

Thermodynamic Properties of Rare Earth Complexes. XX. Free Energy, Enthalpy and Entropy Changes for the Formation of Rare Earth(III) Complexes with Dicarboxylates, $-\text{OCOCH}_2\text{RCH}_2\text{CH}_2\text{RCH}_2\text{COO}-$, $\text{R}=\text{S}$, O , or NH

INGMAR GRENTHE and GÖRAN GÄRDHAMMAR

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

The changes in free energy, enthalpy and entropy for the formation of lanthanoid(III) complexes with anions, A^{2-} , of dicarboxylic acids of the type $(-\text{CH}_2\text{RCH}_2\text{COOH})_2$, $\text{R}=\text{S}$, O , or NH , have been determined at 25°C in 1 M NaClO_4 . For 1,2-bis(carboxymethylthio)ethane ($\text{R}=\text{S}$), complexes of the stoichiometry MA^+ , MA_2^- and MHA_2^{3+} were formed. For 1,2-bis(carboxymethyloxy)ethane ($\text{R}=\text{O}$) the dominating species were MA^+ and MA_2^- . Small amounts of a ternary complex MHA_2 were formed in the solutions with low pH. At high ligand concentrations the presence of a weak complex MA_3^{3-} was indicated. In the 1,2-bis(carboxymethylamino)ethane system complexes of the compositions MA^+ , MA_2^- and MH_2A^{3+} were formed. MH_2A is present in significant amount only in solutions of pH around 3.

The ligand containing sulphur donors gives only weak complexes, in keeping with the poor donor ability of sulphur to hard acceptors such as the lanthanoids. There is a large difference in the magnitude of the variation of β_2 within the rare earth series for the two other ligands. When $\text{R}=\text{NH}$, this variation is equal to 2×10^5 , while it is only a factor of 9 when $\text{R}=\text{O}$. From calorimetric determinations of the enthalpy changes for the complexation reactions it was shown that this difference is nearly entirely an enthalpy effect. We suggest that these differences between the two ligands are related to differences in geometry between the two series of complexes.

In a previous part of this series¹ we discussed the changes in thermodynamic functions such as ΔG_f° , ΔH_f° and ΔS_f° for the formation of lanthanoid(III) complexes in a series of tri-

dentate dicarboxylate ligands *viz.*, thiodiacetate, oxydiacetate, iminodiacetate, and 2,6-pyridinedicarboxylate (dipicolinate). These ligands form complexes of quite different stability and have β_1 values ranging from 2×10^8 for thiodiacetate to 10^6 in dipicolinate. This large difference in stability is nearly entirely an enthalpy effect, *i.e.* the ΔS° for the formation of a complex with a given lanthanoid ion is almost the same for all four ligands. The differences in ΔH_{101}° between the sulphur containing ligand and the other three are approximately -15.0 kJ/mol, -15.6 kJ/mol, and -29 kJ/mol, respectively. In spite of these large differences one finds that the variation in ΔH° through the rare earth series is very nearly the same for all four ligands (*cf.* Fig. 1). It is tempting to relate the differences in ΔH° between the various ligands to differences in affinity of the various donor atoms, R , to the lanthanoid ions. However, variations in ΔH° (or β_1) between different ligands depend on many factors. One is the relative affinity of the various donor atoms, others are the coordination geometry of the ligand and the basicity of its donor groups. It is difficult to estimate the relative importance of these factors in ligands which contain more than one donor atom and no quantitative values of the differences in affinity between the various donors can thus be obtained.

The rare earth oxydiacetates and dipicolinates have approximately the same coordination

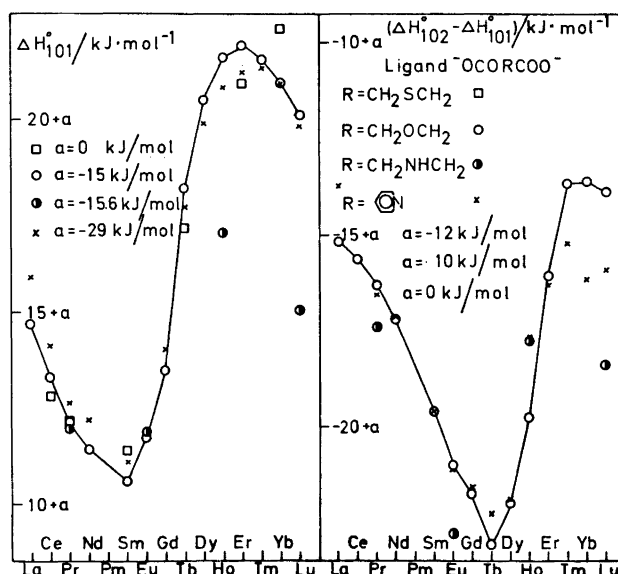


Fig. 1. ΔH_{101}° and $(\Delta H_{102}^{\circ} - \Delta H_{101}^{\circ})$ for the formation of rare earth complexes with thiodiacetate, oxydiacetate, iminodiacetate, and 2,6-pyridinedicarboxylate. The enthalpy changes for the various systems have been displaced by the quantity a given in the figure, in order to illustrate the very similar pattern of variation through the lanthanoid series.

geometry in the solid state,^{16,17} and presumably also in solution. However, the difference in ΔH° is due not only to differences in affinity between O and N, but also to some extent to the different basicities of the carboxylate groups in the two ligands due to different inductive effects from the groups R. Oxydiacetate and thiodiacetate have, on the other hand, about the same basicity towards protons, hence the observed difference in ΔH° may be a rather good estimate of the difference in affinity of O and S to the lanthanoid ion.

In this investigation we have extended the previous study to include potentially tetradentate dicarboxylate ligands of the type $^-\text{OCOCH}_2\text{RCH}_2\text{CH}_2\text{RCH}_2\text{COO}^-$, where R equals S, O, or NH.

The points of main interest to us were

a. To investigate how a change from a tridentate to a tetradentate ligand affects the variation of thermodynamic quantities through the rare earth series.

b. To try to get an estimate of how a change in geometry of the ligand affects the relative affinities of the various donor atoms in R, as measured by differences in ΔH° or β_1 .

c. To study the possible formation of ternary complexes MH_pA_q .

Point a is of interest for the problem of separating the various rare earth elements from one another. The efficiency of a separation process depends, among other things on differences in stability constants between the various elements. These are approximately the same for most of the tridentate ligands, *i.e.* they have all about the same *size specificity* and thus the same efficiency in a separation process. It seems reasonable to assume that the size specificity of a ligand increases with the number of donor atoms, until all of them no longer are coordinated to the central ion. One also expects size specific effects to be more important in the higher complexes formed with a given ligand. We intend to illustrate these points by a comparison of the tri- and tetradentate ligands.

No previous measurements of stability constants have been reported between rare earths and 1,2-bis(carboxymethylthio)ethane or 1,2-bis(carboxymethyloxy)ethane. Stability constants for the rare earth complexes MA^+ and MA_2^- with A equal to 1,2-bis(carboxymethylamino)ethane have been published.^{2,3} This in-

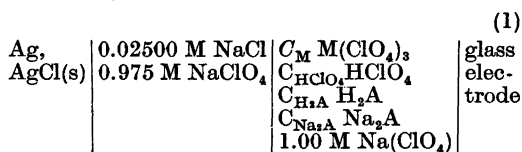
vestigation will extend the previous studies to include measurements of the corresponding enthalpy changes. We have also made determinations of the stability constants of the La, Nd, Sm, Tb, Er, and Yb systems at the ionic strength $I = 1.00$ M as the data previously published refer to a medium with an ionic strength of 0.1 M.

