{n}$, is defined as

$$\bar{n} = \frac{C_A - [A]}{C_M} . \qquad (12)$$

Combination of Equations 11 and 12 with elimination of [M] yields

$$\frac{\bar{n}}{[A]} = \frac{X'}{X}, \qquad (13)$$

which after integration gives

$$\ln X([A]_j) = \int_0^{[A]_j} \frac{\bar{n}}{[A]} d[A] . \qquad (14)$$

This integration gives us corresponding values of the function, X for various values of [A], the free ligand concentration.

The complexity constants, β_n, can now be calculated by successive extrapolation of the functions X_1, X_2, ... X_N to [A] equal to zero.

$$X_1 = \frac{X - 1}{[A]} = \beta_1 + \beta_2 [A] + \beta_3 [A]^2 + \dots\dots$$

$$X_2 = \frac{X_1 - \beta_1}{[A]} = \beta_2 + \beta_3 [A] + \dots\dots \qquad (15)$$

for all of the constants of the system.

After the determination of the consecutive complex formation constants, the results can be checked by computing $\bar{n}$ values and comparing with the experimental values using Equation 4.

IV. THE ACETATE COMPLEXES OF THE RARE-EARTH AND SEVERAL TRANSITION METAL IONS

A. Introduction

It is a well known fact that trivalent lanthanon ions exhibit extensive hydrolysis when placed in an aqueous medium. Thus, when neutral rare-earth salts are dissolved in water, a distinct lowering of the pH is noted. The extent of the lowering depends on the concentration of the rare-earth salt and the particular rare-earth. The ability of a metal ion to displace a hydrogen ion from a water molecule to form a hydroxide complex is a function of the charge density of the ion. Since the ionic radius decreases from lanthanum to lutetium, the heavier the rare-earth the greater is the tendency to hydrolyze.

Measurements made on rare-earth solutions must often be corrected for hydrolysis. The necessity for correction can frequently be eliminated by making the measurements in solutions in which hydrolysis has been suppressed by the addition of excess hydrogen ions. This is conveniently achieved by introducing an acid buffer into the solution. It has been found that acetic acid-sodium acetate buffer systems provide the pH necessary to prevent hydrolysis of dilute rare-earth solutions. This buffer has been used in the determination of stability constants of the rare-earth chelates with ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA) (27) and N'-hydroxyethylethylenediamine-N,N,N'-triacetic acid (HEDTA) (35). Since measurement of stability constants involves either direct or indirect determination of free metal-ion concentrations, it is imperative to consider the possibility of complex formation between the various metal ions and the buffer ligand.

Sonesson has shown that complexes between the lanthanons and acetate do form (36, 37, 38). He determined the stepwise formation constants of rare-earth-acetate species at an ionic strength of 2.0, but data for lower ionic strengths are not available. The present investigation, therefore, considers the magnitude of these formation constants at an ionic strength of 0.1.

In many systems used to determine chelate stability constants, competing metal ions are involved (27, 35). For this reason the stepwise formation constants of the acetate complexes of divalent copper, zinc, cadmium and lead ions have also been included in the present investigation.

The determination of the acetate formation constants has an additional purpose. The variation in stability of the complexes formed with members of the rare-earth sequence has thus far been studied extensively only for the case of polydentate ligands, and the observed trends have not yet been explained satisfactorily. The distinct drop in stability at gadolinium is presently a subject of much discussion. A study involving monodentate ligands such as acetate may lead to a better understanding of such phenomena.

B. Method Used for the Calculation of Acetate Formation Constants

In a solution containing metal ions and acetate ions, the hydrogen-ion concentration affords a means of measuring the degree of complexation of the metal ion. From the initial concentrations of metal ion and acetate buffer (sodium acetate-acetic acid) and the dissociation constant of acetic acid, the amount of ligand bound to the central metal ion can be determined by potentiometric measurement of the hydrogen-ion concentration.

We define the following symbols.

C_{HA} : total amount of acetic acid initially added to system.

C_A : total amount of acetate ion added to system.

C_M : total amount of metal added to system.

$[H^+]$: hydrogen-ion concentration of system at equilibrium.

$[Ac^-]$: amount of free acetate ion in system at equilibrium.

C_H : excess hydrogen ion added to system originally.

Knowing the ionization constant of acetic acid, K_{ion}, and the hydrogen-ion concentration at equilibrium, the amount of free acetate ion in the system can then be calculated from the expression

$$[Ac^-] = \frac{K_{ion} \; (C_{HA} - [H^+] + C_H)}{[H^+]} \; . \qquad (16)$$

The $\bar{n}$ value for the system can then be calculated by

$$\bar{n} = \frac{C_A + [H^+] - C_H - [Ac^-]}{C_M} \; . \qquad (17)$$

From the known values of $\bar{n}$ and $[Ac^-]$ in solutions of varying amounts of initial acetate added, a plot of $\bar{n}/[Ac^-]$ versus $[Ac^-]$ can be made. Graphical integration of this curve from 0 to increasingly higher values of free $[Ac^-]$ will yield the values of ln X ($[Ac^-]_j$) as expressed in Equation 14, Section III. From these values, the functions X_1, X_2, X_3 etc. can be formed (see Equation 15, Section III). Extrapolation of the curves X_1 versus $[Ac^-]$, X_2 versus $[Ac^-]$ etc. to an $[Ac^-]$ value of zero will yield the values of the complex formation constants.

C. Experimental

Standard solutions were prepared from rare-earth oxides supplied by the rare-earth separation group of the Ames

Laboratory of the U. S. Atomic Energy Commission. All of the oxides were of 99.9% or greater purity as determined by emission spectroscopy. Each rare-earth oxide was dissolved in perchloric acid and the excess acid was removed by evaporation to incipient dryness. The resulting basic perchlorate was then dissolved in water and a portion titrated with perchloric acid to determine the equivalence point. This titrated portion was then mixed with the remaining solution and the entire solution was brought to the desired pH. In the case of cerium, it was found that the cerium(III) reverted to the original cerium(IV) oxide before all of the excess acid could be removed. Excess cerium(IV) oxide was mixed with perchloric acid and the mixture heated and stirred for several hours with hydrogen peroxide being added continually. The resulting slurry was filtered and the unused acid was determined by titration with standard base. This excess acid was then taken into account in subsequent calculations. Each solution was standardized by precipitation of the rare-earth content as the oxalate and ignition to the oxide.

Standard solutions of copper, zinc, cadmium and lead were prepared by dissolving the corresponding nitrates in water. The copper solution was standardized by electrodeposition of the copper on platinum and weighing. The zinc, cadmium and lead solutions were analyzed by titration with a standard solution of EDTA using Eriochrome Black T as an indicator. The chelate solution was standardized by using pure metallic zinc. All chemicals used to prepare the solutions were of reagent grade quality.

A buffer solution of acetic acid and sodium acetate was made up by adding a measured amount of standard sodium hydroxide solution to a known amount of standard acetic acid solution. An aliquot of the resulting buffer solution was then titrated with base as a check. Varying amounts of the buffer were added to a series of 50-ml. volumetric flasks and a known amount of metal ion was added. The ionic strength was adjusted to 0.1 using a sodium perchlorate solution and the samples were placed in a 20°C bath for 12 hours. Since the ionic strength changes as the metal ion associates with acetate, the formation constants were first determined roughly and new solutions were prepared taking into account the change in ionic strength. All pH measurements were made with a Beckman Model GS pH meter using a glass electrode. A pH 4.0 ± 0.01 buffer was used to calibrate the instrument. The same buffer solution was used throughout the experiments so that errors due to pH changes in different buffer samples were eliminated. The observed pH measurements were converted into hydrogen-ion concentrations before being used in the calculations. A correction of -0.1 pH units was applied to the pH readings.

The dissociation constant of acetic acid was determined at 20°C and an ionic strength of 0.1 in sodium perchlorate. The constant was evaluated by titrating a 0.01M acetic acid solution with standard potassium hydroxide and calculating the constant at various degrees of neutralization. The constant agreed well with that calculated from the observed pH of the buffer solution used in the experiments. The constant was used for comparison with the ionization constants of acetic acid determined previously at an ionic strength of 0.1 with other supporting electrolytes.

D. Determination of Acetate Constants

The observed pH's of a number of solutions containing metal ion, acetate ion and acetic acid are tabulated in Table 6. Only a few rare earths were chosen for purposes of illustration. The complete set of data is tabulated in the Appendix. It is apparent that significant variations in hydrogen-ion concentration occur from one metal ion to another. Bjerrum defines the average ligand number, $\bar{n}$, as the average number of ligand molecules bound to the central metal ion. By plotting $\bar{n}$ versus $[Ac^-]$, where $[Ac^-]$ is the free ligand concentration in the solution, one obtains the complex formation curve. This curve presents a graphical picture of the complexing that occurs. The complex formation curves of several of the metals studied are shown in

Table 6. Observed pH's of acetate buffer solutions

ml. Buffer[a] / 50 ml. Solution	Metal Cu^{+2}	Zn^{+2}	Cd^{+2}	La^{+3}	Eu^{+3}	Gd^{+3}	Tb^{+3}
2.50	4.353	4.519	4.467	4.479	4.400	4.432	4.458
3.75	4.357	4.526	4.471	4.489	4.412	4.438	4.458
5.00	4.364	4.526	4.474	4.500	4.422	4.447	4.463
7.50	4.376	4.524	4.472	4.503	4.438	4.454	4.467
10.00	4.391	4.524	4.475	4.511	4.455	4.467	4.475
15.00	4.409	4.527	4.481	4.525	4.473	4.486	4.484
20.00	4.433	4.530	4.486	4.534	4.492	4.499	4.496
25.00	4.450	4.535	4.491	4.542	4.505	4.509	4.506
30.00	4.464	4.538	4.502	4.550	4.516	4.520	4.515
35.00	4.475	4.543	4.507	4.556	4.525	4.528	4.523
45.00	4.506	4.548	4.526	4.570	4.538	4.542	4.540

[a] Buffer solution: 0.08807<u>M</u> acetic acid - 0.07740<u>M</u> sodium acetate
Cu^{+2}: 0.01132$\underline{M}$
Zn^{+2}: 0.01041$\underline{M}$
Cd^{+2}: 0.01004$\underline{M}$
Rare earth: 0.0040$\underline{M}$.

