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STEP FORMATION CONSTANTS OF SOME MALONATO
LANTHANIDE CHELATE SPECIES.

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STEP FORMATION CONSTANTS OF SOME MALONATO LANTHANIDE CHELATE SPECIES

by

Marvin Lee Adolphson

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DOCTOR OF PHILOSOPHY

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Approved:

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In Charge of Major Work

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Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Ames, Iowa

1969

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INTRODUCTION

The motivations for this research were fourfold. First, stability constants were needed to ascertain whether substituted malonic acids would be useful as eluants for ion-exchange separation of rare earths. Secondly, there was a paucity of experimental data in the literature regarding malonate complexes of the rare earths. Thirdly, stability constant data can sometimes be used indirectly to infer the structure of species in solution. Lastly, increasing the length of the substituent group on the central carbon atom of the malonate ligand should cause a greater degree of disruption of the outer hydration sphere around the rare-earth cation. Thus the length of the alkyl substituent group should serve as a probe to detect whether there is a significant entropy effect associated with disordering of the outer hydration sphere of rare-earth cations when complexing occurs.

A good review of the coordination chemistry of the rare earths is given in Chem. Reviews 65 (1). A review of the effects of substitutions on ligands which complex the rare earths is given by Schoeb (2).

Equilibrium studies of lanthanon-malonate systems has, to this time, been very limited in scope. The earliest work was performed by Ryabchikov and Terentéva (3). They predicted the existence of strong complexes between the rare-earth cations and malonic acid. Their prediction was based on the observation that no precipitates formed when the precipitating agent $Fe(CN)_6^{-4}$ was added to solutions containing rare-earth cations and malonic acid. However, they gave no indication as to kind or number of complex species formed or of the values of the stability constants for these complexes. They also studied the homologous dibasic acids (succinic, glutaric, and adipic). Many of the light rare-earth cations gave precipitates with anions of these acids; whereas, the heavy rare earths tended to form much more soluble species.

Gelles and Nancollas (4) were the next to examine malonato complexes of the rare earths. They studied the malonato complexes of lanthanum, gadolinium, and lutetium at 25° and 35°C. Their data were consistent with the formation of 1:1 and 2:1 malonato rare-earth chelate species. However, the authors only reported stability constant values for the 1:1 complex. The reported values are given below.

Table 1. K_1 for the 1:1 malonato species of lanthanum, gadolinium, and lutetium at $\mu=0$, data of Gelles and Nancollas (4)

rare-earth	K_1 25°C	K_1 35°C
La	1.00×10^5	1.30×10^5
Gd	2.45×10^5	3.25×10^5
Lu	5.25×10^5	7.00×10^5

These values were calculated at $\mu=0$ by using the Davies equation (5) for the activity coefficients involved in the equilibria.

Subsequent work was performed by Powell and co-workers (6). They studied the stability trends within the complete series of 1:1 and 2:1 malonato rare-earth chelate species at an ionic strength of 0.1<u>M</u>. Several dialkylmalonato rare-earth species were also investigated.

COMPUTATIONS

Stability Constants

A method for the computation of stability constants in labile systems from the function $\bar{n}(a)$ was first devised by J. Bjerrum (7). His method has been used for quite some time and by many workers in complex chemistry. The method takes advantage of our ability to follow the free ligand concentration by following the pH with a glass electrode and a potentiometer. This method is a particularly convenient and successful method when one has a ligand which is the anion of a weak organic acid.

It has been shown by others (8, 9, 10) that rare-earth cations do not complex with undissociated carboxylic acid. Thus, when a carboxylic acid complexes a cation there is an addition of hydrogen ion to the system. The hydrogen-ion concentration in such a metal-organic acid system can be accurately measured by means of a sensitive pH meter. If one also knows the ionization constants controlling the dissociation equilibria of the organic acid, one can easily calculate the free anion concentration in this system.

The experimentally determined quantity $\bar{n}$ can be expressed as a function of free anion concentration with the stability constants appearing as coefficients in this function. Thus knowing $\bar{n}$ and being able to determine free anion concentration allows one to compute stability constants.

In this study the coordinated waters about a rare-earth cation were replaced by a negatively charged organic ligand. A general equation would be:

$$B(H_2O)_x^h + A_{(aq)}^{-j} \rightleftarrows BA(H_2O)_{x-y}^{h-j} + yH_2O \ .$$

B represents the metal cation and A represents the organic anion. For simplicity, the hydration and charge of the species involved will not be shown in the equilibrium expressions. Thus the stepwise equilibrium will be written as:

$$B + A \rightleftarrows BA \ , \qquad (1)$$

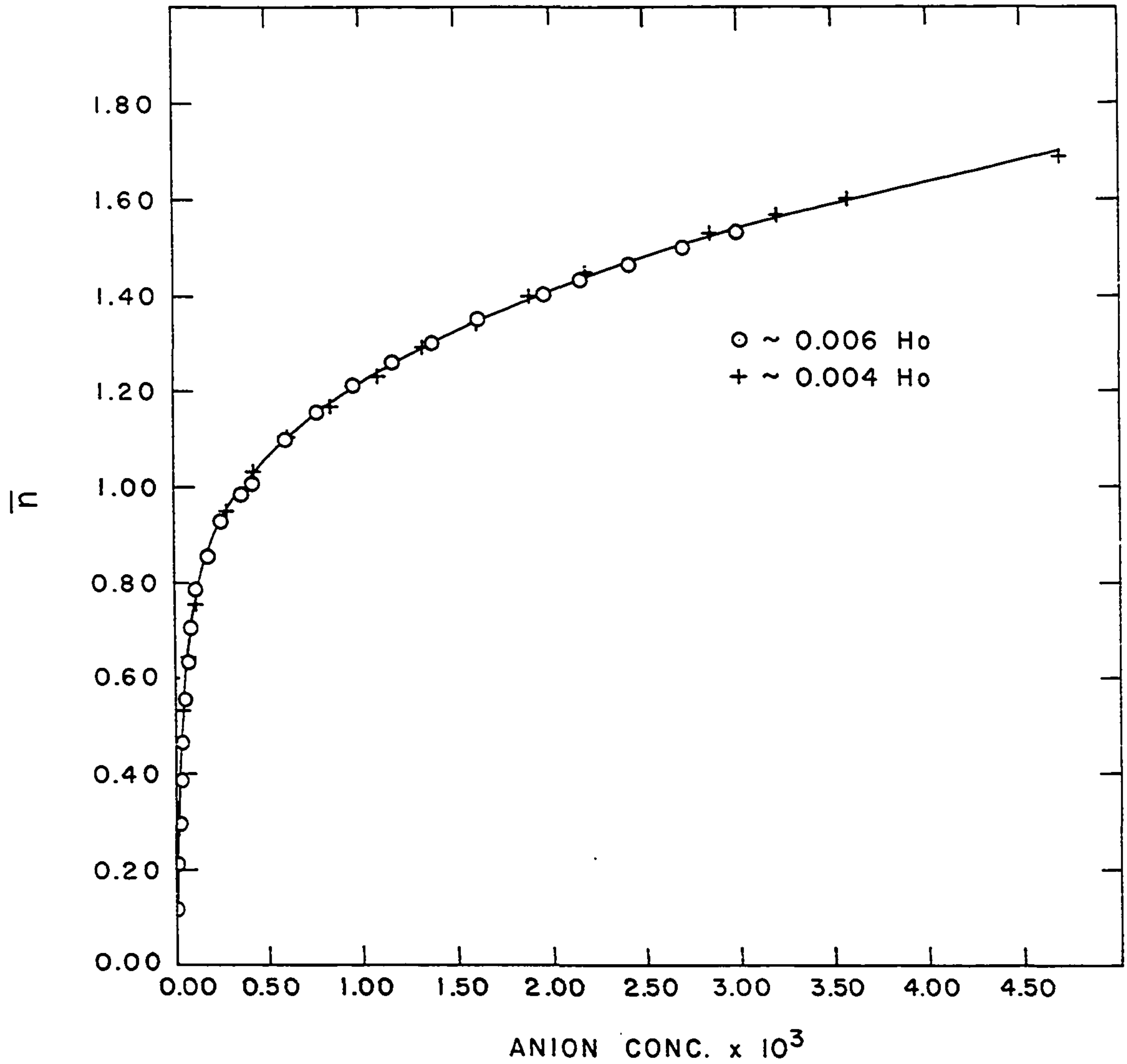
$$BA + A \rightleftarrows BA_2 \ , \qquad (2)$$

$$\cdots$$

$$BA_{N-1} + A \rightleftarrows BA_N \ . \qquad (3)$$

Since for mononuclear complexes $\bar{n}$ is a function only of free anion concentration, plots of $\bar{n}$ vs. free anion concentration at different metal concentrations should show different trends if polynuclear complexing is occurring. Plots of $\bar{n}$ vs. free anion concentration were determined for holmium ethylmalonato species at holmium concentration of 0.004<u>M</u> and 0.006<u>M</u>. The data is shown in Figure 1, and the points are seen to fall on the same curve at both concentrations. Polynuclear complexing of the form $pB + qA \rightleftarrows BpAq$ was thus shown not to occur (at least not to any appreciable

Figure 1. $\bar{n}$ versus anion concentration for holmium ethylmalonato species at two different concentrations of holmium



n̄
ANION CONC. x 10^3
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
1.80
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
○ ~ 0.006 Ho
+ ~ 0.004 Ho

extent) in the systems herein investigated.

In this study the calculated equilibrium constants are based on concentrations and are, therefore, not thermodynamic constants. To calculate thermodynamic constants one must determine the activity coefficients of the N+2 different species in the system. This oftentimes is a quite formidable task. However, for our purposes the stoichiometric constants are just as useful and much easier to obtain.

If the activity coefficients of all the species are held effectively constant throughout the investigation, measurements of at least N sets of data leads to N stoichiometric stability constants. The activity coefficients in these studies were held constant by the constant-ionic-medium method described by Rossotti and Rossotti (11). The ionic strength was maintained at 0.100M by addition of potassium nitrate.

The consecutive step formation constants representing Equations 1 through 3 can now be given as:

$$b_1 = \frac{[BA]}{[B][A]} , \qquad (4)$$

$$b_2 = \frac{[BA_2]}{[BA][A]} , \qquad (5)$$

$$b_3 = \frac{[BA_N]}{[BA_{N-1}][A]} . \qquad (6)$$

The brackets represent concentration of the species contained therein. The equilibria can also be written as:

$$B + A \rightleftarrows BA\ , \tag{7}$$

$$B + 2A \rightleftarrows BA_2\ , \tag{8}$$

$$\cdot\ \cdot\ \cdot$$

$$B + NA \rightleftarrows BA_N\ . \tag{9}$$

The constants representing these equilibria are:

$$\beta_1 = \frac{[BA]}{[B][A]}\ , \tag{10}$$

$$\beta_2 = \frac{[BA_2]}{[B][A]^2}\ , \tag{11}$$

$$\beta_N = \frac{[BA_N]}{[B][A]^N}\ . \tag{12}$$

The relationship between the b's and β's is

$$\beta_n = \prod_{i=1}^{n} b_i\ , \tag{13}$$

where β_o is defined as unity. The reader is again reminded that the b_n and β_n values are stoichiometric constants and are related to the thermodynamic constants b_n and β_n as follows:

$$b_n = \frac{[BA_n]}{[BA_{n-1}][A]} = b_n^* \frac{\gamma_{BA_{n-1}}\gamma_A}{\gamma_{BA_n}}\ ,$$

and

$$\beta_n = \frac{[BA_n]}{[B][A]^n} = \beta_n^* \frac{\gamma_B \gamma_A{}^n}{\gamma_{BA_n}} ,$$

where the brackets represent molar concentrations and the γ's are activity coefficients.

If the activity coefficients are defined with respect to the solute standard state, they will approach one as the concentrations of all the species approach zero. Thus, at infinite dilution β_n^* will equal β_n. One can therefore estimate the thermodynamic stability constants by extrapolating stoichiometric stability constants at various ionic strengths to zero ionic strength.

At this point the following quantities will be defined:

A = total ligand concentration in solution,

a = free (uncomplexed) ligand concentration,

B = total metal ion concentration,

b = free (uncomplexed) metal cation concentration.

Values of A and B are known from the preparation of each solution. The quantity a can be determined from the pH of the solution and the dissociation constants of the ligand acid being investigated. The mean ligand number is now defined as

$$\bar{n} = \frac{A-a}{B} . \qquad (14)$$

We note that A and B can be written as:

$$A = a + b \sum_{n=0}^{N} n\beta_n a^n , \qquad (15)$$

$$B = b \sum_{n=0}^{N} \beta_n a^n . \qquad (16)$$

If we substitute these expressions into Equations 14 we have

$$\bar{n} = \frac{A-a}{B} = \frac{\sum_{n=0}^{N} n\beta_n a^n}{\sum_{n=0}^{N} \beta_n a^n} . \qquad (17)$$

Equation 17 may be rearranged to give

$$\sum_{n=0}^{N} (A_i - a_i - nB_i)\beta_n a^n = 0 , \qquad (18)$$

where the subscript i identifies a discrete experimental data set (A_i, a_i, B_i). Equation 18 can be fitted to a set of data points by the method of least squares. Since Equation 18 does not exactly fit a given set of data points we can expect a residual, U_i, for each data point in the set. Thus,

$$\sum_{n=0}^{N} (A_i - a_i - n\ _i)\beta_n a^n = U_i \; .. \qquad (19)$$

These residuals are squared, weighted, (using the procedure of Sullivan, Rydberg, and Miller (12) and Rydberg (13)), and finally summed. Hence,

$$S = \sum_{i=1}^{I} w_i U_i^{\,2} , \qquad (20)$$

where

$$W_i = 1/\delta U_i^{\,2} \qquad (21)$$

and

$$\delta U_i = \frac{\partial U_i}{\partial a_i}\, a_i m \;. \qquad (22)$$

The quantity m is the estimated relative error in evaluating a_i from pH_c measurements and is set at 0.002. $\frac{\partial U_i}{\partial a_i}$ is evaluated from Equation 19 using estimated β_n values. The quantity S is minimized with respect to each of the β_n parameters. This yields N equations which are solved to give the best individual β_n values. These β_n values are used to recalculate a new set of W_i and the process is repeated until the latest β_n values differ from the previous β_n values by less than 0.01%.

The above mathematical operations were written into a computer program by W. R. Stagg (14). All calculations were performed on the IBM 360 computer.

Ionization Constants for Dibasic Acids

For a weak dibasic acid, the following equilibria exist:

$$H_2A \rightleftarrows HA^- + H^+ , \qquad (23)$$

$$HA^- \rightleftarrows H^+ + A^= \;. \qquad (24)$$

Ionization constants for these equilibria are defined as

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]} , \tag{25}$$

$$K_2 = \frac{[H^+][A^=]}{[HA^-]} , \tag{26}$$

and their product is

$$K_1K_2 = \frac{[H^+]^2[A^=]}{[H_2A]} . \tag{27}$$

We now introduce two material balance equations:

$$C_H = 2[H_2A] + [HA^-] + [H^+] , \tag{28}$$

$$C_A = [H_2A] + [HA^-] + [A^=] . \tag{29}$$

If we add a known amount of base (KOH) to the system, we will then have the additional equations:

$$C_H = 2C_A - [K^+] + [OH^-] , \tag{30}$$

$$[K^+] + [H^+] = [HA^-] + 2[A^=] + [OH^-], \tag{31}$$

where $[K^+]$ equals the concentration of base in the system. From Equations 28 and 30 we obtain

$$2C_A - [K^+] - [H^+] + [OH^-] = 2[H_2A] + [HA] \tag{32}$$

and from Equation 31 we have

$$[K^+] + [H^+] - [OH^-] = [HA^-] + 2[A^=] . \tag{33}$$

The $[OH^-]$ is negligible for solutions whose pH is below 7. We now divide Equation 32 by Equation 33.

$$\frac{2C_A - [K^+] - [H^+]}{[K^+] + [H^+]} = \frac{2[H_2A] + [HA^-]}{[HA^=]+2[A^=]} \qquad (34)$$

We may now substitute for $[H_2A]$ and $[HA^-]$ from the equilibrium expressions 25 and 27

$$[HA^-] = [H^+][A^=]1/K_2 = [H^+][A^=]\alpha_1 \qquad (35)$$

$$[H_2A] = [H^+]^2[A^=]\frac{1}{K_1K_2} = [H^+]^2[A^=]\alpha_2 \qquad (36)$$

where $\alpha_1 = 1/K_2$ and $\alpha_2 = 1/K_1K_2$.

Now

$$\frac{2C_A-[K^+]-[H^+]}{[K^+]+[H^+]} = \frac{2\alpha_2[H^+]^2[A^=]+\alpha_1[H^+][A^=]}{\alpha_1[H^+][A^=]+2[A^=]} \qquad (37)$$

By cross multiplying Equation 37 and rearranging we can obtain

$$\frac{2C_A-[K^+]-[H^+]}{([K^+]+[H^+])[H^+]^2} = \frac{([K^+]+[H^+]-C_A)}{[H^+]([K^+]+[H^+])}\alpha_1 + \alpha_2 \qquad (38)$$

which is a straight line equation of the form $y=mx+b$. This equation is fit to a set of data points by the method of least squares; whereupon, we may obtain $1/K_2$ from the slope and $1/K_1K_2$ from the intercept.

EXPERIMENTAL DETAILS

Preparation of Reagents

Rare-earth nitrate stock solutions

Rare-earth nitrate stock solutions, ∿0.5M in $Ln(NO_3)_3$, were prepared by an adaptation of the procedure described by Stagg and Powell (14) for preparing neutral rare-earth perchlorate solutions. These stock solutions were prepared from 99.99% pure rare-earth oxides (obtained from the Ames Laboratory rare-earth separation group of Dr. J. E. Powell) and "Analyzed Reagent" nitric acid from the J. T. Baker Chemical Company. The solutions were prepared by combining a slight excess of oxide with nitric acid and heating at approximately 80°C for six hours. The reaction is:

$$M_2O_3 + 6HNO_3 = 2M(NO_3)_3 + 3H_2O .$$

The resulting reaction mixtures were diluted to a volume of one liter. These mixtures were acid deficient and approximately 1M in rare-earth concentration. The solutions were then filtered to remove undissolved material. An aliquot was taken from each solution and titrated with 1M HNO_3. The equivalence point pH was determined by constructing plots of (pH) versus (volume of titrant), (ΔpH/Δvolume) versus (volume titrant), and Δ(ΔpH)/Δ(Δvolume) versus volume titrant. All solutions yielded very good titration curves and representative plots are presented in Figures 2, 3, and 4. Each stock solution was then titrated to its respective equivalence point pH. Praseodymium, neodymium and samarium were titrated at room temperature. The remaining rare-earth solutions were titrated at 50°C in a constant temperature bath. Titration at room temperature was kinetically slow as indicated by drifting pH values. However, titration at 50°C gave immediately steady pH readings and a sharp change in pH at the equivalence point. The constant temperature bath and accompanying equipment are pictured in Figure 5. After the solutions were brought to their equivalence point pH's, they were heated for 24 hours at 86°C. The solution pH was then checked and adjusted if necessary by adding additional HNO_3. The above procedure was continued until no further change in pH occurred. These solutions were then diluted to a final volume of two liters.

Aliquots of each of these solutions were analyzed for rare-earth metal content by oxalate precipitation and ignition (15), as well as by the EDTA titration (16). A comparison of the two methods is given in Table 2. The nitrate content was determined by passing aliquots through a bed of cation-exchange resin in the H^+ form, and titrating the combined effluent and washings with standard base. With all the rare-earth solutions, except $Ce(NO_3)_3$, the ratio of nitrate to rare-earth was $3.000 \pm .005$. the cerium nitrate

Figure 2. Titration curve for gadolinium nitrate at 50°C

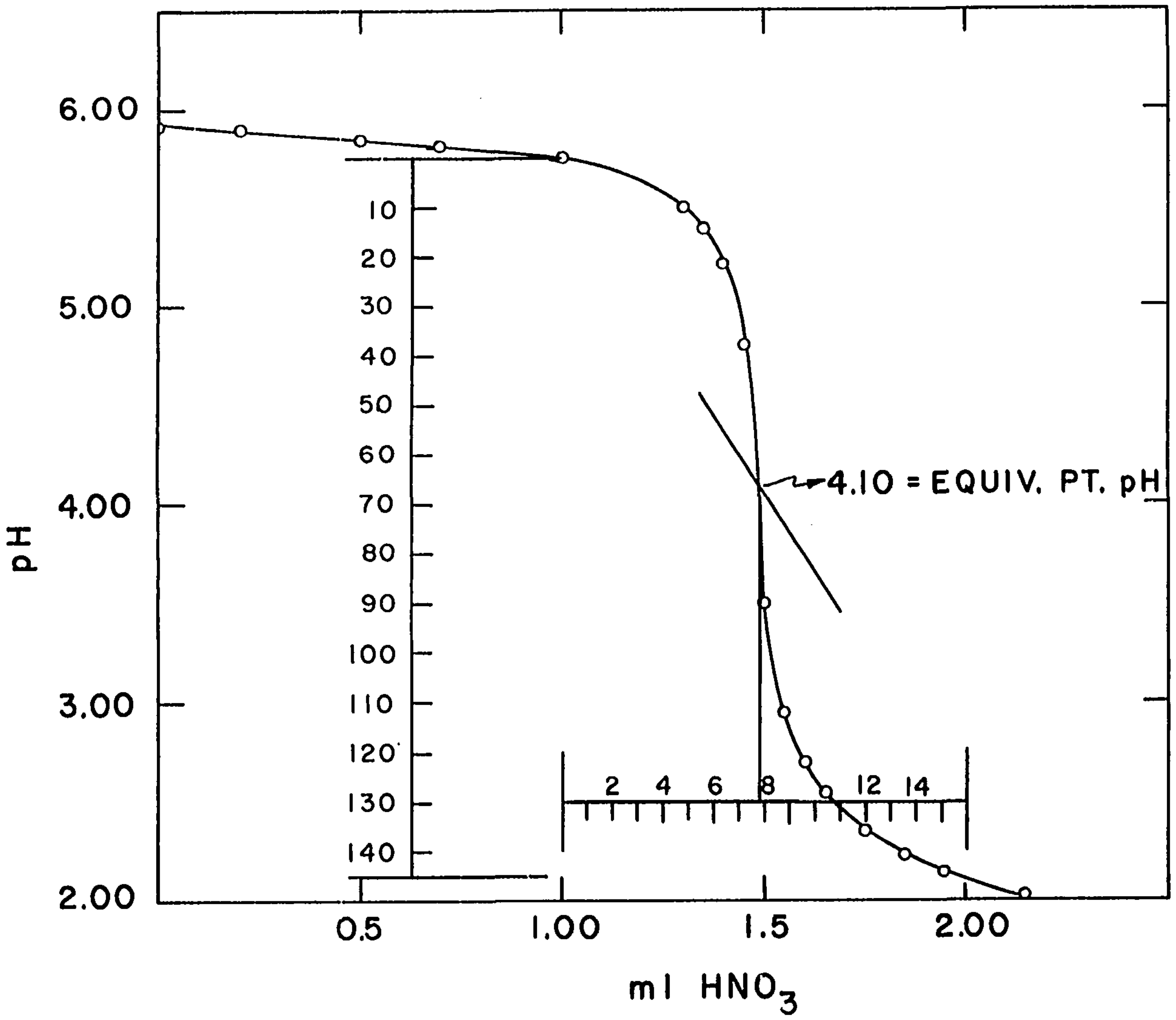

6.00
5.00
4.00
3.00
2.00
pH
10
20
30
40
50
60
70
80
90
100
110
120
130
140
2
4
6
8
12
14
4.10 = EQUIV. PT. pH
0.5
1.00
1.5
2.00
ml HNO$_3$

Figure 3. ΔpH/Δvolume versus volume titrant for gadolinium nitrate at 50°C.