All symbols used are defined in Refs. 4, 5, and 6. The calculation procedure is the same as used before.⁴⁻⁶

EXPERIMENTAL

All measurements have been performed at 25.0°C in a medium with the ionic strength 1.0 M using sodium perchlorate as the neutral salt. The stability constants were determined by the potentiometric standard method of emf-measurements of the hydrogen ion concentration. The enthalpy changes were obtained from calorimetric titrations.

Potentiometric measurements. The emf E of galvanic elements of the following type was measured:



The experimental details have been described before.⁴ The system was calibrated before and after each titration by measuring the emf, E_R , when the right half-cell of (1) contained a solution with known hydrogen ion concentration, h_R . The unknown hydrogen ion concentration, h , was then calculated from eqn. 2.

$$-(RT/F) \log h/h_R = (E_R - E_j') - (E - E_j'') \quad (2)$$

where E_j' and E_j'' are liquid junction potentials which depend both on the hydrogen ion concentration and on the perchlorate ion concentration, i.e. $E_j = E_{h,j} + E_{a,j}$. These two terms were measured as described in Ref. 4, p. 1393. The glass electrode used was of type Jena "Thalamide" and the potentiometer of type Orion 801 or Radiometer pHM4d. The reproducibility of the emf was usually within 0.1 mV. The temperature was controlled at $25.0 \pm 0.1^\circ\text{C}$ by using a water thermostat. The various proton-ligand systems were examined by using a cell of type (1) with $C_M = 0$.

Calorimetric measurements. The titration calorimeter described by Ots⁷ was used in all the calorimetric titrations. The experimental procedure is the same as described before.⁶ The inner vessel was initially filled with a volume V_0 of a solution S . Titrant T was then added

successively, in portions varying between 1.00 and 3.00 ml. The system was calibrated electrically, usually at ten different values of the total volume.

The $(-\text{CH}_2\text{SCH}_2\text{COO})_2$ system. The ligand acid was obtained by the courtesy of Dr. A. Sandell. Its purity was checked by an alkalimetric determination of the formula weight; found 210.3 ± 0.5 , calc. 210.2. The samarium system was investigated potentiometrically at three different values of C_M (10, 20 and 30 mM) using two different buffers with the ratio $C_{\text{H}_2\text{A}}/C_{\text{Na}_2\text{A}}$ equal to 1:1 and 1:3. Some experimental data are given in Table 1. The dysprosium and erbium systems were investigated at only one metal ion concentration equal to 20 mM. The correction for the diffusion potential was

$$E_j/\text{mV} = -0.065h/\text{mM} + 0.042C_{\text{Na}_2\text{A}}/\text{mM}$$

The lighter rare earths were not investigated due to the formation of a sparingly soluble solid $\text{M}_2\text{A}_3 \cdot x\text{H}_2\text{O}$.

The calorimetric titrations were made at $C_M = 20$ mM using a buffer with $C_{\text{H}_2\text{A}}/C_{\text{Na}_2\text{A}} = 1:4$. Only very small amounts of the ternary complexes are formed in these titrations, hence ΔH°_{111} cannot be calculated. Experimental data for the samarium system are given in Table 2. The protonation enthalpies of the ligand were determined by titration of a Na_2A solution with perchloric acid.

The $(-\text{CH}_2\text{OCH}_2\text{COO})_2$ system. The ligand was prepared by oxidation of triethyleneglycol with nitric acid using ammonium vanadate as catalyst.⁸ It was difficult to purify the product. Several different methods were tried and recrystallization from a mixture of acetone and water seemed to work best. The purity was checked by NMR, elemental analyses and alkalimetric determinations of the formula weight. Several different batches of the acid were used throughout this study. The purity, as judged from the alkalimetric formula weight determinations, varied somewhat. Some samples had a formula weight of 178.0, others had values as low as 176.2, calc. 178.1. Repeated recrystallizations of the latter product did not improve its purity. We have not been able to determine the nature of the impurity.

The cerium and erbium systems were investigated potentiometrically at three different values of C_M (10 mM, 20 mM, and 30 mM) using four different buffers with $C_{\text{H}_2\text{A}}/C_{\text{Na}_2\text{A}}$ ratios equal to 3:1, 1:1, 1:3, and 1:5, respectively. The other systems were studied at $C_M = 20$ mM using the 3:1, 1:1, and 1:3 buffers. The correction for the diffusion potential was

$$E_j/\text{mV} = -0.065h/\text{mM} + 0.024C_{\text{Na}_2\text{A}}/\text{mM}$$

This correction was checked by measuring the protonation constants of the ligand using a diffusion free cell as described in Ref. 4, p. 1393.

Table 1. Corresponding values of v/ml , $-\log(h/M)$ and $[(C_{H,\text{calc}} - C_{H,\text{obs}})/C_A] \times 10^3$ for some potentiometric measurements in the $(-\text{CH}_2\text{R} - \text{CH}_2\text{COO}^-)_2$ systems. Half the experimental material in each titration series has been included.

The $\text{Sm}^{3+} - (-\text{CH}_2\text{SCH}_2\text{COO}^-)_2$ system

Series 1: $C_{H(S)} = 0.00008 \text{ M}$, $C_{A(S)} = 0 \text{ M}$, $C_{M(S)} = 0.02000 \text{ M}$, $C_{H(T)} = 0.07500 \text{ M}$, $C_{A(T)} = 0.1500 \text{ M}$, $C_{M(T)} = 0.02000 \text{ M}$, $V_0 = 19.97 \text{ ml}$.

0.00, 4.084, 0.00; 0.20, 3.717, -4.1; 0.60, 3.680, -4.7; 1.20, 3.685, -5.9; 2.10, 3.704, -4.7; 3.40, 3.733, -3.6; 5.10, 3.763, -1.5; 7.00, 3.790, -0.9; 9.00, 3.810, -0.2; 12.00, 3.832, -0.8; 16.00, 3.853, -0.4; 20.00, 3.868, -0.1; 30.00, 3.885, -1.0.

Series 2: $C_{H(S)} = 0.00008 \text{ M}$, $C_{A(S)} = 0 \text{ M}$, $C_{M(S)} = 0.02000 \text{ M}$, $C_{H(T)} = 0.1500 \text{ M}$, $C_{A(T)} = 0.1500 \text{ M}$, $C_{M(T)} = 0.02000 \text{ M}$, $V_0 = 19.97 \text{ ml}$.

0.20, 3.383, 4.8; 0.60, 3.298, -1.0; 1.20, 3.276, 1.6; 1.60, 3.274, 2.4; 2.70, 3.281, 4.6; 4.20, 3.296, 6.5; 6.00, 3.310, 12.8; 8.00, 3.323, 16.8; 10.00, 3.339, 14.7; 14.00, 3.357, 15.9; 18.00, 3.369, 17.5; 25.00, 3.384, 17.2.