Figure 7. The $\bar{n}/[Ac^-]$ versus $[Ac^-]$ curve for one of the rare-earth systems is shown in Figure 8. Figures 9 and 10 show the functions X_1 and X_2 versus the free acetate-ion concentration. Only one of the rare earths has been chosen for purposes of illustration. The constants calculated for all of the metals studied are shown in Table 7. The constants are defined as follows:

$$MA_{n-1} + A \rightleftharpoons MA_n$$

$$M + nA \rightleftharpoons MA_n$$

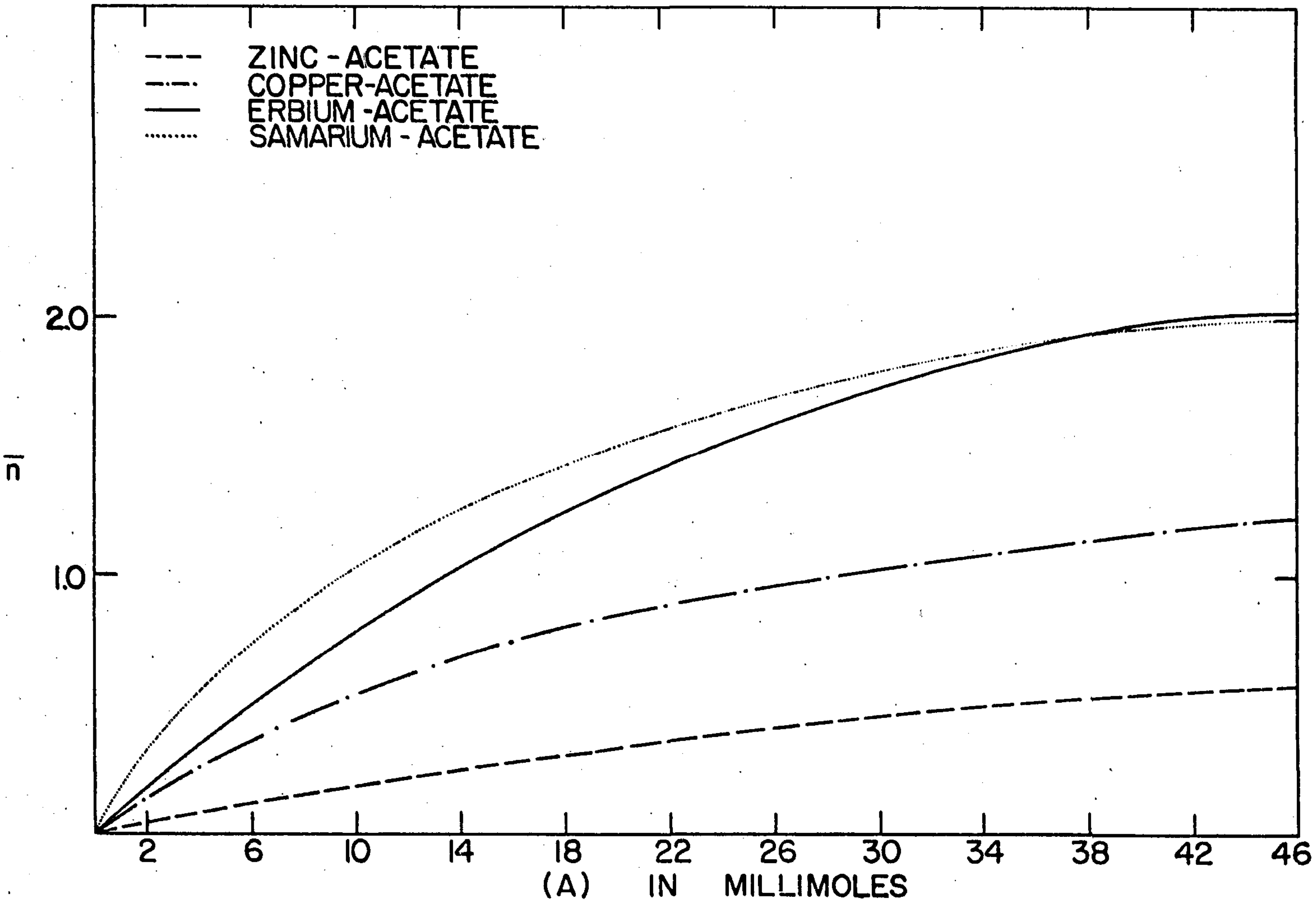
$$b_n = \frac{[MA_n]}{[MA_{n-1}]\ [A]}$$

$$\beta_n = \frac{[MA_n]}{[M]\ [A]^n}$$

E. Discussion of Results

One must first consider the applicability of the glass electrode to the determination of the acetate constants. The pH meter will detect variations of ±0.0025 pH units; therefore, the relative values of the individual constants are very good. Using the above variation in the pH reading and errors involved in the calculations, an error of about ±3% is probable between the constants. As will be shown later, this fact is important when both rare-earth and competing metal-ion (either copper, zinc or cadmium) acetate

Fig. 7. Complex formation curves of several acetate systems



ZINC - ACETATE
COPPER-ACETATE
ERBIUM -ACETATE
SAMARIUM - ACETATE
$\bar{n}$
2.0
1.0
2
6
10
14
18
22
26
30
34
38
42
46
(A) IN MILLIMOLES

Fig. 8. Example of the $\overline{n}/[Ac^-]$ versus $[Ac^-]$ curve. The Sm-acetate system

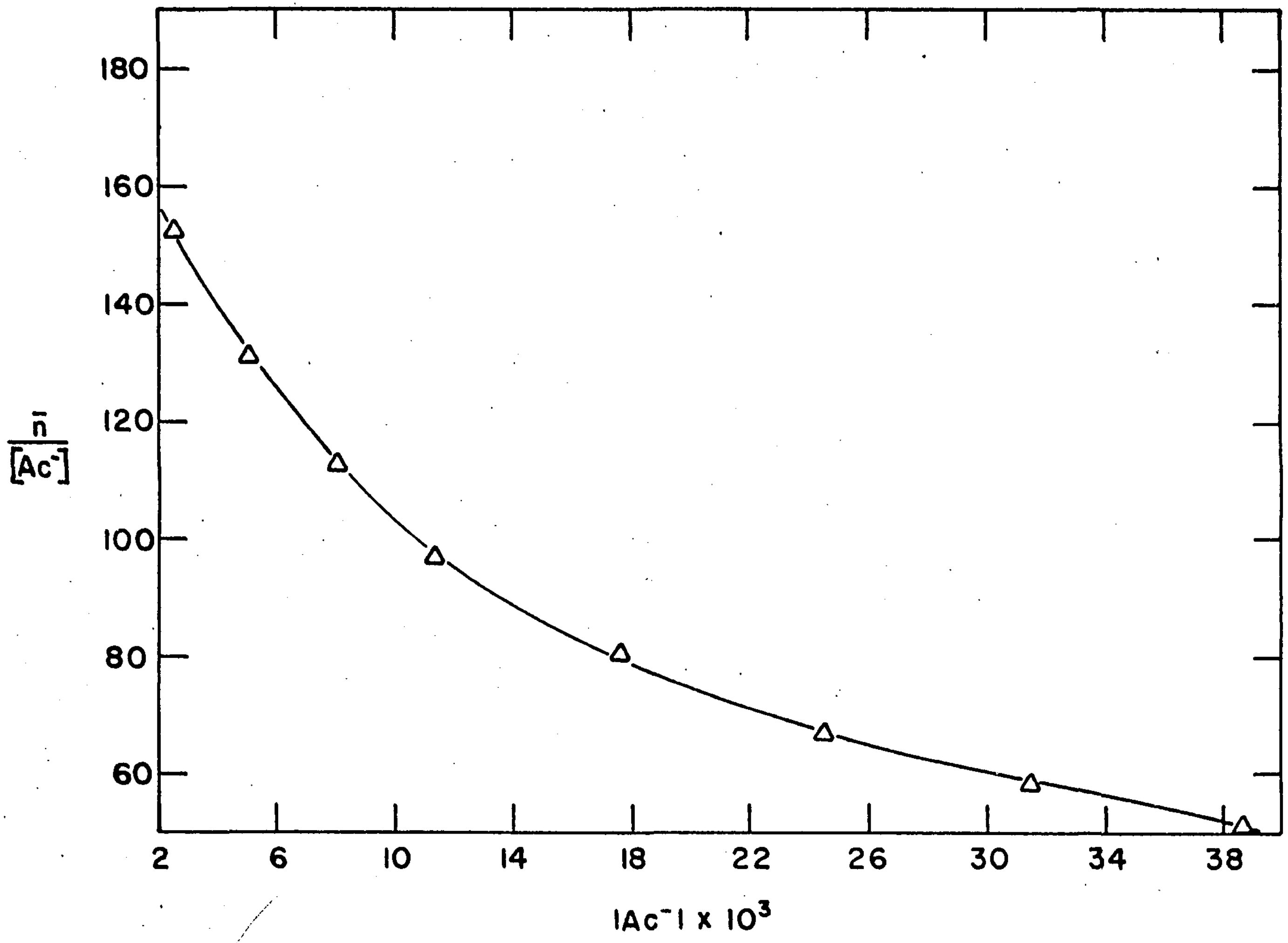

180
160
140
120
100
80
60
$\frac{\bar{n}}{[Ac^-]}$
2
6
10
14
18
22
26
30
34
38
$|Ac^-| \times 10^3$

Fig. 9. Example of the extrapolation of the function X_1 to zero free acetate concentration. The Sm-acetate system

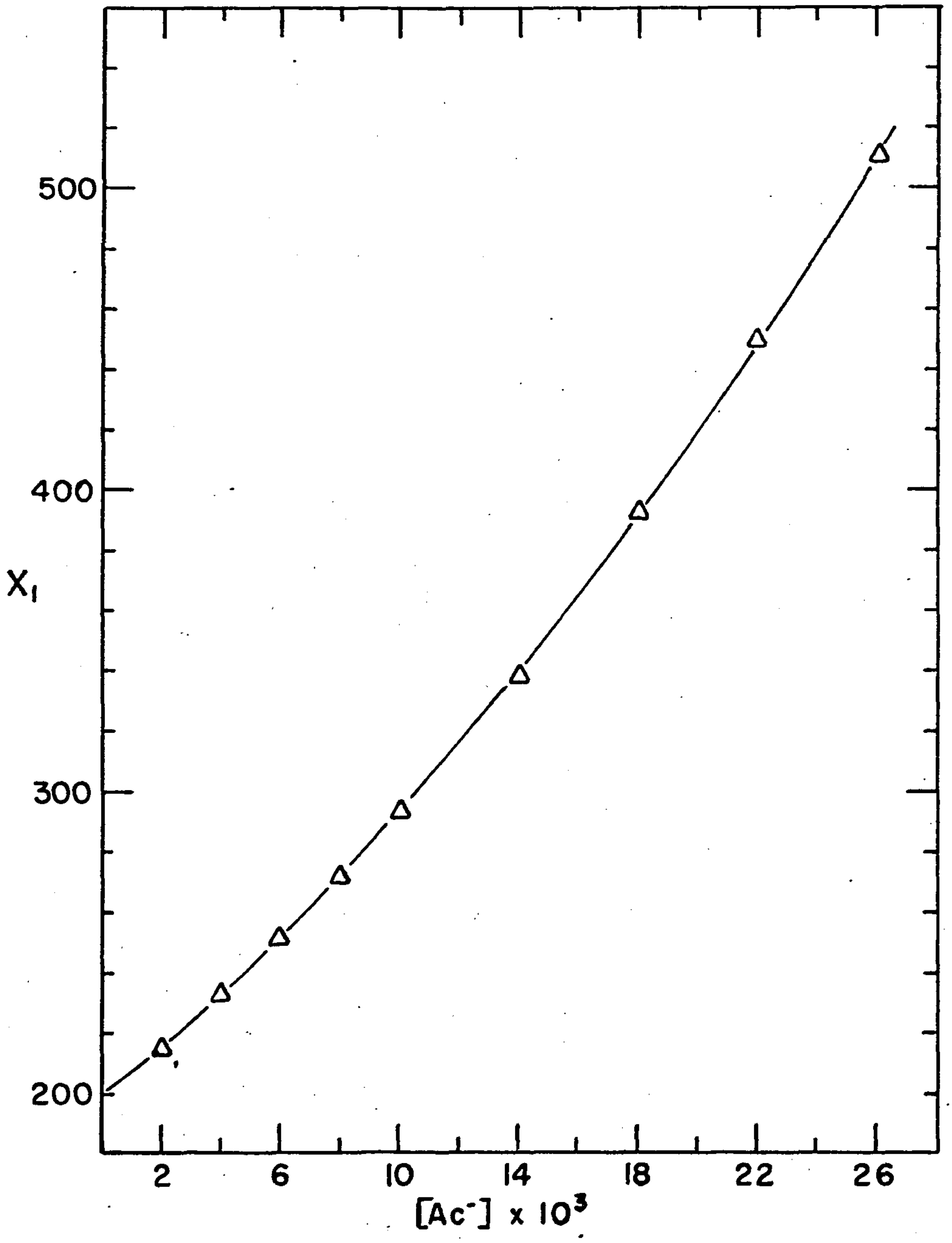

500
400
300
200
X_1
2
6
10
14
18
22
26
$[Ac^-] \times 10^3$

Fig. 10. Example of the extrapolation of the function X_2 to zero free acetate concentration. The Sm-acetate system