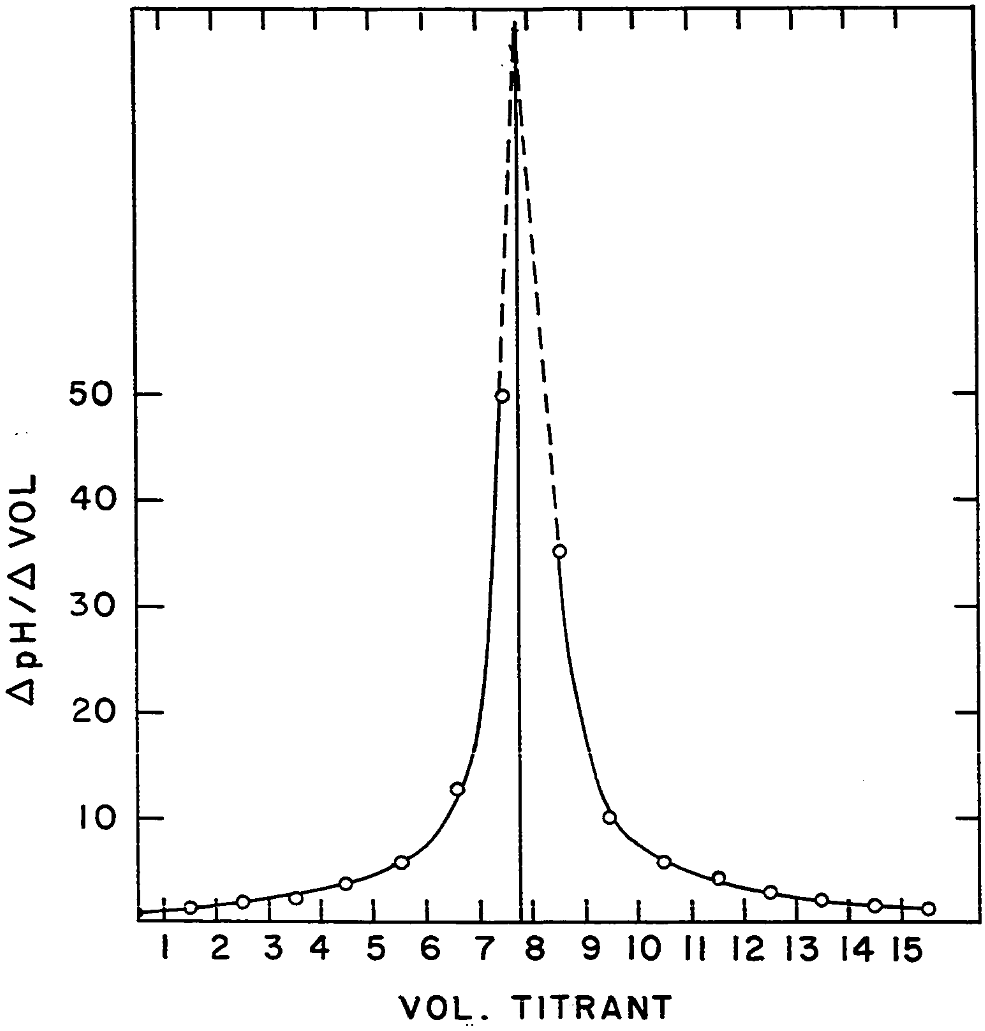

50
40
30
20
10
ΔpH/Δ VOL
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
VOL. TITRANT

Figure 4. Δ(ΔpH)/Δ(Δvolume) versus volume titrant for gadolinium nitrate at 50°C

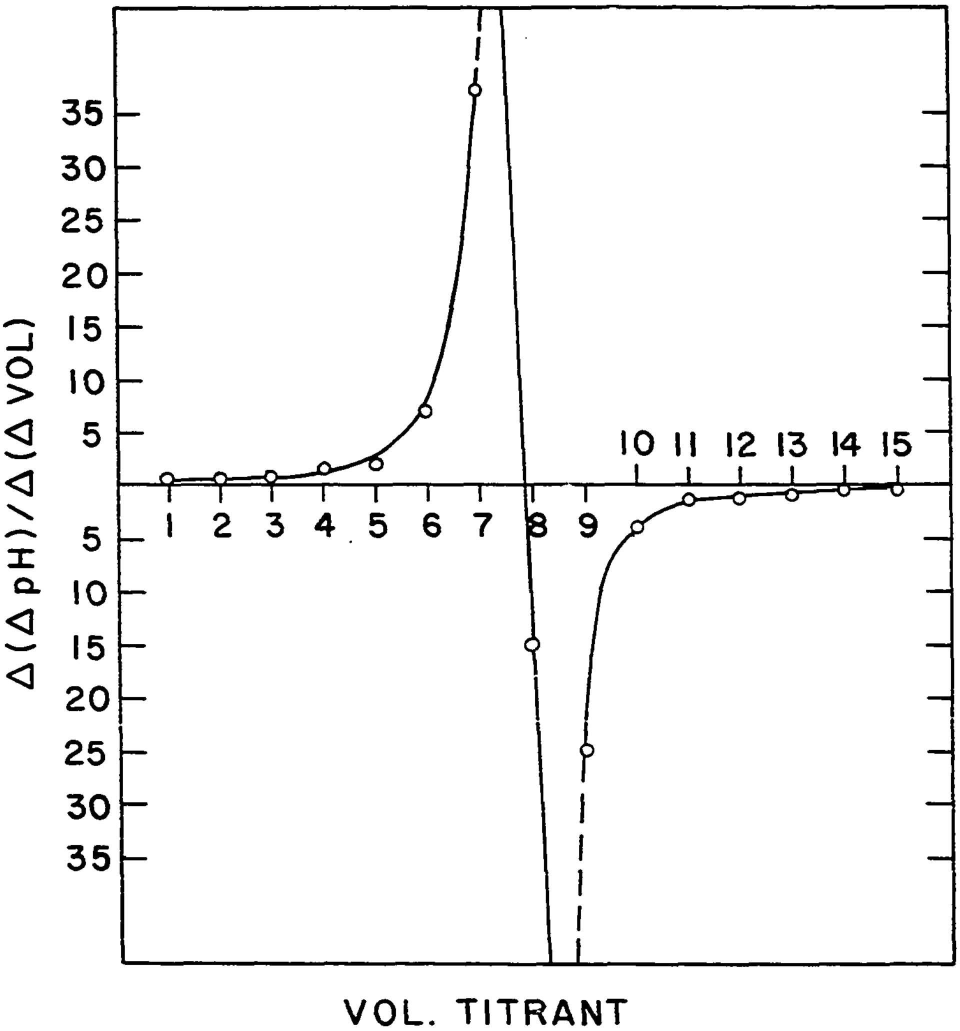

Δ(ΔpH)/Δ(ΔVOL)
35
30
25
20
15
10
5
5
10
15
20
25
30
35
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
VOL. TITRANT

Figure 5. Apparatus used in determining equivalence point pH's of rare-earth nitrate stock solutions

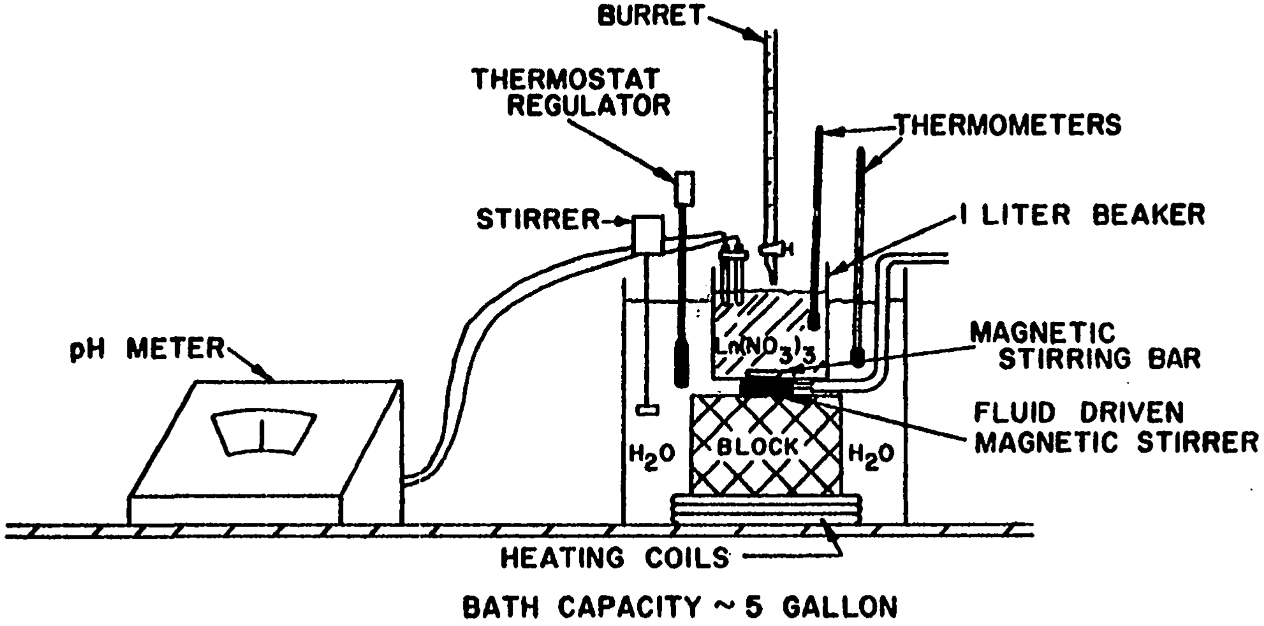

BURRET
THERMOSTAT REGULATOR
THERMOMETERS
STIRRER
1 LITER BEAKER
pH METER
$Ln(NO_3)_3$
MAGNETIC STIRRING BAR
FLUID DRIVEN MAGNETIC STIRRER
H_2O
BLOCK
H_2O
HEATING COILS
BATH CAPACITY ~ 5 GALLON

Table 2. Comparison of concentrations of stock rare-earth nitrate solutions

Rare earth	Method EDTA titration	 Oxalate precipitation
	(concentration in Molarity)	
Ce	0.09989	0.1001
Pr	0.10037	0.1006
Sm	0.1010	0.1018
Gd	0.09970	0.1003
Tb	0.1008	0.1006
Ho	0.1012	0.1016
Tm	0.1002	0.1004
Lu	0.1006	0.1010

solution contained a slight excess of HNO_3 in order to stabilize the Ce^{+3} ion. Rare-earth nitrate solutions of ∿0.1M were prepared by diluting aliquots of the above stock solutions. These dilute solutions were re-analyzed for rare-earth content by oxalate precipitation and ignition. These concentrations were taken as the correct concentrations.

Potassium nitrate solution

A potassium nitrate solution of ∿1.5M was prepared by dissolving Baker "Analyzed Reagent" potassium nitrate in freshly distilled water. The solution was standardized by passing aliquots through a hydrogen-form Dowex 50 ion-exchange resin bed. The resultant nitric acid was titrated with standard base. The average of four determinations was taken as the correct concentration.

Acids

All the acids were made by saponifying their respective diethyl esters. The saponifications were performed in absolute alcohol using KOH as base. The resulting potassium salts were insoluble and precipitated from the reaction mixture. The salts were filtered and washed with absolute alcohol and petroleum ether. These salts were then dried in air, dissolved in distilled water, and finally converted to their respective acids by adding calculated amounts of dilute HCl. The acids were extracted into ether and recovered by evaporation of the ether under vacuum. Methylmalonic, ethylmalonic, and propylmalonic acids were purified by recrystallization from a CCl_4-acetone mixture in which just enough acetone was added to permit complete dissolution of the acid in hot CCl_4. Butylmalonic acid and pentylmalonic acid were re-crystallized from benzene. The purified acids were dried in a vacuum desiccator over magnesium perchlorate. They were analyzed by melting point and equivalent weight titrations with standard base. The melting points and equivalent weights are given in Table 3.

Buffer solutions

Buffer solutions were prepared by 3/4 neutralizing a known amount of acid with an accurately measured volume of standard CO_2-free base. The buffers were prepared in 2-liter

Table 3. Melting points and observed equivalent weights

Acid	mp (°C)		Equivalent weight	
	Found	Lit.	Found	Theory
Methyl Malonic	-	135(d)	59.38	59.05
Ethyl Malonic	111-112	111.5	66.31	66.05
Propyl Malonic	94-96	96	73.0	73.07
Butyl Malonic	103-105	-	78.20	80.0
Pentyl Malonic	81-83	-	85.90	87.0

batches containing 0.05 N acid and 0.15 N salt of the acid. The exact amount of un-neutralized acid was determined by titrating three aliquots of the buffer with standard base.

Potassium hydroxide solution

A standard potassium hydroxide solution was prepared by the method of Powell and Hiller (17) and standardized against oven-dried reagent grade potassium acid phthalate.

Technique

All work involved in the determination of stability constants consisted of carefully preparing and standardizing solutions and making careful pH measurements. The calculations were done by computer and details are given under

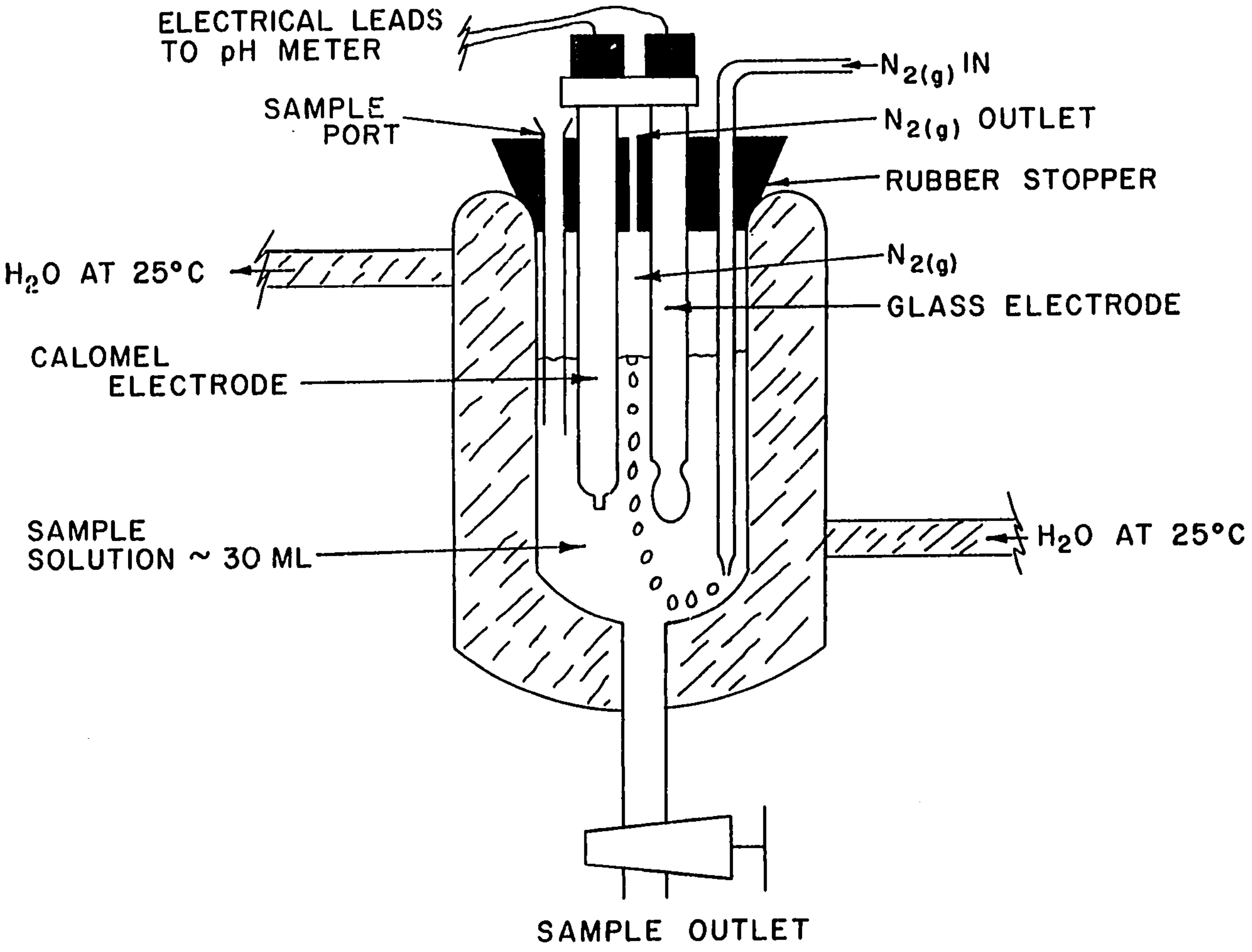
"Computations".

A Beckman Research pH Meter, Model 1019, was used for all pH measurements. A Beckman regular glass electrode was used in conjunction with a carborundum frit Beckman calomel reference electrode. The pH could be read to a precision of 0.001 pH units. The thermostated sample container and electrodes are pictured in Figure 6.

The pH meter was standardized to read hydrogen-ion concentrations at 0.100M ionic strength. Thus, all pH measurements are given in terms of pH based on concentration and will be denoted pH_c. The standard was prepared by diluting a standardized hydrochloric acid solution to yield a solution of defined hydrogen-ion concentration whose ionic strength was adjusted to 0.100M by adding potassium nitrate. The pH_c standard was prepared so as to have a pH_c value near the midpoint of the pH_c range to be investigated. The pH meter was then standardized before each run and again checked at the end of each run.

The ionization constants of each acid must first be evaluated before stability constants can be determined. The ionization constants were evaluated by a method similar to that of Speakman (18). A series of twenty 100-ml. solutions was prepared for each acid. Each solution contained 10.00 ml. of a standard acid solution (∿0.1M), varying amounts of standard KOH, and enough KNO_3 to maintain the ionic strength

Figure 6. Cross section of constant temperature cell and electrodes used for pH measurements


ELECTRICAL LEADS TO pH METER
SAMPLE PORT
$N_{2(g)}$ IN
$N_{2(g)}$ OUTLET
RUBBER STOPPER
H_2O AT 25°C
$N_{2(g)}$
GLASS ELECTRODE
CALOMEL ELECTRODE
SAMPLE SOLUTION ~ 30 ML
H_2O AT 25°C
SAMPLE OUTLET

at 0.100M. Along this series the degree of acid neutralization ranged from 1/4 neutralized to 3/4 neutralized. The pH_c of these solutions was then read by means of the Beckman Research pH Meter. The first and second ionization constants were then calculated as shown under "Computations."

The complex studies involved preparing a series of twenty-five solutions (similar to those used for determining the acid ionization constants) for each metal cation investigated. A complete series of twenty-five solutions could not be prepared for some of the light rare-earths with the bulky butyl and pentyl substituted ligands since precipitation occurred in these solutions. The solutions were prepared in 100-ml. volumetric flasks. Each flask in the series contained a constant amount of rare-earth nitrate and varying amounts of buffer and KNO_3. Enough KNO_3 was added to maintain the ionic strength at 0.100M. The amount of buffer varied along the series such that the metal to ligand ratio ranged from 4:1 to 1:6. These solutions were then allowed to equilibrate in a constant temperature bath at 25.00±0.05°C for a period of six hours. The pH_c of each solution was then read by means of the Beckman Research pH Meter. Each 100-ml. solution was divided into three portions. The first portion was used to rinse the electrodes, the second portion was used to soak the electrodes, and the third portion was used to obtain the pH_c reading.