Series 3: $C_{H(S)} = 0.00004 \text{ M}$, $C_{A(S)} = 0 \text{ M}$, $C_{M(S)} = 0.01000 \text{ M}$, $C_{H(T)} = 0.0750 \text{ M}$, $C_{A(T)} = 0.1500 \text{ M}$, $C_{M(T)} = 0.01000 \text{ M}$, $V_0 = 19.97 \text{ ml}$.

0.20, 3.841, -8.4; 0.60, 3.809, -7.4; 1.20, 3.819, -6.8; 2.10, 3.842, -5.9; 3.40, -3.866, -0.8; 5.10, 3.890, 0.0; 7.00, 3.910, 0.1; 9.00, 3.924, 0.0; 12.00, 3.934, 0.2; 16.00, 3.944, 0.2; 20.00, 3.951, 0.3; 30.00, 3.959, 0.5.

Series 4: $C_{H(S)} = 0.00012 \text{ M}$, $C_{A(S)} = 0 \text{ M}$, $C_{M(S)} = 0.03000 \text{ M}$, $C_{H(T)} = 0.0750 \text{ M}$, $C_{A(T)} = 0.1500 \text{ M}$, $C_{M(T)} = 0.03000 \text{ M}$, $V_0 = 19.97 \text{ ml}$.

0.20, 3.628, 12.1; 0.40, 3.604, 3.7; 0.80, 3.597, -1.7; 1.60, 3.606, -3.2; 2.70, 3.626, -4.1; 4.20, 3.655, -5.5; 6.00, 3.684, -5.3; 8.00, 3.711, -6.0; 10.00, 3.731, -5.4; 14.00, 3.765, -8.3; 18.00, 3.785, -8.1; 20.00, 3.793, -8.5; 30.00, 3.817, -6.3.

The $\text{Ce}^{3+} - (-\text{CH}_2\text{OCH}_2\text{COO}^-)_2$ system

Series 1: $C_{H(S)} = 0.00086 \text{ M}$, $C_{A(S)} = 0 \text{ M}$, $C_{M(S)} = 0.02000 \text{ M}$, $C_{H(T)} = 0.2303 \text{ M}$, $C_{A(T)} = 0.1526 \text{ M}$, $C_{M(T)} = 0.02000 \text{ M}$, $V_0 = 19.97 \text{ ml}$.

0.00, 3.067, 0; 0.60, 2.235, 24.4; 0.80, 2.174, 12.9; 1.20, 2.101, -0.5; 2.10, 2.023, -1.3; 3.40, 1.983, -4.4; 5.10, 1.964, 1.9; 7.00, 1.966, -0.9; 9.00, 1.973, 1.9; 12.00, 1.990, 3.4; 16.00, 2.015, 3.8; 20.00, 2.040, 2.3; 30.00, 2.084, 5.1.

Series 2: $C_{H(S)} = 0.00086 \text{ M}$, $C_{A(S)} = 0 \text{ M}$, $C_{M(S)} = 0.02000 \text{ M}$, $C_{H(T)} = 0.1565 \text{ M}$, $C_{A(T)} = 0.1532 \text{ M}$, $C_{M(T)} = 0.02000 \text{ M}$, $V_0 = 19.97 \text{ ml}$.

0.60, 2.372, -3.0; 0.80, 2.313, -4.2; 1.20, 2.248, -12.8; 1.60, 2.215, -12.5; 2.70, 2.187, -11.3;

4.20, 2.204, -5.3; 6.00, 2.253, -1.8; 8.00, 2.319, -2.8; 10.00, 2.378, 0.0; 14.00, 2.483, -1.7; 18.00, 2.561, 1.0; 20.00, 2.593, 2.5; 30.00, 2.713, 5.6.

Series 3: $C_{H(S)} = 0.00086 \text{ M}$, $C_{A(S)} = 0 \text{ M}$, $C_{M(S)} = 0.02000 \text{ M}$, $C_{H(T)} = 0.08005 \text{ M}$, $C_{A(T)} = 0.1523 \text{ M}$, $C_{M(T)} = 0.02000 \text{ M}$, $V_0 = 19.97 \text{ ml}$.

0.60, 2.571, 9.1; 0.80, 2.519, 5.3; 1.20, 2.461, 1.3; 2.10, 2.433, -1.5; 3.40, 2.480, 0.4; 5.10, 2.598, -2.2; 7.00, 2.730, -2.0; 9.00, 2.859, -4.0; 12.00, 3.024, -1.3; 16.00, 3.187, 1.0; 20.00, 3.286, 1.3; 30.00, 3.410, -1.4.

Series 4: $C_{H(S)} = 0.00086 \text{ M}$, $C_{A(S)} = 0 \text{ M}$, $C_{M(S)} = 0.02000 \text{ M}$, $C_{H(T)} = 0.05408 \text{ M}$, $C_{A(T)} = 0.1516 \text{ M}$, $C_{M(T)} = 0.02000 \text{ M}$, $V_0 = 19.97 \text{ ml}$.

0.60, 2.684, -2.3; 0.80, 2.635, -3.0; 2.10, 2.563, -8.6; 3.40, 2.629, -3.6; 5.10, 2.776, -3.4; 7.00, 2.938, -4.2; 10.00, 3.175, -1.6; 14.00, 3.408, -2.0; 18.00, 3.531, -3.5; 25.00, 3.638, -6.1.

Series 5: $C_{H(S)} = 0.00038 \text{ M}$, $C_{A(S)} = 0 \text{ M}$, $C_{M(S)} = 0.01000 \text{ M}$, $C_{H(T)} = 0.08005 \text{ M}$, $C_{A(T)} = 0.1523 \text{ M}$, $C_{M(T)} = 0.01000 \text{ M}$, $V_0 = 19.95 \text{ ml}$.

0.60, 2.706, -2.3; 0.80, 2.668, -3.1; 1.20, 2.652, -2.4; 2.10, 2.747, 0.7; 3.40, 2.950, -1.7; 5.10, 3.175, 4.5; 7.00, 3.747, 4.3; 9.00, 3.447, 3.3; 12.00, 3.526, 1.8; 16.00, 3.579, 2.0; 20.00, 3.609, 1.4; 30.00, 3.648, 0.3.

Series 6: $C_{H(S)} = 0.00130 \text{ M}$, $C_{A(S)} = 0 \text{ M}$, $C_{M(S)} = 0.03000 \text{ M}$, $C_{H(T)} = 0.08005 \text{ M}$, $C_{A(T)} = 0.1523 \text{ M}$, $C_{M(T)} = 0.03000 \text{ M}$, $V_0 = 19.97 \text{ ml}$.

0.60, 2.483, 18.3; 0.80, 2.433, 14.5; 1.20, 2.370, 8.8; 2.10, 2.314, 4.0; 3.40, 2.309, 4.0; 5.10, 2.350, 6.1; 7.00, 2.419, 8.2; 9.00, 2.502, 4.8; 12.00, 2.612, 3.6; 16.00, 2.737, 0.9; 20.00, 2.842, 1.4; 30.00, 3.036, 4.4.