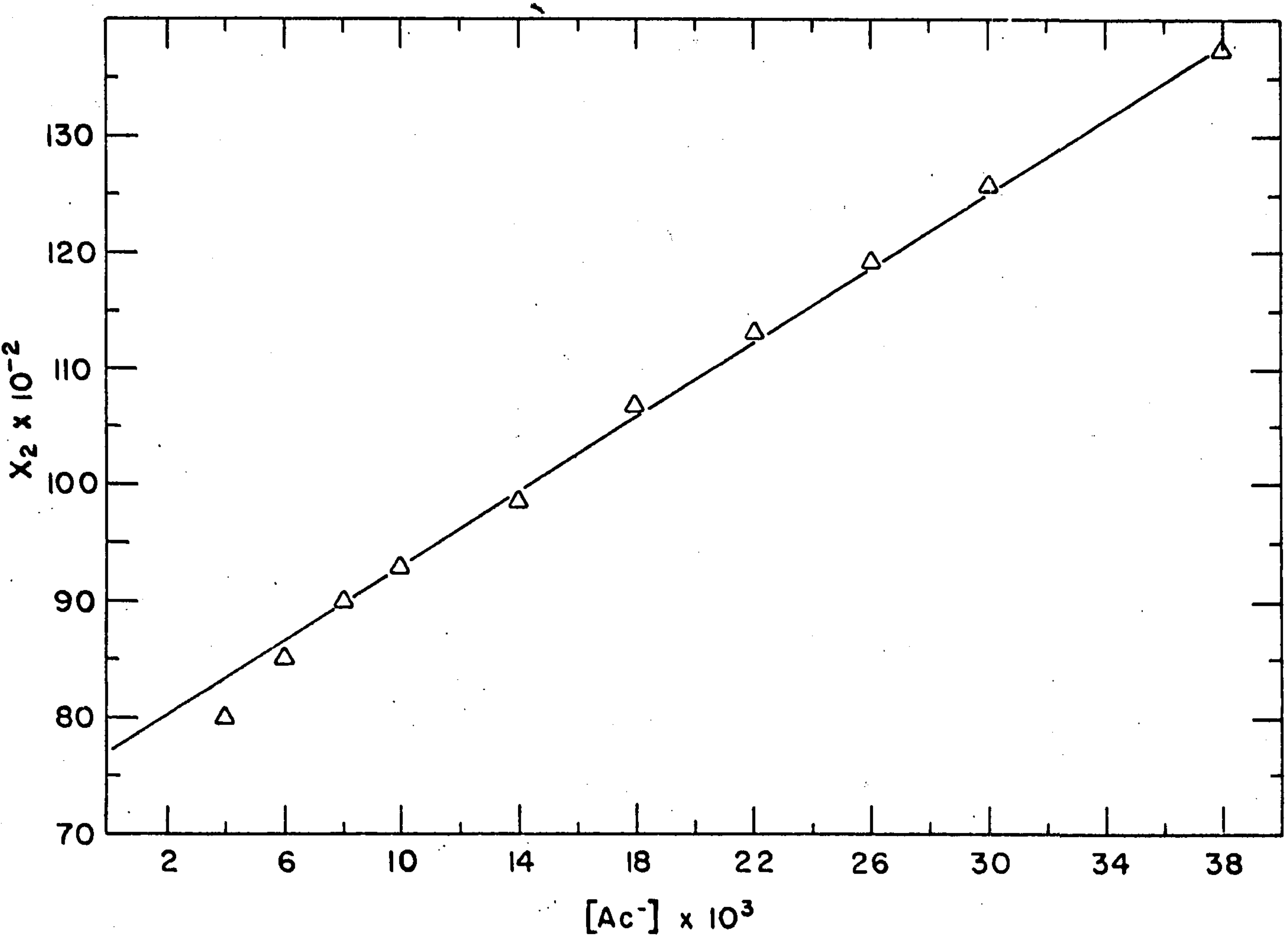

130
120
110
100
90
80
70
$X_2 \times 10^{-2}$
2
6
10
14
18
22
26
30
34
38
$[Ac^-] \times 10^3$

Table 7. Complex formation constants of the acetate ligand

Metal	$b_1 = \beta_1$	b_2	β_2	$\frac{b_1}{b_2}$
La^{3}	105	17.2	1810	6.1
Ce^{3}	124	27.5	3410	4.5
Pr^{3}	150	28.1	4220	5.3
Nd^{3}	166	34.8	5780	4.8
Sm^{3}	201	38.4	7710	5.2
Eu^{3}	202	39.7	8020	5.3
Gd^{3}	146	39.8	5810	3.7
Tb^{3}	118	39.3	4640	3.0
Dy^{3}	108	40.4	4360	2.7
Ho^{3}	101	39.3	3970	2.6
Er^{3}	102	38.8	3960	2.6
Tm^{3}	104	38.9	4050	2.7
Yb^{3}	107	43.3	4630	2.5
Lu^{3}	111	43.6	4840	2.5
Y^{3}	94	42.7	4010	2.2
Cu^{2}	78	15.8	1230	4.9
Zn^{2}	19	6.5	123	2.9
Cd^{2}	41	11.7	482	3.5
Pb^{2}	159	24.6	3910	6.5

complexes enter into the calculations. The absolute error in the constants is much greater than the relative error. The error in the standard buffer pH used in the experiments, for example, is ±0.01 pH units. The variation in converting the observed activity of the hydrogen ion to concentration of hydrogen ion by various workers in this laboratory amounts to ±0.02 pH units. Considering these possible deviations, an error of approximately ±10% is probable in the absolute magnitude of the first stepwise formation constant. Errors in the second constant, b_2, are of the order of 15% while b_3 constants may be in error by as much as 25%. It should also be mentioned that indeterminate errors due to salt bridge effects (39) and the thermodynamic definition of pH (40) are not considered in the above errors; but some of these errors would be accounted for in the ±0.02 pH unit variation.

Sonesson (36) has shown that at least three, and possibly four, acetate groups will attach themselves to a central rare-earth ion. Only the first two constants are reported in this paper, since the amount of acetate ion added to the solutions was limited by the low ionic strength value. The b_1 constants obtained at μ equal to 0.1 are approximately two and one-half times as large as those obtained at μ equal to 2.0 (37). This factor is about the same for b_2, the second constant. Using this as a basis, one may predict the values of b_3 and b_4 at μ equal 0.1 from the known values of b_3 and b_4 at μ equal 2.0. b_3 should be of the order of 8 for the lighter members and 15 for the heavier members of the rare-earth sequence. Likewise, b_4 should be of the order of 2 to 3 for all of the rare earths. The ratio b_1/b_2 for the complexes at μ equal 0.1 compare well with those obtained at μ equal 2.0.

Variations in the acetate stability constants of the rare earths, as one proceeds through the series, are very interesting. From lanthanum through samarium there is a definite rise in the first complexation constant which may be explained by the decrease in the ionic radius of the central atom. The europium constant is about the same as samarium. Since the ionic radius of europium is smaller than that of samarium, this constant is lower than expected from the previous trend. If the generally observed trend for rare-earth stability constants were followed, one would expect the constant to drop at gadolinium and then rise again at terbium. However, with the acetates the constant for terbium drops below that of gadolinium and the downward trend continues through holmium. The erbium constant is about the same as that of holmium, but a small rising trend is noted throughout the remainder of the series.

The lack of ligand-field stabilization has been postulated as an explanation for the usual downward displacement of the gadolinium constant relative to europium and terbium (41, 42). It will be noted from Table 7 that the drop between europium and gadolinium is much larger than that between gadolinium and terbium. Consequently, the ligand-field postulation is not disproven by the fact that the terbium constant continues to decrease. Yttrium has no <u>f</u> orbitals and therefore should not have any ligand-field stabilization. It is of interest to note that the first acetate constant for yttrium is lower than any rare earth. In view of the continued decrease in the stability of the heavier members, it would certainly seem that factors other than ligand-field stabilization are involved. With the second constant, b_2, the anomaly disappears and the trend more or less substantiates the ionic radii concept. Variations are noted, but it is difficult to say whether these are real or simply due to experimental error. The b_2 values of holmium, erbium and thulium, for example, appear to be slightly depressed. Similar trends have been found at μ equal to 2.0 lending credence to the observed variations.

The constants calculated for the transition metal ions are in the vicinity of those reported by other workers. As is generally the case for extremely weak constants, large variations in magnitude are observed when different methods of measurement are applied. In the case of copper, Pederson (43) reports a value of 144 for b_1 and 11 for b_2 using a glass electrode and μ extrapolated to 0. Fronaeus (34) has determined the copper acetate constants spectrophotometrically at μ equal 1.0 and reports b_1 equal to 41.7 and b_2 equal to 9.6. The reported values for the cadmium complex range from 20.0 and 9.6 at μ equal to 3.0 (44) for b_1 and b_2, respectively, to b_1 equal to 50 at μ equal 0.55 (45). Only the first constant has been reported in the case of zinc (46).

A value of 10.7 was found at μ equal to 0.2 using a hydrogen electrode. This compares rather well with the value of 19 reported in this paper. The authors feel that the determination of weak constants is significant as a measure of the relative complexing ability of the various metals but that the glass electrode is not appropriate for an absolute evaluation of constants which are of the magnitude of those of cadmium and zinc. As will be shown later, the relative values of the individual formation constants are the primary objective of this work.

Sodium perchlorate was used as the supporting electrolyte in this work. Quite frequently other highly ionized salts are used. That the constants obtained in this work are applicable to solutions containing other supporting electrolytes is indicated by a comparison of the ionization constants of acetic acid obtained in various media. The constant found using sodium perchlorate was 2.799×10^{-5} at μ equal 0.1, whereas Harned and Owen (47) list values of 2.874, 2.891 and 2.850×10^{-5} at μ equal 0.11 using lithium chloride, sodium chloride and potassium chloride, respectively. The behavior of acetate complexes in the different solutions should be similar to acetic acid.