Solid Malonates

Most of the Nd, Pr, Ce, and La malonate solids were obtained as precipitates from the samples which were prepared for stability constant measurements. The remaining solids were prepared by concentrating a 3:1 solution of buffered acid and rare-earth nitrate by evaporation. The solids were filtered, washed and then air-dried.

Samples of approximately 0.2 g. were weighed out into small platinum crucibles for thermogravimetric analysis. Thermograms were recorded over a temperature range of 465°C. A heating rate of 0.5 deg./min. was used and a maximum temperature of 480°C was reached.

After the thermobalance run, the samples were placed in a muffle furnace and ignited to the oxides. The oxides were weighed and the moles of metal per sample were calculated. The molecular weight of the starting material could then be calculated. Four significant figures were carried through the calculations. The molecular weights calculated were found to be consistent with the general formula $\mathrm{Ln(malonate)}_{1.5}x\mathrm{H_2O}$ where x has integral values only.

Since copper sulfate forms a well-defined five hydrate, a thermobalance run was also made on this compound. The temperature at which these coordinated waters were lost were hoped to be of some value in determining coordinated versus uncoordinated water in the rare-earth compounds. The condition of bound versus trapped or adsorbed water can sometimes be difficult to ascertain. The above thermobalance data is summarized in Table 13 of the "Results" section. As a check on the thermogravimetric analysis a carbon hydrogen and metal analysis was performed on erbium butylmalonate and on neodymium butylmalonate. The analytical work was performed by the Analytical Chemistry Gruop I of Ames Laboratory and the results are given below.

Table 4. Elemental analysis of solids

	$Er(butylmalonate)_{1.5} \cdot 3H_2O$				$Nd(butylmalonate)_{1.5} \cdot 4H_2O$			
	1st	2nd	Avg.	Theory	1st	2nd	Avg.	Theory
%C	28.40	28.51	28.46	27.4	25.89	25.89	25.89	27.7
%H	4.60	4.30	4.45	4.56	4.06	4.13	4.10	5.05
%Ln	36.55	36.55	36.55	36.3	34.55	34.62	34.6	31.6

Several IR spectra were taken of the solid rare-earth malonates. The spectra were recorded by Dr. Fassel's analytical group of Ames Laboratory. Structural data could not be inferred from the spectra, but absorption bands due to hydrated water could be assigned. The IR results are given in Tables 11 and 12 of the "Results" section. Sketches of the spectra are shown in the Appendix.

An attempt to obtain the coordination number of Lu^{+3} by means of NMR spectra was made. It had been demonstrated by Fratiello and Schuster (19, 20) that at low temperatures separate NMR signals can be seen for coordinated water and bulk water in diamagnetic salt-mixed solvent systems. Knowing all initial concentrations and integrating the separate water signals will permit calculation of coordination number. This method has been applied to the diamagnetic ions Al(III) (19, 20, 21, 22), Be (II), Ga (III), In (III) (21), and Mg (II) (22, 23).

Several lutetium nitrate solutions were prepared using the mixed solvents, water-acetone and water-DMSO. The lutetium nitrate concentration, the ratio of water:acetone, and the ratio of water:DMSO were all varied from one sample solution to another. NMR spectra were run on these solutions at various temperatures down to their freezing points. The spectra were run on a Varian HA-100 NMR spectrometer by Dr. Roy King's group at Iowa State University.

Separation of the water peak was not observed for any of the solutions. The last sample solution (with the composition $Lu(NO_3)_3 = 1\underline{M}$, 1 mole H_2O:1 mole acetone) was lowered to a temperature of -80°C, but no separation of the water peak was observed. The spectra for this sample are shown in the Appendix.

EXPERIMENTAL RESULTS

The data for the rare-earth complexes with the substituted malonate ligands are tabulated in Tables 5 through 9. Plots of Log K_1 versus atomic radius, Log K_2 versus atomic radius and Log β_2 versus atomic radius are presented in Figures 7 through 10.

The computer prints out the calculated $\bar{n}$, ($\bar{n}_{calc.}$), and the experimental $\bar{n}$, ($\bar{n}_{exp.}$). The calculated $\bar{n}$ is compared with $\bar{n}_{exp.}$ and data points for which $\bar{n}_{exp.}$ differed from $\bar{n}_{calc.}$ by 1% or greater were discarded from the data set.

Convergence of the β's was obtained in five iterations or less. The standard deviation in each β was computed by the equation

$$\sigma_{\beta_n} = \pm \sqrt{r_{nn} \, S/(I-N)}$$

where r_{nn} is the diagonal element of the inverse coefficient matrix. These deviations are the errors of internal consistency and reflect the overall fit of the calculated curve to the experimental points. In order to reveal something about the errors in the β's caused by errors in volume measurements, concentrations, ionization constants of the acids, etc., these data were varied within their estimated maximum limits of error and the effects on the β's noted. It was found that the maximum variation in the β's could be

Table 5. Stability constants for 1:1, 1:2, and 1:3 rare-earth methylmalonate species at 25°C, μ=0.100 (KNO_3 used as supporting electrolyte)

rare earth	$\bar{n}_{max}$ achieved	$(\beta_1=b_1)\text{x}10^{-4}$	$\beta_2\text{x}10^{-6}$	$\beta_3\text{x}10^{-7}$	$b_2\text{x}10^{-2}$	b_1/b_2	b_3	b_2/b_3
La	1.47	0.303±0.02	0.476±0.01	-	1.57	19	-	-
Ce	1.30	0.563±0.0007	1.22±0.07	-	2.17	26	-	-
Pr	1.56	0.595±0.002	1.55±0.01	-	2.62	23	-	-
Nd	1.58	0.659±0.002	1.68±0.02	-	2.54	26	-	-
Sm	1.64	1.18±0.007	3.66±0.04	2.31±0.6	3.09	38	7	49
Eu	1.64	1.43±0.01	4.47±0.05	3.48±0.8	3.13	45	8	40
Gd	1.63	1.50±0.01	4.20±0.05	3.33±0.8	2.79	54	9	35
Tb	1.70	1.98±0.007	6.82±0.03	10.5±0.6	3.44	58	15	22
Dy	1.75	2.31±0.01	8.50±0.06	23.4±1.2	3.68	63	27	13
Ho	1.71	2.14±0.01	7.27±0.05	15.1±0.9	3.39	63	21	16
Er	1.66	2.07±0.01	6.68±0.06	8.79±1.0	3.23	64	13	24
Tm	1.70	2.12±0.01	7.43±0.07	10.7±1.1	3.50	61	14	24
Yb	1.68	2.27±0.01	8.63±0.08	12.4±1.5	3.80	60	14	26
Lu	1.69	2.01±0.01	7.73±0.04	11.5±0.4	3.84	52	15	26
Y	1.57	1.61±0.02	4.00±0.5	3.51±1.0	2.48	65	8.7	28

Table 6. Stability constants for 1:1, 1:2, and 1:3 rare-earth ethylmalonate species at 25°C, $\mu=0.100$ (KNO_3 used as supporting electrolyte)

rare earth	$\bar{n}_{max}$ achieved	$(\beta_1=b_1)x10^{-4}$	β_2x10^{-6}	β_3x10^{-8}	b_2x10^{-2}	b_1/b_2	b_3	b_2/b_3
La	1.28	0.379±0.002	0.823±0.02	0.303±0.06	2.17	17	36	5.8
Ce	1.61	0.487±0.002	1.45±0.01	0.0847±0.02	2.97	16	5.8	51
Pr	1.73	0.62±0.002	2.11±0.01	0.409±0.02	3.36	19	19	17
Nd	1.75	0.708±0.003	2.43±0.02	0.536±0.03	3.43	21	22	15
Sm	1.75	1.31±0.01	4.27±0.06	1.75±0.1	3.26	40	41	7.9
Eu	1.80	1.79±0.01	7.52±0.08	2.91±0.1	4.20	43	38	11
Gd	1.74	1.86±0.01	6.61±0.09	2.74±0.2	3.55	52	42	8.5
Tb	1.75	2.42±0.02	9.75±0.08	3.59±0.2	4.03	60	37	11
Dy	1.95	2.84±0.01	12.3±0.1	7.86±0.2	4.33	65	63	6.9
Ho	1.83	2.52±0.009	9.37±0.07	4.91±0.1	3.72	68	52	7.1
Er	1.81	2.41±0.007	9.27±0.07	4.07±0.1	3.84	63	44	8.7
Tm	1.83	2.46±0.008	9.98±0.006	4.00±0.1	4.06	61	45	9.7
Yb	1.86	2.57±0.007	11.3±0.05	5.08±0.1	4.37	59	40	10
Lu	1.77	2.28±0.02	9.65±0.1	3.24±0.3	4.23	54	34	13
Y	1.67	2.11±0.004	6.65±0.04	1.57±0.7	3.16	66	24	13
Cu	1.62	7.59±0.04	84.1±0.8	18.0 ±4	11.1	68	23	51

Table 7. Stability constants for 1:1, 1:2, and 1:3 rare-earth propylmalonate species at 25°C, μ=0.100 (KNO_3 used as supporting electrolyte)

rare earth	$\bar{n}_{max}$ achieved	$(\beta_1=b_1)x10^{-4}$	β_2x10^{-6}	β_3x10^{-8}	b_2x10^{-2}	b_1/b_2	b_3	b_2/b_3
La								
Ce		NO VALUES DUE TO PRECIPITATION						
Pr								
Nd	0.75	0.674±0.05	4.72±1.0	-	7.00	9.6	-	-
Sm	1.76	1.54±0.007	6.92±0.04	1.61±0.09	4.51	34	23	19
Eu	1.75	1.97±0.01	8.50±0.08	2.10±0.10	4.31	46	25	17
Gd	1.74	2.06±0.007	7.95±0.04	2.09±0.08	3.85	54	26	15
Tb	1.78	2.79±0.01	12.4±0.01	4.24±0.3	4.42	63	34	12
Dy	1.77	3.05±0.007	13.2±0.007	3.32±0.1	4.32	71	25	17
Ho	1.76	2.88±0.009	11.5±0.009	3.50±0.2	3.97	72	31	13
Er	1.75	2.88±0.01	11.4±0.01	3.40±0.2	3.97	73	30	13
Tm	1.79	2.86±0.01	12.2±0.01	4.00±0.2	4.25	67	33	13
Yb	1.80	3.02±0.008	14.5±0.01	4.78±0.2	4.81	63	33	15
Lu	1.82	2.66±0.009	12.8±0.009	4.79±0.2	4.79	55	37	13
Y	1.73	2.32±0.01	7.14±0.08	2.56±0.1	3.09	75	36	8.6

Table 8. Stability constants for 1:1, 1:2, and 1:3 rare-earth butylmalonate species at 25°C, μ=0.100 (KNO_3 used as supporting electrolyte)

rare earth	$\bar{n}_{max}$ achieved	$(\beta_1=b_1)\times10^{-4}$	$\beta_2\times10^{-6}$	$\beta_3\times10^{-8}$	$b_2\times10^{-2}$	b_1/b_2	b_3	b_2/b_3
La								
Ce	NO VALUES DUE TO PRECIPITATION							
Pr								
Nd	0.56	0.77±0.03	2.40±0.1	-	3.11	25	-	-
Sm	1.83	1.42±0.008	6.17±0.09	1.17±0.06	4.35	33	19	23
Eu	1.72	1.76±0.01	7.18±0.08	1.20±0.1	4.07	43	17	24
Gd	1.70	1.83±0.02	6.68±0.10	1.05±0.2	3.65	50	16	23
Tb	1.66	2.41±0.01	9.74±0.10	2.09±0.2	4.03	60	22	19
Dy	1.73	2.58±0.01	10.3±0.01	1.77±0.1	3.98	65	17	23
Ho	1.55	2.40±0.01	8.85±0.1	2.61±0.3	3.68	65	30	12
Er	1.71	2.43±0.01	9.12±0.1	1.80±0.2	3.75	65	20	19
Tm	1.69	2.47±0.009	10.1±0.007	2.09±0.1	4.09	60	21	20
Yb	1.72	2.55±0.01	11.6±0.009	2.64±0.2	4.56	56	23	20
Lu	1.77	2.30±0.01	10.6±0.01	2.46±0.2	4.62	50	23	20
Y	1.63	1.95±0.01	5.38±0.08	0.748±0.1	2.76	71	14	20

Table 9. Stability constants for 1:1, 1:2, and 1:3 rare-earth pentylmalonate species at 25°C, μ=0.100 (KNO_3 used as supporting electrolyte)

rare earth	$\bar{n}_{max}$ achieved	$(\beta_1=b_1)\times10^{-4}$	$\beta_2\times10^{-6}$	$\beta_3\times10^{-9}$	$b_2\times10^{-2}$	b_1/b_2	b_3	b_2/b_3
La								
Ce		NO VALUES DUE TO PRECIPITATION						
Pr								
Nd								
Sm								
Eu	1.26	2.09±0.03	8.88±0.9	3.25±1.0	4.24	49	366	1.2
Gd	1.57	2.13±0.01	9.48±0.3	1.16±0.1	4.44	48	122	3.6
Tb	1.55	2.77±0.02	12.5±0.04	1.70±0.2	4.50	62	136	3.3
Dy	1.59	3.07±0.02	14.0±0.04	1.82±0.1	4.56	67	130	3.7
Ho	1.64	2.84±0.01	11.8±0.03	1.37±0.1	4.17	68	115	3.6
Er	1.42	2.91±0.05	12.3±0.1	1.77±0.7	4.22	69	145	2.9
Tm	1.59	2.85±0.01	13.6_0.02	1.57±0.1	4.76	60	116	4.1
Yb	1.47	2.98±0.03	15.8±0.07	2.20±0.4	5.30	56	139	3.8
Lu	1.90	2.67±0.01	14.9±0.02	1.20±0.05	5.58	48	81	6.9
Y	1.49	2.27±0.02	8.14±0.3	0.758±0.1	3.58	64	93	3.8

Figure 7. Log K_1 versus ionic radius

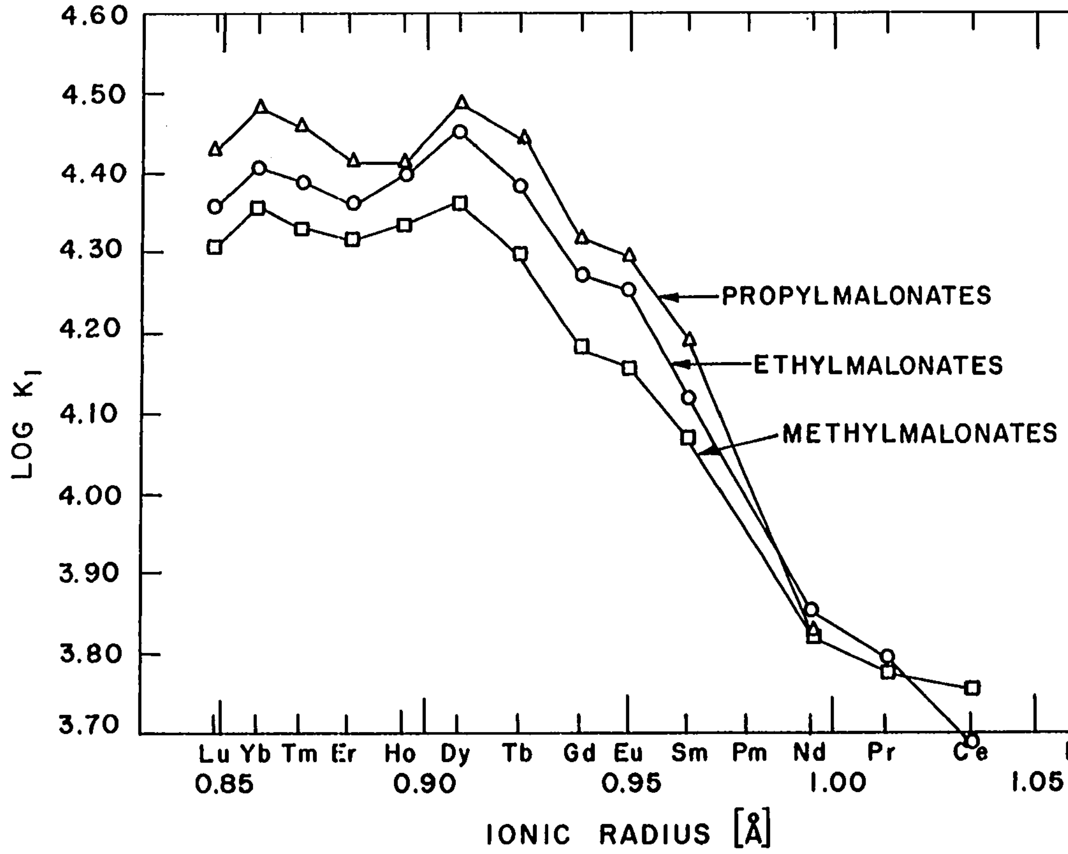

4.60
4.50
4.40
4.30
4.20
4.10
4.00
3.90
3.80
3.70
LOG K_1
PROPYLMALONATES
ETHYLMALONATES
METHYLMALONATES
Lu Yb Tm Er Ho Dy Tb Gd Eu Sm Pm Nd Pr Ce La
0.85
0.90
0.95
1.00
1.05
IONIC RADIUS [Å]

Figure 8. Log K_1 versus ionic radius

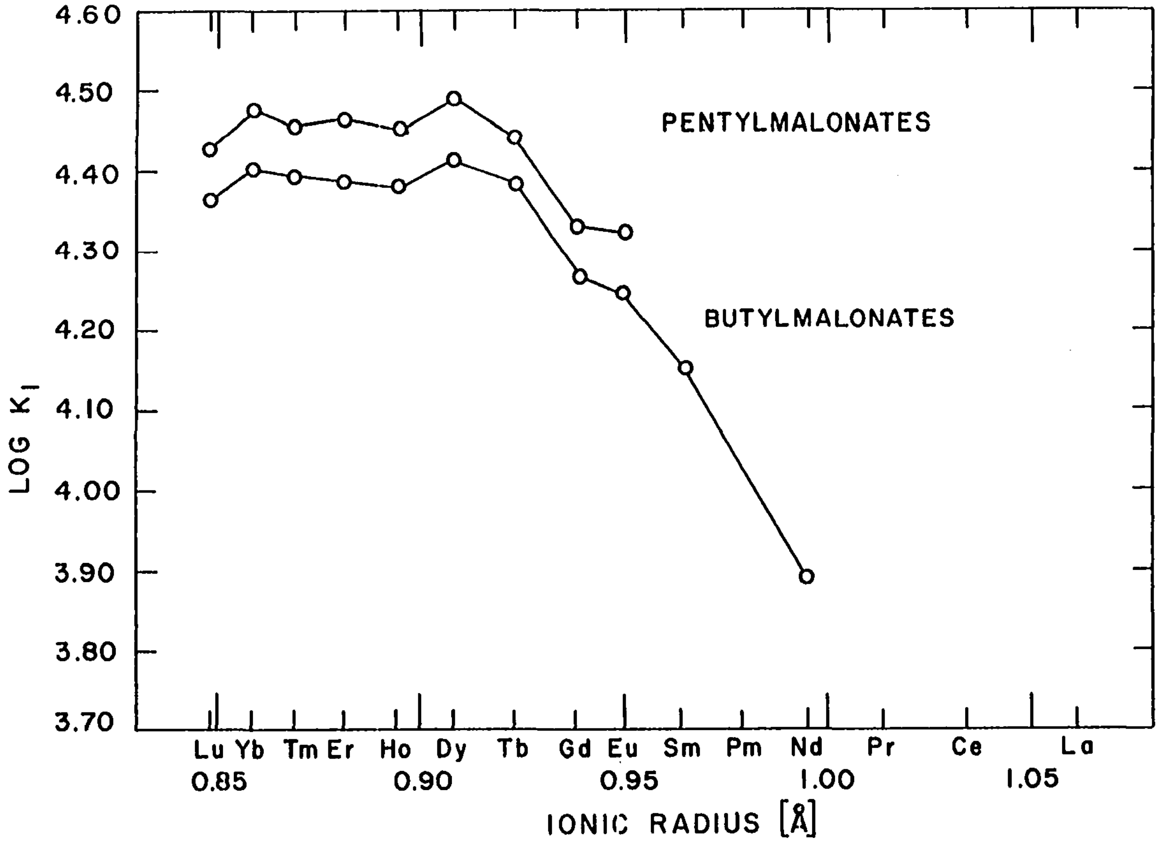

PENTYLMALONATES
BUTYLMALONATES
LOG K_1
4.60
4.50
4.40
4.30
4.20
4.10
4.00
3.90
3.80
3.70
Lu Yb Tm Er Ho Dy Tb Gd Eu Sm Pm Nd Pr Ce La
0.85
0.90
0.95
1.00
1.05
IONIC RADIUS [Å]

