Thermodynamic Properties of Rare Earth Complexes

IX. Stability Constants for the Lanthanoid Malonate and Hydrogen Malonate Complexes

INGEMAR DELLIEN and INGMAR GRENTHE

*Division of Physical Chemistry 1, Chemical Center, University of Lund,
P.O.B. 740, S-220 07 Lund 7, Sweden*

The stability constants for the formation of lanthanoid(III) malonate and bimalonate complexes of the compositions MA, MA_2, MA_3, MHA, and MHA_2 have been determined. All data refer to a temperature of 25.0°C and a sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M. The various systems were investigated by determining the concentration of free hydrogen ion by means of a glass electrode. Stability constants were obtained from the experimental data by a least-squares method ("Letagrop Vrid").

Thermodynamic studies of the complexes formed between the tervalent rare earths and a number of dicarboxylates have been reported in the previous parts of this series.[1-8] These studies have been extended to include the ligands malonate, maleate, thiodiacetate, and iminodiacetate. All ligands are potential chelating agents containing two carboxylate groups. The size of the chelate ring, if formed, varies from five atoms in oxalate to six in malonate, and seven in maleate.

Oxydiacetate, thiodiacetate, iminodiacetate, and 2,6-pyridine dicarboxylate are potential three-dentate ligands, where one donor atom is an ether oxygen, an ether sulfur, an aliphatic and an aromatic nitrogen, respectively. The various ligands have been chosen in this way in order to permit a discussion of the following points.

a. How are the stability constants influenced by the third donor atom in the three-dentate ligands and by the size of the chelate ring?

b. One expects a correlation between the stability of the chelate complex and the tendency to form acid or polynuclear complexes — the weaker the chelate the stronger the tendency for formation of mixed complexes. The occurrence of effects of this type may be studied as a function of the distance between the donor atoms in the series oxalate — malonate —

maleate and as a function of the donor atoms in the series dipicolinate — oxydiacetate — thiodiacetate.

c. The rare earth elements presumably have coordination numbers larger than six in aqueous solution. An estimate of the coordination number is obtained from the maximum number of ligands coordinated in solution. The lanthanoids can coordinate three oxydiacetate [2] and dipicolinate [1] ligands, indicating a coordination number of at least nine in solution. The maximum number of oxalate groups coordinated is four [6], a fact which also implies a coordination number larger than six. Also scandium(III) coordinates four oxalate ions, whereas only three malonate ions are bound.[7] It is thus of interest to determine the maximum number of coordinated malonate ions for the rare earth elements to see whether the difference between the number of coordinated oxalate and malonate ions is due to the ligand or to the size of the central ion.

Discussion along the lines mentioned should be facilitated if more than one characteristic of the reactions is studied. We have for this reason studied both the free energy and enthalpy changes for most of the systems.

This paper will describe the stoichiometric composition and the stability constants for the complexes formed between the various lanthanoids and the ligands malonate and hydrogen malonate. There are some earlier communications on this subject. Ke *et al.*[9] have studied rare earth bimalonate complexes using an ion-exchange method and reported stability constants for the complexes MHA and M(HA)$_2$. Powell *et al.*[10] have used the same potentiometric method as the present authors and found evidence for the formation of the species MA and MA$_2$. Only Paramonova *et al.*[11] have clearly taken into consideration the fact that both malonate and bimalonate ions act as ligands to lanthanoid ions.

None of the studies published so far have shown the existence of complexes with more than two malonate ions coordinated.

The method chosen for the present study was one of the potentiometric standard methods, *viz.* the determination of the concentration of free hydrogen ion by means of a glass electrode.

All measurements refer to a sodium perchlorate medium with a constant sodium ion concentration equal to 1.00 M and a temperature of 25.0°C.

NOTATIONS

Malonic acid, CH$_2$ (COOH)$_2$, is written as H$_2$A. C_M, C_H, C_A denote the total concentration of metal ion, free and dissociable hydrogen ions, and malonate ion, respectively. m, h, a, denote the concentrations of free metal ion, hydrogen ion, and malonate ion, respectively.

$\beta_{p,q,r}$ = the over-all stability constant for the complex M$_p$H$_q$A$_r$, defined as .

$$\beta_{p,q,r} = [M_pH_qA_r] \, m^{-p} \, h^{-q} \, a^{-r}; \, p \geqslant 0, \, q \geqslant 0, \, r \geqslant 0, \, p+q+r \geqslant 2$$

$$\bar{n} = (C_A - \sum_{j=0}^{2} [H_jA])/C_M$$

$\bar{n}_H$ = the mean number of hydrogen ions bound per malonate ion, *i.e.*

$$\bar{n}_{\mathrm{H}} = (C_{\mathrm{H}} - h)/C_{\mathrm{A}}$$

$\alpha_{p,q,r} =$ the fraction of the total metal ion concentration existing as the complex $M_pH_qA_r$

$$\alpha_{p,q,r} = p[M_pH_qA_r]/C_{\mathrm{M}}$$

$V_0 =$ the initial volume of the titrand solution.
$v\ \ =$ the added volume of the titrator solution.

CALCULATION OF THE STABILITY CONSTANTS

The complex formation in the lanthanoid malonate systems has been studied by measuring the change in hydrogen ion concentration when a solution of the metal ion is titrated with a buffer of the ligand and its corresponding acid. This is a standard method, often used in systems where the ligand is the anion of a weak acid and where suitable electrodes, reversible with respect to the metal ion, are lacking.

From the total concentrations C_{M}, C_{H}, and C_{A} and the concentration of free hydrogen ion, h, one can compute the quantities a^* and $\bar{n}^*$ given below:

$$a^* = (C_{\mathrm{H}} - h)/(\beta_{0,1,1}h + 2\beta_{0,2,1}h^2) \tag{1}$$

$$\bar{n}^* = [C_{\mathrm{A}} - a^* (1 + \beta_{0,1,1}h + \beta_{0,2,1}h^2)]/C_{\mathrm{M}} \tag{2}$$

If all complexes formed are of the type MA_r, $r = 1, \ldots, N$, the left members of eqns. (1) and (2) are equal to a and $\bar{n}$, respectively. The stability constants can be calculated from corresponding values of $\bar{n}$ and a. The possible existence of acid or polynuclear complexes of the type $M_pH_qA_r$ is often checked by determining the function $\bar{n}^* (a^*)$ in solutions where the total concentrations C_{M}, C_{H}, and C_{A} are varied systematically. If $\bar{n}^* (a^*)$ turns out to depend on C_{H} and/or C_{M} this is taken as an indication of the existence of species other than MA_r.