The $\text{Sm}^{3+} - (-\text{CH}_2\text{NHCH}_2\text{COO}^-)_2$ system

The error is $[(C_{H,\text{calc}} - C_{H,\text{obs}})/C_A] \times 10^4$

Series 1: $C_{H(S)} = 0.0622 \text{ M}$, $C_{A(S)} = 0.03078 \text{ M}$, $C_{M(S)} = 0.00950 \text{ M}$, $C_{OH(T)} = 0.1485 \text{ M}$, $C_{A(T)} = 0 \text{ M}$, $C_{M(T)} = 0 \text{ M}$, $V_0 = 20.00 \text{ ml}$.

0.20, 4.319, -14; 0.45, 4.549, -23; 0.95, 4.796, -38; 1.67, 5.053, -58; 2.40, 5.327, -28; 3.00, 5.595, 4; 3.65, 5.861, -14; 4.50, 6.155, -21; 5.28, 6.458, -25; 5.80, 6.730, -11; 6.20, 7.041, -19.

Series 2: $C_{H(S)} = 0.1007 \text{ M}$, $C_{A(S)} = 0.0497 \text{ M}$, $C_{M(S)} = 0.01900 \text{ M}$, $C_{OH(T)} = 0.1490 \text{ M}$, $C_{A(T)} = 0 \text{ M}$, $C_{M(T)} = 0 \text{ M}$, $V_0 = 20.00 \text{ ml}$.

0.00, 3.797, 2; 0.20, 4.066, -2; 0.49, 4.301, 9; 1.05, 4.530, 25; 2.06, 4.767, 32; 3.40, 5.011, 22; 4.70, 5.266, 37; 5.80, 5.533, 31; 7.00, 5.808, 1; 8.30, 6.069, 4; 9.60, 6.356, 15; 10.55, 6.650, 19; 11.10, 6.917, 16.

Table 1. Continued.

Series 3: $C_{H(S)} = 0.0798$ M, $C_{A(S)} = 0.0399$ M, $C_{M(S)} = 0.01900$ M, $C_{H(T)} = 0.2328$ M, $C_{A(T)} = 0$ M, $C_{M(T)} = 0$ M, $V_0 = 20.00$ ml.

0.00, 4.001, 14; 0.20, 3.521, 18; 0.40, 3.236, 24; 0.67, 3.006, 25; 1.08, 2.779, 31; 1.70, 2.553, 11; 2.60, 2.321, -13; 3.90, 2.074, -17; 5.70, 1.819, -17.

Series 4: $C_{H(S)} = 0.03147$ M, $C_{A(S)} = 0.01530$ M, $C_{M(S)} = 0.01330$ M, $C_{H(T)} = 0.2328$ M, $C_{A(T)} = 0$ M, $C_{M(T)} = 0$ M, $V_0 = 20.00$ ml.

0.00, 3.628, 2; 0.10, 3.276, 5; 0.20, 3.070, 20; 0.40, 2.815, 30; 0.69, 2.583, 18.

Series 5: $C_{H(S)} = 0.04200$ M, $C_{A(S)} = 0.02036$ M, $C_{M(S)} = 0.01900$ M, $C_{H(T)} = 0.2328$ M, $C_{A(T)} = 0$ M, $C_{M(T)} = 0$ M, $V_0 = 20.00$ ml.

0.00, 3.555, -4; 0.10, 3.286, -15; 0.24, 3.051, -7; 0.46, 2.821, -7.

Series 6: $C_{H(S)} = 0.04160$ M, $C_{A(S)} = 0.02049$ M, $C_{M(S)} = 0.00950$ M, $C_{H(T)} = 0.2328$ M, $C_{A(T)} = 0$ M, $C_{M(H)} = 0$, $V_0 = 20.00$ ml.

0.00, 3.834, 4; 0.10, 3.442, 17; 0.20, 3.220, 28; 0.40, 2.955, 30; 0.67, 2.732, 18; 1.10, 2.493, 7; 1.70, 2.265, -54; 2.60, 2.015, -11.

Table 2. Corresponding values of v/ml , $(Q_{\text{corr}} \times 100)/J$ and $(Q_{\text{corr,calc}} - Q_{\text{corr,obs}}) \times 100 \text{ J}^{-1}$ from selected calorimetric titrations.

The $\text{Sm}^{3+} - (-\text{CH}_2\text{SCH}_2\text{COO}^-)_2$ system

Series 1: $C_{H(S)} = 0.00053$ M, $C_{A(S)} = 0.00038$ M, $C_{M(S)} = 0.01928$ M, $C_{H(T)} = 0.1200$ M, $C_{A(T)} = 0.3000$ M, $C_{M(T)} = 0$ M, $V_0 = 80.07$ ml.

2.00, 375.6, -4.1; 4.00, 321.1, 0.3; 6.00, 257.2, 5.9; 9.00, 294.3, 4.5; 12.00, 212.8, 1.7; 15.00, 158.2, 1.6.

Series 2: The various concentrations are the same as in series 1.

1.00, 181.0, 9.0; 3.00, 353.7, -4.2; 5.00, 289.9, 2.2; 8.00, 339.7, -5.0; 11.00, 243.4, -4.6; 14.00, 176.7, -1.3.

The $\text{Ce}^{3+} - (-\text{CH}_2\text{OCH}_2\text{COO}^-)_2$ system

Series 1: $C_{H(S)} = 0.00081$ M, $C_{A(S)} = 0.00038$ M, $C_{M(S)} = 0.01956$ M, $C_{H(T)} = 0.1510$ M, $C_{A(T)} = 0.3000$ M, $C_{M(T)} = 0$ M, $V_0 = 80.07$ ml.

2.00, 245.0, -1.0; 4.00, 170.4, -1.3; 6.00, 58.5, -1.7; 9.00, -192.8, 2.4; 12.00, -347.3, -0.1; 15.00, -275.9, 2.9.

Series 2: The various concentrations are the same as in series 1.

1.00, 132.9, 4.0; 3.00, 211.1, 0.8; 5.00, 120.4, -1.3; 8.00, -84.3, 0.4; 11.00, -326.1, -0.7; 14.00, -311.5, -3.0; 17.00, -175.0, -0.4.

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The $\text{H}^+ - (-\text{CH}_2\text{NHCH}_2\text{COO}^-)$ system

Series 1: $C_{H(S)} = 0.00680$ M, $C_{A(S)} = 0.01613$ M, $C_{H(T)} = 0.05980$ M, $C_{A(T)} = 0$ M, $V_0 = 86.00$ ml.

2.00, 454, -3; 4.00, 452, -2; 6.00, 448, 1; 8.00, 449, -1; 10.00, 448, 0; 12.00, 444, 3; 14.00, 442, 4.

Series 2: $C_{H(S)} = 0.02346$ M, $C_{A(S)} = 0.02019$ M, $C_{H(T)} = 0.05980$ M, $C_{A(T)} = 0$ M, $V_0 = 80.00$ ml.

2.00, 442, 3; 4.00, 449, -4; 6.00, 450, -5; 8.00, 446, -1; 10.00, 448, -3; 12.00, 446, -1; 14.00, 442, 3; 16.00, 441, 4.

The $\text{Sm}^{3+} - (-\text{CH}_2\text{NHCH}_2\text{COO}^-)_2$ system

Series 1: $C_{H(S)} = 0.00072$ M, $C_{A(S)} = 0.001284$ M, $C_{M(S)} = 0.00938$ M, $C_{H(T)} = 0.00860$ M, $C_{A(T)} = 0.1040$ M, $C_{M(T)} = 0$ M, $V_0 = 81.00$ ml.