Figure 9. Log K_2 versus ionic radius

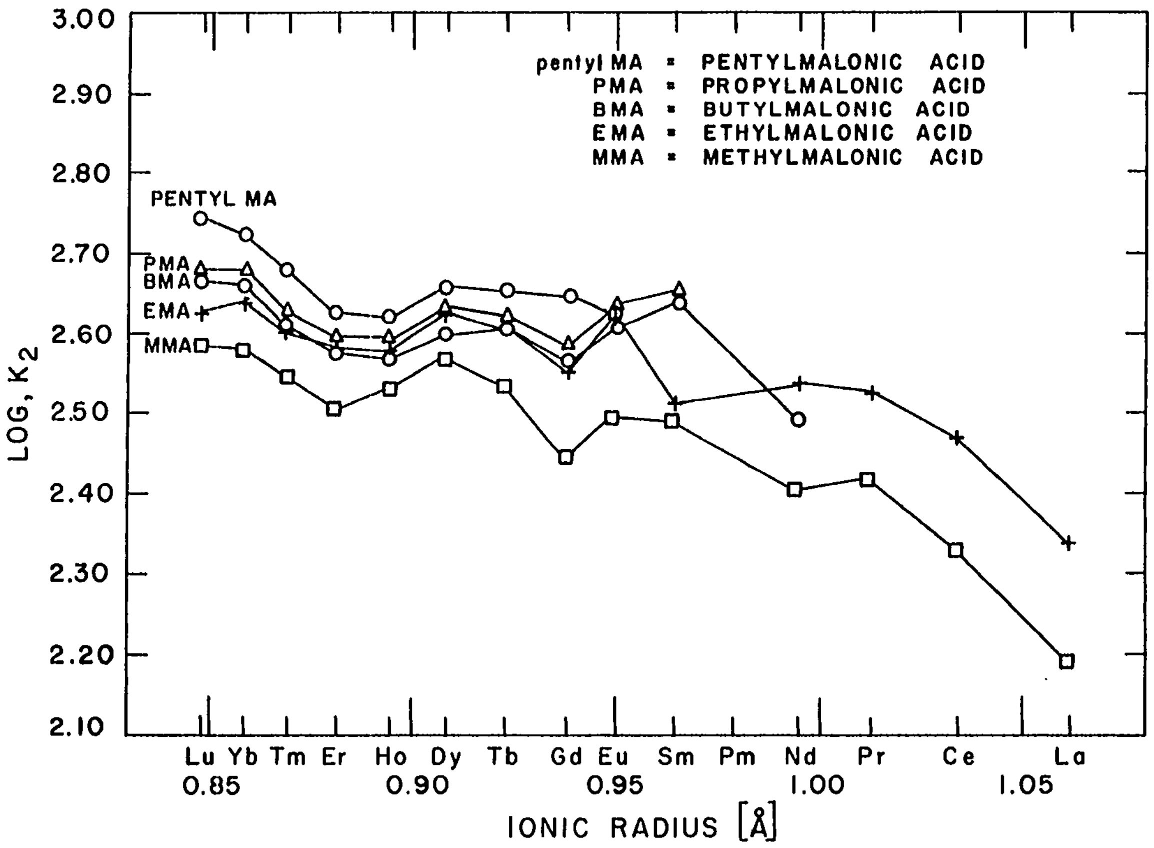
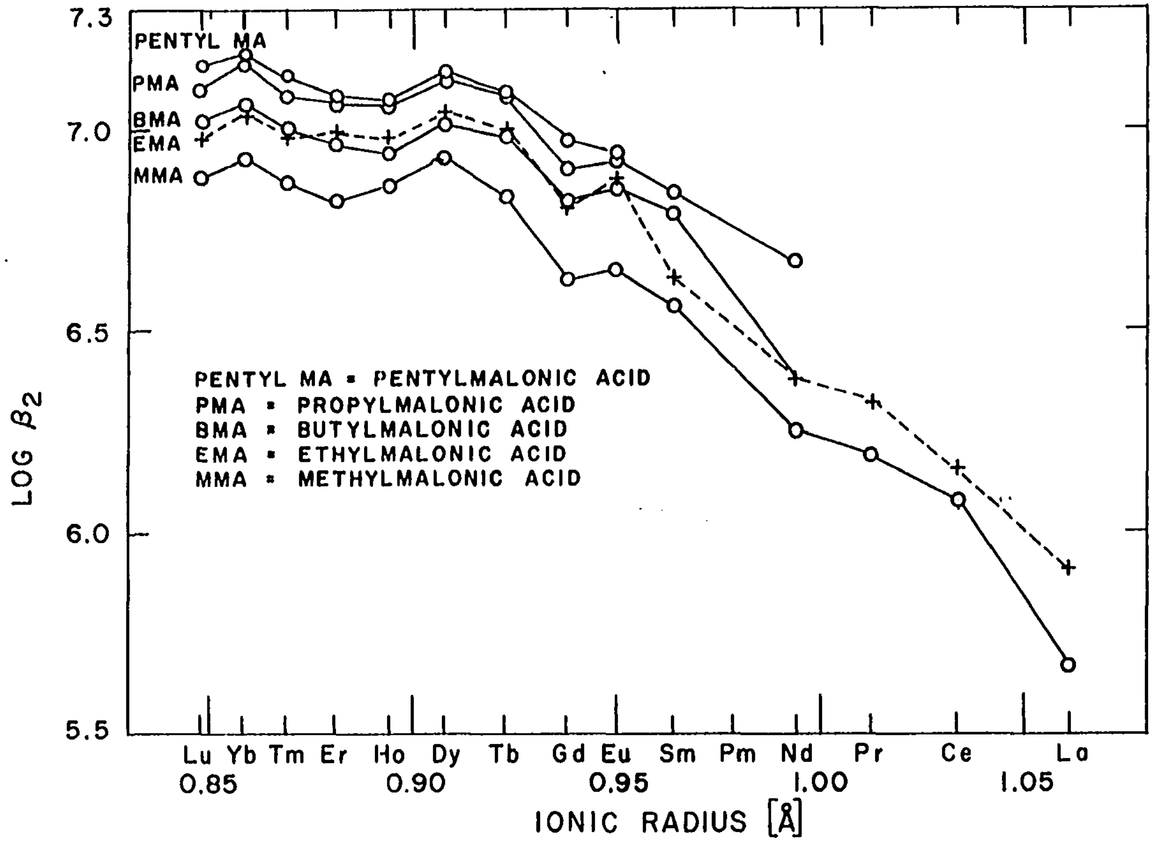

pentyl MA = PENTYLMALONIC ACID
PMA = PROPYLMALONIC ACID
BMA = BUTYLMALONIC ACID
EMA = ETHYLMALONIC ACID
MMA = METHYLMALONIC ACID
PENTYL MA
PMA
BMA
EMA
MMA
LOG, K2
3.00
2.90
2.80
2.70
2.60
2.50
2.40
2.30
2.20
2.10
Lu Yb Tm Er Ho Dy Tb Gd Eu Sm Pm Nd Pr Ce La
0.85
0.90
0.95
1.00
1.05
IONIC RADIUS [Å]

Figure 10. Log β_2 versus ionic radius


7.3
7.0
6.5
6.0
5.5
LOG β_2
PENTYL MA
PMA
BMA
EMA
MMA
PENTYL MA = PENTYLMALONIC ACID
PMA = PROPYLMALONIC ACID
BMA = BUTYLMALONIC ACID
EMA = ETHYLMALONIC ACID
MMA = METHYLMALONIC ACID
Lu Yb Tm Er Ho Dy Tb Gd Eu Sm Pm Nd Pr Ce La
0.85
0.90
0.95
1.00
1.05
IONIC RADIUS [Å]

± 10% in β_1, ± 25% in β_2, and ± 50% in β_3. Since 5 input variables were fed into the computations (each of which can be positive or negative) there should be some cancellation of errors. Therefore a more reasonable estimate of errors would be ± 3% in β_1, ± 8% in β_2, and ± 25% in β_3. Stagg (24) also found a maximum variation of ± 10% in β_1, ± 25% in β_2, and ± 50% in β_3 for the rare-earth complexes formed with several uninegative carboxylate ligands.

The number of samples used to calculate the stability constants, the sample composition, and the pH_c of each sample are tabulated in the Appendix.

The acid dissociation constants for the acids used in these complex studies are given in Table 10. The quantities α_1 and α_2 are also listed. The straight line data for determining α_1 and α_2 for propylmalonic acid is given in Figure 11. This straight line is typical of the straight line plots obtained for the other acids investigated. The Appendix contains the sample compositions and pH_c readings used in determining the acid dissociation constants.

Table 10. Acid dissociation constants at μ=0.100 M

Acid	α_1	α_2	K_{1a}	K_{2a}
methylmalonic	$2.455\text{x}10^5$	$1.549\text{x}10^8$	$1.584\text{x}10^{-3}$	$4.073\text{x}10^{-6}$
ethylmalonic	$3.006\text{x}10^5$	$1.510\text{x}10^8$	$1.991\text{x}10^{-3}$	$3.326\text{x}10^{-6}$
propylmalonic	$3.097\text{x}10^5$	$2.440\text{x}10^8$	$1.269\text{x}10^{-3}$	$3.228\text{x}10^{-6}$
butylmalonic	$3.302\text{x}10^5$	$1.459\text{x}10^8$	$2.262\text{x}10^{-3}$	$3.028\text{x}10^{-6}$
pentylmalonic	$3.505\text{x}10^5$	$2.197\text{x}10^8$	$1.595\text{x}10^{-3}$	$2.853\text{x}10^{-6}$

Figure 11. Straight line data obtained for determining α_1 and α_2 for propylmalonic acid. This data is typical of the data obtained for the other acids investigated

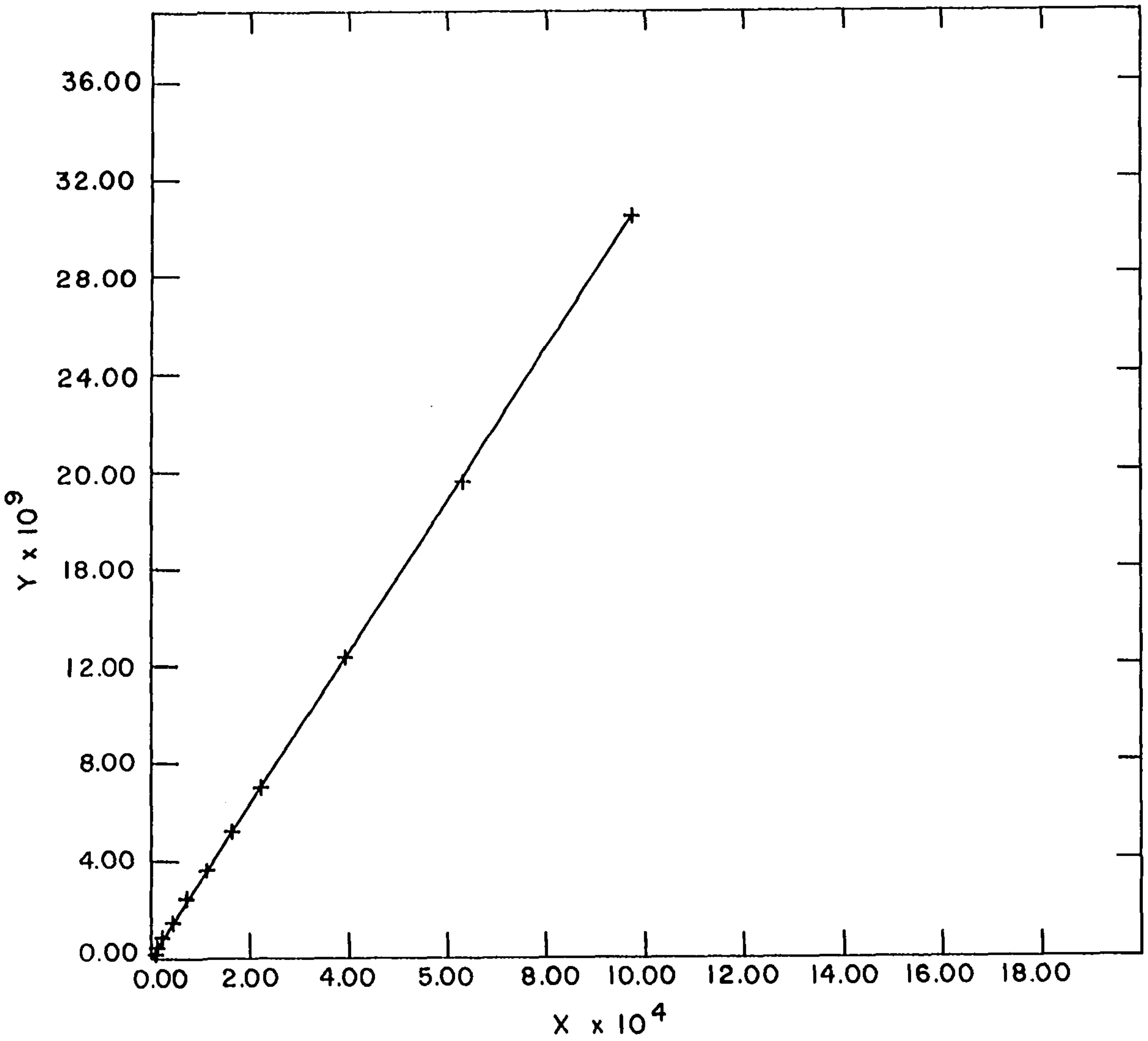

36.00
32.00
28.00
24.00
20.00
18.00
12.00
8.00
4.00
0.00
Y x 10^9
0.00
2.00
4.00
5.00
8.00
10.00
12.00
14.00
16.00
18.00
X x 10^4

Table 11. IR spectra from 600 cm^{-1} - 4000 cm^{-1}

pentyl malonic acid	ND pentyl-malonate ·6 H_2O	Nd pentyl-malonate anhydrous	Er pentyl-malonate ·3 H_2O	Lu pentyl-malonate ·1 H_2O
675	675	675	675	675
725	725	725	725 (s)[a]	725 (s)
780	780 (w)[b]	780 (w)	-	-
820	820 (w)	820 (w)	-	850 (w)
925	-	-	-	930 (w)
1060	-	-	-	975 (w)
1120	1120 (w)	1120 (w)	-	-
1190	-	-	-	-
1220	broad band no sharp peaks	broad band no sharp peaks	-	-
1270			-	-
1300	-	-	-	-
1400-1425	1400 (w)	-	1380	1375
1465-1470	1465 (w)	1465 (w)	1470 (s)	1470 (s)
-	1570	1570	1575	1575
-	1680	-	1680 (w)	-
1720	-	-	-	-
2350	-	2400	-	-
2900	2900	2900	2900	2900
-	3400	-	3400 (w)	3400
2200-3400	much less intense	very weak	very weak	very weak

[a] s=strong.

[b] w=weak.

Table 12. IR spectra from 200 cm^{-1} - 600 cm^{-1}

Pentyl malonic acid	ND (pentylmalonate)$_{1.}$ ·6 H_2O	Nd (pentylmalonate)$_{1.5}$
Frequency (cm^{-1})	Frequency (cm^{-1})	Frequency (cm^{-1})
230	230 (much broader and more intense)	230
320	-	-
370	-	-
-	430 (due to H_2O)	disappears
450	-	-
470	-	-
530	-	-
580	-	-

Table 13. Hydration number (X) for Ln(-malonate)$_{1.5}$ · x H_2O with accompanying temperature range for H_2O loss during thermogravimetric analysis

	Methyl malonate	Ethyl malonate	Propyl malonate	Butyl malonate	Pentyl malonate
Lu					1
Er		1 (180°-190°) 3 (197°-210°) 4	3 (50°-125°)	3 (90°-120°)	3 (45°-100°)
Nd	1 (60°-80°) 1 (100°-134°) 1 (184°-220°) 3	4 (100°-120°)	4(90°-113°)	4-5?(100°-140°)	2 (70°-103°) 4 (130°-157°) 6
Pr	1 (37°-50°) 1 (102°-130°) 1 (184°-203°) 3	4 (50°-210°)	3 (160°-200°)	2 (134°-137°)	
Ce	1 (38°-50°) 1 (108°-130°) 1 (184°-210°) 3				
La	1 (35°-100°) 1 (150°-200°) 2	2 (50°-210°)			

Compd.	H_2O Loss	Temp. °C
Cu SO_4 · 5 H_2O	2	(50°-70°)
	2	(90°-108°)
	1	(220°-240°)
	5	total H_2O

DISCUSSION

A bulk type separation of the rare earths is easily performed and many flow-schemes and techniques have been used (25, pp. 31-61). The separation of adjacent pairs is usually performed by ion exchange using a complexing agent as the eluant. The first successful eluant was citric acid buffered with ammonium citrate (26). Many other complexing agents have since been used as eluants. To date, the eluants EDTA and HEDTA produce the best separation of rare-earth elements (27). Studies of ion-exchange separation of rare-earth pairs at elevated temperatures have been carried out by Powell and Burkholder (28, 29, 30) in order to improve the separation factors for several of these adjacent pairs. The possibility of obtaining good separation of adjacent pairs of rare earths was one incentive for this investigation.

The effectiveness of the separation of two similar metal ions, A and B, by ion exchange can be measured by the separation factor. The separation factor is defined as

$$\alpha_B^A = \frac{K_{dB}}{K_{dA}} ,$$

where

$$K_{dB} = \frac{[\bar{B}]}{[B]}$$

and

$$K_{dA} = \frac{[\bar{A}]}{[A]} .$$

The brackets represent concentration. The bar above A and B signifies metal ions bound to the resin and the unmarked A and B represent metal ions in solution. If A and B cations have nearly identical affinities for cation-exchange resin, then

$$\alpha_B^A = \frac{K_{dB}}{K_{dA}} = \frac{[A][\bar{B}]}{[\bar{A}][B]} \simeq 1.0$$

Separation in such a system can be enhanced by the use of a complexing ligand L. When the complexing ligand forms a simple neutral or anionic 1:1 complex and if the 1:1 complex is the only important species, one can write for the separation factor:

$$\alpha_B^A = \frac{\{[A]+[AL]\}[\bar{B}]}{\{[B]+[BL]\}[\bar{A}]} .$$

The equilibria in solution are $A + L \rightleftarrows AL$ and $B + L \rightleftarrows BL$, for which

$$K_{AL} = \frac{[AL]}{[A][L]}$$

and

$$K_{BL} = \frac{[BL]}{[B][L]} .$$

Upon substituting [AL] and [BL] from the above expressions into the separation factor one obtains

$$\alpha \simeq \frac{1+K_{AL}[L]}{1+K_{BL}[L]} .$$

It has been found for strong complexing ligands, where the neutral or negatively charged 1:1 complex is the predominant species, that α can be reduced further to

$$\alpha \simeq \frac{K_{AL}}{K_{BL}}$$

(31, pp. 62-66). Thus we see that the separation factor, or effectiveness of separation, can, in certain cases, be estimated by the ratio of the first stability constants of the cations being eluted. For this work the first negative species formed is ML_2^{-1}. The β values for this species can therefore be used to estimate the separation factors.

The stability constant data of this investigation show that the ligands studied would not promote an improved separation of any adjacent rare-earth pairs. As indicated by the Log β_2 versus cationic radius curves, the separation factors for the Tb-Gd pair ought to be the largest. A rough estimation of the separation factors for this pair from β_2 values shows a maximum value of 1.6. A separation factor of approximately 4.8 is possible when using EDTA at 25°C (27).

A theoretical explanation of stability constant data necessitates proposing a reasonable model for the complex formation process. This model includes assumptions concerning the dentate character of the ligand, as well as the coordination number of the cation. Several models and some of the other theoretical aspects of rare-earth complex formation have been discussed by J. E. Powell, (32), Devine (33) and Moeller et al., (1).

Aqueous rare-earth cations are known to be heavily hydrated, (see, for instance, Brady (34)). The hydration sphere is thought to consist of two regions: an inner hydration sphere made up of water molecules in direct contact with the metal cation, and an outer hydration sphere comprised of water molecules, not in contact with the rare-earth cation, but oriented with respect to it, whose motion is restricted by electrostatic dipole attraction to the rare-earth cation. The numbers of water molecules in these hydration spheres are very difficult to ascertain. The number of water molecules in the inner hydration sphere (the coordination number) is thought to be greater than six and possible as high as ten. The number of water molecules in the outer hydration sheath is virtually impossible to determine. However, the work of Spedding and co-workers on the properties of rare-earth salt solutions indicates an overall size for such hydrated cations. The data, which include measurements of equivalent conductances (35), activity coefficients (35), heats of dilution (36), relative viscosities (37), and apparent molal volumes (38), shows an irregular change in the hydration sphere as the rare-earth series is traversed. These irregularities have been attributed to a change in the coordination number of the rare-earth cations as the ionic radius decreases.

In the early work by Wheelwright, Spedding, and Schwarzenbach (39) on the EDTA complexes of the rare earths, it was suggested that EDTA acted as a hexadentate ligand with the light rare earths and as a pentadentate ligand with the heavies. The coordination change was suggested to take place at gadolinium. It is now believed that the rare-earths from lanthanum through samarium have a coordination number of nine or ten. (Nine is the most likely number since many solid rare-earth compounds investigated by x-ray crystallography have been found to have this number). This coordination number is believed to decrease by one somewhere between the rare earths europium and holmium. The exact point at which the coordination change occurs cannot be established. The elements europium through holmium seem to comprise a transition group which sometimes have the higher coordination number and sometimes the lower coordination number. A coordination number of nine has been definitely established by x-ray crystallography for the solid compounds $Nd(H_2O)_9(BrO_3)_3$ (40) and $M(C_2H_5OSO_3)_3(H_2O)_9$ where M represents lanthanum, praseodymium, erbium and yttrium (41). The nine water molecules surround the cation with six molecules at the apices of a right triangular prism and the other three molecules situated beyond the centers of the three rectangular faces of the prism. Wells (42, pp. 74, 340, 553) reports the following compounds to have this nine-coordination structure also: the trihydroxides of lanthanum, praseodymium, neodymium, samarium, gadolinium, dysprosium, erbium, and yttrium; the trichlorides of lanthanum through gadolinium; and the tribromides of lanthanum, cerium, and praseodymium. A slightly distorted nine-coordinate array has been found for the anionic species $[M(EDTA)(H_2O)_3]^-$, where M represents all the rare earths from lanthanum through terbium (43). We also find a coordination number of ten reported for compounds of the type $HM(EDTA)(H_2O)_4$ (43). On the other hand, a coordination number of eight has been found for the gadolinium ion in crystals of $Gd\ Cl_3 \cdot 6H_2O$ (44).