It was mentioned earlier that, in systems containing both rare-earth and transition-metal ions, acetate complexing of both metals must be considered. Whether or not such complexing affects the measurements to a significant degree remains to be seen. The stability constants of the rare-earths with several aminopolyacetic acids have been determined by measuring the concentration of free copper, cadmium, zinc or lead ions in a solution containing equimolar amounts of rare-earth, transition metal and the aminopolyacetic acid (27, 35, 48, 49). The following equilibrium is obtained:

$$MY^{-n} + Ln^{+3} \rightleftharpoons M^{+2} + LnY^{-n+1}$$

where M denotes the transition metal, Ln is the rare-earth and Y is the aminopolyacetic acid anion. To control the pH of the solutions, the investigators used a 0.01$\underline{M}$ acetic acid-0.01$\underline{M}$ sodium acetate buffer system. M, Ln and Y each had an initial concentration of 0.001$\underline{M}$. An equilibrium constant, K_{EX}, can be written for the reaction above,

$$K_{EX} = \frac{[M^{+2}]\ [LnY^{-n+1}]}{[MY^{-n}]\ [Ln^{+3}]} . \qquad (18)$$

In order to obtain an expression for K_{EX} the following material balance equations can be written.

$$\text{Total chelate} = Y_T = [LnY^{-n+1}] + [HLnY^{-n+2}] + \ldots . \quad [My^{-n}] + [HMY^{-n+1}] + \ldots . \quad [Y^{-n-2}] + [HY^{-n-1}] + \ldots . \tag{19}$$

$$\text{Total rare-earth} = Ln_T = [Ln^{+3}] + [LnY^{-n+1}] + [HLnY^{-n+2}] + \ldots . \quad [LnAc^{+2}] + [Ln(Ac)_2^{+}] + [Ln(Ac)_3] + \ldots \ldots \tag{20}$$

$$\text{Total transition metal} = M_T = [M^{+2}] + [MY^{-n}] + [HMY^{-n+1}] + \ldots . \quad [MAc^{+}] + [M(Ac)_2] + \ldots . \tag{21}$$

Since equimolar concentrations of M, Y and Ln were used

$$M_T = Ln_T = Y_T \tag{22}$$

The concentration of free Y^{-n-2} and protonated species of this anion may be neglected since the stability constants of the metals with Y are very large. Also since the solution pH is approximately 4.6, the protonated metal chelate species are also negligible in the calculations (50, 51). Using Equations 20 and 21 the total rare-earth and transition-metal ion concentrations can be written as

$$Ln_T = [LnY^{-n+1}] + [Ln^{+3}] \times F(Ac), \tag{23}$$

$$M_T = [My^{-n}] + [M^{+2}] \times f(Ac), \tag{24}$$

where F(Ac) is the function

$$1 + \beta_1 [Ac^-] + \beta_2 [Ac^-]^2 + \beta_3 [Ac^-]^3 + \ldots \qquad (25)$$

and f(Ac) is the corresponding function for the transition metal ion. Equations 23 and 24 can now be used in Equation 18 to obtain

$$K_{EX} = \frac{[LnY^{-n+1}] \left(M_T - [MY^{-n}] \right)}{[MY^{-n}] \left(Ln_T - [LnY^{-n+1}] \right)} \times \frac{F(Ac)}{f(Ac)} \; . \qquad (26)$$

Since

$$K_{EX} = \frac{K_{LnY}}{K_{MY}} \; , \qquad (27)$$

it can be seen that evaluation of K_{EX} plus a knowledge of K_{MY} will yield the desired K_{LnY} for the rare-earth ion. Also it is seen from Equation 26 that it is the ratio of the acetate formation constants which determines the correction factor for acetate complexing so that relative values of these constants are important.

The rare-earth-chelate formation constants of EDTA (49) and HEDTA (35) found in the literature were determined polarographically using transition metals as the competing ions in acetate buffer solutions. To correct these constants for the presence of acetate, it was necessary to see what effect acetate had on the transition metal polarograms.

Polarograms of copper, zinc and cadmium, with and without acetate buffer, were made with sodium perchlorate as the supporting electrolyte. The half-wave potential of a 0.001M copper solution containing 0.05M acetate ion shifted about -0.03 volts from that of the free copper solution. Similar experiments with zinc and cadmium showed that the acetate had little effect of the half-wave potential. A comparison of the i_d values of the transition metal solutions with varying amounts of acetate ligand showed little change in the diffusion current. Similar effects were noted in the study of lead-acetate systems (52). These data were interpreted as meaning that only the total concentration of M^{+2}, MAc^{+}, $M(Ac)_2$... is obtained from a polarogram due to lack of resolution of the individual waves. Hence Equation 4 can be expressed as

$$K_{EX} = \frac{(\%M)^2}{(100-\%M)^2} \times \frac{f(Ac)}{f'(Ac)} \qquad (28)$$

where %M is percentage of the original transition-metal ion not complexed by the very powerful aminopolyacetate anion--a value readily obtained from the polarograph.

If accurate pH measurements are made, the amount of free acetate ion can be calculated from the ionization constant of acetic acid at the ionic strength of the solution. The final pH's of the solutions used in the determination of the

EDTA and HEDTA constants were not recorded. However, since the initial acetate concentration was 10 times that of the resulting unchelated-metal-ion concentration, one can get an approximate value of the free acetate ion from the known values of the acetate constants. The reported constants of EDTA and HEDTA with the rare-earth and several transition-metal ions have been corrected for acetate complexing on this basis and are listed in Tables 8 and 9.

The corrected values of the constants in the above-mentioned tables were obtained using the assumption that at most, only the first two metal complexes of acetate are formed. This assumption is certainly valid at the low acetate concentrations used. It can be seen from Table 8 that the corrections are significant since they are greater than the experimental error involved in the determination of the constants. The constants in Table 8 were originally determined using the cadmium-EDTA constant as a standard. These values were corrected for the difference between the cadmium-acetate and individual metal-acetate constants. The constants in Table 9 were based on the copper-HEDTA constant and hence were corrected for copper-acetate complexing. It should be mentioned that the acetate correction applied to the constants does not necessarily involve the metal used as the direct competing ion in the above experiments. If

Table 8. Stability constants of EDTA,[a] T = 20°C, μ = 0.1 with KNO_3

Metal	Log K_{LnY}(rept.)	Log K_{LnY}(corr.)
La	15.50±0.05	15.67±0.05
Ce	15.98±0.05	16.21±0.05
Pr	16.40±0.05	16.68±0.05
Nd	16.61±0.05	16.93±0.05
Sm	17.14±0.05	17.53±0.05
Eu	17.35±0.06	17.74±0.06
Gd	17.37±0.05	17.67±0.05
Tb	17.93±0.05	18.17±0.05
Dy	18.30±0.05	18.52±0.05
Eu	18.85±0.06	19.05±0.06
Tm	19.32±0.06	19.53±0.06
Yb	19.51±0.07	19.73±0.07
Lu	19.83±0.07	20.06±0.07
Y	18.09±0.04	18.28±0.04
Cu	18.80±0.04	18.91±0.04
Pb	18.04±0.04	18.33±0.04

[a] Values taken from ref. (49).

Table 9. Stability of rare-earth chelates with Hedta;[a] T = 25°C, μ = 0.1 with KNO_3

Metal	Log K_{LnY}(rept.)	Log K_{LnY}(corr.)
Sm	15.3	15.6
Gd	15.4	15.6
Dy	15.3	15.4
Ho	15.4	15.5
Er	15.4	15.5
Tm	15.5	15.6
Yb	15.8	15.9
Lu	16.0	16.1
Y	14.8	14.9

[a] Values taken from ref. (35).

the constant of the competing ion with the chelating agent was originally determined in the same manner, then the acetate correction involves only the preceding competing ion. Thus, although lead and copper were used as competing ions in the determination of several of the rare-earth-EDTA constants; their acetate values were not involved in the corrections since the chelate stability constants of these metals with EDTA were originally measured using cadmium as competing ion.

V. COMPLEX FORMATION CONSTANTS OF THE RARE EARTHS WITH α-HYDROXISOBUTYRIC ACID

A. Introduction

The study of complexes of the rare earths has been concerned primarily with the polydentate chelating agents. This section is concerned with a ligand that has the ability to behave as a bidentate chelating agent, the α-hydroxyisobutyrate anion.

The examination of the stability constants of the rare earths with this ligand has a dual purpose. These constants will add to the knowledge of rare-earth chemistry. Also, this ligand has been cited (53) for its ability to separate the rare earths using ion-exchange chromatography. Since these separations depend to a large degree on the differences between the stability constants of the various rare earths, the quantitative measure of these constants leads to a better understanding of the ion-exchange process.

Sonesson (54) has studied the glycolate systems at an ionic strength of 2.0. Chopoorian (55) has studied the glycolate, lactate and α-hydroxyisobutyrate systems at an ionic strength of 2.0. Karraker (56) has studied the glycolates and lactates at an ionic strength of 0.1. The constants determined in this section were measured at an ionic strength of 0.1 so that complete sets of data for these ligands will be available at two ionic strengths.

B. Experimental

The α-hydroxyisobutyric acid (Eastman Organic Chem. Co.) used in these experiments was first decolorized using activated charcoal. After filtering, the acid solution was standardized using carbonate-free potassium hydroxide (20). As with the acetates, a buffer solution containing the acid and its sodium salt was made and various amounts were added to rare-earth perchlorate. Sodium perchlorate was used to bring the ionic strength up to 0.1. The same general procedure was used in these experiments as was described in the determination of the acetate constants (Section IV, B and C).

C. Determination of α-hydroxyisobutyrate Constants

The observed pH's of a number of solutions containing rare-earth, ligand acid and sodium salt of the ligand acid are listed in Table 10. Only several sets of data are shown here for purposes of illustration. The complete data are listed in the Appendix. The complex formation curves of several of the systems are shown in Figure 11. The α-hydroxyisobutyrate constants are listed in Table 11 along with the reported values (55) for these constants at an ionic strength 2.0. Also listed are the constants of the

Table 10. Observed pH's of α-hydroxyisobutyrate buffer solutions

ml. Buffer[a] / 50 ml. Solution	Pr^{+3}	Eu^{+3}	Gd^{+3}	Ho^{+3}	Tm^{+3}
0.50	3.632	3.526	3.529	3.436	3.367
1.00	3.574	3.429	3.433	3.330	3.254
1.50	3.567	3.409	3.422	3.295	3.223
2.50	3.556	3.415	3.436	3.305	3.250
3.75	3.608	3.484	3.491	3.371	3.309
5.00	3.622	3.529	3.543	3.433	3.381
6.25	3.642	3.563	3.560	3.488	3.443
7.50	3.680	3.598	3.594	3.539	3.491
8.75	3.704	3.629	3.632	3.556	3.529
10.00	3.722	3.663	3.660	3.598	3.563
11.25	3.732	3.673	3.680	3.622	3.598
12.50	3.752	3.680	3.691	3.666	3.636

[a] Buffer solution: 0.1000*M* acid - 0.1000*M* sodium salt
Rare-earth: 0.0040*M*.