2.00, 250, -4; 4.00, 248, -3; 6.00, 245, 0; 8.00, 241, 5; 10.00, 248, 0; 12.00, 246, -1; 14.00, 242, -9.

Series 2: $C_{H(S)} = 0.00081$ M, $C_{A(S)} = 0.002537$ M, $C_{M(S)} = 0.00927$ M, $C_{H(T)} = 0.00860$ M, $C_{A(T)} = 0.1040$ M, $C_{M(T)} = 0$ M, $V_0 = 82.00$ ml.

2.00, 248, -2; 4.00, 243, 2; 6.00, 242, 3; 8.00, 239, 9; 10.00, 244, 3; 12.00, 245, -4.

Experimental data for the cerium system are given in Table 1.

As our main interest was to determine the enthalpy changes for the formation of the first two complexes the calorimetric titrations were designed with this object in mind. Only one buffer with $C_{\text{H}_2\text{A}^+}/C_{\text{Na}_2\text{A}}$ ratio equal to 1:3 was used. The titrations were made at one value of C_{M} equal to 20 mM and extended to a $C_{\text{A}}/C_{\text{M}}$ ratio equal to 3:1. Hence, no accurate information can be obtained about ΔH°_{103} , cf. Fig. 3. The enthalpy change for the formation of MHA_2 was also rather uncertain. Within the estimated error limits ΔH°_{103} seemed to have approximately constant values equal to -10 kJ/mol throughout the rare earth series. In the final least-squares calculation we refined only the constants ΔH°_{101} , ΔH°_{102} and ΔH°_{112} while keeping ΔH°_{103} constant at -10 kJ/mol. Refinements where the enthalpy changes for the formation of MA^+ and MA_2^- were varied while keeping both ΔH°_{103} and ΔH°_{112} at given constant values always resulted in *sig y* values three or four times larger than in the method we used.

The experimental data for the cerium system are shown in Table 2.

The $(-\text{CH}_2\text{NHCH}_2\text{COO}^-)_2$ systems. 1,2-Bis-(carboxymethylamino)ethane (La Mont Laboratories) was purified by repeated recrystallizations from water. The purity was determined by a complexometric titration with copper(II) using murexide as indicator. Formula weight: found 176.3, calc. 176.2.

The experimental procedure used in the potentiometric titrations differed slightly from that described previously. The *S* solution contained the metal ion and a buffer of Na_2A and H_2A . This solution was then titrated with a solution *T* containing either sodium hydroxide or perchloric acid. The compositions of the *S* and *T* solutions are shown in Table 1, where some of the experimental findings for the samarium system are given. The change in the perchlorate ion concentration was so small that only the hydrogen ion dependent term was included in E_j .

The calorimetric titrations were made in solutions of such a low hydrogen ion concentration that the complex MH_2A^{3+} was negligible. Hence the values of ΔH_{101}° and ΔH_{102}° are not influenced by an error in β_{121} (cf. Fig. 3). Both the potentiometric and the calorimetric titrations were made in fairly alkaline solutions. Hence the possible formation of hydroxocomplexes, and in the calorimetric titrations also the enthalpy change for the process $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$, had to be taken into account. This was done as described in Ref. 6, pp. 3212–3213.

Experimental data from the calorimetric titrations of the samarium system are given in Table 2.

It has been possible to include only a small part of the experimental material in this communication. However, these data are representative of all the systems studied with a given ligand. An estimate of the precision of the experiments is obtained from the standard deviations of the experimental quantities $C_{\text{H}}/C_{\text{A}}$, and Q_{corr} given in Tables 3–8. The complete experimental material may be obtained from the authors.

Calculations. Stability constants and molar enthalpy changes were calculated by using a

least-squares procedure with equal weight to all the experimental points. Two programmes in the "Letagrop" series were used: ETITER⁹ for the potentiometric data, with $C_{\text{H}}/C_{\text{A}}$ as the error carrying variable, and LETAGROP KALLE¹⁰ with Q_{corr} as the error carrying variable for the calorimetric data.

RESULTS

The equilibrium models used for the description of the various metal-ligand systems were deduced from measurements where the various total concentrations of metal, ligand and protons were varied over a fairly large concentration range. Only data for one or two elements were used to deduce the model. This was then applied to all other rare earth systems investigated with a given ligand. By this procedure the total number of experimental determinations decreased considerably with only a small loss of accuracy in the stability constants.

The potentiometric data showed that ternary complexes were present only in small amounts. Hence the calorimetric titrations were designed to give their main information about the binary complexes, cf. Figs. 2 and 3 which show the distribution of the various species in the terbium 1,2-bis(carboxymethoxy)ethane system for the potentiometric and calorimetric titrations, respectively.

The 1,2-bis(carboxymethylthio)ethane systems. The protonation constants of the ligand were

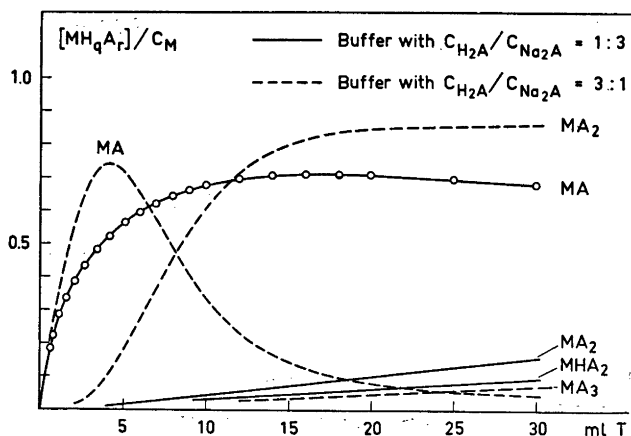


Fig. 2. The relative concentrations of the various complexes formed in the terbium 1,2-bis(carboxymethoxy)ethane system in the potentiometric investigations. The circles indicate the total volumes of titrant added in the various titrations.

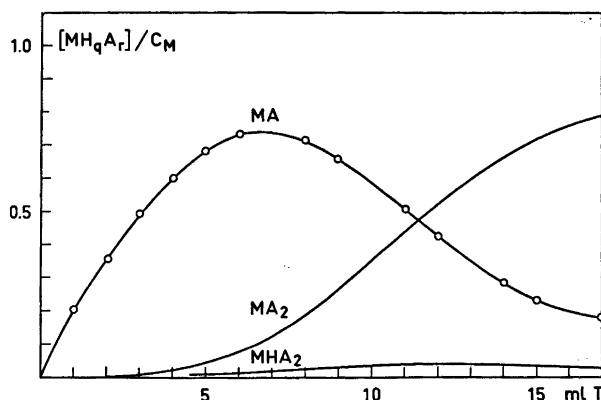


Fig. 3. The relative amounts of the various complexes formed in the calorimetric study of the terbium 1,2-bis(carboxymethyloxy)ethane system. The circles denote the total volume of titrant added.