Thermogravimetric data tends to support a change in coordination number as we traverse the rare-earth series and suggests that a transition group exists near the middle of the series. The problem encountered in thermogravimetric analysis is that one cannot be certain whether all water molecules found are really coordinated. Any weight lost below 50°C is most likely due to water simply trapped in the crystal lattice. The well established five hydrate of copper sulfate loses the first two water molecules from 50°-70°C and thus typifies a compound from which coordinated water is lost at quite a low temperature.

E. L. Head et al. (45, pp. 55-62) studied thermal decomposition of several rare-earth carbonates. Their investigations did not always reveal the same number of waters of hydration for a given rare-earth carbonate. Therefore in this case and others it is quite probable that the degree of hydration depends on the conditions extant during compound preparation. However, for the carbonates the hydrated water is usually lost near 100°C and general thermal decomposition commences at approximately 300°C.

Thermal decomposition studies of the oxalates (46, p. 290) again shows varying hydration numbers as we traverse the rare-earth series. Several of these hydrates are reported to begin to lose water at 40°C and many are not completely anhydrous until approximately 400°C.

The solid rare-earth compounds studied in this work were analyzed by TGA, IR, and elemental analysis. The solids formed as powders and no well-defined crystals could be produced. Therefore, x-ray data could not be of any benefit in structural analysis. However, using the TGA data and the requirements of electro-neutrality, a molecular formula of $\mathrm{Ln(\text{-malonate})_{1.5} \cdot xH_2O)}$ was deduced. The value of x ranged from two to six with three being the most frequent value encountered.

Generally speaking, thermogravimetric data is not very revealing as to compound structure or exact coordination number. It does indicate that the solid compounds are hydrated and that the hydration number usually varies as the rare-earth series is traversed.

In summary, we find that most of the available data for solid rare-earth compounds shows a coordination number of nine for the rare-earth cations. On this basis a coordination number of at least nine for the rare-earth cation in solution seems a very reasonable assumption. However we must keep in mind that coordination numbers other than nine have been reported (at least for the solid compounds) and that there seems to be a change in coordination number as the rare-earth series is traversed.

A comparison of the effects of dentate character on stability constants is given by Schoeb (47, pp. 7-8). A comparison of the atoms through which coordination to the rare earths occurs best and the effects of various substitutions on complexing ligands is also given by Schoeb et al. (47, pp. 5-10).

All of the ligands studied in this work contain four oxygen atoms which are potential donors. For the rare-earth complexes with EDTA and other carboxylic acids, workers believe that coordination generally occurs through only one oxygen atom of each carboxylate group. Coordination through both oxygens has been considered but size considerations and angle requirements show this situation to be highly strained. Therefore, one's first inclination is to consider malonate ligands as bidentate, coordinating through only one oxygen atom from each carboxyl group.

Scale models of the ligands and rare-earth cations were constructed from styrofoam balls. Using these space filling models, various ways of placing the ligands around a rare-earth cation were considered. First one could assume the ligands to act as monodentate ligands. This seemed quite unlikely just from the values of the first stability constants. The values of the first stability constants are of the order of 10-20 thousand. Nearly all monodentate ligands investigated have a first stability constant of the order of 100 or below. The affinity of the ligand is significantly increased if a donor group is introduced on an initially monodentate ligand in such a way that a chelate ring can form. As an example, the first stability constant of Lu^{+3} with acetate anion is reported as 71.1 (48) while the logarithm of the first stability constant of lutetium glycolate (hydroxyacetate) is reported as 3.14 (49). This corresponds to a stability constant value of 1390. Thus we see that hydroxyl substitution on the acetate anion has increased the affinity approximately twenty-fold. The glycolate ligand ostensibly forms a chelate ring and the increased stability is referred to as the "chelate effect." This was first recognized by Schwarzenbach (50) and was also named by him.

One could consider substituted malonate ligands as quadradentate (using all the oxygen atoms as coordination sites), but this seems highly unlikely from size and angle considerations. A tridentate arrangement could be formed by having one carboxyl group in a perpendicular position in relation to the other carboxyl group. Again such an arrangement is not flexible and also does not fit the rare-earth models very well.

Now let us consider the bidentate case. One can consider malonic acid as an organic acid with a second carboxyl group substituted on the α carbon. This substitution should cause a chelating effect. Since the first stability constants of rare-earth malonates are of the order of 10-20 thousand, we indeed believe that a chelate is formed. This chelate effect is attributed mostly to displacement of several coordinated water molecules and other ordered water molecules around the cation. Further disruption could be caused by substituting an alkyl group on the α carbon. This should further disrupt the sheath of oriented water molecules and enhance the stability constants by an entropy effect. This entropy effect should be evident if the ordered hydration sphere has not already been completely disrupted by introduction of the unsubstituted malonate ligand itself. We also note that when a bidentate malonate ligand complexes a rare-earth cation a six-membered ring is formed. Five and six-membered rings are considered the least strained of organic ring systems. Thus it seems that a bidentate ligand complexing a rare-earth cation to form a six-membered ring should be a favorable configuration.

The stability constants of the copper ethylmalonato species were also measured. This data also tends to support the bidentate character of the malonate ligands. The copper malonate data is listed below and compared with the data for ytterbium ethylmalonato species.

Table 14a. Comparison of the Cu and Yb ethylmalonato step formation constants

	ethylmalonato		stability	constants	ionic	coordination
	K_1	K_2	K_3	K_1/K_2	radius	number
Yb	$2.57\text{x}10^4$	437	40	59	0.858Å	8-10
Cu	$7.59\text{x}10^4$	1110	23	68	0.69Å	6

It is first noted that three stepwise stability constants are calculable for each cation. It is further noted that the values of the respective constants are of the same order of magnitude. One would suspect from such data that the ligand behaves similarly in both systems. Since the data indicates that the species BA_3 forms for the copper system, and since a coordination number of six is firmly established for copper, a model of a bidentate ligand on a six-coordinate cation is a very pleasing picture. If we assume that the ligand is behaving similarly in the rare-earth system we would conclude that the ligand is bidentate.

It is also noted that the malonate ligand is unique in that each COO^- group can rotate. Since the COO^- groups can rotate and if the ligand bonds bidentately through one of the oxygen atoms on each carboxyl group, then the chelate formed can adjust to many differently sized cations. As we traverse the rare-earth series there is a gradual decrease in the size of the rare-earth cations. It appears as though a bidentate malonate ligand should be able to easily adjust to this size decrease and thus fit all the cations equally well. Therefore as one complexes the cations of the rare-earth series with a malonate ligand, effects on the stability of the complexes other than those due to the ligand straining to fit the various sized cations, could possibly be observed.

Various authors have attempted to establish ligand dentate character and metal ion coordination number by comparing ratios of successive step formation constants. The procedure is to assume a dentate character for the ligand and a coordination number for the cation. Using this proposed model, a ratio of successive constants is then calculated. These calculated values are then compared with experimentally determined ratios to test the originally assumed model. J. Bjerrum (7, p. 39) suggested that the ratio of thermodynamic step formation constants, $\underline{P}^*$, should equal the product of three terms; $\underline{S}$, $\underline{T}$, and $\underline{R}$.

$$\underline{P}^* = \frac{K_1^*}{K_2^*} = \underline{S} \cdot \underline{T} \cdot \underline{R}$$

$\underline{S}$, the statistical factor, is obtained by taking the ratio of successive statistical step formation constants. Included in $\underline{S}$ is the assumption that the mechanism by which the BA_{n+1} species is formed from BA_n is identical to the mechanism by which BA_n is formed from BA_{n-1}. Such successive statistical constants are then each proportional to the number of ways an incoming ligand can attach to the existing species divided by the number of ways the new complex entity can revert to the previous species. Therefore, the statistical ratios depend solely on the number and configuration of coordination sites and the dentate character of the ligand.

$\underline{T}$ is the electrostatic or coulombic factor. When a negatively charged ligand attaches to a positively charged cation the complex species becomes less positive and the process of complexing another ligand is less favored. N. Bjerrum (51) studied the association constants for some dibasic acids and derived the following equation for evaluating $\underline{T}$ for his systems.

$$\underline{T} = e^{\frac{\varepsilon^2 No}{DRTr}}$$

where No = Avogadro's number

ε = electronic charge,

D = dielectric constant,

r = equilibrium separation of charged species given in Å,

R = gas constant,

T = absolute temperature.

The quantity $\underline{T}$ is thought of as the work done in bringing a second ligand from infinity to its equilibrium position, r, in the complex. The relationship was developed from Coulomb's law and is likely an oversimplification.

$\underline{R}$ is called the rest term and includes all other factors involved in the complexing process but is considered to be primarily a term reflecting steric hindrance. R is usually assumed to be close to 1, at least for most small or simple ligands.

The usefulness and validity of the relationship $\underline{P}^* = \underline{S} \cdot \underline{R} \cdot \underline{T}$ is rather questionable since many assumptions are made in evaluating $\underline{S}$, $\underline{R}$, and $\underline{T}$. Nevertheless, the relationship has been applied to several uninegative ligands which complex with rare earths and good agreement between many of the calculated and experimental ratios has been obtained (32). The above mentioned systems were studied at an ionic strength of 0.100M and activity coefficients were involved as follows:

$$P^* = \frac{K_1}{K_2^*} = \frac{b_1}{b_2} f(\gamma) = \frac{[BA]^2}{[BA_2][B]} \cdot \frac{\gamma^2 BA}{\gamma BA_2\ \gamma B} = \underline{S} \cdot \underline{R} \cdot \underline{T}$$

R for these systems was assumed to be one. If one uses the Debye-Hückel or Davies equation to evaluate the γ's we find that the function $f(\gamma)$ is $\sim$1.5. T has been evaluated by Devine (33) and by Manning (52, 53, 54) for uninegative ligands complexing rare-earth cations and a value of $\sim$1.5 was concluded. Thus we see that for these systems $f(\gamma)$ cancels T and the observed ratio should equal the statistical ratio S. As mentioned earlier good agreement has been obtained between measured ratios and the statistical factor S, but one major difficulty still exists in trying to deduce dentate character and coordination number from these data. It is found that the values of the b_1/b_2 ratios for several models are quite similar to one another and thus no definite model can be assigned. A list of various models and b_1/b_2 ratios for these models is given in Table 14b, taken from reference 32, p. 9.

It is noted that the b_1/b_2 ratios from this work are unusually high compared to ratios observed for uninegative ligands. (uninegative ligands usually have b_1/b_2 ratios which range from 2-5). A theoretical calculation of b_1/b_2 ratios for this work was carried out to establish whether an agreement with theory could be obtained. T was calculated using the equation of N. Bjerrum which yields

$$T = e^{\frac{7.15}{r}} .$$

If we assume an equilibrium distance of r=2Å we obtain

$$T = e^{3.5} \simeq 33.$$

Since the statistical factor S is roughly three, assuming a nine-coordinate cation and a bidentate ligand, the product of S and T is 99. If we calculate log f(γ) by the Debye-Hückel equation we obtain log f(γ)=0.80. A calculation of log f(γ) by the Davies equation gives log f(γ)=0.72. This value is considered the better value since the ionic strength is at 0.1M. Multiplying the observed ratios for the heavy rare earths by f(γ) from the Davies equation gives values for P* which range from 250-300. Thus the experimental values of P* are much higher than the theoretical value which one obtains by assuming R≃1 and r=2Å.

The value of P* theoretical can be increased by increasing T. If we assume the equilibrium distance is closer to 1.5Å than 2Å we can calculate for T

$$T = e^{\frac{7.15}{1.55}} = e^{4.6} \simeq 100.$$

The product of S and T will now be approximately 300. In either of the above cases the experimental value is of the right order of magnitude. However the latter value of T gives better agreement with experiment.

On the other hand one could reduce the theoretical P*by evoking steric hindrance arguments (i.e. R values < 1) or by

Table 14b. Statistical ratios of successive stability constants

C.N.	Configuration	Dentate Character	K_1/K_2
10	Archimedean antiprism + 2	tridentate	4.92
		bidentate	3.13
		monodentate	2.22
9	trigonal prism + 3	tridentate	4.92
		bidentate	3.27
		monodentate	2.25
8	cubic	tridentate	7.33
		bidentate	3.43
		monodentate	2.29
8	dodecahedral	tridentate	7.11
		bidentate	3.64
		monodentate	2.29
8	Archimedean antiprism	tridentate[a]	5.33
		bidentate	3.56
		monodentate	2.29
7	pentagonal bipyramid	tridentate	10.00
		bidentate	4.09
		monodentate	2.33
6	octahedral	tridentate	16.00
		bidentate	4.80
		monodentate	2.40

[a] It is assumed that the ligand would only be accommodated on equilateral triangular faces of the square antiprism.

modifying the expression for T. A modification of T is suggested by a comparison of Bjerrum's system and the malonate systems. Sine T is associated with the electrical work involved in bringing the second ligand to its equilibrium position in the complex, let's compare the electrostatics of these processes for the two different systems.

Bjerrum's system: $H\overline{A} + H^+ \rightleftarrows H_2A$.

The malonate systems: $BL^+ + L^= \rightleftarrows BL_2^-$.

Let's imagine the malonate system as proceeding in the following steps:

$BL^+ + L^- \rightleftarrows BL_2$ (A)

$BL_2 + e^- \rightleftarrows BL_2^-$ (B)

Step A is electrostatically similar to Bjerrum's system and a $\underline{T}_A$ for this step can be evaluated by Bjerrum's equation. For steps B, one no longer has a positive species attracting a negative species but has a negative species being formed from a neutral species. Thus $\underline{T}_B$ is assumed opposite in sign from $\underline{T}_A$. If one now lets $\underline{T} = \underline{T}_A + \underline{T}_B$, the previously calculated $\underline{T}$ can be reduced by the term $\underline{T}_B$.

It is interesting to note that Schoeb obtained some rather high (b_1/b_2) ratios for the dilactates. She, however, proposed that the high values were due to the first ligand bonding tetradentately or pseudopentadentately. She did not consider electrostatic effects as a possible solution.

It was mentioned earlier, under the experimental section, that an attempt to obtain the rare-earth coordination number was made using an NMR technique. The lutetium cation was studied but no useful data were obtained. If the coordination number could be obtained by this technique, it was proposed that the system should then be studied with a malonate complexing ligand present. If any water molecules are still in the first hydration sphere after complexing occurs their presence and concentration should be discernable. This type of information could certainly help to further characterize the system. At least the dentate character could be established for the ligand when forming the first complex species BA.

The present work also involved investigating effects upon rare-earth chelate stability constants due to successive addition of the $-CH_2-$ entity to the basic malonate ligand. Many kinds of substitutions can be made on this ligand but the simplest substitution was chosen as a starting point. Since the formation of the 1:1 complexes is strongly endothermic ($\Delta H \sim 5$kcal/mole), the stability is principally due to a high entropy of formation (4). Thus a substitution which does not change the basic nature of the ligand but which causes more extensive disruption of the hydration sphere about a rare-earth cation could indicate the approximate extent of the hydration sphere and the entropy contribution arising from disruption of this sphere. A look at Figures 7 and 8 shows that the stability constants increase in the order methylmalonato<ethylmalonato<propylmalonato. The stabilities of the pentylmalonato species, however, are nearly the same as those found for corresponding propylmalonato species, and the stabilities of the butylmalonato

species closely parallel the values for corresponding ethylmalonato complexes. The stability constants seem to follow a trend related to the dissociation constants of the acids. It appears that the major effect of $-CH_2-$ substitution on malonic acid is to influence the dissociation constants of the acid. The change in acid dissociation constants is in turn reflected by a change in stability constants of the complexes formed. Below is a table showing the observed trend:

Table 15. Effect of $-CH_2-$ substitution on the acid first dissociation constant and the first stability constants

substituted acid	first acid dissociation constant (K_{1a})	first stability constant (K_1)
pentyl→butyl	increased	decreased
butyl→propyl	decreased	increased
propyl→ethyl	increased	decreased
ethyl→methyl	decreased	decreased

With the exception of methylmalonic acid, the data show that the acids with greater affinity for hydrogen ion have a stronger tendency to complex rare-earth cations. The exception noted with methylmalonic acid is believed to be due to the marked increase in K_{2a}. From ethyl malonic acid through pentyl malonic acid the value of K_{2a} remains almost constant while K_{1a} varies (see Figure 12). Since the stability constants seem to follow the formation constants of the acids, it seems that alkyl substitution promotes little entropy change in the complexing process. Thus it may be concluded that the cation hydration sphere does not extend beyond the protrudence of the unsubstituted malonate ligand.

The log b_n versus ionic radius curves are observed to follow the trend shown for the malonato species which were investigated by Powell, Farrell, Neillie, and Russell (6). Their results are given in Table 16 and Figure 13. The malonato species are slightly more stable than the alkyl substituted malonato species studied in this work, showing that single alkyl substitution does not enhance the stability of the malonato complexes. Recent data (55) show that dimethyl substitution on malonic acid likewise decreases the stability constants, but that diethyl, di-n-propyl, and di-n-butyl substitutions increase the stability constants as compared to malonate (6). This stability decrease, caused by single alkyl substitution, was also observed by Schoeb (47) when comparing the 1:1 stability constants for the dilactates and the diglycolates. Dilactic acid can be thought of as diglycolic acid with two methyl groups substituted for two hydrogen atoms at the two and four positions of diglycolic acid. For monobasic organic acids, methyl or ethyl substitution on the α carbon usually produces

Figure 12. Dissociation constants of some substituted malonic acids at $\mu=0{,}1M$ and $T=25°C$

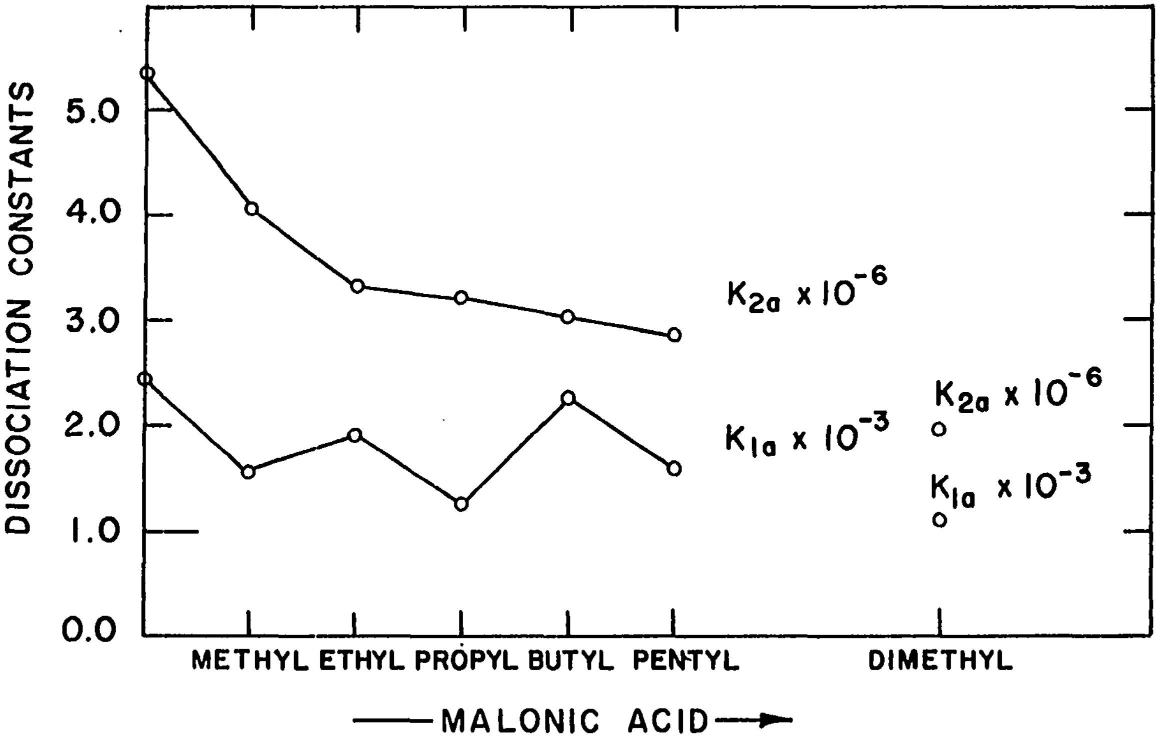

DISSOCIATION CONSTANTS
5.0
4.0
3.0
2.0
1.0
0.0
$K_{2a} \times 10^{-6}$
$K_{1a} \times 10^{-3}$
$K_{2a} \times 10^{-6}$
$K_{1a} \times 10^{-3}$
METHYL
ETHYL
PROPYL
BUTYL
PENTYL
DIMETHYL
MALONIC ACID

Figure 13. The step formation constants of the malonato rare-earth chelate species at $\mu=0.1M$ and $T=25°C$, data of Powell (6)

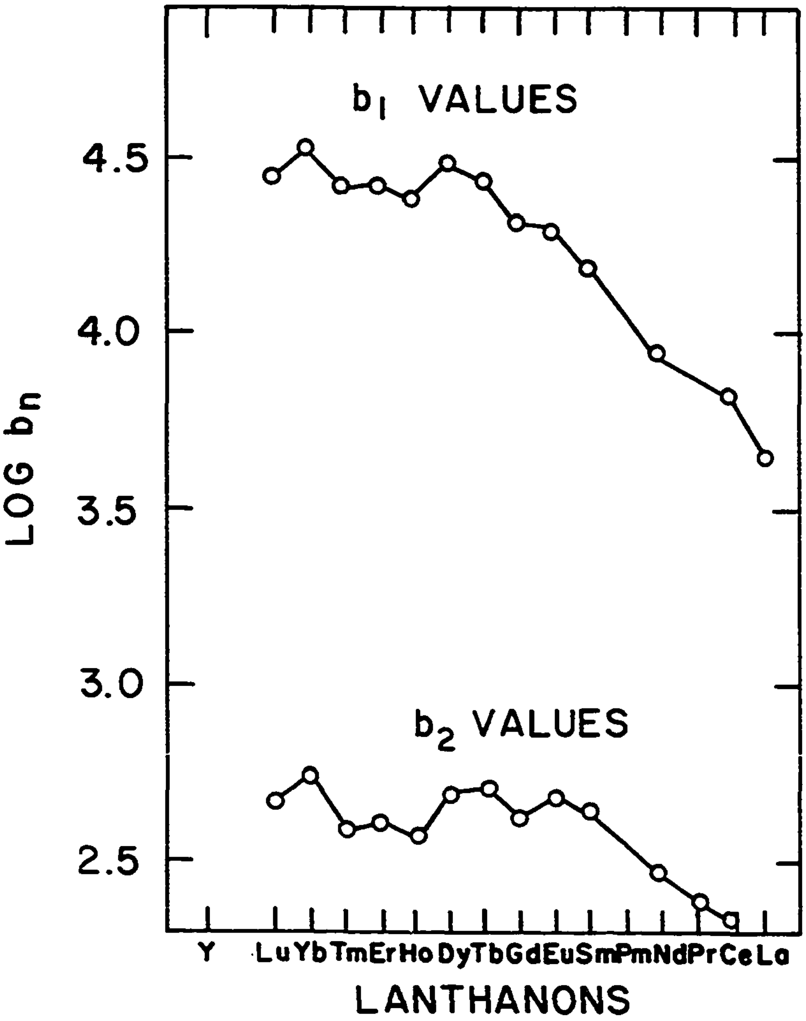

b1 VALUES
b2 VALUES
LOG bn
4.5
4.0
3.5
3.0
2.5
Y
Lu Yb Tm Er Ho Dy Tb Gd Eu Sm Pm Nd Pr Ce La
LANTHANONS

Table 16. Stability and step formation constants for 1:1 and 1:2 rare-earth malonate species at 25.0°C, $\mu=0.100(KNO_3)$; computations based on $K_1=2.47 \times 10^{-3}$, $K_2=5.34 \times 10^{-6}$

rare earth	$\bar{n}_{max}$ achieved	$(\beta_1=b_1)\times10^{-4}$	$\beta_2\times10^{-6}$	$b_2\times10^{-2}$	b_1/b_2
La	1.86	0.49	0.8	1.6	30
Ce	1.65	0.68	1.5	2.2	31
Pr	1.90	0.82	2.0	2.5	33
Nd	1.68	0.88	2.6	3.0	30
Sm	1.80	1.56	7.0	4.5	35
Eu	1.80	2.03	9.8	4.9	42
Gd	1.79	2.09	9.3	4.4	47
Tb	1.76	2.74	14.1	5.1	53
Dy	1.58	3.00	14.9	5.0	60
Ho	1.56	2.45	9.3	3.8	65
Er	1.60	2.63	11.1	4.2	63
Tm	1.56	2.65	10.3	3.9	68
Yb	1.71	3.40	18.9	5.6	61
Lu	1.71	2.82	13.5	4.8	59
Y	1.74	2.51	11.1	4.4	57

an increase in the stability constants. Thus it seems that no trend exists between alkyl substitution on monobasic acids and substitution on dibasic acids and possibly even an inverse trend exists.