A graphical integration method due to Österberg [2] can in some cases be used to calculate the concentration of free ligand. Values of a/a_0, where a_0 is an integration constant, are obtained. In order to determine a_0, the measurements must be extended to a high hydrogen ion concentration, h_0, where all metal complex formation is completely suppressed. This gives $a_0 = C_{\mathrm{A}}/(1 + \beta_{0,1,1} h_0 + \beta_{0,2,1} h_0^2)$. In the present case, however, it was not experimentally possible to measure h accurately in such strongly acidic solutions.

The various stability constants were instead obtained by using a computer and a least-squares program in the series "Letagrop Vrid", written by Ingri and Sillén.[13] As starting values of $\beta_{p,q,r}$ we used estimates of $\beta_{1,0,r}$ obtained from $\bar{n}^* - a^*$ data in solutions with low hydrogen ion concentrations. Starting values of the constants $\beta_{1,1,1}$ were obtained by assuming that the complexes formed between the lanthanoids and hydrogen malonate ion had the same strength as the corresponding acetate complexes.[14,15] $C_{\mathrm{H}}/C_{\mathrm{A}}$ was chosen as the error-carrying variable. The "best" set of constants was the one that minimized the error square sum U, given by

$$U = \sum_i [(C_{\mathrm{H},i,\mathrm{calc}} - C_{\mathrm{H},i,\mathrm{exp}})/C_{\mathrm{A},i}]^2$$

where $C_{H,i,calc}$ is the value of the total hydrogen ion concentration calculated from $C_{A,i}$, $C_{M,i}$, h_i, and the values of $\beta_{p,q,r}$. The summation is taken over all experimental points "i", all of which were given the weight one.

Some properties of $\bar{n}^* = f(a^*)$ *curves.* It may in some cases be difficult to interpret titration data obtained by using the method described here. It is, for instance, easy to overlook the existence of mixed complexes, and this seems to have been done in some investigations of the complex formation between the rare earths and the dicarboxylates which we are presently studying.[16] The following discussion will point out some of the reasons for these misinterpretations.

If it is assumed that a system forms complexes only of the type MA_r, a and $\bar{n}$ can be calculated from eqns. (1) and (2) and $\bar{n}$ is a function of a only. The experimental proof of the assumption is often given by showing that the curves $\bar{n} = f(a)$ coincide in solutions with different compositions. However, if an acid complex is formed, the experimentally determined quantities are $\bar{n}^*$ and a^*. Therefore, one must know the properties of the function $\bar{n}^*$ (a^*) under different experimental conditions. This will be discussed in the following example.

For simplicity we assume that only two metal complexes, MA and MHA, are formed in a system. The ligand A forms two complexes with protons, *viz.* HA and H_2A. Eqns. (3) and (4) give the relations between a and a^*, and $\bar{n}$ and $\bar{n}^*$, respectively.

$$a/a^* = 1 - \beta_{1,1,1}\, m/(\beta_{0,1,1} + 2\beta_{0,2,1}\, h + \beta_{1,1,1}\, m) \tag{3}$$

$$\bar{n}^* = \bar{n} + \frac{\beta_{1,1,1}\, m\, a(\beta_{0,2,1}\, h^2 - 1)}{C_M\,(\beta_{0,1,1} + 2\beta_{0,2,1}\, h)} + \frac{[MHA]}{C_M} \tag{4}$$

In solutions where C_H is small enough compared to C_A, the term $2\beta_{0,2,1}\, h$ will be negligible in comparison with $\beta_{0,1,1}$, and $\beta_{0,2,1}\, h^2$ much smaller than unity. Eqns. (3) and (4) can then be written as $a^*/a = 1 + \beta_{1,1,1}\, m\, \beta_{0,1,1}^{-1}$ and $\bar{n}^* = \bar{n}(1 - \beta_{1,1,1}\, \beta_{0,1,1}^{-1}\, \beta_{1,0,1}^{-1})$, respectively. For a given value of a^*, the value of $1 + \beta_{1,1,1} m\, \beta_{0,1,1}^{-1}$ does not vary very much in solutions where the previous approximations are valid. This means that it is possible to get an $\bar{n}^*$ *vs.* a^* curve, independent of the ratio C_H/C_A, as long as the ratio is small. In the lutetium system (*vide infra* p. 1394) this occurs when the ratio C_H/C_A is smaller than 1:2 (*cf.* Fig. 2).

The above discussions can be formulated quantitatively by studying the variation of the constant β^*, obtained from the $\bar{n}^*$ *vs.* a^* data. β^* is defined as

$$\beta^* = (\bar{n}^* \times C_M)/(m^* \times a^*)$$

and can be expressed as

$$\beta^* = \left[\frac{(\beta_{0,1,1} + 2h\beta_{0,2,1})\beta_{1,0,1} + \beta_{1,1,1}(\beta_{0,2,1}h^2 - 1)}{\beta_{0,1,1} + 2h\beta_{0,2,1} + m\beta_{1,1,1}} \right]\frac{m}{m^*} \tag{5}$$

It is difficult to estimate how the value of β^* varies during a titration by studying eqn. (5). We have therefore calculated the variation of β^* for two different hypothetical complex systems with the composition of the buffer

used. The value of C_M has been constant, equal to 20 mM, and the ratio C_H/C_A has been varied between 3:2 and 1:10.

System 1 has the following constants: $\beta_{1,0,1} = 7.6 \times 10^3$ M^{-1}, $\beta_{1,1,1} = 1.8 \times 10^6$ M^{-2}, $\beta_{0,1,1} = 1.0 \times 10^5$ M^{-1}, $\beta_{0,2,1} = 4.5 \times 10^7$ M^{-2}.