Table 3. Stability constants for complexes formed in the rare earth-1,2 bis(carboxymethylthio)-ethane system at 25°C, $I=1.00$ M. All errors are given as 3σ , where σ is the estimated standard deviation in the constant, referring to the least significant digit. *Sig y* is the standard deviation in the error carrying variable C_H/C_A and N denotes the number of experimental points. The protonation constants are $\beta_{011}=7.41(5)\times 10^3$ M $^{-1}$ and $\beta_{021}=1.361(74)\times 10^7$ M $^{-2}$. *Sig y* = 3.9×10^{-3} and $N=154$.

Metal	$\beta_{101}\times 10^{-2}\times M$	$\beta_{102}\times 10^{-3}\times M^2$	$\beta_{111}\times 10^{-5}\times M^2$	<i>sig y</i> $\times 10^3$	N
Sm	2.09(5)	3.1(2)	2.3(1)	7.2	96
Dy	1.22(7)	3.0(2)	1.9(7)	12.0	48
Er	1.02(5)	1.4(4)	1.4(4)	7.4	46

$\beta_{011}=7.41(5)\times 10^3$ M $^{-1}$ and $\beta_{021}=1.36(7)\times 10^7$ M $^{-2}$. The numbers in parantheses are here and in the following equal to 3σ , where σ is the estimated standard deviation in the constant referring to the least significant digit. The constants were determined in solutions where the total ligand concentration, C_A , was constant in each titration series. C_A -values of 25, 50, 100, and 150 mM were used. The data could be well described (*sig y* = 3.9×10^{-3}) by the above two constants in spite of the fairly large correction for the diffusion potential (at most 6.3 mV).

The potentiometric data for the samarium system were described by using a model with the metal complexes MA^+ , MA_2^- and MHA_2^{2+} . This model gives a satisfactory description of the measurements as judged by the value of *sig y* = 7.2×10^{-3} . The same model also gives a fairly good description of the experimental data for the other two systems. The stability con-

stants are given in Table 3. ΔH° and ΔS° values are given in Table 4.

The 1,2-bis(carboxymethyloxy)ethane systems. The protonation constants of the ligand were $\beta_{011}=4.75(3)\times 10^3$ M $^{-1}$ and $\beta_{021}=5.38(3)\times 10^6$ M $^{-2}$. These data are based on 263 experimental points collected from ten different titration series at C_A/mM = 10, 25, 50, 100, and 150. The protonation constants fit these data well as judged by the value of *sig y* = 4.2×10^{-3} .

The metal ligand systems were described by a model with the species MA^+ , MA_2^- , MA_3^{3-} , and MHA_2 . We have tested other possible models which include complexes of the type MHA_2^{2+} and $M_2A_4^{4+}$ on the cerium and erbium systems. In the least-squares refinement we found that the corresponding stability constants β_{111} and β_{201} were negative or zero. Hence these models were discarded.

The dominating species are MA^+ and MA_2^-

Table 4. Over-all enthalpy and entropy changes for the formation of some rare earth 1,2-bis-(carboxymethylthio)ethane complexes at 25.00°C and $I=1.00$ M. The enthalpy changes for the formation of MHA complexes have not been determined. All errors are equal to 3σ , referring to the least significant digit. The units for the enthalpy and entropy changes are kJ/mol and kJ/(K mol), respectively.

Metal	ΔH°_{101}	ΔH°_{102}	ΔS°_{101}	ΔS°_{102}	sig Q/J
Sm	12.3(17)	21.2(26)	86	138	0.050
Dy	20.4(29)	24.3(22)	108	148	0.048
Er	19.6(25)	33.0(28)	104	171	0.037

Table 5. Stability constants for complexes formed in the rare earth 1,2-bis(carboxymethyloxy)-ethane system at 25°C, $I=1.00$ M. The error carrying variable and the method used to estimate the errors are defined in Table 3. The protonation constants are $\beta_{011}=4.748(27) \times 10^9 \text{M}^{-1}$ and $\beta_{021}=5.384(26) \times 10^9 \text{M}^{-2}$. Sig $y=4.2 \times 10^{-3}$ and $N=263$.

Metal	$\beta_{101} \times 10^{-4} \times \text{M}$	$\beta_{102} \times 10^{-7} \times \text{M}^2$	$\beta_{103} \times 10^{-9} \times \text{M}^3$	$\beta_{112} \times 10^{-10} \times \text{M}^3$	sig $y \times 10^3$	N
La	2.26(1)	5.18(9)	0.40(11)	0.266(2)	4.2	66
Ce	4.41(3)	7.71(12)	0.67(14)	0.315(5)	5.3	132
Pr	6.40(15)	7.79(65)	0.39(2)	0.35(4)	8.7	71
Nd	8.32(26)	9.02(79)	0.43(1)	0.73(3)	9.5	66
Sm	11.87(14)	9.61(30)	0.89(8)	2.16(17)	6.6	66
Gd	7.83(13)	7.45(31)	0.68(1)	1.61(17)	7.2	66
Tb	5.66(12)	7.91(48)	0.49(3)	0.55(2)	10.1	70
Dy	4.66(5)	8.44(34)	0.60(1)	0.89(1)	7.6	66
Er	4.04(9)	10.91(40)	0.88(3)	0.26(15)	9.7	130
Tm	4.34(8)	17.13(49)	0.29(3)	0.32(6)	6.4	70
Yb	7.03(15)	47.4(15)	0.33(8)	0.59(24)	9.3	66

Table 6. Over-all enthalpy and entropy changes for the formation of rare earth complexes with 1,2-bis(carboxymethyloxy)ethane at 25.00°C and $I=1.00$ M. MA^- and MA_2^- are the dominating species. The enthalpy value ΔH°_{103} has been assumed to be constant -10.0 kJ/mol throughout the rare earth series. The protonation enthalpies of the ligand are $\Delta H^\circ_{011}=1.10(6)$ kJ/mol and $\Delta H^\circ_{021}=2.10(6)$ kJ/mol, respectively.

Metal	ΔH°_{101}	ΔH°_{102}	ΔH°_{112}	ΔS°_{101}	ΔS°_{102}	sig Q/J
La	6.75(12)	-4.04(15)	-16.5(23)	106	153	0.025
Ce	5.52(11)	-3.27(17)	-17.8(35)	107	159	0.040
Pr	4.31(21)	-2.12(35)	-44(66)	106	144	0.061
Nd	3.30(13)	0.58(22)	3.9(31)	105	154	0.038
Sm	1.58(7)	7.94(15)	-0.8(9)	102	178	0.023
Gd	3.56(9)	12.23(18)	-1.0(9)	106	192	0.027
Tb	7.30(17)	14.06(30)	-1.8(41)	115	198	0.049
Dy	10.84(15)	17.77(23)	9.5(15)	126	211	0.043
Ho	12.97(30)	19.43(59)	7(9)	132	216	0.077
Er	15.61(17)	29.04(26)	11(8)	141	251	0.047
Tm	16.74(26)	31.78(31)	38(11)	145	264	0.065
Yb	15.95(28)	31.53(31)	48(11)	146	272	0.077
Lu	15.22(21)	29.43(24)	21.0(6)	143	268	0.049

(cf. Fig. 2). The \bar{n} -curves have a plateau at $\bar{n}=2$ but with a slight increase at high ligand concentrations indicating the possible formation of a third complex MA_3^{3-} . The value of the third stepwise stability constant is rather small, varying between 1 M^{-1} and 10 M^{-1} . The magnitude of the constant is very sensitive towards systematic errors in the diffusion potential correction and/or in the various total concentrations. An impurity in the acid may cause an error in the total concentration of ligand. We have investigated how this may effect the magnitude of the stability constants by repeating the potentiometric titrations for the neodymium system by using two different batches of ligand acid with formula weights differing by one percent. The stability constants agreed within 3σ . Furthermore both \bar{n} -curves show a pronounced inflexion at $\bar{n}=2$ and this would not have been the case if the ratio C_A/C_M had been in error. In view of this we judge the third complex to be real and not an artefact brought about by impure chemicals. The various stability constants are given in Table 5, ΔH° and ΔS° values in Table 6.