As far as the disubstituted acids are concerned, we note that with the exception of dimethylmalonic acid, all have smaller dissociation constants than malonic and the monosubstituted malonic acids. One would expect from our previous discussion that the stability constants for lanthanon chelates of these acids would be greater than those of malonic acid or the monosubstituted malonic acids. This is indeed the case. For dimethylmalonic acid the dissociation constants are near the values for the monosubstituted acids. The stability constants for this acid also fall with the stability constants of the monosubstituted acids.

One other significant effect observed from this work was a decrease in species solubility with increasing $-CH_2-$ substitution. Many of the lighter rare earths could not be studied with the propyl, butyl, and pentyl substituted malonic acids since precipitation resulted even at very dilute metal and ligand concentrations.

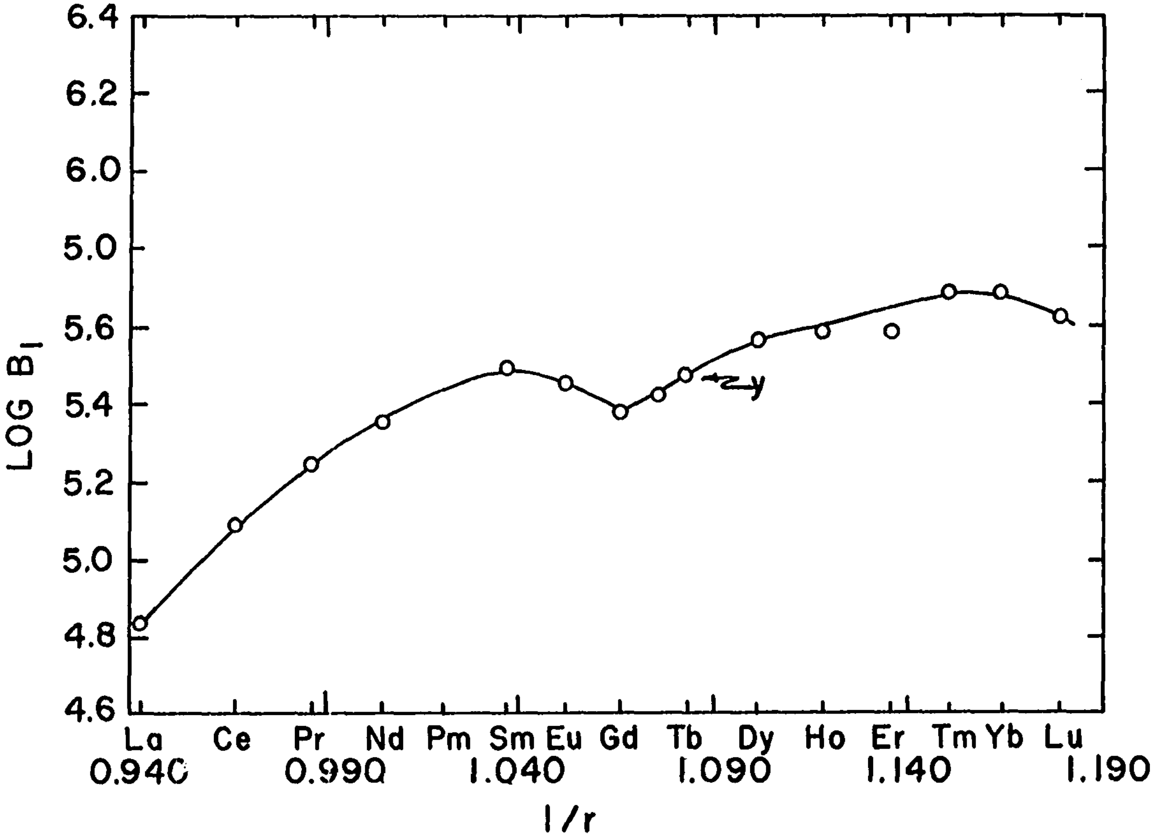
An irregularity noted for the stability constants of the 1:1 species is the greater stability of ytterbium over lutetium and the greater stability of dysprosium over holmium. These irregularities were also observed for the malonato species, which were investigated by Powell, Farrell, Neillie, and Russell (6), but no attempt was made to explain these irregularities. These irregularities are well outside of experimental error and have been verified for the malonato species by ion-exchange elution (56).

The greater stability of ytterbium over lutetium was also observed by Schoeb (47) for the 1:1 dilactate species (see Table 17 and Figure 14).

Table 17. Stability constants of the rare-earth dilactate complexes (T = 25°C; $\mu=0.1$ ($NaClO_4$); $\alpha_1=7.71\times10^{-5}$, $\alpha_2=1.19\times10^{-7}$)

Metal	$\beta_1\times10^{-5}$	$\beta_2\times10^{-8}$	$b_2\times10^{-4}$	b_1/b_2
La	0.69±0.03	0.75±0.05	0.11±0.01	65
Ce	1.24±0.06	3.09±0.20	0.25±0.02	50
Pr	1.78±0.09	7.05±0.49	0.40±0.03	45
Nd	2.25±0.12	14.1±0.9	0.63±0.05	36
Sm	3.09±0.20	37.5±2.7	1.21±0.11	26
Eu	2.85±0.23	46.7±3.9	1.64±0.19	17
Gd	2.42±0.16	44.7±2.9	1.85±0.17	13
Tb	2.96±0.13	71.0±2.7	2.40±0.14	12
Dy	3.69±0.25	111 ±6	3.01±0.26	12
Ho	3.89±0.34	144 ±11	3.72±0.43	10
Er	3.87±0.61	207 ±26	5.34±1.08	7.2
Tm	4.77±0.72	328 ±40	6.88±1.34	6.9
Yb	4.71±0.97	451 ±69	9.57±2.45	4.9
Lu	4.20±1.01	556 ±86	13.2 ±3.8	3.2
Y	2.74±0.31	79.8±8.3	2.91±0.45	9.4

Figure 14. One over the radius (in angstroms) versus the logarithm of the first stability constants of the rare-earth dilactates at $\mu=0.1M$, data of Schoeb (47)


LOG B_1
6.4
6.2
6.0
5.0
5.6
5.4
5.2
5.0
4.8
4.6
Y
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
0.940
0.990
1.040
1.090
1.140
1.190
1/r

The plot of log b_1 versus 1/ionic radius for Schoeb's dilactate results also shows a similarity to the log b_1 plots of this work, especially in the region of the heavy rare earths. This similarity may be a reflection of the similar dentate character of these ligands.

A number of authors (57, 58, 59) have considered the possibility of ligand field stabilization in rare-earth complexes. The electronic properties of crystalline rare-earth compounds have been studied (60, 61) and it is found that spin orbit coupling is far more important in determining the energy of the 4f orbitals than crystal-field splitting. The spin-orbit couplings for these electrons are of the order of several thousand wave numbers. Crystal-field splittings are only one or two hundred wave numbers (62, p. 114). Several authors have studied the electronic properties of rare-earth complexes in solution (63, 64, 65). The crystal-field splitting for these complexes is found to be nearly the same as for crystals. However, since the geometry of the complexes is uncertain, one cannot be certain of the symmetry of the ligand field. Without a knowledge of the symmetry of the ligand field, the exact manner in which the 4f orbitals can be split cannot be determined. Stavely and Randall (58) noted that ligand field stabilization should be absent in the complexes of La, Gd, Lu, and Y since these ions contain empty or half-filled 4f orbitals.

We note that the differences in stability between the ytterbium-lutetium pair is nearly a constant value. We observe also that the stability differences for the dysprosium-holmium and europium-gadolinium pairs are again nearly constant. Since one of the regularities occurs when the 4f orbitals are half filled and another occurs when the 4f orbitals are full, it seems that ligand field effects are being observed. If the differences are truly caused by the ligand field the various regular differences which are observed should be a measure of the energy differences for various energy levels in the splitting diagram for the 4f orbitals.

SUMMARY

The data from this investigation shows alkyl substituted malonate ligands to be of little value in ion-exchange separation of the rare earths. The $-CH_2-$ substitution causes an increase in the acid dissociation constants which in turn is reflected as a decrease in rare-earth stability constants. Increased $-CH_2-$ substitution also causes a decrease in the solubility of the solution species.

At least from the data available, a good model seems to be a nine-coordinate rare-earth cation and a bidentate ligand.

The increase in stability as we proceed from La to Lu is primarily due to the decrease in ionic radius of the rare-earth cations. This decrease causes an increased charge density (charge/radius) for the cation and thus an increase in the ionic attraction between ligand and cation. The irregularities observed (Lu-Yb, Dy-Ho) may be due to ligand field effects. With the data presented it is very difficult to do any more than hypothesize about the complexing process, the ligand field effects, and the species structure. More precise and definite information will depend on devising a method of accurately determining the structure of these species in solution.

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APPENDIX

Experimental Data for the Rare-Earth Methylmalonates

$\left.\begin{array}{l}\text{Buffer Acid Concentration} = 0.04780N \\ \text{Buffer Salt Concentration} = 0.14230N\end{array}\right\} A$

$\left.\begin{array}{l}\text{Buffer Acid Concentration} = 0.04957N \\ \text{Buffer Salt Concentration} = 0.14933N\end{array}\right\} B$

Lu $(NO_3)_3$ - 0.1010M

Yb $(NO_3)_3$ - 0.1003M

Tm $(NO_3)_3$ - 0.1004M

Volume of Metal Solution Used = 4.00 ml.

A		A		B	
Lu		Yb		Tm	
VB	pH_c	VB	pH_c	VB	pH_c
6.00	4.0406	4.00	3.8675	5.00	3.9780
7.00	4.1381	5.00	3.9360	6.00	4.0783
8.00	4.2430	6.00	4.0210	7.00	4.1850
9.00	4.3445	7.00	4.1220	8.00	4.3070
10.00	4.4423	8.00	4.2340	9.00	4.4200
11.00	4.5257	9.00	4.3440	10.00	4.5110
12.00	4.5996	10.00	4.4403	11.00	4.5970
13.00	4.6560	11.00	4.5264	12.00	4.6625
14.00	4.7082	12.00	4.5990	13.00	4.7220
15.00	4.7550	13.00	4.6620	14.00	4.7710
16.00	4.7970	14.00	4.7120	15.00	4.8140
17.00	4.8321	15.00	4.7640	16.00	4.8500
18.00	4.8630	16.00	4.8010	17.00	4.8846
19.00	4.8925	17.00	4.8377	18.00	4.9122
20.00	4.9180	18.00	4.8678	19.00	4.9415
21.00	4.9418	19.00	4.8980	20.00	4.9638
22.00	4.9639	20.00	4.9233	21.00	4.9840
23.00	4.9816	21.00	4.9476	22.00	5.0055
24.00	5.0000	22.00	4.9678	23.00	5.0210
		23.00	4.9870	24.00	5.0382
		24.00	5.0060		

Buffer Acid Concentration = 0.04957N
Buffer Salt Concentration = 0.14933N

Er $(NO_3)_3$ - 0.1046M

Ho $(NO_3)_3$ - 0.1016M

Dy $(NO_3)_3$ - 0.1003M

Volume of Metal Solution Used = 4.00 ml.

Er		Ho		Dy	
VB	pH_c	VB	pH_c	VB	pH_c
4.00	3.8900	5.00	3.9690	4.00	3.8823
5.00	3.9602	6.00	4.0640	5.00	3.9595
6.00	4.0500	7.00	4.1740	6.00	4.0560
7.00	4.1560	8.00	4.2922	7.00	4.1676
8.00	4.2663	9.00	4.4059	8.00	4.2899
9.00	4.3840	10.00	4.5020	9.00	4.4002
10.00	4.4794	11.00	4.5877	10.00	4.4980
11.00	4.5661	12.00	4.6560	11.00	4.5800
12.00	4.6378	13.00	4.7120	12.00	4.6502
13.00	4.6980	14.00	4.7621	13.00	4.7064
14.00	4.7484	15.00	4.8041	14.00	4.7540
15.00	4.7940	16.00	4.8410	15.00	4.7990
16.00	4.8357	17.00	4.8740	16.00	4.8359
17.00	4.8670	18.00	4.9036	17.00	4.8682
18.00	4.8977	19.00	4.9315	18.00	4.8971
19.00	4.9263	20.00	4.9543	19.00	4.9258
20.00	4.9510	21.00	4.9740	20.00	4.9460
21.00	4.9710	22.00	4.9955	21.00	4.9677
22.00	4.9915	23.00	5.0110	22.00	4.9877
23.00	5.0070	24.00	5.0280	23.00	5.0055
24.00	5.0262			24.00	5.0220

$$\left.\begin{array}{l}\text{Buffer Acid Concentration} = 0.04957\text{N} \\ \text{Buffer Salt Concentration} = 0.14933\text{N}\end{array}\right\} \text{A}$$

$$\left.\begin{array}{l}\text{Buffer Acid Concentration} = 0.04934\text{N} \\ \text{Buffer Salt Concentration} = 0.14930\text{N}\end{array}\right\} \text{B}$$

$Tb(NO_3)_3$ - 0.1006M

$Gd(NO_3)_3$ - 0.1010M

$Eu(NO_3)_3$ - 0.1028M

Volume of Metal Solution Used = 4.00 ml.

A		B		B	
Tb		Gd		Eu	
VB	pH_c	VB	pH_c	VB	pH_c
5.00	3.9980	5.00	4.0810	5.00	4.0750
6.00	4.0910	6.00	4.1723	6.00	4.1620
7.00	4.2000	7.00	4.2780	7.00	4.2602
8.00	4.3157	8.00	4.3870	8.00	4.3600
9.00	4.4220	9.00	4.4830	9.00	4.4553
10.00	4.5180	10.00	4.5700	10.00	4.5410
11.00	4.6010	11.00	4.6463	11.00	4.6158
12.00	4.6670	12.00	4.7080	12.00	4.6800
13.00	4.7241	13.00	4.7630	13.00	4.7360
14.00	4.7725	14.00	4.8070	14.00	4.7810
15.00	4.8156	15.00	4.8500	15.00	4.8230
16.00	4.8525	16.00	4.8855	16.00	4.8595
17.00	4.8841	17.00	4.9152	17.00	4.8920
18.00	4.9140	18.00	4.9424	18.00	4.9240
19.00	4.9414	19.00	4.9683	19.00	4.9457
20.00	4.9620	20.00	4.9683	20.00	4.9737
21.00	4.9837	21.00	5.0114	21.00	4.9925
22.00	5.0042	22.00	5.0279	22.00	5.0140
23.00	5.0200	23.00	5.0462	23.00	5.0318
24.00	5.0370	24.00	5.0620	24.00	5.0482

Buffer Acid Concentration = 0.04934N
Buffer Salt Concentration - 0.14930N .

$Sm(NO_3)_3$ - 0.1018M

$Pr(NO_3)_3$ - 0.1006M

$Nd(NO_3)_3$ - 0.1016M

Volume of Metal Solution Used = 4.00 ml.

Sm		Pr		Nd	
VB	pH_c	VB	pH_c	VB	pH_c
4.00	4.0727	3.00	4.2402	1.00	4.1695
5.00	4.1430	4.00	4.2904	2.00	4.1735
6.00	4.2237	5.00	4.3500	3.00	4.2106
7.00	4.3120	6.00	4.4165	4.00	4.2498
8.00	4.4038	7.00	4.4824	5.00	4.3227
9.00	4.4918	8.00	4.5480	6.00	4.3710
10.00	4.5664	9.00	4.6102	7.00	4.4580
11.00	4.6400	10.00	4.6700	8.00	4.5280
12.00	4.6940	11.00	4.7232	9.00	4.5953
13.00	4.7518	12.00	4.7724	10.00	4.6505
14.00	4.7960	13.00	4.8158	11.00	4.7093
15.00	4.8350	14.00	4.8531	12.00	4.7586
16.00	4.8717	16.00	4.9210	13.00	4.8056
17.00	4.9010	17.00	4.9481	14.00	4.8443
18.00	4.9300	18.00	4.9735	15.00	4.8810
19.00	4.9575	19.00	4.9977	16.00	4.9125
20.00	4.9800	20.00	5.0170	17.00	4.9387
21.00	5.0010	21.00	5.0360	18.00	4.9644
22.00	5.0200	22.00	5.0530	19.00	4.9890
23.00	5.0390	23.00	5.0690	20.00	5.0086
24.00	5.0540	24.00	5.0840	21.00	5.0323
				22.00	5.0472
				23.00	5.0632
				24.00	5.0720

Buffer Acid Concentration = 0.04780N
Buffer Salt Concentration = 0.14230N } A

Buffer Acid Concentration = 0.04930N
Buffer Salt Concentration = 0.14930N } B

$Ce(NO_3)_3$ - 0.09989M

$La(NO_3)_3$ - 0.1042M

$Y(NO_3)_3$ - 0.1027M

Volume of Metal Solution Used = 4.00 ml.

A

Ce[a]

VB	pH_c
2.00	4.1908
3.00	4.2414
4.00	4.2950
5.00	4.3540
6.00	4.4140
7.00	4.4720
8.00	4.5328
9.00	4.5920
10.00	4.6461
11.00	4.6995
12.00	4.7461
13.00	4.7918
14.00	4.8260
15.00	4.8604
16.00	4.8938

B

La

VB	pH_c
1.00	4.4090
2.00	4.4118
3.00	4.4444
4.00	4.4850
5.00	4.5458
6.00	4.5900
7.00	4.6375
8.00	4.6917
9.00	4.7330
10.00	4.7721
11.00	4.8155
12.00	4.8440
13.00	4.8804
14.00	4.9080
15.00	4.9320
16.00	4.9590
17.00	4.9760
18.00	4.9900
19.00	5.0200
20.00	5.0340
21.00	5.0535
22.00	5.0600
23.00	5.0760

A

Y

VB	pH_c
6.00	4.1007
7.00	4.1941
8.00	4.3060
9.00	4.4140
10.00	4.5078
11.00	4.5892
12.00	4.6590
13.00	4.7100
14.00	4.7675
15.00	4.8090
16.00	4.8476
17.00	4.8800
18.00	4.9120
19.00	4.9340
20.00	4.9586
21.00	4.9793
22.00	4.9990
23.00	5.0158
24.00	5.0306

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[a] $Ce(NO_3)_3$ solution has excess HNO_3 = 0.0004N.

Experimental Data for the Rare-Earth Ethylmalonates

Buffer Acid Concentration = 0.04940N
Buffer Salt Concentration = 0.14890N } A

Buffer Acid Concentration = 0.04844N
Buffer Salt Concentration = 0.15000N } B

Lu $(NO_3)_3$ - 0.1014M

Yb $(NO_3)_3$ - 0.09907M

Tm $(NO_3)_3$ - 0.09835M

Volume of Metal Solution Used = 4.00 ml.