System 2 has the same values of $\beta_{1,0,1}$ and $\beta_{1,1,1}$, while the values of $\beta_{0,1,1}$ and $\beta_{0,2,1}$ are 4.0×10^5 M^{-1} and 1.5×10^7 M^{-2}, respectively. The calculated values of β^* as a function of $\bar{n}^*$ are given in Fig. 1 for the various values of C_H/C_A used.
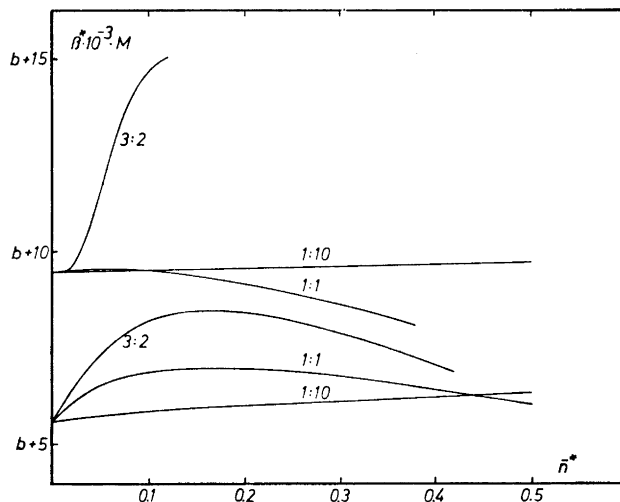

Fig. 1. β^* as a function of $\bar{n}^*$ for system 1 (lower curves) and system 2 (upper curves). The constants of the systems are given above. The ratio C_H/C_A is indicated at each curve. b equals zero for system 1 and -2.5 for system 2. The curves are drawn to $\bar{n}^* = 0.5$ or $C_A = 100$ mM.

In the region $0.1 < \bar{n}^* < 0.5$, the total variation of β^* is 10 % for the 1:10 buffer in system 1, and 4 % in system 2. The experimental data can thus be described by assuming only one complex MA with, for system 1, a stability constant equal to $(6.0 \pm 0.3) \times 10^3$ M^{-1}. When an actual titration is performed, the ratio C_H/C_A is usually not constant, due to the presence of an excess of acid in the metal stock solutions. This fact can make the apparent constancy of β^* even better. If an S-solution with $C_M = 20$ mM and $C_H = 0.2$ mM is titrated with a buffer solution where C_H/C_A is equal to 1:3, the measurements can be described by a constant β^* equal to $(6.2 \pm 0.2) \times 10^3$ M^{-1} in the region $0.05 < \bar{n}^* < 0.9$. If the concentration of acid in the metal solution is high, and the ratio C_H/C_A in the buffer is small, the calculated values of β^* will decrease monotonously when $\bar{n}^*$ increases.

When the values of C_A are small, eqn. (5) is reduced to

$$\beta^* \approx \frac{(\beta_{0,1,1} + 2h\,\beta_{0,2,1})\,\beta_{1,0,1} + \beta_{1,1,1}\,(\beta_{0,2,1}\,h^2 - 1)}{\beta_{0,1,1} + 2h\,\beta_{0,2,1} + C_M\,\beta_{1,1,1}} \tag{6}$$

$\bar{n}^*$

15

10

0.5

0

	Solution S			Solution T		
	$\dfrac{C_H}{mM}$	$\dfrac{C_M}{mM}$	$\dfrac{C_A}{mM}$	$\dfrac{C_H}{mM}$	$\dfrac{C_M}{mM}$	$\dfrac{C_A}{mM}$
O	0.2	20	0.0	300	20	200
□	0.2	20	0.0	100	20	200
▽	0.2	20	0.0	68	20	200
△	2.0	40	0.0	100	40	200

$-\log a^*/M$

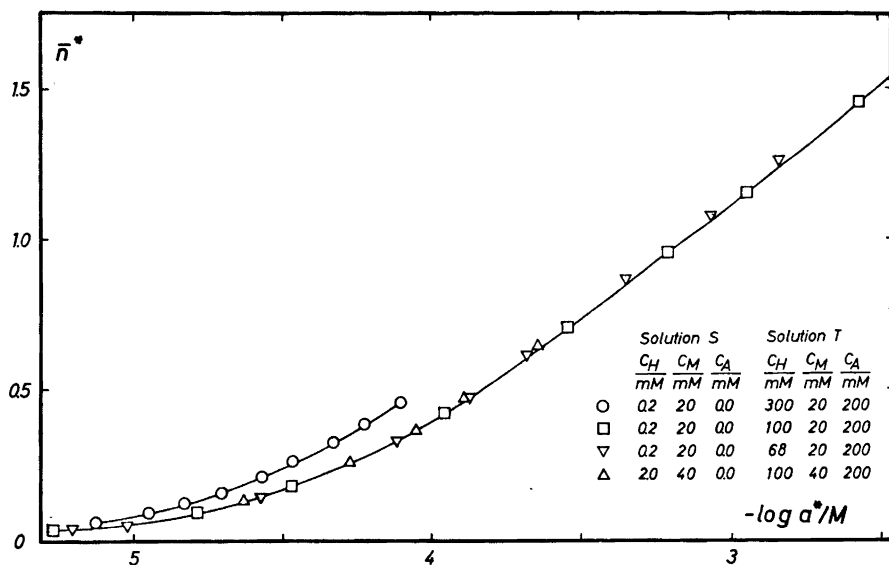5   4   3

Fig. 2. Experimental $\bar{n}^*$ *vs.* $-\log(a^*/M)$ curves for the lutetium malonate system.

It is in principle possible to calculate the constants $\beta_{1,1,1}$ and $\beta_{1,0,1}$ from this relation by measurements of β^* at various values of h and C_M. In actual practice, one finds that it is not possible to determine small values of $\bar{n}^*$ with a sufficiently high accuracy to permit the use of eqn. (6).

The following conclusion can be drawn from this discussion.

a. When complex formation is studied, using hydrogen ion as a competitor, in a system where the ligand A is a polyprotic base, the possibility that the species H_jA act as ligands must be kept in mind.

b. It is possible to get an $\bar{n}^*$ *vs.* a^* curve independent of C_H even in the presence of mixed complexes of the type MH_qA_r. The fact that the curve can be described with a set of stability constants $\beta_{1,0,r}$ is no conclusive proof of the non-existence of mixed complexes.

c. The variations in the total hydrogen ion concentration in the solutions used must be made as large as the experimental technique allows.

d. At low values of $\bar{n}^*$ it is easier to see variations in the function $\bar{n}^*/a^*$ *vs.* a^* than in $\bar{n}^*$ *vs.* a^*.