Fig. 11. The complex formation curves of several α-hydroxyisobutyrate systems

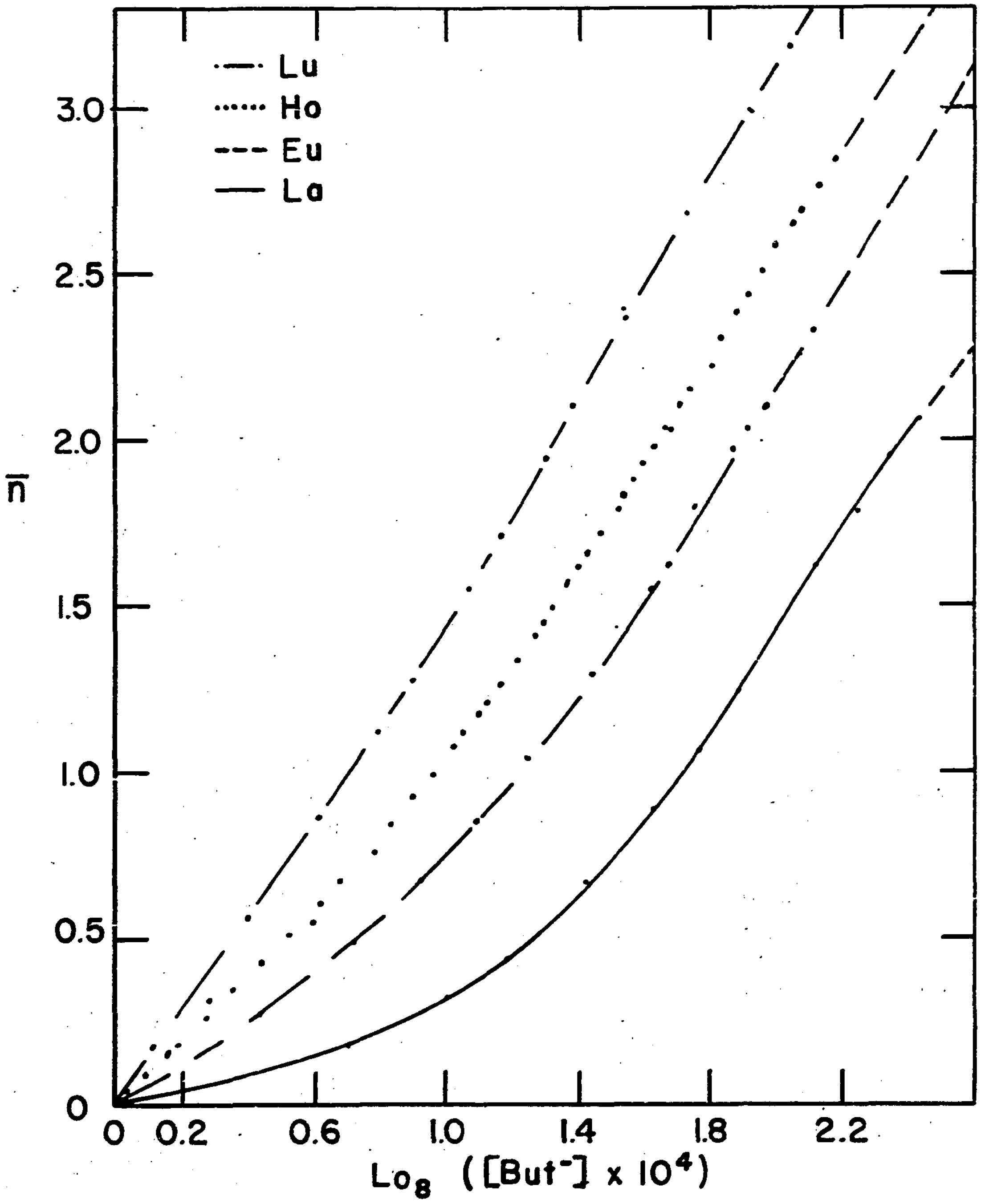

Lu
Ho
Eu
La
n̄
0
0.5
1.0
1.5
2.0
2.5
3.0
0
0.2
0.6
1.0
1.4
1.8
2.2
Log ([But⁻] x 10⁴)

Table 11. Complex formation constants of the α-hydroxy-carboxylate ligands

Metal	b_1	b_2	b_3	b_1	b_2	b_3
			A. α -Hydroxyisobutyrate			
	Temp. 20°C μ = 0.1 with $HaClO_4$			Temp. 25°C μ = 2.0 with $NaClO_4$		
La	412	63	13	---	---	---
Ce	628	88	16	270	77	10
Pr	698	116	20	---	---	---
Nd	752	140	19	420	111	25
Sm	985	247	24	560	141	38
Eu	1230	281	60	503	174	38
Gd	1190	274	47	660	213	42
Tb	1280	331	63	673	261	60
Dy	1870	420	94	---	---	---
Ho	2060	464	95	1127	392	106
Er	2240	491	122	1168	453	117
Tm	3270	505	148	---	---	---
Yb	4400	600	187	1400	715	132
Lu	4620	636	223	---	---	---
Y	1590	385	52	730	380	72

Table 11 (Continued)

Metal	b_1	b_2	b_3	b_1	b_2	b_3
	B. Glycolate			C. Lactate		
	Temp. 20°C μ = 0.1 with $NaClO_4$			Temp. 20°C μ = 0.1 with $NaClO_4$		
La	355	49	6	400	55	20
Ce	495	71	7	570	93	17
Pr	600	80	15	705	113	16
Nd	780	92	18	740	126	26
Sm	820	126	36	760	162	18
Eu	860	137	28	890	169	18
Gd	620	116	14	780	141	16
Tb	660	123	13	790	203	14
Dy	840	111	38	1020	220	21
Ho	980	112	34	1050	250	26
Er	1010	153	46	1460	288	38
Tm	1135	188	47	1550	329	53
Yb	1350	174	55	1700	388	58
Lu	1400	214	63	1875	405	79
Y	610	123	8	1040	216	42

glycolate and lactate anions (56).

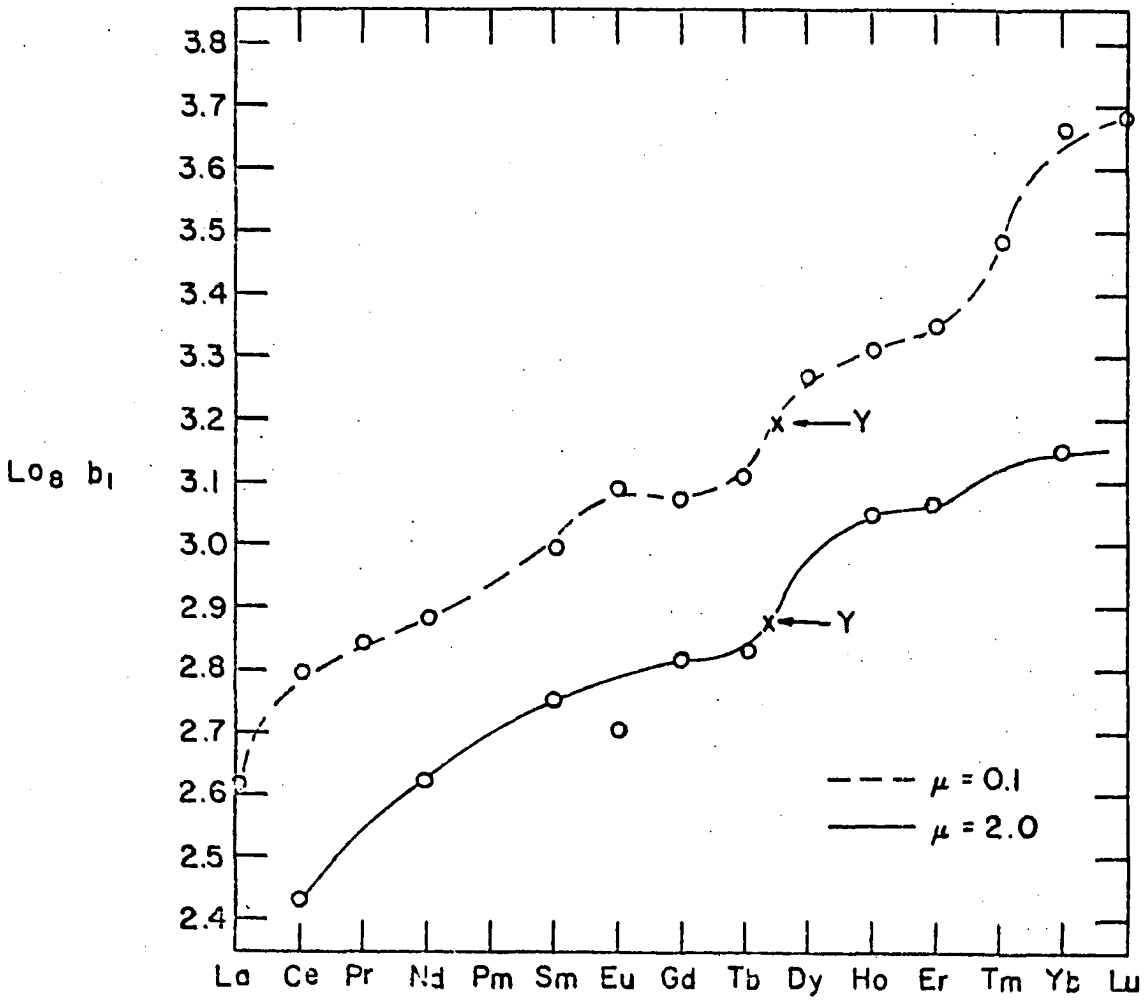
D. Discussion of Results

The errors involved in the determinations of these constants are of the same order of magnitude as those discussed on page 67 of this manuscript.

The values for the first stability constants, b_1, are plotted in Figure 12 versus the atomic number of the rare-earth. For purposes of comparison, the values of the constants (55) reported for an ionic strength 2.0 are also listed. Except for several discrepancies the two curves are similar. The position of europium is lower than that of gadolinium or samarium in the data at an ionic strength of 2.0 reported by Chopoorian while in this manuscript a higher value is found. In the work done in this laboratory on the glycolate and lactate constants (56) europium is found to be higher than either samarium or gadolinium. It would seem plausible to accept the higher value of the europium constant in view of the agreement found in this laboratory by different workers employing similar ligands.

Another discrepancy occurs with the thulium-ytterbium-lutetium triad. In the work reported in this manuscript, there is a very large break between these three elements and erbium. A similar break occurs in the constants measured at ionic strength 2.0 but it is not nearly as large. Similar

Fig. 12. Plot showing the variation in the first stepwise formation constants of the rare earths


Log b1
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Y
Y
μ = 0.1
μ = 2.0

breaks are also apparent in the glycolate and lactate constants.

It will be shown later that, from a consideration of the separation factors of the rare earths observed with α-hydroxyisobutyric acid, the break in stability at thulium apparently is not as large as indicated by the complex formation constants at ionic strength of 0.1. A further experiment was therefore carried out with lutetium. If some phenomenon such as loss of more than one hydrogen from the complexed ligand is occurring, then changing the pH of the buffer used in the experiments should result in finding a new complex formation constant. Therefore, the lutetium constant was redetermined using an acid:salt buffer ratio of 3:7 and compared with the constant obtained with the 1:1 buffer. A constant of 4410 was found as compared with the value of 4620 reported. Since these two values are well within the range of the experimental error, it is apparent that no reactions other than the ones considered in the calculations are taking place. The values of the constants for the heavy rare earths are quite large. It may be possible, however, that these constants are somewhat in error, since the extrapolations involved in the computational method become more inaccurate as stronger constants are measured.

Table 11 lists the constants found for the glycolate, lactate and α-hydroxyisobutyrate complexes of the rare earths found in this laboratory at ionic strength 0.1. The general trend observed is glycolate $<$ lactate $<$ α-hydroxyisobutyrate. This trend follows inversely the trend in the ionization constants of the ligand acids, $2.72 \times 10^{-4} > 2.33 \times 10^{-4} > 1.61 \times 10^{-4}$, respectively. It is noted that the α-hydroxyisobutyrate constants are much larger than those for the lactates while the lactate constants are slightly greater than those for the glycolates. A comparison of the magnitudes of the ionization constants of the ligand acids shows a similar trend. This suggests that the phenomenon is probably due to the electronic induction effects of the methyl groups rather than properties attributable to the rare earths or possible steric effects.