The 1,2-bis(carboxymethylamino)ethane systems. The samarium system is used as a model for all the other systems. The equilibrium model suggested from these data includes the complexes MA^+ , MA_2^- and MH_2A^{2+} . The possible existence of a complex MHA^{2+} was also tested. A stability constant $\beta_{111}=7.1(3) \times 10^{11} \text{ M}^{-2}$, corresponding to an equilibrium constant of $1.4 \times 10^2 \text{ M}^{-1}$ for the reaction $\text{M}^{3+} + \text{HA}^- \rightleftharpoons \text{MHA}^{2+}$, was obtained. A calculation of the concentrations of the various species in the

solutions studied showed that at most 2 % of the metal ion was present as MHA^{2+} . Hence, the existence of the complex cannot be unequivocally decided, e.g. a very slight change in the total concentrations C_H and/or C_A gave a negative value of β_{111} . For this reason the complex has not been included in the equilibrium model used.

The magnitude of the stability constants and their estimated errors are to some extent influenced by the number of titration series used. This difference is illustrated for the samarium system in Table 7, where the second set of stability constants refers to titration series of similar stoichiometric compositions as those used in the other lanthanoid systems investigated.

The variation within the rare earth series of the stability constants obtained in this study agrees well with earlier results.^{2,3} The ratio between our stability constants and those of Thompson is equal to 0.6 and 0.8 for β_1 and β_2 , respectively. This difference is presumably due to the different ionic media used. In view of the constant ratio between the two sets of stability constants the magnitude of the constants for the seven elements which were not investigated potentiometrically at $I=1.0 \text{ M}$, viz. Ce, Pr, Gd, Dy, and Tm may be estimated from the constants given by Thompson.²

The stability constants are given in Table 7, ΔH° and ΔS° values in Table 8.

Comparison between models and experimental data. The models suggested for the various metal-ligand systems give estimates of the standard-deviations in the quantity C_H/C_A

Table 7. Stability constants for complexes formed in the rare earth 1,2-bis(carboxymethylamino)-ethane system at 25°C and $I=1.00 \text{ M}$. The error carrying variable and the method used to estimate the errors are defined in Table 3. The protonation constants are $\beta_{011}=4.95(7) \times 10^9 \text{ M}^{-1}$, $\beta_{021}=2.574(41) \times 10^{16} \text{ M}^{-2}$, $\beta_{031}=6.02(12) \times 10^{18} \text{ M}^{-3}$ and $\beta_{041}=2.775(54) \times 10^{20} \text{ M}^{-4}$. $\text{Sig } y = 3.6 \times 10^{-3}$ and $N=140$.

Metal	$\beta_{101} \times 10^{-6} \times \text{M}$	$\beta_{102} \times 10^{-11} \times \text{M}^2$	$\beta_{121} \times 10^{-17} \times \text{M}^3$	$\text{sig } y \times 10^3$	N
La	9.02(28)	3.57(18)	4.53(39)	3.8	36
Nd	94.7(17)	$3.88(10) \times 10^2$	3.98(23)	2.7	39
Sm	181.7(19)	$2.75(4) \times 10^3$	3.98(10)	2.2	97
Sm	175.8(44)	$2.62(8) \times 10^3$	4.01(27)	1.7	37
Tb	183.4(59)	$1.12(4) \times 10^4$	4.50(35)	2.3	38
Er	322(7)	$8.68(23) \times 10^4$	3.69(60)	2.1	39
Yb	672(24)	$8.65(28) \times 10^5$	2.83(24)	2.1	38

Table 8. Over-all enthalpy and entropy changes for the formation of proton and rare earth 1,2-bis-(carboxymethylamino)ethane complexes at 25.00°C and $I = 1.00$ M.

Proto-nation	$-\Delta H^\circ_{011}$	$-\Delta H^\circ_{021}$	ΔS°_{011}	ΔS°_{021}	<i>sig</i> Q/J
	37.3(11)	74.5(14)	61	64	0.035
Metal	$-\Delta H^\circ_{101}$	$-\Delta H^\circ_{102}$	ΔS°_{101}	ΔS°_{102}	<i>sig</i> Q/J
La	4.69(50)	13.22(66)	117	177	0.076
Ce	7.22(20)	12.94(29)	117	191	0.031
Pr	8.76(39)	15.90(54)	119	194	0.061
Nd	10.50(18)	19.21(24)	117	196	0.029
Sm	12.20(36)	25.17(47)	117	192	0.055
Gd	8.89(68)	24.95(87)	127	194	0.101
Tb	4.76(58)	22.12(70)	142	214	0.082
Dy	3.54(85)	19.82(97)	148	229	0.114
Ho	2.02(67)	13.99(82)	153	260	0.092
Er	1.40(47)	14.39(49)	158	257	0.059
Tm	1.63(42)	15.69(39)	160	264	0.044
Yb	3.24(35)	19.15(33)	158	260	0.041

which are in the range $3 \times 10^{-3} - 10 \times 10^{-3}$. In order to decide whether a model gives a fair description of the experimental data or not, one has to decide whether this range of *sig y* values corresponds to reasonably small errors in the various system variables or not. These variables are, *e.g.*, the various total concentrations and the measured E and E_R values.

Dellien¹¹ has given an account of one possible method for checking this: the measured emf-values are adjusted until an exact fit is obtained with the final set of constants. Reasonable "random errors" are then added to the various total concentrations and emf values and a new set of stability constants is then calculated. In this way one can for each estimate of the random errors obtain an estimate both of *sig y* and the errors in the various constants. The mean errors expected from our experimental procedure are 0.1 mV in E and 0.15 % in the various total concentrations. These errors give *sig y* values in the range $3 \times 10^{-3} - 7 \times 10^{-3}$. The equilibrium models we have used, all have *sig y* values in this range and we can thus conclude that the models do give a satisfactory description of the experimental data.

It is obvious from the data presented in Table 1 that systematic errors are present in some of the titration series. However, these errors are small and we did not feel it justified

to decrease them by variations of the system variables.

Sillén¹² has given an account of how the errors in the constants are estimated in the "Letagrop" procedure. However, the magnitude of the error estimate is strongly dependent on the weighting of the experimental data. It is at best very difficult to assign weights to the various experimental data in measurements of the kind discussed here. For this reason one must not take the error estimates of the various constants literally. A better estimate may be obtained by the previously outlined procedure of assigning random errors to the system variables. This procedure indicates that mean errors of the magnitude mentioned above for the system variables give errors in the stability constants which are approximately 3σ for the dominating complexes, while the errors in the species present in small amounts might be 10–20 times their estimated standard deviations.