EXPERIMENTAL

Chemicals used. Sodium perchlorate was prepared from perchloric acid (Baker's Analyzed) and sodium carbonate (Merck *p.a*), as described by Gerding.[17] Lanthanum perchlorate was prepared from the carbonate (Fluka *p.a.*). Cerium(III) perchlorate was prepared in the following way: a solution of cerium(IV) sulfate (Merck *p.a.*) was reduced with hydrogen peroxide. The sulfate ions were then precipitated by adding barium perchlorate, and the cerium(III) hydroxide was precipitated by ammonia. The precipitate was dissolved in perchloric acid, and then the cerium was precipitated with ammonium carbonate. An 0.2 M cerium perchlorate stock solution was prepared

by dissolving the carbonate in perchloric acid. Stock solutions of the other rare earth perchlorates were made by dissolving the oxide (Lindsay Chemical Co., > 99.9 %) in warm perchloric acid. The metal content of the solutions was determined by titration with EDTA in urotropin buffer, using xylenolorange as indicator (*cf.* Ref. 18). The hydrogen ion concentration of the solutions was approximately 0.02 M, the exact values being determined potentiometrically.

Malonic acid (Fischer Sci. Co.) was purified by repeated recrystallization from diethyl ether. The formula weight as determined by alkalimetric titration was 104.3 (calc. 104.1).

The various malonate buffer solutions were prepared by mixing appropiate amounts of stock solutions of malonic acid and disodium malonate. The latter solution was prepared by neutralizing malonic acid to 99 % with sodium hydroxide. The small excess of acid was determined potentiometrically.
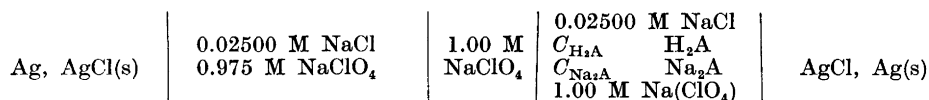
Potentiometric measurements. The emf E of galvanic cells of the following type was measured:

$$\text{Ag, AgCl(s)} \left| \begin{array}{c} \text{0.02500 M NaCl} \\ \text{0.975 M NaClO}_4 \end{array} \right| \left| \begin{array}{c} \text{1.00 M} \\ \text{NaClO}_4 \end{array} \right| \left| \begin{array}{cc} C_{\text{M}} & \text{M(ClO}_4)_3 \\ C_{\text{HClO}_4} & \text{HClO}_4 \\ C_{\text{H}_2\text{A}} & \text{H}_2\text{A} \\ C_{\text{Na}_2\text{A}} & \text{Na}_2\text{A} \\ \multicolumn{2}{c}{\text{1.00 M Na(ClO}_4)} \end{array} \right| \begin{array}{c} \text{glass} \\ \text{electrode} \end{array} \quad (7)$$
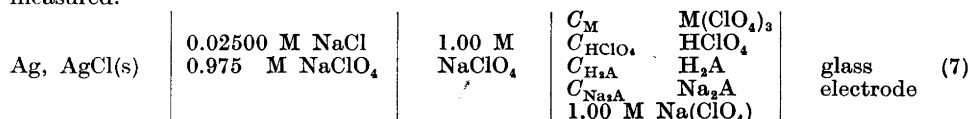
The solution in the right half-cell was prepared by adding known amounts of a solution T from a piston burette to a known volume of a solution S. The additions were made with an error of at most 0.005 ml. The value of C_{M} was constant during a titration series. The system was calibrated before each titration by measuring the emf, E_{R}, when the right half-cell of (7) contained a solution with known hydrogen ion concentration, h_{R}. The unknown hydrogen ion concentration, h, is then calculated from eqn. (8),

$$-59.16 \log h/h_{\text{R}} = (E_{\text{R}}/\text{mV} - E_{\text{j}}'/\text{mV}) - (E/\text{mV} - E_{\text{j}}''/\text{mV}) \quad (8)$$
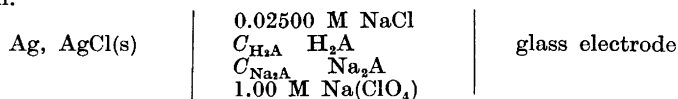
where E_{j}' and E_{j}'' are liquid junction potentials. The liquid junction potentials depend both on the hydrogen ion concentration and on the perchlorate ion (or the malonate ion) concentration in the solution, *i.e.* $E_{\text{j}} = E_{h,\text{j}} + E_{a,\text{j}}$. The hydrogen ion concentration dependent term, $E_{h,\text{j}}$, was determined as described by Ahrland and Rosengren.[19] The perchlorate ion concentration dependent term, $E_{a,\text{j}}$, was determined from emf measurements of cells of the following type:

$$\text{Ag, AgCl(s)} \left| \begin{array}{c} \text{0.02500 M NaCl} \\ \text{0.975 M NaClO}_4 \end{array} \right| \left| \begin{array}{c} \text{1.00 M} \\ \text{NaClO}_4 \end{array} \right| \left| \begin{array}{cc} \multicolumn{2}{c}{\text{0.02500 M NaCl}} \\ C_{\text{H}_2\text{A}} & \text{H}_2\text{A} \\ C_{\text{Na}_2\text{A}} & \text{Na}_2\text{A} \\ \multicolumn{2}{c}{\text{1.00 M Na(ClO}_4)} \end{array} \right| \text{AgCl, Ag(s)}$$

The term $E_{a,\text{j}}$ is only of importance when a fairly large part of the sodium perchlorate has been exchanged with sodium malonate and is equal to 0.8 mV when C_{NaClO_4} is 0.900 M.

The liquid junction potentials were measured by using a Jena glass electrode of the "Thalamide" type and a Fluke 885 AB differential voltmeter. A Beckman glass electrode (type 40498) and a Radiometer pHM4d pH-meter were used in the other titrations. The Ag,AgCl electrodes were prepared according to Brown.[20] A quinhydrone electrode did not work well in these solutions. The reproducibility of the emf was usually within 0.1 mV. The temperature was controlled within ± 0.1°C by using a water thermostat.