A

Lu

VB	pH_c
1.00	3.8810
3.00	3.8691
4.00	3.9365
5.00	3.9970
6.00	4.0920
7.00	4.2079
8.00	4.3220
9.00	4.4315
10.00	4.5321
11.00	4.6160
12.00	4.6897
13.00	4.7461
14.00	4.8020
15.00	4.8455
16.00	4.8837
18.00	4.9447
19.00	4.9776
20.00	4.9980
21.00	5.0260
22.00	5.0546
23.00	5.0739
24.00	5.0898

B

Yb

VB	pH_c
3.00	3.8658
4.00	3.9255
5.00	4.0060
6.00	4.1093
7.00	4.2297
8.00	4.3579
9.00	4.4730
10.00	4.5757
11.00	4.6597
12.00	4.7320
13.00	4.7900
14.00	4.8390
15.00	4.8810
16.00	4.9210
17.00	4.9538
18.00	4.9820
19.00	5.0080
20.00	5.0320
21.00	5.0530
22.00	5.0738
23.00	5.0877
24.00	5.1050

B

Tm

VB	pH_c
3.00	3.8840
4.00	3.9444
5.00	4.0300
6.00	4.1340
7.00	4.2520
8.00	4.3793
9.00	4.5010
10.00	4.6015
11.00	4.6841
12.00	4.7540
13.00	4.8125
14.00	4.8615
15.00	4.9039
16.00	4.9385
17.00	4.9740
18.00	4.9998
19.00	5.0240
20.00	5.0470
21.00	5.0662
22.00	5.0841
23.00	5.1005
24.00	5.1170

Buffer Acid Concentration = 0.04844N } A
Buffer Salt Concentration = 0.15000N

Buffer Acid Concentration = 0.04116N } B
Buffer Salt Concentration = 0.15000N

Er $(NO_3)_3$ - 0.1038M

Ho $(NO_3)_3$ - 0.10046M

Dy $(NO_3)_3$ - 0.09976M

Volume of Metal Solution Used = 4.00 ml.

A

Er

VB	pH_c
1.00	3.8765
2.00	3.8360
3.00	3.8620
4.00	3.9203
5.00	3.9906
6.00	4.0870
7.00	4.1976
8.00	4.3220
9.00	4.4380
10.00	4.5457
11.00	4.6340
12.00	4.7080
13.00	4.7754
14.00	4.8237
15.00	4.8650
16.00	4.9063
17.00	4.9381
18.00	4.9680
19.00	4.9945
20.00	5.0191
21.00	5.0380
22.00	5.0583
23.00	5.0745
24.00	5.0898

A

Ho

VB	pH_c
3.00	3.8657
4.00	3.9255
5.00	4.0080
6.00	4.1092
7.00	4.2320
8.00	4.3596
9.00	4.4837
10.00	4.5862
11.00	4.6701
12.00	4.7428
13.00	4.8060
14.00	4.8484
15.00	4.8920
16.00	4.9280
17.00	4.9560
18.00	4.9850
19.00	5.0095
20.00	5.0336
21.00	5.0520
22.00	5.0696
23.00	5.0871
24.00	5.1058

B

Dy

VB	pH_c
3.00	3.9240
4.00	3.9915
5.00	4.0846
6.00	4.2060
7.00	4.3480
8.00	4.4864
9.00	4.6120
10.00	4.7172
11.00	4.7967
12.00	4.8638
13.00	4.9210
14.00	4.9635
15.00	5.0039
16.00	5.0400
17.00	5.0700
18.00	5.0960
19.00	5.1206
20.00	5.1421
21.00	5.1610
22.00	5.1800
23.00	5.1925
24.00	5.2100

Buffer Acid Concentration = 0.04934N
Buffer Salt Concentration = 0.14930N } A

Buffer Acid Concentration = 0.04920N
Buffer Salt Concentration = 0.14910N } B

Tb $(NO_3)_3$ - 0.1055M

Eu $(NO_3)_3$ - 0.1000M

Gd $(NO_3)_3$ - 0.1010M

Volume of Metal Solution Used = 4.00 ml.

A		A		B	
Tb		Eu		Gd	
VB	pH_c	VB	pH_c	VB	pH_c
5.00	3.9564	5.00	4.0840	5.00	4.0810
6.00	4.0480	6.00	4.1757	6.00	4.1723
8.00	4.2720	7.00	4.2650	7.00	4.2780
9.00	4.3810	8.00	4.3814	8.00	4.3870
10.00	4.4920	9.00	4.4858	9.00	4.4830
11.00	4.5810	10.00	4.5700	10.00	4.5700
12.00	4.6596	11.00	4.6456	11.00	4.6463
13.00	4.7225	12.00	4.7199	12.00	4.7080
14.00	4.7778	13.00	4.7692	13.00	4.7630
15.00	4.8280	14.00	4.8250	14.00	4.8070
16.00	4.8634	15.00	4.8676	15.00	4.8500
17.00	4.9040	16.00	4.9015	16.00	4.8855
18.00	4.9370	17.00	4.9340	17.00	4.9152
19.00	4.9640	18.00	4.9661	18.00	4.9424
20.00	4.9850	19.00	4.9864	19.00	4.9683
21.00	5.0110	20.00	5.0130	20.00	4.9900
22.00	5.0280	21.00	5.0345	21.00	4.0114
23.00	5.0478	22.00	5.0537	22.00	5.0279
24.00	5.0640	23.00	5.0770	23.00	5.0462
		24.00	5.0940	24.00	5.0620

Buffer Acid Concentration = 0.04920N
Buffer Salt Concentration = 0.14910N

$Sm(NO_3)_3$ - 0.0962M

$Nd(NO_3)_3$ - 0.08865M

$Pr(NO_3)_3$ - 0.09143M

Volume of Metal Solution Used = 4.00 ml.

Sm	
VB	pH_c
4.00	2.1282
5.00	4.2120
6.00	4.3083
7.00	4.4061
8.00	4.5059
9.00	4.5993
10.00	4.6730
11.00	4.7396
12.00	4.7983
13.00	4.8475
14.00	4.8885
15.00	4.9270
16.00	4.9593
17.00	4.9900
19.00	5.0380
20.00	5.0587
21.00	5.0780
22.00	5.0941
23.00	5.1090

Nd	
VB	pH_c
3.00	4.3100
4.00	4.3740
5.00	4.4445
6.00	4.5177
7.00	4.5941
8.00	4.6675
9.00	4.7316
10.00	4.7900
11.00	4.8423
12.00	4.8850
13.00	4.9280
14.00	4.9618
15.00	4.9943
16.00	5.0260
17.00	5.0510
18.00	5.0737
19.00	5.0940
20.00	5.1114
21.00	5.1277
22.00	5.1455
23.00	5.1580
24.00	5.1716

Pr	
VB	pH_c
2.00	4.2906
3.00	4.3360
4.00	4.3940
6.00	4.5240
7.00	4.5940
8.00	4.6598
9.00	4.7220
10.00	4.7777
11.00	4.8297
12.00	4.8750
13.00	4.9180
14.00	4.9500
15.00	4.9830
16.00	5.0135
17.00	5.0390
18.00	5.0610
19.00	5.0818
21.00	5.1197
22.00	5.1350
23.00	5.1517
24.00	5.1643

Buffer Acid Concentration = 0.05080N
Buffer Salt Concentration = 0.14910N

$Ce(NO_3)_3$ - 0.1025M

$La(NO_3)_3$ - 0.09990M

Volume of Metal Solution Used = 4.00 ml.

Ce		La		Cu*	
VB	pH_c	VB	pH_c	VB	pH_c
2.00	4.2380	1.00	4.3942	5.00	3.616
3.00	4.2897	2.00	4.4061	20.00	3.578
4.00	4.3424	3.00	4.4441	25.00	3.649
5.00	4.3983	4.00	4.4921	30.00	3.736
6.00	4.4560	5.00	4.5420	35.00	3.854
7.00	4.5043	6.00	4.5943	40.00	3.983
8.00	4.5736	7.00	4.6450	45.00	4.114
9.00	4.6304	8.00	4.6950	50.00	4.242
10.00	4.6855	9.00	4.7435	55.00	4.348
11.00	4.7382	10.00	4.7887	60.00	4.447
12.00	4.7858	11.00	4.8302	65.00	4.530
13.00	4.8265	12.00	4.8680	70.00	4.600
14.00	4.8643	13.00	4.9061	75.00	4.662
15.00	4.9017	14.00	4.9380	80.00	4.726
16.00	4.9337	15.00	4.9642		
17.00	4.9615				
18.00	4.9890				
19.00	5.0120				
20.00	5.0342				
22.00	5.0726				
23.00	5.0892				
24.00	5.1043				

Excess acid (HNO_3) in $Ce(NO_3)_3$ soln. = 0.00240 N

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*Concentrations for Cu solutions:
buffer salt conc. = 0.07491 M
buffer acid conc. = 0.02492 M
volume of metal used = 10.00 ml.
conc. of metal solution = 0.1032 M
excess acid in metal solution = 0.00024 M
final sample volume = 250 ml. .

Experimental Data for the Rare-Earth Propylmalonates

Buffer Acid Concentration = 0.05150N
Buffer Salt Concentration = 0.15010N

Lu $(NO_3)_3$ - 0.1010M

Yb $(NO_3)_3$ - 0.1003M

Tm $(NO_3)_3$ - 0.1004M

Volume of Metal Solution Used = 4.00 ml.

Lu		Yb		Tm	
VB	pH_c	VB	pH_c	VB	pH_c
1.00	3.8580	1.00	3.8304	1.00	3.8450
2.00	3.8266	2.00	3.7964	2.00	3.8087
3.00	3.8540	3.00	3.8250	3.00	3.8380
4.00	3.9138	4.00	3.8800	4.00	3.8958
5.00	3.9824	5.00	3.9562	5.00	3.9730
6.00	4.0733	6.00	4.0500	6.00	4.0700
7.00	4.1810	7.00	4.1642	7.00	4.1835
8.00	4.2979	8.00	4.2840	8.00	4.3048
9.00	4.4026	9.00	4.4000	9.00	4.4223
10.00	4.5024	10.00	4.5036	10.00	4.5252
11.00	4.5884	11.00	4.5922	12.00	4.6879
12.00	4.6617	13.00	4.7258	13.00	4.7493
13.00	4.7219	14.00	4.7800	15.00	4.8453
14.00	4.7750	15.00	4.8283	16.00	4.8841
15.00	4.8207	16.00	4.8680	17.00	4.9182
16.00	4.8618	17.00	4.9061	19.00	4.9765
17.00	4.8960	18.00	4.9370	20.00	5.0017
18.00	4.9280	19.00	4.9640	21.00	5.0256
19.00	4.9573	20.00	4.9906	22.00	5.0458
20.00	4.9835	21.00	4.0140	23.00	5.0639
21.00	5.0070	22.00	5.0342	24.00	5.0807
22.00	5.0280	23.00	5.0557		
23.00	5.0477	24.00	5.0742		
24.00	5.0660				

$$\left.\begin{array}{l}\text{Buffer Acid Concentration} = 0.05150\text{N} \\ \text{Buffer Salt Concentration} = 0.15010\text{N}\end{array}\right\} \text{A}$$

$$\left.\begin{array}{l}\text{Buffer Acid Concentration} = 0.05160\text{N} \\ \text{Buffer Salt Concentration} = 0.15000\text{N}\end{array}\right\} \text{B}$$

$Er(NO_3)_3$ - 0.1046M

$Ho(NO_3)_3$ - 0.1016M

$Dy(NO_3)_3$ - 0.1003M

Volume of Metal Solution Used = 4.00 ml.

A		A		B	
Er		Ho		Dy	
VB	pH_c	VB	pH_c	VB	pH_c
1.00	3.8303	1.00	3.8379	1.00	3.8279
2.00	3.7924	2.00	3.8038	2.00	3.7030
3.00	3.8170	3.00	3.8318	3.00	3.8220
4.00	3.8700	4.00	3.8879	4.00	3.8770
5.00	3.9419	5.00	3.9612	5.00	3.9542
6.00	4.0320	6.00	4.0599	6.00	4.0483
7.00	4.1420	7.00	4.1742	7.00	4.1672
8.00	4.2604	8.00	4.2980	8.00	4.2923
9.00	4.3795	9.00	4.4164	9.00	4.4097
10.00	4.4890	10.00	4.5243	10.00	4.5220
11.00	4.5810	11.00	4.6153	11.00	4.6104
12.00	4.6566	12.00	4.6867	12.00	4.6839
13.00	4.7210	13.00	4.7501	13.00	4.7475
14.00	4.7763	14.00	4.8015	14.00	4.8002
15.00	4.8240	15.00	4.8464	15.00	4.8442
16.00	4.8650	16.00	4.8860	16.00	4.8850
17.00	4.9000	17.00	4.9206	17.00	4.9210
18.00	4.9323	18.00	4.9516	18.00	4.9523
19.00	4.9615	19.00	4.9777	19.00	4.9795
20.00	4.9863	20.00	5.0045	20.00	5.0057
21.00	5.0101	21.00	5.0261	21.00	4.0276
22.00	5.0318	22.00	5.0459	22.00	5.0482
23.00	5.0517	23.00	5.0659	23.00	5.0675
24.00	5.0690	24.00	5.0835	24.00	5.0861

Buffer Acid Concentration = 0.05160N
Buffer Salt Concentration = 0.15000N

$Tb\ (NO_3)_3$ - 0.09996M

$Gd\ (NO_3)_3$ - 0.1010M

$Eu\ (NO_3)_3$ - 0.1028M

Volume of Metal Solution Used = 4.00 ml.

Tb*		Gd		Eu	
VB	pH_c	VB	pH_c	VB	pH_c
2.00	3.8837	4.00	3.9800	4.00	3.9778
3.00	3.9317	5.00	4.0538	5.00	4.0467
4.00	3.9964	6.00	4.1420	6.00	4.1340
5.00	4.0805	7.00	4.2465	7.00	4.2296
6.00	4.1800	8.00	4.3562	8.00	4.3338
7.00	4.3197	9.00	4.4625	9.00	4.4359
8.00	4.4540	10.00	4.5581	10.00	4.5257
9.00	4.5780	11.00	4.6395	11.00	4.6040
10.00	4.6760	12.00	4.7078	12.00	4.6710
11.00	4.7581	13.00	4.7660	13.00	4.7317
12.00	4.8264	14.00	4.8160	14.00	4.7825
13.00	4.8910	15.00	4.8599	15.00	4.8282
14.00	4.9400	16.00	4.8967	16.00	4.8700
15.00	4.9820	17.00	4.9302	17.00	4.9058
16.00	5.0189	18.00	4.9600	18.00	4.9360
17.00	5.0510	19.00	4.9882	19.00	4.9670
18.00	5.0780	20.00	5.0122	20.00	4.9920
19.00	5.1040	21.00	5.0342	21.00	5.0176
20.00	5.1285	22.00	5.0500	22.00	5.0387
21.00	5.1482	23.00	5.0739	23.00	5.0580
22.00	5.1716	24.00	5.0919	24.00	5.0760

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*Buffer acid conc. = 0.04348 N
Buffer salt conc. = 0.14890 N

Buffer Acid Concentration = 0.05160N } A
Buffer Salt Concentration = 0.15000N }

Buffer Acid Concentration = 0.04916N } B
Buffer Salt Concentration = 0.15000N }

Sm $(NO_3)_3$ - 0.1018M

Nd $(NO_3)_3$ - 0.1016M

Y $(NO_3)_3$ - 0.1029 M

For Y and Sm run Volume of Metal Solution Used = 4.00 ml.

For Nd run Volume of Metal Solution Used = 1.00 ml.

A		A		B	
Sm		Nd		Y	
VB	pH_c	VB	pH_c	VB	pH_c
4.00	4.0545	0.50	4.7457	3.00	3.9095
5.00	4.1220	1.00	4.7390	4.00	3.9681
6.00	4.2018	1.50	4.8210	5.00	4.0461
7.00	4.2898	2.00	4.8843	7.00	4.2596
8.00	4.3798			8.00	4.3900
9.00	4.4675			9.00	4.5080
10.00	4.5480			10.00	4.6080
11.00	4.6220			11.00	4.6941
12.00	4.6860			12.00	4.7640
13.00	4.7421			13.00	4.8218
14.00	4.7920			14.00	4.8696
15.00	4.8360			15.00	4.9122
16.00	4.8740			16.00	4.9490
17.00	4.9097			17.00	4.9810
18.00	4.9439			18.00	5.0083
19.00	4.9696			19.00	4.0341
20.00	4.9967			20.00	5.0567
21.00	5.0190			21.00	5.0780
22.00	5.0420			22.00	5.0957
23.00	5.0603			23.00	5.1030
24.00	5.0797			24.00	5.1300

Experimental Data for the Rare-Earth Butylmalonates

Buffer Acid Concentration = 0.05000N } A
Buffer Salt Concentration = 0.15010N } A

Buffer Acid Concentration = 0.04990N } B
Buffer Salt Concentration = 0.15010N } B

Lu $(NO_3)_3$ - 0.1010M

Yb $(NO_3)_3$ - 0.1003M

Tm $(NO_3)_3$ - 0.1004M

Volume of Metal Solution Used = 4.00 ml.

A

Lu

VB	pH_c
3.00	3.8938
4.00	3.9448
5.00	4.0241
6.00	4.1220
7.00	4.2286
8.00	4.3490
9.00	4.4601
10.00	4.5602
11.00	4.6445
12.00	4.7176
13.00	4.7804
14.00	4.8325
15.00	4.8810
16.00	4.9237
17.00	4.9592
18.00	4.9910
19.00	5.0210
20.00	5.0471
21.00	5.0700
22.00	5.0938
23.00	5.1150
24.00	5.1321

A

Yb

VB	pH_c
4.00	3.9209
5.00	4.0002
6.00	4.1011
7.00	4.2184
8.00	4.3403
9.00	4.4632
10.00	4.5643
11.00	4.6520
12.00	4.7260
13.00	4.7908
14.00	4.8442
15.00	4.8908
16.00	4.9304
17.00	4.9700
18.00	5.0000
19.00	5.0290
20.00	5.0559
21.00	5.0790
22.00	5.1000

B

Tm

VB	pH_c
3.00	3.8770
4.00	3.9365
5.00	4.0125
6.00	4.1121
7.00	4.2297
8.00	4.3598
9.00	4.4792
10.00	4.5880
11.00	4.6737
12.00	4.7480
13.00	4.8085
14.00	4.8610
15.00	4.9065
16.00	4.9461
17.00	4.9810
18.00	5.0122
19.00	5.0400
20.00	5.0670
21.00	5.0902
22.00	5.1143

$$\left.\begin{array}{l}\text{Buffer Acid Concentration} = 0.04990\text{N} \\ \text{Buffer Salt Concentration} = 0.15010\text{N}\end{array}\right\} \text{A}$$

$$\left.\begin{array}{l}\text{Buffer Acid Concentration} = 0.04980\text{N} \\ \text{Buffer Salt Concentration} = 0.15010\text{N}\end{array}\right\} \text{B}$$

$Er(NO_3)_3$ - 0.1046M

$Ho(NO_3)_3$ - 0.1016M

$Dy(NO_3)_3$ - 0.1003M

Volume of Metal Solution Used = 4.00 ml.

A

Er

VB	pH_c
4.00	3.9098
5.00	3.9861
6.00	4.0796
7.00	4.1986
8.00	4.3185
9.00	4.4400
10.00	4.5541
11.00	4.6420
12.00	4.7200
13.00	4.7839
14.00	4.8410
15.00	4.8858
16.00	4.9277
17.00	4.9640
18.00	4.9962
19.00	5.0245
20.00	5.0512
21.00	5.0740
22.00	5.0962
23.00	5.1181
24.00	5.1336

A

Ho

VB	pH_c
5.00	4.0117
6.00	4.1110
7.00	4.2300
8.00	4.3640
9.00	4.4782
10.00	4.5872
11.00	4.6793
12.00	4.7510
13.00	4.8122
14.00	4.8640
15.00	4.9102
16.00	4.9480
17.00	4.9800
18.00	5.0124

B

Dy

VB	pH_c
4.00	3.9196
5.00	4.0020
6.00	4.1039
7.00	4.2290
8.00	4.3600
9.00	4.4840
10.00	4.5938
11.00	4.6807
12.00	4.7541
13.00	4.8160
14.00	4.8700
15.00	4.9156
16.00	4.9540
17.00	4.9900
18.00	5.0200
19.00	5.0482
20.00	5.0765
21.00	5.0964
22.00	5.1181
23.00	5.1370
24.00	5.1555

Buffer Acid Concentration = 0.04980N
Buffer Salt Concentration = 0.15010N

$Tb(NO_3)_3$ - 0.1006M

$Gd(NO_3)_3$ - 0.1010M

$Eu(NO_3)_3$ - 0.1028M

Volume of Metal Solution Used = 4.00 ml.