Due to the presence of two methyl groups on the α-carbon atom in α-hydroxyisobutyrate, one might expect steric hindrances to appear after the first or second ligand has been bonded to the rare-earth ion. Unfortunately, the uncertainies in b_2 and b_3 do not permit a definite conclusion to be drawn. It may be mentioned, however, that the average ligand number, $\bar{n}$, frequently is greater than three for the heavier members of the series indicating that anionic chelate species are formed.

Evidence that the hydroxyl group is bonded to the rare-earth central ion to form a bidentate chelate is found both in the magnitude and the ratios of the individual constants. The constants are all much greater than the acetate constants Table 7, Page 76) indicating that a change in coordination number of the ligand is taking place. Bjerrum (33) proposes, from a statistical viewpoint, that a bidentate ligand occupying adjacent sites of an octahedrally coordinated metal ion will exhibit the following relationship between successive constants

$$b_1 : b_2 : b_3 = 12 : 2 : 1/3.$$

The values of b_1/b_2 are in the vicinity of 5 for the α-hydroxyisobutyrate constants. It is seen from Table 7, Page 76, that the acetate ration b_1/b_2 are generally much lower than this. Although one cannot be sure of the octahedral symmetry of the rare-earth ions, the increase in the ratios suggest strongly that another coordination position is being occupied by the α-hydroxyisobutyrate ligand.

It was pointed out earlier that α-hydroxyisobutyric acid has the ability to promote separation of rare-earth metals when used in ion-exchange chromatography. A convenient means of expressing quantitatively the extent of separation of two species [A] and [B] in an ion-exchange system is the separation factor,

$$\lambda = \frac{[\bar{A}]\ [B]_T}{[\bar{B}]\ [A]_T} \qquad (29)$$

where $[\bar{A}]$ stands for the mole fraction of rare-earth A in the resin phase and $[A]_T$ stands for the total concentration in moles per liter of rare-earth A in the aqueous phase. An approximate expression for λ may then be calculated (3) from a knowledge of the stability constants of the complexing agent, Y^-, being used in the separation experiments. The total rare earth in solution $[A]_T$, is given by

$$[A]_T = [A^{+3}] + [AY^{+2}] + [AY_2^{+}] + \ldots . \qquad (30)$$

plus any rare-earth hydroxy species present. If experiments are carried out in an acid medium, these latter species will be negligible. If the ligand, Y^-, is quite strong, then the free metal ion concentrations will be negligible in comparison to the complexed species and

$$\frac{[B]_T}{[A]_T} = \frac{\sum_{n=1}^{N} [BY_n{}^{3-n}]}{\sum_{n=1}^{N} [AY_n{}^{3-n}]} . \qquad (31)$$

If the selectivity coefficient is unity, that is, if the free rare-earth ions have identical affinities for the resin,

$$\frac{[\bar{A}]}{[\bar{B}]} = \frac{[A^{+3}]}{[B^{+3}]} \tag{32}$$

then Equation 29 becomes

$$\lambda = \frac{[A^{+3}]}{[B^{+3}]} \times \frac{\sum_{n=1}^{N} [BY_n{}^{3-n}]}{\sum_{n=1}^{N} [AY_n{}^{3-n}]} \; . \tag{33}$$

Since

$$\begin{aligned} b_1 &= \frac{[ABuT^{+2}]}{[A^{+3}]\ [BuT^-]} \\ b_2 &= \frac{[ABuT_2^{+}]}{[ABuT^{\;2}\ \ [BuT^-]} \\ &\cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ &\cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ &\cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \end{aligned} \tag{34}$$

Equation 33 reduces to

$$\lambda = \frac{b_1\ [BuT^-] + b_1 b_2\ [BuT^-]^{2} + \ldots .}{b_1'\ [BuT^-] + b_1' b_2'\ [BuT^-]^{2} + \ldots .} \tag{35}$$

where b_n, b_n' are the corresponding formation constants of the two rare-earths being considered.

The experimental separation factors have been determined for the rare earths and α-hydroxyisobutyric acid (53) at a temperature of 87°C. No data were reported for lower temperatures, but it was mentioned that little difference was noted when the ion-exchange columns were run at room temperature. The experimental and the calculated factors are listed in Table 12. A free ligand concentration of 0.1*M* was arbitrarily chosen for the calculated values. b_1, b_2 and b_3 were used in the calculations. All of separation factors were determined relative to gadolinium.

Table 12. Separation factors of the rare earths with α-hydroxyisobutyrate

Metal	Expt., T = 87°C ref. (53)	Calc., T = 20°C μ = 0.1 this work	Calc., T = 25°C μ = 2.0 ref. (55)
La^{+3}	34.10	29.1	-----
Ce^{+3}	16.70	12.5	16.6
Pr^{+3}	10.45	7.53	-----
Nd^{+3}	6.60	5.98	4.40
Pm^{+3}	4.10	----	-----
Sm^{+3}	2.25	2.22	1.92
Eu^{+3}	1.40	0.77	1.73
Gd^{+3}	1.00	1.00	1.00
Tb^{+3}	0.49	0.61	0.60
Dy^{+3}	0.26	0.23	-----
Ho^{+3}	0.16	0.19	0.14
Er^{+3}	0.13	0.13	0.11
Tm^{+3}	0.10	0.05	-----
Yb^{+3}	0.075	0.036	0.052
Lu^{+3}	0.055	0.027	-----
Y^{+3}	0.25	0.49	0.32

On the whole, the agreement between the calculated and the experimental values is not too bad. There are some notable exceptions in which reversals of adjacent rare earths occur. It is also interesting to note that the previously discussed thulium-ytterbium-lutetium triad does not appear to have as large separation factors as might be expected from inspection of their complex stability constants.

VI. THE RARE-EARTH COMPLEXES OF METHOXYACETIC AND THIOGLYCOLIC ACIDS

A. Introduction

Thus far the formation constants of a monodentate ligand, acetate, and a bidentate ligand, α-hydroxyisobutyrate, have been discussed. It was observed that the hydroxyl group can donate a pair of electrons to the rare-earth ion to form a five-membered chelate ring. This section is concerned with determining whether other functional groups can also coordinate with the rare-earths to form bidentate complexes.

The ether group is capable of coordinating with metal ions. The best known of the ether coordination compounds are those formed with Grignard reagents. Although ethereal oxygen atoms can act as electron donors, it is generally observed that the compounds formed are not as stable as those formed with alcohols.

Sulfur, being a congener of oxygen, has the potential of behaving as an electron donor, although the sulfur atom is more selective in the acceptor atoms to which it bonds. The coordination chemistry of sulfur in relation to the rare earths is virtually unknown. Therefore, a beginning to that study is made here.

B. Experimental

As with the previously discussed complexing agents, the methoxyacetic and thioglycolic acids (Eastman Organic Co.) were standardized by titration with base, and buffer solutions were prepared by addition of sodium hydroxide. In order to prevent air oxidation of the thioglycolic acid, oxygen free water was used in preparing all solutions. The water was purged of oxygen by bubbling in purified nitrogen and all measurements of the thioglycolate solutions were made under a stream of nitrogen. The experimental procedure was the same as that described in connection with the acetate and α-hydroxyisobutyrate experiments. Complete experimental data for the methoxyacetate and thioglycolate runs are tabulated in the Appendix.

C. Discussion of Results

The constants found for the methoxyacetate and thioglycolate complexes of the lanthanons and yttrium are listed in Table 13. The acetate constants are included for comparison. Only the first two constants are reported in each case, since the amount of ligand added to the solutions was limited by the low ionic strength value chosen. Even the second constants reported for these complex species should be regarded as only intelligent estimates rather than true

Table 13. Stability constants of the acetate, methoxyacetate and thioglycolate ligands

Temp. 20°C; μ = 0.1($NaClO_4$)

Metal	Acetate		Methoxyacetate		Thioglycolate	
	b_1	b_2	b_1	b_2	b_1	b_2
La	105	17.2	106	7.2	96	10
Ce	124	27.5	114	10.4	98	11
Pr	150	29.1	118	15.0	106	11
Nd	166	34.8	128	16.6	117	16
Sm	201	38.4	134	17.8	129	23
Eu	202	39.7	131	20.2	117	22
Gd	146	39.8	115	9.4	103	20
Tb	118	39.3	111	9.2	91	18
Dy	108	40.4	113	12.0	86	21
Ho	101	39.3	117	14.3	83	21
Er	102	38.8	119	14.4	87	21
Tm	104	38.9	119	14.2	95	13
Yb	107	43.3	120	18.8	96	21
Lu	111	43.6	124	19.2	102	20
Y	94	42.7	99	12.9	82	19

constants, since the $\bar{n}$ values for these experiments did not reach 1.5 in most of the cases studied.

The methoxyacetate constants are indeed surprising. One might expect that the ether group would form fairly strong bonds with rare-earth ions to form complexes of greater stability than the corresponding acetates. The data in Table 13 reveal that only the methoxyacetate complexes of rare earths heavier than terbium are stronger than their acetate counterparts. Even here the difference is less than experimental accuracy of the method. There is no ready explanation for this apparent anomaly. Intuitively, one feels that the ether group should donate electrons into the rare-earth coordination sphere, thus stabilizing the complex since the ether group is similar to the hydroxyl group with respect to its donor properties. With the glycolate anion, the first lanthanum constant, b_1, is approximately four times as great as the corresponding constant for lanthanum acetate. The ratio increases with atomic number of the rare earth and reaches ten with the heavy rare earths. An enhancement in complex stability is not observed with the methoxyacetate ligand.

Some degree of explanation for the low magnitude of the methoxyacetate constants is found in a comparison of the ionization constants of the ligand acids. These constants are 2.72×10^{-4}, 4.91×10^{-4} and 2.80×10^{-5} for glycolic

(56), methoxyacetic and acetic acid, respectively. If we suppose, for the moment, that the anions of these acids all form complexes by bonding only through the carboxylate group, then the order of complex stabilities should be acetate > glycolate > methoxyacetate. That is, the strength of the carboxylate bond to a metal ion should parallel the bonding to hydrogen. From this viewpoint it appears that the ether group does bond weakly to the rare earths, since there is no great loss in complex stability from acetates to methoxyacetates corresponding to the loss in affinity of the ligand for hydrogen.

Another possibility, and a more probable one, is that steric factors are introduced by the presence of the methyl group on the ethereal oxygen as compared to the hydrogen on the hydroxyl group. If the steric hindrance is such that the oxygen is prevented from closely approaching the rare earth, then a good deal of complexing strength would be lost. This type of behavior is substantiated to some degree by the trends observed in the methoxyacetate constants. The Ln(methoxyacetate) species of the intermediate atomic number rare-earths are considerably less stable than the corresponding acetates whereas the Ln(methoxyacetate) species of the heavy lanthanons are more stable than the corresponding acetate species. Due to the lanthanide contraction, the steric hindrance of the methyl group might be less pronounced when methoxyacetate complexes form with the heavier lanthanons. In this respect, the values reported for the complexes of the divalent calcium ion are interesting. The calcium-acetate constant (57) has a value of 5.9. The calcium-glycolate and calcium-methoxyacetate constants (58) have values of 38.9 and 13.2, respectively. Here the methoxyacetate constant is larger than the acetate constant and the glycolate constant is much larger. The crystal radius of the Ca(II) ion is 0.99 Å as compared to 1.16 Å for La(III) and 0.93 Å for Lu(III) (31). A steric factor due to the methyl group seems to be substantiated by these data, since the radius of calcium is comparable to the radii of the heavy rare earths. Unfortunately these are the only data available for methoxyacetate complexes.