The proton malonate system was examined in a cell of type (7) with $C_{\text{M}} = 0$, and using different constant values of C_{A}, *viz.* 10, 50, and 100 mM, respectively. After correction for the liquid junction potential, all titration series could be described with the same set of proton-malonate stability constants. If $E_{a,\text{j}}$ is neglected, the stability constants increase about 5 % as C_{A} increases from 10 mM to 100 mM. This result was confirmed by measurements in a cell without liquid junction potential. This cell had the following composition:

$$\text{Ag, AgCl(s)} \left| \begin{array}{cc} \multicolumn{2}{c}{\text{0.02500 M NaCl}} \\ C_{\text{H}_2\text{A}} & \text{H}_2\text{A} \\ C_{\text{Na}_2\text{A}} & \text{Na}_2\text{A} \\ \multicolumn{2}{c}{\text{1.00 M Na(ClO}_4)} \end{array} \right| \text{glass electrode}$$

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The lanthanoid-malonate systems were measured in galvanic cells of the type (7), where the total concentrations C_M, C_H, and C_A were known, and h was determined.

The formation of a slightly soluble compound of the composition $M_2A_3.nH_2O$ complicated the measurements. The solubility is smallest for the light lanthanoids. No quantitative determination of the solubility has been made, but the heaviest elements can be titrated in solutions with $C_M = 15$ mM, whereas lanthanum and cerium form a precipitate in solutions with $C_M < 2.5$ mM.

The minimum solubility occurs when $\bar{n}$ equals 1.5. When a metal solution is titrated with a malonate buffer, the precipitate is formed before $\bar{n}$ reaches this value, and $\beta_{1,0,3}$ can thus not be determined from these data. In order to obtain information on $\beta_{1,0,3}$ some titrations have been made by adding an acid buffer to a metal solution with a high ligand concentration. In this way some $\bar{n}$-values in the region $1.8 < \bar{n} < 2.5$ were obtained. These solutions are supersaturated, and a precipitate is easily formed. The precision in these determinations is also lower than in the region of low $\bar{n}$-values.

RESULTS

The proton-malonate system. All data could be described by assuming the existence of two acidic species, HA and H_2A. The stability constants have been calculated *via* graphical integration of the curve $\bar{n}_H/h$ vs. h and by the least-squares program "Letagrop Vrid". The stability constants as calculated by the graphical method were:

$$\beta_{0,1,1} = (1.155 \pm 0.010) \times 10^5 \ M^{-1}$$

$$\beta_{0,2,1} = (4.49 \pm 0.08) \times 10^7 \ M^{-2}$$

The quoted errors are estimated maximum errors. This set of constants has been used for the later calculations.

The least-squares method gave the following values:

$$\beta_{0,1,1} = (1.158 \pm 0.005) \times 10^5 \ M^{-1}$$

$$\beta_{0,2,1} = (4.51 \pm 0.03) \times 10^7 \ M^{-2}$$

The quoted errors here and in the following are equal to three standard deviations. The standard deviation in C_H/C_A was 2.91×10^{-3}. The calculation was based on 13 different titration series with a total of 288 experimental values.

The proton-malonate complexes have been studied by Szilard [21] at 20°C in 1 M $NaClO_4$. A recalculation of his measurements to 25°C by using the known enthalpy values for the protonation reactions [7] gave values which agreed within 1 % with our constants.

We have assumed that the constants remain the same when $C_M \neq 0$ as when $C_M = 0$.

The lanthanoid-malonate systems. Fig. 2 shows some experimental values of $\bar{n}^*$ vs. $-\log(a^*/M)$ for the lutetium malonate system. The values of a^* and $\bar{n}^*$ have been calculated from eqns. (1) and (2). The experimental material was obtained from three titration series with C_M equal to 20 mM, and the ratio C_H/C_A in the T-solution equal to 3:2, 1:2, and 1:3, respectively. A fourth series had C_M equal to 40 mM, and C_H/C_A equal to 1:2. For the series with $C_H/C_A > 1/2$ (but not for those with $C_H/C_A \leq 1/2$), the experiments show clearly that $\bar{n}^*$ is a function of both a^* and h, *i.e.* complexes containing both A and

Table 1. Experimental results for the lanthanum and lutetium malonate systems. The results are given as v/ml, $(E-E_j)$/mV, $\bar{n}_H$, $(\bar{n}_{H,calc}-\bar{n}_{H,exp})\times 10^3$. The sodium ion concentration is 1.00 M in all solutions. Approximately one half of the experimental results is given.

a. The lanthanum malonate system

Series 1. S: $C_H=0.06132$ M, $C_M=0.01372$ M, $C_A=0.03020$ M, $C_{NaClO_4}=1.000$ M;
T: $C_H=0.00128$ M, $C_M=0.01371$ M, $C_A=0.03027$ M, $C_{NaClO_4}=0.940$ M;
$V_0=19.97$ ml, $E_0=500.0$ mV;

0.000,	379.1,	*1.731*,	6.09;	3.000,	363.8,	*1.605*,	− 2.90;
6.000,	351.0,	*1.470*,	− 1.29;	9.000,	340.0,	*1.347*,	0.78;
12.00,	330.1,	*1.239*,	0.28;	15.00,	321.2,	*1.145*,	0.68;
18.00,	313.2,	*1.064*,	2.82;	21.00,	305.9,	*0.993*,	5.39;
24.00,	299.0,	*0.931*,	6.02;				

Series 2. S: $C_H=0.1217$ M, $C_M=0.01372$ M, $C_A=0.06040$ M, $C_{NaClO_4}=1.000$ M;
T: $C_H=0.00164$ M, $C_M=0.01371$ M, $C_A=0.06038$ M, $C_{NaClO_4}=0.879$ M;
$V_0=19.97$ ml, $E_0=500.4$ mV;

0.000,	389.1,	*1.797*,	8.56;	1.500,	378.7,	*1.731*,	3.48;
4.500,	361.0,	*1.577*,	0.23;	7.500,	347.1,	*1.430*,	0.69;
10.50,	335.4,	*1.303*,	0.66;	13.50,	325.1,	*1.195*,	1.84;