Tb		Gd		Eu	
VB	pH_c	VB	pH_c	VB	pH_c
3.00	3.8819	4.00	4.0180	4.00	4.0180
4.00	3.9418	5.00	4.0982	5.00	4.0935
5.00	4.0215	6.00	4.1957	6.00	4.1830
6.00	4.1194	7.00	4.3063	7.00	4.2855
7.00	4.2405	8.00	4.4285	8.00	4.3941
8.00	4.3662	9.00	4.5280	9.00	4.4940
9.00	4.4820	10.00	4.6240	10.00	4.5910
10.00	4.5900	11.00	4.7000	11.00	4.6700
11.00	4.6765	12.00	4.7712	12.00	4.7361
12.00	4.7480	13.00	4.8325	13.00	4.7977
13.00	4.8117	14.00	4.8820	14.00	4.8500
14.00	4.8638	15.00	4.9260	15.00	4.8971
15.00	4.9097	16.00	4.9663	16.00	4.9360
16.00	4.9479	17.00	4.9998	17.00	4.9710
17.00	4.9840	18.00	5.0292	18.00	5.0042
18.00	5.0155	19.00	5.0545	19.00	5.0339
19.00	5.0438	20.00	5.0800	20.00	5.0600
20.00	5.0700	21.00	5.1030	21.00	5.0823
21.00	5.0916	22.00	5.1240	22.00	5.1033
		23.00	5.1433	23.00	5.1260
		24.00	5.1600	24.00	5.1437

Buffer Acid Concentration = 0.04980N}
Buffer Salt Concentration = 0.15010N} A

Buffer Acid Concentration = 0.05010N}
Buffer Salt Concentration = 0.15010N} B

$Sm(NO_3)_3$ - 0.1018M

$Nd(NO_3)_3$ - 0.1016M

$Y(NO_3)_3$ - 0.1027M

Y run used 4.00 ml. metal solution

Sm run used 3.00 ml. metal solution

Nd run used 2.00 ml. metal solution

A		B		B	
Sm		Nd		Y	
VB	pH_c	VB	pH_c	VB	pH_c
4.00	4.2910	1.00	4.4721	4.00	3.9900
5.00	4.4020	1.25	4.4885	5.00	4.0679
6.00	4.5218	1.50	4.5058	6.00	4.1706
7.00	4.6340	1.75	4.5260	7.00	4.2895
8.00	4.7320	2.00	4.5501	8.00	4.4167
9.00	4.8120	2.25	4.5738	9.00	4.5324
10.00	4.8774	2.50	4.6001	10.00	4.6364
11.00	4.9340			11.00	4.7222
12.00	4.9810			12.00	4.7940
13.00	5.0220			13.00	4.8530
14.00	5.0591			14.00	4.9042
15.00	5.0898			15.00	4.9460
16.00	5.1177			16.00	4.9842
17.00	5.1419			17.00	5.0142
18.00	5.1633			18.00	5.0459
19.00	5.1820			19.00	5.0700
20.00	5.1998			20.00	5.0942
21.00	5.2157			21.00	5.1150
22.00	5.2300			22.00	5.1346
23.00	5.2438			23.00	5.1525
24.00	5.2556			24.00	5.1686

Experimental Data for the Rare-Earth Pentylmalonates

Buffer Acid Concentration = 0.05030N
Buffer Salt Concentration = 0.15010N

Lu $(NO_3)_3$ - 0.1010M

Yb $(NO_3)_3$ - 0.1003M

Tm $(NO_3)_3$ - 0.1004

Volume of Metal Solution Used = 1.00 ml.

Lu		Yb		Tm	
VB	pH_c	VB	pH_c	VB	pH_c
1.00	4.4483	0.50	4.3650	0.50	4.3760
1.50	4.5784	1.00	4.4175	1.00	4.4360
2.00	4.7218	1.50	4.5575	2.00	4.7343
2.50	4.8681	2.00	4.7191	2.50	4.8820
3.00	4.9761	2.50	4.8658	3.00	4.9871
3.50	5.0540	3.00	4.9720	3.50	5.0659
4.00	5.1092	3.50	5.0519	4.00	5.1200
4.50	5.1555	4.00	5.1123	4.50	5.1630
5.00	5.1880			5.00	5.1975
5.50	5.2158			5.50	5.2218
6.00	5.2399			6.00	5.2401
6.50	5.2608			6.50	5.2670
7.00	5.2780			7.00	5.2830
7.50	5.2935				
8.00	5.3061				
8.50	5.3178				
9.00	5.3280				
9.50	5.3387				
10.00	5.3460				
10.50	5.3510				
11.00	5.3623				
11.50	5.3688				

Buffer Acid Concentration = 0.05030N
Buffer Salt Concentration = 0.15010N

Er $(NO_3)_3$ - 0.1046M

Ho $(NO_3)_3$ - 0.1016M

Dy $(NO_3)_3$ - 0.1003M

Volume of Metal Solution Used = 1.00 ml.

Er		Ho		Dy	
VB	pH_c	VB	pH_c	VB	pH_c
0.50	4.3584	0.50	4.3717	0.50	4.3584
1.00	4.4163	1.00	4.4316	1.00	4.4103
1.50	4.5156	1.50	4.5662	1.50	4.5550
2.00	4.7082	2.00	4.7312	2.00	4.7302
2.50	4.8559	2.50	4.8880	2.50	4.8770
3.00	4.9650	3.00	4.9925	3.00	4.9860
3.50	5.0482	3.50	5.0695	3.50	5.0675
4.00	5.1030	4.00	5.1236	4.00	5.1220
4.50	5.1540	4.50	5.1674	4.50	5.1623
5.00	5.1835	5.00	5.1980	5.00	5.1954
5.50	5.2119	5.50	5.2260	5.50	5.2240
		6.00	5.2500	6.00	5.2442
		6.50	5.2690	6.50	5.2640
		7.00	5.2857	7.00	5.2830
		7.50	5.2997		
		8.00	5.3125		

Buffer Acid Concentration = 0.05030N
Buffer Salt Concentration = 0.15010N

$Tb\ (NO_3)_3$ - 0.1006M

$Gd\ (NO_3)_3$ - 0.1010M

$Eu\ (NO_3)_3$ - 0.1028M

$Y\ (NO_3)_3$ - 0.1027

Volume of Metal Solution Used = 1.00 ml.

Tb		Gd		Eu		Y	
VB	pH_c	VB	pH_c	VB	pH_c	VB	pH_c
0.50	4.3818	0.50	4.4523	0.50	4.4516	0.50	4.4282
1.00	4.4428	1.00	4.5170	1.00	4.5130	1.00	4.4898
1.50	4.5757	1.50	4.6445	1.50	4.6323	1.50	4.6230
2.00	4.7460	2.00	4.7834	2.00	4.7770	2.00	4.7780
2.50	4.8860	2.50	4.9098	2.50	4.8863	2.50	4.9001
3.00	4.9860	3.00	5.0059	3.00	4.9758	3.00	5.0110
3.50	5.0661	3.50	5.0746	3.50	5.0483	3.50	5.0870
4.00	5.1258	4.00	5.1241	4.00	5.1040	4.00	5.1380
4.50	5.1635	4.50	5.1657			4.50	5.1819
5.00	5.1965	5.00	5.1985			5.00	5.2131
5.50	5.2220	5.50	5.2270			5.50	5.2400
6.00	5.2438	6.00	5.2491			6.00	5.2602
6.50	5.2657	6.50	5.2692			6.50	5.2819
		7.00	5.2841			7.00	5.2961

Experimental Data for the Acid Dissociation Constants

methyl malonic acid

conc. acid = 0.09950M
conc. base = 0.09936M
final sample volume = 100 ml.
10.00 ml. acid/sample

sample	vol. base	pH_c
1	4.50	2.9670
2	5.00	3.0280
3	5.50	3.0956
4	6.00	3.1700
5	6.50	3.2443
6	7.00	3.3300
7	8.00	3.5343
8	9.00	3.8110
9	11.00	4.5343
10	12.00	4.8090
11	12.50	4.9300
12	13.00	5.0290
13	13.50	5.1240
14	14.00	5.2136
15	14.50	5.3030
16	15.00	5.3863
17	15.50	5.4742
18	16.00	5.5684

ethylmalonic acid

conc. acid = 0.03814M
conc. salt = 0.03716M
final sample volume = 250 ml.

vol. base	pH_c
5.00	4.3390
10.00	4.2340
15.00	4.1890
20.00	4.1640
25.00	4.1410
30.00	4.1060
40.00	4.0890
45.00	4.0750
50.00	4.0710
55.00	4.0690
60.00	4.0670
65.00	4.0660
70.00	4.0630
75.00	4.0620
80.00	4.0610

ethyl malonic acid

conc. acid = 0.4918M
conc. base = 0.09936M
final sample volume = 100.0 ml.
2.00 ml. acid/sample

propyl malonic acid

conc. acid = 0.1270M
conc. base = 0.09936M
final sample volume = 100 ml.
10.00 ml. acid/sample

sample	vol. base	pH_c	vol. base	pH_c
1	4.00	2.8480	4.50	2.7760
2	4.50	2.9022	5.00	2.8195
3	5.00	2.9618	5.50	2.8690
4	5.50	3.0278	6.00	2.9180
5	6.00	3.0944	6.50	2.9700
6	6.50	3.1715	7.00	3.0277
7	7.00	3.2580	8.00	3.1438
8	8.00	3.4541	9.00	3.2818
9	9.00	3.7380	11.00	3.6616
10	11.00	4.5882	12.00	3.9576
11	12.00	4.8737	12.50	4.1321
12	12.50	4.9905	13.00	4.3178
13	13.00	5.0950	13.50	4.4841
14	13.50	5.1840	14.00	4.6300
15	14.00	5.2785	14.50	4.7530
16	14.50	5.3720	15.00	4.8557
17	15.00	5.4610	15.50	4.9523
18			16.00	5.0340
19			17.00	5.1935
20			18.00	5.3336
21			19.00	5.4720

butylmalonic acid

conc. acid = 0.1009M
conc. base = 0.09936M
final sample volume = 100 ml.
10.00 ml. acid/sample

pentylmalonic acid

conc. acid = 0.1008M
conc. acid = 0.09936M
final sample volume = 100.0 ml.
10.00 ml. acid/sample

sample	vol. base	pH_c	vol. base	pH_c
1	4.50	2.9182	4.50	2.9238
2	5.00	2.9758	5.00	2.9817
3	5.50	3.0497	5.50	3.0471
4	6.00	3.1080	6.00	3.1179
5	6.50	3.1085	6.50	3.1963
6	7.00	3.2700	7.00	3.2800
7	8.00	3.4718	8.00	3.4820
8	9.00	3.7525	9.00	3.7640
9	11.00	4.5901	11.00	4.6160
10	12.00	4.8841	12.00	4.9217
11	12.50	5.0163	12.50	5.0399
12	13.00	5.1101	13.00	5.1422
13	13.50	5.2061	13.50	5.2353
14	14.00	5.3058	14.00	5.3501
15	14.50	5.3881	14.50	5.4217
16	15.00	5.4780	15.00	5.5093
17	15.50	5.5671	15.50	5.5926
18	16.00	5.6560	16.00	5.6839

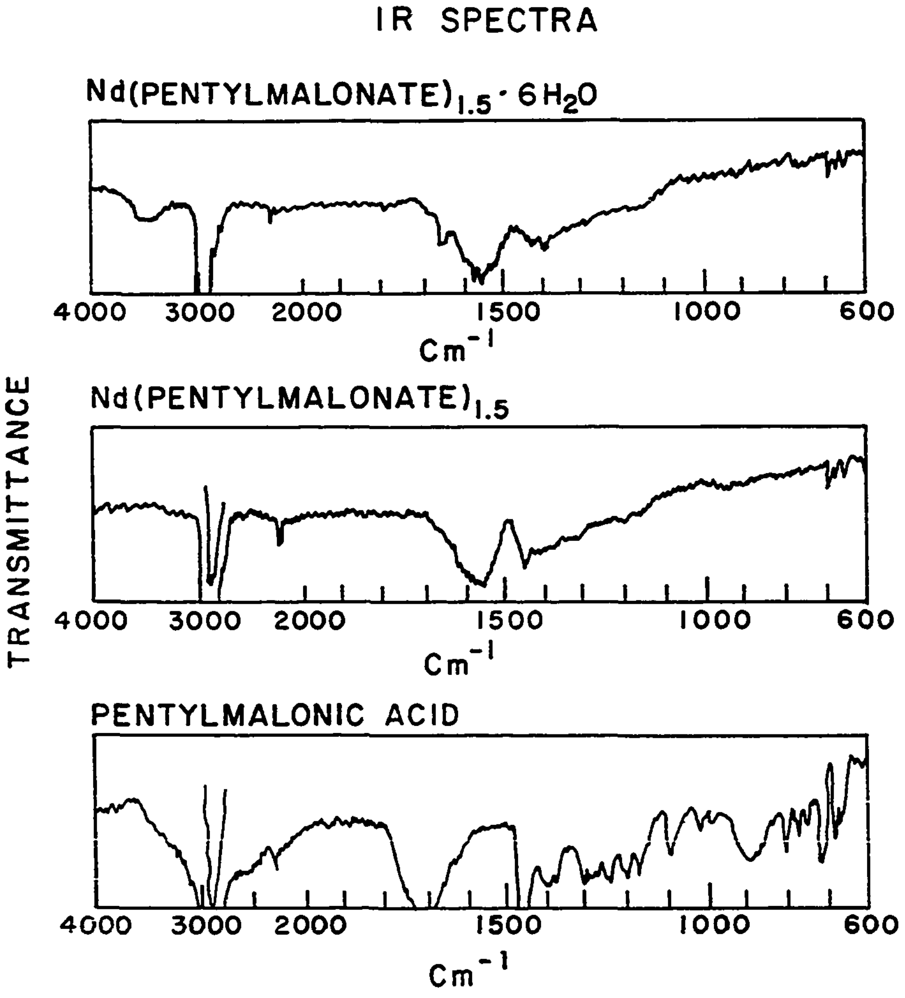

Figure 16. IR spectra from from 600 cm^{-1} to 4000 cm^{-1}

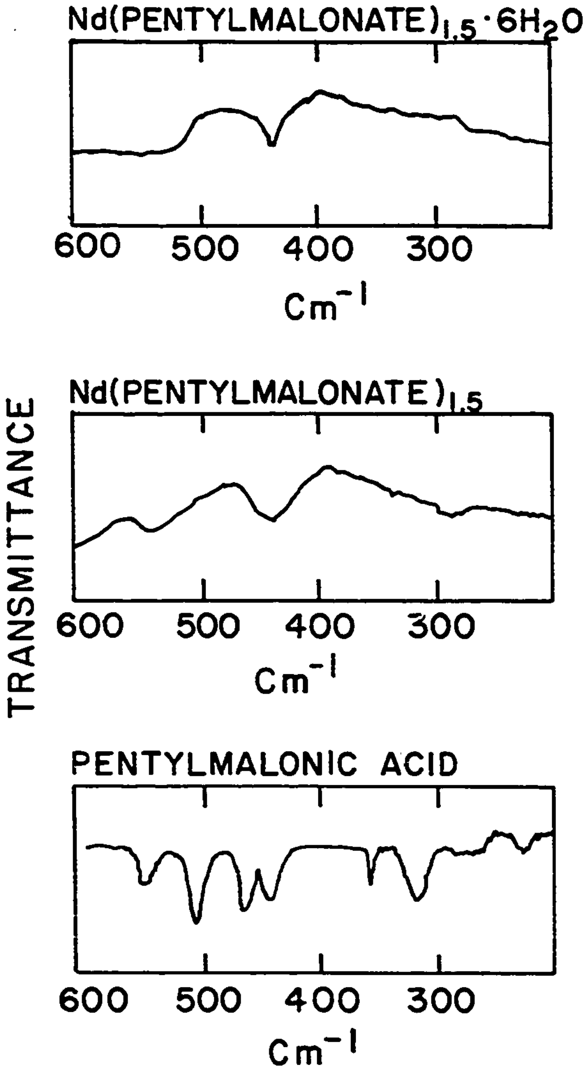

Figure 17. IR spectra from 200 cm^{-1} to 600 cm^{-1}

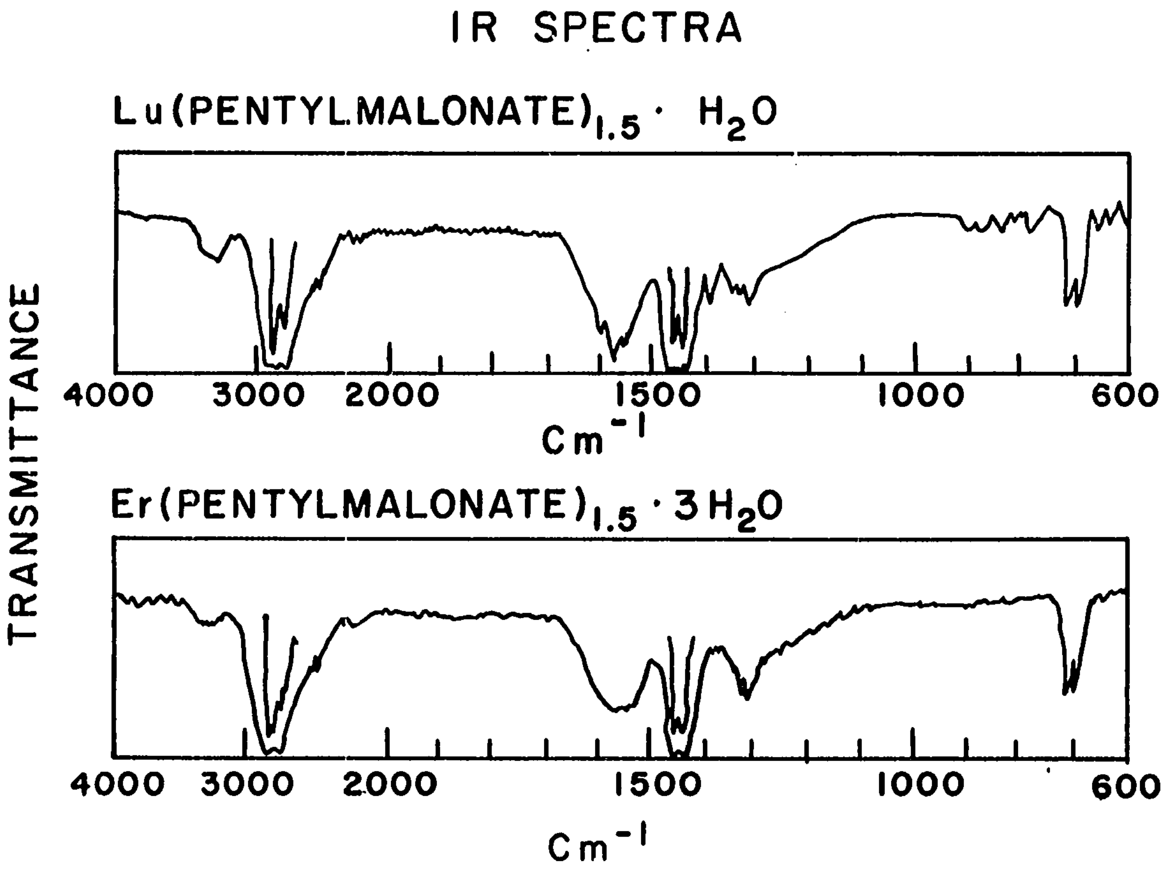

Figure 18. IR spectra from 600 cm^{-1} to 4000 cm^{-1}

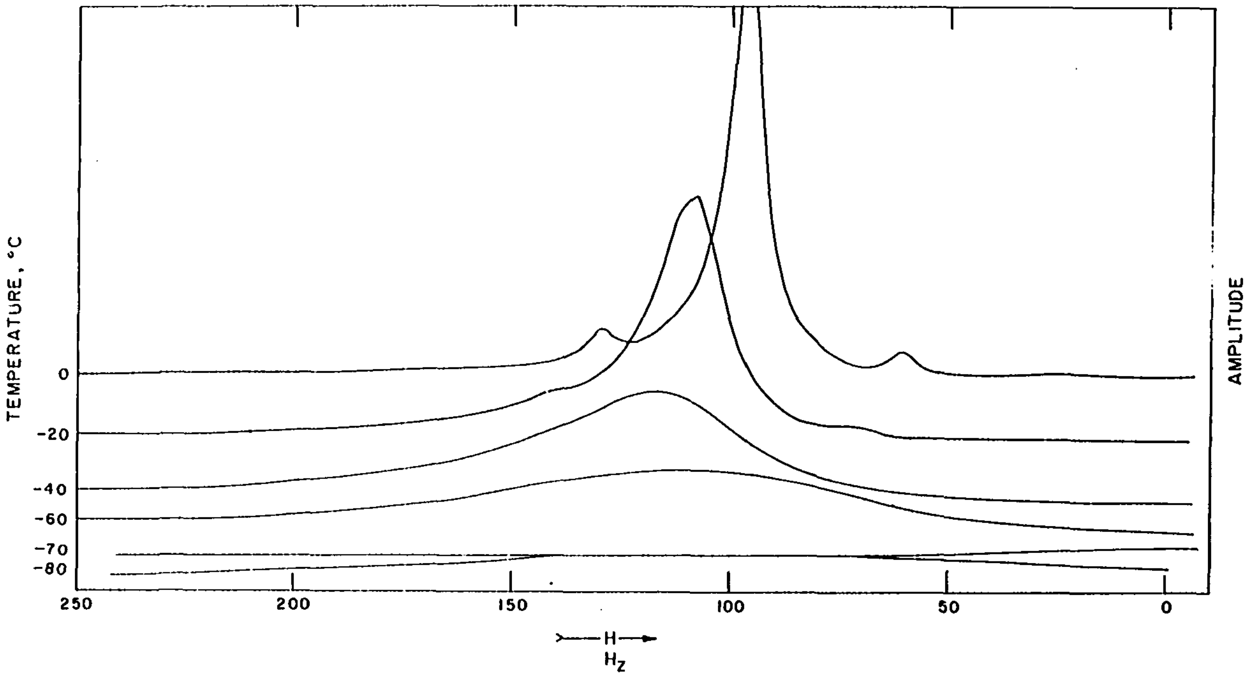

Figure 19. NMR spectra