The stability constants of the thioglycolate complexes with rare earths are also quite surprising. Thioglycolic acid is a dibasic acid with K_1 equal to 3.89×10^{-4} and K_2 equal to 1.66×10^{-10} at an ionic strength of 0.1 (determined in this laboratory using the glass electrode). In the determination of the constants of divalent lead and zinc ions (59) with this ligand, it was found that both hydrogens were lost and strong complexes were formed, involving both the carboxylate group and the sulfur. The stability constants were of the order of 10^8. Since the rare earths have one more unit of positive charge, one might be tempted to predict that they would also expel the second acidic hydrogen and form strong complexes by bridging the uninegative carboxyl and sulfur groups. Attempts to calculate $\bar{n}$, the average ligand number, on this basis led to negative values. This could only mean that other species were present in the solutions which were not accounted for in the material balance equations. The constants in Table 13 were calculated assuming that the sulfur-hydrogen bond remained intact on complexing with the rare earth. In order to check the possibility of both types of complexes being formed, the pH of the buffer (that is, the ratio of ligand acid to ligand salt) was changed and several of the constants redetermined using this buffer. In all cases, the values remained constant within the experimental error of the determinations. One may conclude that the acidic hydrogen on the sulfur atom remains intact even with the trivalent rare-earth ion in close proximity.

It can be seen from Table 13 that little if any contribution is made by the sulfur atom to complex stability. Here again the electronegativity of the sulfur atom and its effect on the carboxyl group is evident. No steric effects are present in this ligand, as may be the case with the methoxyacetates, and both acids are of similar strength. Yet, the thioglycolate constants are lower than the methoxyacetate constants. From the values reported in this manuscript, one may conclude that the order of electron donating ability of the functional groups (at least in the case of rare-earth ions) is

$$OH > OCH_3 > SH .$$

VII. SUMMARY

The solid rare-earth chelates of ethylenediaminetetraacetic acid have been examined using thermobalance, infrared and X-ray diffraction techniques. The lighter members are monohydrates while the heavier members are anhydrous. Infrared studies indicate that the light-member chelates have a pentadentate EDTA structure while the remaining rare earths assume a hexadentate configuration. X-ray diffraction studies substantiate this structural change. Ionization constant determinations of these acids indicate that a corresponding change does not occur in solution.

The complex formation constants of the rare earths with the acetate, α-hydroxyisobutyrate, methoxyacetate and thioglycolate ligands have been determined. It is found that the acetate constants do not follow the ionic radius trend. The acetate constants are found to be lower for the heavier members than the light members. Similar results are found with methoxyacetate and thioglycolate. α-hydroxyisobutyrate forms very strong bidentate chelates with the rare earths and the usual order of stability magnitudes is noted. The methoxy group and the sulfhydryl group contribute little if any to chelate formation with the rare-earth ions.

VIII. BIBLIOGRAPHY

1. Meggars, W. F., *Science*, *105*, 514 (1947).

2. Moeller, T., "Inorganic Chemistry", John Wiley and Sons, New York (1952).

3. Powell, J. E. and Spedding, F. H., "Basic Principles Involved in the Macro-Separation of Adjacent Rare-Earths from Each Other by Means of Ion Exchange", U. S. Atomic Energy Commission Report ISC-857, Ames Lab., Ames, Iowa (1956).

4. ______ and ______, *Chem*. *Eng*. *Progr*. *Symposium* *Ser*., *55*, No. 24, 101 (1959).

5. Spedding, F. H., Powell, J. E. and Wheelwright, E. J., *J*. *Am*. *Chem*. *Soc*., *76*, 612, 2557 (1954).

6. ______ and ______, *J*. *Am*. *Chem*. *Soc*., *76*, 2545, 2550 (1954).

7. Bellamy, L. J., "The Infrared Spectra of Complex Molecules", John Wiley and Sons, New York (1958).

8. Busch, D. H. and Bailar, J. C., *J*. *Am*. *Chem*. *Soc*., *75*, 4574 (1953).

9. Brintzinger, H., Thiele, H. and Muller, U., *Z*. *Anorg*. *Chem*., *251*, 285 (1943).

10. Schwarzenbach, G., *Helv*. *Chim*. *Acta*, *32*, 839 (1949).

11. Busch, D. H. and Bailar, J. C., *J*. *Am*. *Chem*. *Soc*., *78*, 716 (1956).

12. Pecsok, R. L., *J*. *Chem*. *Educ*., *29*, 597 (1952).

13. Weakliem, H. A. and Hoard, J. L., *J*. *Am*. *Chem*. *Soc*., *81*, 549 (1959).

14. Kirschner, S., *J*. *Am*. *Chem*. *Soc*., *78*, 2372 (1956).

15. Smith, G. S. and Hoard, J. L., *J*. *Am*. *Chem*. *Soc*., *81*, 556 (1959).

16. Brintzinger, H. and Munkett, S., Z. Anorg. Chem., 256, 285 (1948).

17. Moeller, T., Moss, F. A. J. and Marshall, R. H., J. Am. Chem. Soc., 77, 3182 (1955).

18. Marsh, J. K., J. Chem. Soc., 1819 (1950).

19. Schmid, R. W. and Reilly, C. N., J. Am. Chem. Soc., 78, 5513 (1956).

20. Powell, J. E. and Hiller, M. A., J. Chem. Educ., 34, 330 (1957).

21. Flett, M. St. C., J. Chem. Soc., 962 (1951).

22. Sawyer, D. T. and McKinnie, J. M., J. Am. Chem. Soc., 82, 4191 (1960).

23. ______, Ann. N. Y. Acad. Sci., 88, 307 (1960).

24. Morris, M. L. and Busch, D. H., J. Am. Chem. Soc., 78, 5178 (1956).

25. Brunisholz, G., Chimia, 11, 97 (1957).

26. Moeller, T. and Horwitz, E. P., J. Inorg. Nuclear Chem., 12, 49 (1959).

27. Wheelwright, E. J., Spedding, F. H. and Schwarzenbach, G., J. Am. Chem. Soc., 75, 4196 (1953).

28. Marsh, J. K., J. Chem. Soc., 451 (1955).

29. Moeller, T., Record Chem. Prog., 14, 69 (1953).

30. Minczewski, J. and Dybczynski, R., "Separation of Rare Earths on Anion Exchange Resins-H", Polish Academy of Sciences, Institute of Nuclear Research Report No. 229/VIII, (1961).

31. Kleinberg, J., Argersinger, W. J., Jr. and Griswold, E., "Inorganic Chemistry", D. C. Heath and Co., Boston (1960).

32. Rossotti, F. J. C. and Rossotti, H., "The Determination of Stability Constants", McGraw-Hill Co., New York (1961).

33. Bjerrum, J., "Metal Ammine Formation in Aqueous Solution", P. Haase and Son, Copenhagen (1941).

34. Fronaeus, S., "Komplexsystem hos koppar", Unpublished Ph.D. Thesis, Gleerupska Universitets-Bokhandeln, Lund (1948). (Original not available for examination; cited in Rossotti, F. J. C. and Rossotti, H., "The Determination of Stability Constants", McGraw-Hill Co., New York (1961).)

35. Spedding, F. H., Powell, J. E. and Wheelwright, E. J., J. Am. Chem. Soc., 78, 34 (1956).

36. Sonesson, A., Acta Chem. Scand., 12, 165 (1958).

37. ______, Acta Chem. Scand., 12, 1937 (1958).

38. ______, Acta Chem. Scand., 14, 1495 (1960).

39. Bates, R. G., Pinching, G. D. and Smith, E. R., J. Research Nat. Bur. Standards, 45, 418 (1950).

40. Feldman, I., Anal. Chem., 28, 1859 (1956).

41. George, P., McClure, D. S., Griffith, J. S. and Orgel, L. E., J. Chem. Phys., 24, 1269 (1956).

42. Staveley, L. A. K. and Randall, T., Discussions Faraday Soc., No. 26, 157 (1958).

43. Pederson, K. J., Kgl. Danske Videnskab. Selskab, Mat-fys Medd., 22, No. 12 (1945).

44. Leden, J., Svensk Kem. Tidskr., 58, 129 (1946).

45. Ferrell, E., Ridgion, J. M. and Riley, H. L., J. Chem. Soc., 1440 (1934).

46. Cannan, R. K. and Kibrick, A., J. Am. Chem. Soc., 60, 2314 (1938).

47. Harned, H. S. and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions", Reinhold Pub. Corp., New York (1958).

48. Hiller, M. A., "Some Physical and Chemical Properties of Scandium and the Rare Earths", Unpublished Ph.D Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa (1959).

49. Schwarzenbach, G., Gut, R. and Anderegg, G., Helv. Chim. Acta, 37, 937 (1954).

50. Hagiwara, Z., Data from titration studies, (Manuscript), (1959). U. S. Atomic Energy Commission, Ames Laboratory, Document Library, Data Book No. ZEN-1, p. 234 (1956).

51. James, D. B., "Ion-Exchange Elution Sequences with Chelating Eluants", Unpublished Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa (1960).

52. Toropova, F. V., Zhur. Anal. Khim., 4, 337 (1949).

53. Choppin, G. R. and Silve, R. J., J. Inorg. Nuclear Chem., 3, 153 (1956).

54. Sonesson, A., Acta Chem. Scand., 13, 998 (1959).

55. Chopoorian, J. A., "The Complex Stabilities of the Lanthanides with a Series of α-hydroxy Carboxylate Ligands", Unpublished Ph.D. Thesis, Library, The Florida State University, Tallahassee, Fla. (1961).

56. Karraker, Robert H., "Stability Constants of Some Rare-Earth-Metal Chelates", Unpublished Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa (1961).

57. Colman-Porter, C. A. and Monk, C. B., J. Chem. Soc., 4363 (1952).

58. Davies, C. W., J. Chem. Soc., 277 (1938).

59. Li, N. C. and Manning, R. A., J. Am. Chem. Soc., 77, 5225 (1955).

IX. ACKNOWLEDGMENTS

The author wishes to express his thanks to Dr. J. E. Powell for his encouragement and helpful advice in carrying out the research presented in this thesis. His willingness to discuss the problems involved was always greatly appreciated.

The author would also like to thank his wife, Maxine, for her constant encouragement throughout his graduate college career.