Series 3. S: $C_H=0.000510$ M, $C_M=0.009138$ M, $C_A=0.000$ M, $C_{NaClO_4}=1.000$ M;
T: $C_H=0.02156$ M, $C_M=0.009138$ M, $C_A=0.1625$ M, $C_{NaClO_4}=0.680$ M;
$V_0=20.01$ ml, $E_0=385.8$ mV;

0.200,	133.5,	*0.413*,	− 0.52;	0.300,	123.1,	*0.327*,	− 1.40;
0.400,	116.5,	*0.281*,	− 0.56;	0.500,	111.5,	*0.252*,	− 0.91;
0.600,	107.5,	*0.233*,	− 1.11;	0.700,	104.2,	*0.219*,	− 0.75;

Series 4. S: $C_H=0.000510$ M, $C_M=0.009138$ M, $C_A=0.000$ M, $C_{NaClO_4}=1.000$ M;
T: $C_H=0.02134$ M, $C_M=0.009138$ M, $C_A=0.1415$ M, $C_{NaClO_4}=0.720$ M;
$V_0=20.02$ ml, $E_0=385.8$ mV;

0.100,	158.5,	*0.668*,	− 0.27;	0.200,	138.8,	*0.464*,	− 0.65;
0.300,	128.4,	*0.370*,	− 0.85;	0.400,	121.7,	*0.319*,	− 1.14;
0.500,	116.9,	*0.287*,	− 0.63;	0.600,	113.1,	*0.265*,	− 0.39;
0.700,	110.1,	*0.249*,	0.97;	0.800,	107.2,	*0.237*,	− 0.05;
0.900,	104.9,	*0.228*,	0.96,	1.000,	102.7,	*0.221*,	1.11;

b. The lutetium malonate system

Series 1. S: $C_H=0.000200$ M, $C_M=0.01990$ M, $C_A=0.000$ M, $C_{NaClO_4}=1.000$ M;
T: $C_H=0.1018$ M, $C_M=0.01990$ M, $C_A=0.2014$ M, $C_{NaClO_4}=0.699$ M;
$V_0=20.11$ ml, $E_0=472.4$ mV;

0.200,	274.0,	*0.382*,	3.19;	0.400,	276.3,	*0.432*,	− 3.50;
0.800,	276.3,	*0.468*,	− 9.50;	1.300,	274.5,	*0.484*,	− 11.29;
2.000,	271.0,	*0.494*,	− 10.49;	2.500,	268.3,	*0.498*,	− 7.37;
3.000,	265.3,	*0.500*,	− 5.44;	3.500,	262.2,	*0.502*,	− 3.46;
4.000,	259.0,	*0.503*,	− 2.17;	4.500,	255.9,	*0.504*,	− 0.54;
5.000,	252.8,	*0.505*,	0.15;	6.000,	247.4,	*0.505*,	3.49;

Series 2. S: $C_H=0.00020$ M, $C_M=0.01991$ M, $C_A=0.000$ M, $C_{NaClO_4}=1.000$ M;
T: $C_H=0.06833$ M, $C_M=0.01981$ M, $C_A=0.2007$ M, $C_{NaClO_4}=0.667$ M;
$V_0=20.11$ ml, $E_0=474.9$ mV;

0.300,	267.7,	*0.301*,	− 5.13;	0.750,	266.7,	*0.325*,	− 8.39;
1.000,	265.4,	*0.330*,	− 7.72;	1.500,	262.0,	*0.336*,	− 6.83;
2.000,	258.1,	*0.339*,	− 4.23;	3.010,	249.1,	*0.341*,	2.17;
4.000,	239.5,	*0.342*,	4.55;	5.000,	230.6,	*0.343*,	4.38;

Table 1. Continued.

Series 3. S: $C_H = 0.00171$ M, $C_M = 0.03964$ M, $C_A = 0.000$ M, $C_{NaClO_4} = 1.000$ M;
T: $C_H = 0.1031$ M, $C_M = 0.03961$ M, $C_A = 0.2011$ M, $C_{NaClO_4} = 0.702$ M;
$V_0 = 20.11$ ml, $E_0 = 475.0$ mV;

1.000,	299.7,	*0.569,*	20.91;	2.000,	295.7,	*0.547,*	13.17;
3.000,	292.7,	*0.538,*	10.89;	4.000,	290.1,	*0.533,*	11.68;
6.000,	285.3,	*0.528,*	14.96;				

Series 4. S: $C_H = 0.05165$ M, $C_M = 0.01943$ M, $C_A = 0.02525$ M, $C_{NaClO_4} = 1.000$ M;
T: $C_H = 0.00141$ M, $C_M = 0.01943$ M, $C_A = 0.02515$ M, $C_{NaClO_4} = 0.950$ M;
$V_0 = 20.11$ ml, $E_0 = 386.1$ mV;

0.000,	265.7,	*1.680,*	13.39;	1.500,	259.8,	*1.618,*	12.73;
3.000,	254.1,	*1.556,*	4.98;	4.500,	249.1,	*1.491,*	1.22;
6.000,	244.8,	*1.428,*	2.06;	7.500,	240.8,	*1.368,*	0.17;
9.000,	237.2,	*1.312,*	− 0.94;	10.50,	234.0,	*1.258,*	− 0.13;
12.00,	230.9,	*1.210,*	− 2.63;	13.50,	228.1,	*1.164,*	− 3.49;
15.00,	225.6,	*1.121,*	− 2.17;	16.50,	223.1,	*1.081,*	− 4.06;
18.00,	220.9,	*1.044,*	− 2.93;	19.50,	218.8,	*1.009,*	− 2.32;
21.00,	216.7,	*0.977,*	− 3.75;				

Series 5. S: $C_H = 0.00020$ M, $C_M = 0.01990$, $C_A = 0.000$ M, $C_{NaClO_4} = 1.000$ M;
T: $C_H = 0.3024$ M, $C_M = 0.01990$ M, $C_A = 0.2010$ M, $C_{NaClO_4} = 0.900$ M;
$V_0 = 20.11$ ml, $E_0 = 472.7$ mV;