DISCUSSION

1,2-Bis(carboxymethylthio)ethane gives complexes of such low stability, $\beta_1 = 10^2 \text{ M}^{-1}$, that one might assume that no chelate is formed and that the metal is bonded to only one carboxylate group. This is in keeping with the poor donor ability of sulphur noted already in thio-

diacetate. The complexes formed by 1,2-bis-(carboxymethyloxy)ethane and 1,2-bis(carboxymethylamino)ethane are much more stable, $\beta_1 = 10^6$ and 10^8 M^{-1} , respectively, suggesting the formation of chelates. The characteristic coordination number for both the latter ligands is two, indicating a coordination number of at least eight for the lanthanoid ions in the various MA_2^- complexes.

The second consecutive stability constant K_2 varies with a factor of 8 through the rare earth series for 1,2-bis(carboxymethyloxy)ethane. In the 1,2-bis(carboxymethylamino)ethane system the variation is much larger, a factor of 3.3×10^3 . In this system K_2 turns out to be an approximately linear function of the atomic number Z . The data in Tables 6 and 8 show that a large part of the observed difference between the two ligands is a ligand specific enthalpy effect (*cf.* Fig. 4). The variation of ΔH°_{101} for the elements La through Tb is very similar to the type of variation previously found for a number of other ligands, *e.g.* those depicted in Fig. 1. Noticeable differences in ΔH°_{101} between the two ligands appear for the smallest lanthanoid ions. These differences are more pronounced in the enthalpy change for the second consecutive complex formation reactions.

The variations in ΔS°_{101} through the rare earth series are for both ligands very nearly the same as those found previously for a number of other ligands.^{1,13} This similarity also extends to the entropy changes for the reactions $\text{MA} + \text{A} \rightarrow \text{MA}_2$, except for the heaviest lanthanoid elements (Er–Lu) in the 1,2-bis(carboxymethyloxy)ethane system where there is an additional increase in ΔS° .

From the study of the tridentate dicarboxylate ligands, we infer that the observed differences in the thermodynamic quantities between 1,2-bis(carboxymethyloxy)ethane and 1,2-bis(carboxymethylamino)ethane cannot be due to the nature of the donor atoms. The fact that the differences between the two ligands are largest (*i.*) for the smallest central ions and (*i.i.*) in the second complexes, indicates that the differences are due to geometric factors. Even the presumably small differences in geometry between these tetradentate ligands give rise to large variations in the thermodynamic parameters with the size of the central ion. 1,2-Bis-(carboxymethylamino)ethane has obviously a much better size specificity than 1,2-bis-(carboxymethyloxy)ethane and the tridentate dicarboxylates and is the ligand to be preferred if one wants to separate the various rare earths

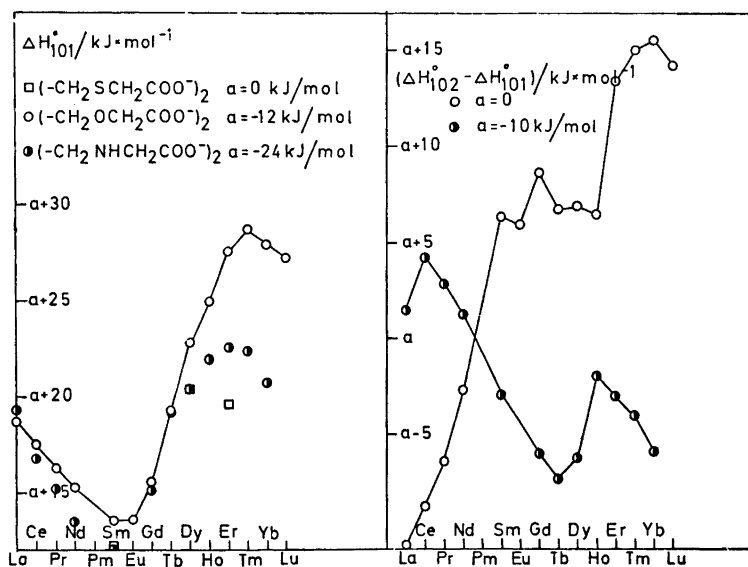
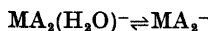


Fig. 4. ΔH°_{101} and $(\Delta H^\circ_{102} - \Delta H^\circ_{101})$ for the formation of rare earth complexes with 1,2-bis-(carboxymethylthio)ethane, 1,2-bis(carboxymethyloxy)ethane, and 1,2-bis(carboxymethylamino)ethane. The various enthalpy values have been displaced by the quantity α given in the figure.

from one another.

From our data it seems as if the coordination geometry is more important for the size of the enthalpy term than for the corresponding entropy term. A similar finding has been noted for the formation of the third oxydiacetate and dipicolinate complexes where the relative decrease in the third consecutive stability constant observed for the rare earth elements with smallest ionic radius, was found to be predominantly an enthalpy effect.

The non-monotonic variation of ΔH°_{102} for the 1,2-bis(carboxymethylamino)ethane system may be due to a solvation equilibrium of the type discussed in previous communications,^{14,15} e.g. a change in coordination number from nine to eight according to the following equilibrium



where K is near unity for Ho. Work is in progress to obtain more quantitative information about the possible occurrence of such equilibria in this system.

The difficulty of getting a quantitative estimate of differences in affinity between various donors is illustrated in Fig. 4. The difference in the quantity $(\Delta H^\circ_{102} - \Delta H^\circ_{101})$ between 1,2-bis(carboxymethyloxy)ethane and 1,2-bis(carboxymethylamino)ethane varies through the lanthanoid series from -3 kJ/mol to $+31.5$ kJ/mol. This variation does not depend on differences in the affinity of ether oxygen and NH or on the basicity of the carboxylate groups, but only on variations in the geometry of the complexes. The differences in ΔH°_{101} between ligands containing ether oxygen, ether sulphur, and iminogroups are quite different for the tri- and the tetradentate ligands. Hence, it seems as if estimates of relative affinities for one series of ligands cannot be used for quantitative prediction of the corresponding values for other ligands.

Ternary complexes are formed for all the three ligands investigated. The magnitude of the stability constants indicates that the ligands HA^- and H_2A are bonded to one carboxylate group only, i.e. that no chelates are formed. The amounts of the ternary complexes formed depend on the basicity of the ligand, the pH of the solution and on the relative magnitude of the stability constants for the ternary and binary complexes. Fairly high concentrations of MHA may be obtained in the 1,2-bis(carboxymethylthio)ethane system because of the low

stability of the binary complexes. In the 1,2-bis(carboxymethyloxy)ethane system the binary complexes are much more stable and the concentration of MHA is thus too small to be detectable in the concentration range available.

No ternary complexes were detected in the earlier investigation of the rare earth 1,2-bis(carboxymethylamino)ethane system. This is not especially surprising since the previous investigators did not study the complexation reactions at high hydrogen ion concentrations. The stability constants for the reaction



are in the range $11 - 18 \text{ M}^{-1}$ in keeping with a unidentate coordination of the H_2A ligand. The acid H_2A exists mainly in the zwitter-ion form, a fact supported both by the magnitude of the protonation constants and the protonation enthalpies; cf. Table 8.

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