X. APPENDIX A: OBSERVED ACETATE BUFFER SOLUTION pH'S

ml.buffer / 50ml.soln.	Cu^{+2}	Zn^{+2}	Cd^{+2}	La^{+3}	Ce^{+3}	Pr^{+3}
2.50	4.251	4.527	4.471	4.479	4.422	4.435
3.75	4.253	4.519	4.467	4.489	4.448	4.452
5.00	4.257	4.526	4.471	4.500	4.460	4.461
7.50	4.264	4.526	4.474	4.503	4.476	4.477
10.00	4.276	4.524	4.472	4.511	4.488	4.486
15.00	4.291	4.524	4.475	4.525	4.505	4.505
20.00	4.309	4.527	4.481	4.534	4.521	4.521
25.00	4.333	4.530	4.486	4.542	4.534	4.533
30.00	4.350	4.535	4.491	4.550	4.538	4.544
35.00	4.364	4.538	4.502	4.556	4.546	4.550
40.00	4.375	4.548	4.507	4.561	4.560	4.557
45.00	4.406	4.548	4.526	4.570	4.566	4.567

	Nd^{+3}	Sm^{+3}	Eu^{+3}	Gd^{+3}	Tb^{+3}	Dy^{+3}
2.50	4.419	4.379	4.385	4.426	4.458	4.465
3.75	4.427	4.401	4.400	4.432	4.458	4.465
5.00	4.445	4.414	4.412	4.438	4.458	4.464
7.50	4.462	4.419	4.422	4.447	4.463	4.467
10.00	4.478	4.438	4.438	4.454	4.467	4.473
15.00	4.502	4.456	4.455	4.467	4.475	4.479
20.00	4.515	4.477	4.473	4.486	4.484	4.488
25.00	4.528	4.495	4.492	4.486	4.484	4.501
30.00	4.543	4.506	4.505	4.509	4.506	4.508
35.00	4.551	4.517	4.516	4.520	4.515	4.517
40.00	4.557	4.528	4.525	4.528	4.523	4.526
45.00	4.566	4.543	4.538	4.542	4.540	4.540

	Ho^{+3}	Er^{+3}	Tm^{+3}	Yb^{+3}	Lu^{+3}	Y^{+3}
2.50	4.475	4.470	4.470	4.472	4.466	4.493
3.75	4.474	4.476	4.478	4.473	4.465	4.492
5.00	4.478	4.477	4.473	4.468	4.467	4.491
7.50	4.479	4.478	4.476	4.473	4.471	4.494
10.00	4.479	4.480	4.480	4.474	4.479	4.496
15.00	4.482	4.485	4.486	4.481	4.485	4.502
20.00	4.493	4.492	4.492	4.497	4.496	4.505
25.00	4.506	4.503	4.508	4.506	4.510	4.518
30.00	4.509	4.510	4.515	4.514	4.515	4.525
35.00	4.519	4.518	4.525	4.523	4.523	4.535
40.00	4.527	4.527	4.530	4.530	4.533	4.529
45.00	4.541	4.541	4.545	4.543	4.549	4.553

Buffer solution: 0.08807*M* acetic acid - 0.07740*M* sodium acetate

Cu^{+2}: 0.01132*M*

Zn^{+2}: 0.01041*M*

Cd^{+2}: 0.01004*M*

Rare Earth : 0.0040*M* except Ce^{+3}

Ce^{+3}: 0.003897*M* + 1.690×10^{-4} perchloric acid

XI. APPENDIX B: OBSERVED α-HYDROXYISOBUTYRATE SOLUTION pH'S

ml.buffer / 50ml.soln.	La^{+3}	Ce^{+3}	Pr^{+3}	Nd^{+3}	Sm^{+3}	Eu^{+3}
0.50	3.749	3.537	3.632	3.629	3.578	3.526
1.00	3.691	3.514	3.574	3.543	3.474	3.429
1.50	3.673	3.501	3.567	3.539	3.462	3.407
2.50	3.660	3.536	3.556	3.563	3.481	3.415
3.75	3.691	3.542	3.608	3.581	3.512	3.484
5.00	3.722	3.591	3.622	3.608	3.556	3.529
6.25	3.742	3.629	3.642	3.642	3.584	3.563
7.50	3.756	3.653	3.680	3.665	3.624	3.598
8.75	3.766	3.665	3.704	3.693	3.662	3.629
10.00	3.770	3.680	3.722	3.722	3.693	3.662
12.50	3.787	3.704	3.752	3.742	3.725	3.680
15.00	3.797	3.723	3.777	3.763	3.756	3.714

	Gd^{+3}	Tb^{+3}	Dy^{+3}	Ho^{+3}	Er^{+3}	Tm^{+3}
0.50	3.529	3.512	3.454	3.436	3.426	3.367
1.00	3.432	3.419	3.343	3.330	3.302	3.254
1.50	3.421	3.378	3.309	3.295	3.275	3.223
2.50	3.436	3.367	3.343	3.305	3.278	3.250
3.75	3.491	3.454	3.391	3.371	3.350	3.309
5.00	3.542	3.501	3.446	3.432	3.405	3.391
6.25	3.560	3.529	3.495	3.488	3.462	3.443
7.50	3.593	3.563	3.550	3.539	3.526	3.491
8.75	3.632	3.591	3.578	3.556	3.550	3.529
10.00	3.660	3.611	3.604	3.598	3.584	3.563
12.50	3.691	3.645	3.632	3.622	3.611	3.598
15.00	3.711	3.677	3.662	3.665	3.642	3.636

	Yb^{+3}	Lu^{+3}	Y^{+3}
0.50	3.330	3.336	3.474
1.00	3.195	3.195	3.378
1.50	3.209	3.168	3.354
2.50	3.220	3.182	3.378
3.75	3.247	3.240	3.440
5.00	3.343	3.281	3.498
6.25	3.436	3.360	3.556
7.50	3.471	3.440	3.584
8.75	3.519	3.495	3.619
10.00	3.560	3.526	3.653
12.50	3.598	3.556	3.683
15.00	3.636	3.587	3.693

Buffer soln.: 0.1000M acid - 0.1000M sodium salt

Rare earth : 0.0040M except Ce^{+3}

Ce^{+3} : 0.003897M + 1.690 x 10^{-4}M $HClO_4$

XII. APPENDIX C: OBSERVED METHOXYACETATE SOLUTION pH'S

ml. buffer / 50ml. soln.	La^{+3}	Ce^{+3}	Pr^{+3}	Nd^{+3}	Sm^{+3}	Eu^{+3}
2.00	3.384	3.347	3.375	3.361	3.354	3.356
3.00	3.365	3.334	3.352	3.343	3.338	3.342
5.00	3.350	3.328	3.335	3.326	3.322	3.326
7.50	3.346	3.332	3.334	3.325	3.320	3.323
10.00	3.342	3.333	3.333	3.327	3.321	3.324
12.50	3.340	3.337	3.334	3.327	3.320	3.330
15.00	3.348	3.339	3.340	3.333	3.325	3.328
17.50	3.351	3.342	3.342	3.337	3.326	3.333
20.00	3.354	3.346	3.345	3.340	3.332	3.338
25.00	3.357	3.352	3.346	3.345	3.340	3.343
30.00	3.360	3.359	3.355	3.349	3.344	3.346
35.00	3.368	3.362	3.364	3.355	3.360	3.359
	Gd^{+3}	Tb^{+3}	Dy^{+3}	Ho^{+3}	Er^{+3}	Tm^{+3}
2.00	3.379	3.385	3.381	3.382	3.379	3.378
3.00	3.363	3.361	3.357	3.351	3.360	3.356
5.00	3.343	3.340	3.336	3.338	3.341	3.329
7.50	3.337	3.337	3.336	3.342	3.335	3.326
10.00	3.341	3.342	3.336	3.336	3.335	3.333
12.50	3.343	3.344	3.337	3.340	3.338	3.340
15.00	3.347	3.346	3.340	3.343	3.336	3.339
17.50	3.349	3.349	3.343	3.343	3.339	3.340
20.00	3.356	3.347	3.347	3.346	3.347	3.342
25.00	3.360	3.351	3.353	3.356	3.353	3.350
30.00	3.369	3.357	3.359	3.353	3.356	3.355
35.00	3.374	3.370	3.369	3.363	3.362	3.360
	Yb^{+3}	Lu^{+3}	Y^{+3}			
2.00	3.374	3.374	3.390			
3.00	3.350	3.353	3.366			
5.00	3.336	3.336	3.350			
7.50	3.328	3.332	3.343			
10.00	3.329	3.330	3.340			
12.50	3.336	3.332	3.339			
15.00	3.341	3.329	3.346			
17.50	3.346	3.336	3.346			
20.00	3.345	3.340	3.349			
25.00	3.354	3.346	3.356			
30.00	3.359	3.360	3.358			
35.00	3.365	3.374	3.366			

Buffer soln.: 0.1018M acid - 0.0982M sodium salt
Rare earth : 0.0040M except Ce^{+3}
Ce^{+3} : 0.003897M + 1.690×10^{-4}M $HClO_4$

XIII. APPENDIX D: OBSERVED THIOGLYCOLIC ACID SOLUTION pH'S

ml.buffer / 50ml.soln.	La^{+3}	Ce^{+3}	Pr^{+3}	Nd^{+3}	Sm^{+3}	Eu^{+3}
2.50	3.308	3.281	3.301	3.390	3.281	3.289
3.75	3.289	3.272	3.285	3.375	3.264	3.270
5.00	3.284	3.268	3.277	3.370	3.259	3.259
6.25	3.279	3.268	3.276	3.368	3.258	3.247
7.50	3.280	3.267	3.272	3.367	3.252	3.252
8.75	3.279	3.267	3.272	3.365	3.253	3.253
10.00	3.277	3.269	3.271	3.367	3.256	3.256
15.00	3.279	3.273	3.273	3.367	3.261	3.260
20.00	3.283	3.279	3.280	3.373	3.269	3.265
25.00	3.288	3.285	3.281	3.378	3.278	3.274
30.00	3.293	3.291	3.290	3.389	3.285	3.284
35.00	3.299	3.298	3.300	3.398	3.292	3.291

	Gd^{+3}	Tb^{+3}	Dy^{+3}	Ho^{+3}	Er^{+3}	Tm^{+3}
2.50	3.298	3.309	3.305	3.310	3.308	3.304
3.75	3.278	3.291	3.288	3.288	3.283	3.284
5.00	3.275	3.280	3.276	3.281	3.281	3.278
6.25	3.267	3.274	3.275	3.277	3.276	3.275
7.50	3.267	3.269	3.267	3.269	3.274	3.278
8.75	3.266	3.267	3.276	3.268	3.271	3.279
10.00	3.267	3.274	3.269	3.271	3.273	3.280
15.00	3.269	3.274	3.269	3.275	3.276	3.276
20.00	3.277	3.280	3.280	3.281	3.279	3.277
25.00	3.279	3.281	3.283	3.285	3.284	3.285
30.00	3.290	3.288	3.285	3.281	3.289	3.291
35.00	3.295	3.299	3.291	3.294	3.292	3.297

	Yb^{+3}	Lu^{+3}	Y^{+3}
2.50	3.301	3.306	3.311
3.75	3.284	3.283	3.297
5.00	3.278	3.273	3.280
6.25	3.270	3.266	3.277
7.50	3.266	3.264	3.271
8.75	3.264	3.263	3.269
10.00	3.266	3.265	3.271
15.00	3.266	3.268	3.274
20.00	3.275	3.271	3.273
25.00	3.279	3.274	3.277
30.00	3.291	3.282	3.291
35.00	3.294	3.285	3.299

Buffer soln.: 0.1089$\underline{M}$ acid - 0.0982$\underline{M}$ sodium salt

Rare earth : 0.0040$\underline{M}$ except Ce^{+3}

Ce^{+3} : 0.003897$\underline{M}$ + 1.690 x $10^{-4}\underline{M}$ $HClO_4$