0.500,	315.4,	*1.095,*	13.42;	1.000,	321.5,	*1.233,*	3.39;
1.600,	324.8,	*1.304,*	1.26;	3.000,	328.1,	*1.373,*	2.76;
4.000,	329.1,	*1.397,*	2.91;	6.000,	330.1,	*1.424,*	4.46;
9.000,	330.6,	*1.443,*	5.65;	13.00,	330.9,	*1.455,*	9.17;
18.00,	330.9,	*1.463,*	10.64;	25.00,	330.8,	*1.469,*	11.93;

Series 6. S: $C_H = 0.02592$ M, $C_M = 0.01943$ M, $C_A = 0.02520$ M, $C_{NaClO_4} = 0.974$ M;
T: $C_H = 0.00141$ M, $C_M = 0.01943$ M, $C_A = 0.02515$ M, $C_{NaClO_4} = 0.950$ M;
$V_0 = 21.00$ ml, $E_0 = 386.6$ mV;

3.000,	209.8,	*0.866,*	− 7.10;	6.000,	203.6,	*0.781,*	− 9.72;
9.000,	198.3,	*0.711,*	− 9.95;	12.00,	193.6,	*0.654,*	− 9.91;
18.00,	185.6,	*0.564,*	− 9.03;	24.00,	178.9,	*0.498,*	− 8.64;
30.00,	173.2,	*0.447,*	− 8.33;	36.00,	168.3,	*0.407,*	− 7.91;

Series 7. S: $C_H = 0.1027$ M, $C_M = 0.01943$ M, $C_A = 0.05078$, $C_{NaClO_4} = 1.000$ M;
T: $C_H = 0.00167$ M, $C_M = 0.01934$ M, $C_A = 0.05038$ M, $C_{NaClO_4} = 0.900$ M;
$V_0 = 20.01$ ml, $E_0 = 386.4$ mV;

1.500,	266.6,	*1.699,*	7.40;	3.000,	259.0,	*1.626,*	1.69;
4.500,	252.4,	*1.552,*	− 2.47;	6.000,	246.9,	*1.480,*	− 1.44;
7.500,	241.9,	*1.412,*	− 2.68;	9.000,	237.5,	*1.349,*	− 2.26;
10.50,	233.5,	*1.290,*	− 1.78;	12.00,	229.9,	*1.236,*	0.05;
13.50,	226.3,	*1.186,*	− 2.23;	15.00,	223.1,	*1.140,*	− 1.42;
18.00,	217.0,	*1.057,*	− 2.60;	21.00,	211.4,	*0.986,*	− 3.39;

H must be formed. The curves obtained at C_M equal to 20 mM and 40 mM are very nearly the same, indicating the absence of polynuclear species. The highest value for $\bar{n}^*$ is 2.7 in this system, that is, complexes with at least three malonate ions per metal ion must be formed. A first attempt to interpret the experimental data was made by assuming the formation of the complexes MHA, MA, MA_2, and MA_3. The calculations were made by using the least-squares program.

The first least-squares refinement showed the presence of a systematic error, the differences $(C_H/C_A)_{calc} - (C_H/C_A)_{exp}$, increasing with increasing concentration of free ligand. This systematic difference became much smaller when a complex MHA_2 was included in the refinements.

Other types of complexes are also possible. The terbium system was investigated to see if inclusion of the binuclear complex M_2A gave a better description of the data. The stability constant $\beta_{2,0,1}$ obtained was $(2.6 \pm 10.0) \times 10^3$ M^{-2}. A similar test for the complex MH_2A_2 was performed for the dysprosium and lutetium systems. The calculated constants $\beta_{1,2,2}$ became $(4.0 \pm 2.0) \times 10^{12}$ M^{-4} for dysprosium and $(2.5 \pm 2.7) \times 10^{12}$ M^{-4} for lutetium. The standard deviations in C_H/C_A decreased from 4.75×10^{-3} to 3.86×10^{-3}, and from 8.73×10^{-3} to 8.19×10^{-3}, respectively. All other constants had practically the same values as in the calculation, where $\beta_{1,2,2}$ was not included. However, their standard deviations had increased with as much as 50 %. It can thus be concluded that inclusion of the constants $\beta_{2,0,1}$ and $\beta_{1,2,2}$ does not improve the description of the experimental data to a significant extent. The complexes M_2A and MH_2A_2 do not occur in any significant amounts, if at all, in the solutions studied.

All experimental results have thus been described by using only the complexes MA, MA_2, MA_3, MHA, and MHA_2. The corresponding stability constants with their estimated errors, equal to three standard deviations, are given in Table 2. The experimental difficulties mentioned before (see p. 1394) made a

Table 2. Stability constants for the lanthanoid malonate systems. The errors are equal to three standard deviations.

Metal ion	Number of experimental points	Standard deviation in C_H/C_A	$\beta_{1,0,1} \times 10^{-3}$ M	$\beta_{1,0,2} \times 10^{-6}$ M²	$\beta_{1,0,3} \times 10^{-7}$ M³	$\beta_{1,1,1} \times 10^{-6}$ M²	$\beta_{1,1,2} \times 10^{-9}$ M³
La	56	4.51×10^{-3}	1.167 ± 0.034	0.139 ± 0.043		2.03 ± 0.26	1.51 ± 0.36
Ce	50	5.42×10^{-3}	1.79 ± 0.07	0.17 ± 0.09		2.41 ± 0.34	2.0 ± 0.7
Pr	98	10.3×10^{-3}	1.96 ± 0.17	0.41 ± 0.36		2.97 ± 0.28	1.8 ± 1.1
Nd	43	1.83×10^{-3}	2.390 ± 0.041	0.830 ± 0.041		3.01 ± 0.17	2.76 ± 0.34
Sm	119	9.91×10^{-3}	4.73 ± 0.16	1.18 ± 0.29		3.94 ± 0.37	7.2 ± 2.1
Eu	82	5.65×10^{-3}	5.25 ± 0.17	1.74 ± 0.21		3.0 ± 0.5	9.7 ± 1.6
Gd	160	10.8×10^{-3}	5.39 ± 0.18	1.74 ± 0.35		3.17 ± 0.28	6.0 ± 1.3
Tb	88	4.94×10^{-3}	6.55 ± 0.16	2.39 ± 0.23		2.33 ± 0.37	12.3 ± 1.7
Dy	74	4.75×10^{-3}	7.05 ± 0.15	2.23 ± 0.20	3.9 ± 1.6	2.03 ± 0.24	6.5 ± 1.8
Ho	83	4.12×10^{-3}	6.79 ± 0.16	2.34 ± 0.16	4.7 ± 1.2	2.02 ± 0.29	9.0 ± 1.3
Er	134	3.77×10^{-3}	7.09 ± 0.13	2.43 ± 0.15	4.1 ± 0.7	2.23 ± 0.24	8.5 ± 1.0
Tm	116	3.73×10^{-3}	7.01 ± 0.14	2.64 ± 0.14	4.2 ± 0.8	1.84 ± 0.25	9.6 ± 1.1
Yb	94	3.45×10^{-3}	7.42 ± 0.15	2.71 ± 0.13	6.0 ± 1.0	1.63 ± 0.22	5.8 ± 1.0
Lu	150	8.73×10^{-3}	7.57 ± 0.22	2.60 ± 0.25	7.6 ± 1.6	1.77 ± 0.25	3.2 ± 1.9

determination of $\beta_{1,0,3}$ impossible for the elements lanthanum to terbium. Tables 1a and 1b give the experimental results for the titrations with lanthanum and lutetium. Fig. 3 shows the relative amounts of the various complexes at different values of h and a.
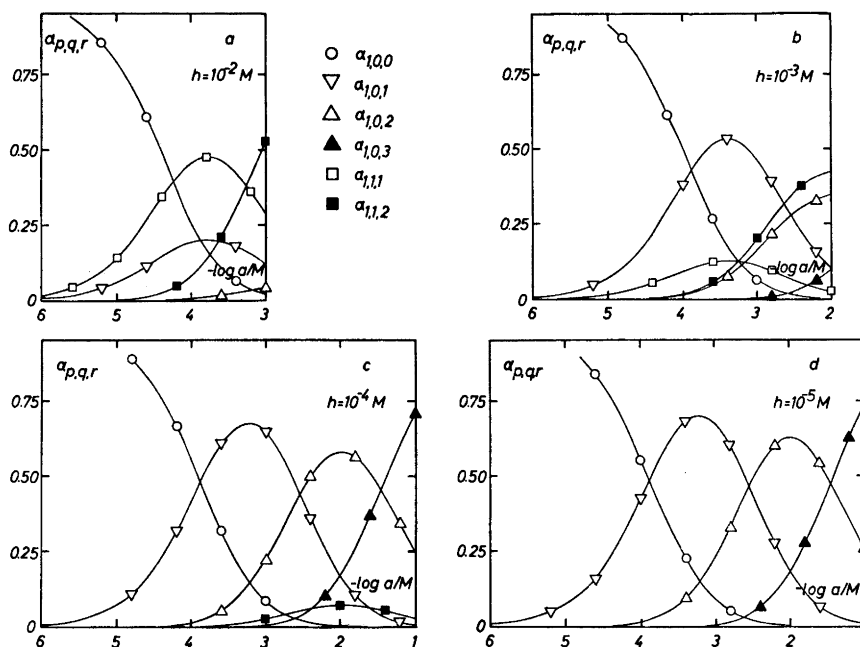

Fig. 3. The relative amounts of the different complexes in the lutetium malonate system at four different values of the hydrogen ion concentration.

DISCUSSION

Even with due allowance for the differences in experimental conditions, the results of Ke *et al.*[9] for acid complexes are not in agreement with those given here.

Powell *et al.*[10] have determined $\beta_{1,0,1}$ and $\beta_{1,0,2}$ for lanthanoid-malonate complexes in 0.1 M KNO_3 at 25°C with the same potentiometric method as used here. Powell does not report any acid complexes, but because of lack of primary data it is not possible to make any close comparison.

Paramonova *et al.*[11] give the following constants for the europium system:

$$\beta_{1,0,1} = (4.0 \pm 0.2) \times 10^3 \text{ M}^{-1}, \quad (\beta_{1,1,1}/\beta_{0,1,1}) = 17.5 \pm 2.0 \text{ M}^{-1}$$

The determination refers to 0.5 M $NaNO_3$ and an ion-exchange method was used. The temperature is not given. The corresponding values found here are:

$$\beta_{1,0,1} = (5.25 \pm 0.17) \times 10^3 \text{ M}^{-1}, \quad (\beta_{1,1,1}/\beta_{0,1,1}) = 26 \pm 4 \text{ M}^{-1}$$

A more detailed discussion will be postponed until the experimental results from the enthalpy measurements have been presented. Some comparisons with a few other carboxylate complexes will, however, be made.

The complex formation in some lanthanoid-oxalate complexes have been studied by Grenthe et al.[6] The oxalate complexes are stronger than the corresponding malonate complexes i.e. the fivemembered chelate ring in the former complexes is more stable than the sixmembered one in the latter complexes. There is no tendency for the formation of acid complexes in the oxalate systems. However, such complexes are formed with the weaker chelated malonate ligand.

A maximum of four oxalate groups are coordinated to the lanthanoid ions, but in the malonate systems there are no indications for the formation of a fourth complex. In the oxydiacetate systems the ratio between the second and third stepwise stability constants, K_2/K_3, increases considerably with decreasing ionic radius, indicating an increasing difficulty for the last complex to be formed. Neither the oxalate nor the malonate systems show any "steric effect" of this kind.

Acetate ion and bimalonate ion act in a similar way as ligands to lanthanoids. The acetate complexes are somewhat stronger, which might be correlated with the higher basicity of the acetate ion compared to the bimalonate ion.

The strength of the acid MHA increases from lanthanum to lutetium. This might be regarded as an effect of the change in electrostatic interaction between proton and metal ion, when the radius of the metal ion diminishes. pK_a for this acid lies in the range from 3.2 to 2.3. It is a much stronger acid than the hydrogen malonate ion. The acidity is comparable to that of malonic acid itself, for which pK_a is 2.46. This suggests that the tendency for the malonate group to form a chelate ring is small.

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