

## Association Reactions of Magnesium(II), Calcium(II), Strontium(II), and Barium(II) with Malate Ion in Aqueous Solution. Influence of Enthalpy and Entropy Factors on the Stability Order of the Complexes

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Calorimetric values are reported for  $\Delta H^\circ$  and  $\Delta S^\circ$  of reactions between alkaline-earth metals and malate ion. The measurements were carried out in aqueous solution, at 25 °C and  $I = 1$  M ( $\text{NaNO}_3$ ). The present results indicate that the stability order of the alkaline-earth metal complexes of malate ( $\text{Mg} < \text{Ca} > \text{Sr} > \text{Ba}$ ) is determined by enthalpic factors. The irregular position of magnesium in comparison with calcium seems to be caused by the difficulty of stable bond formation by the former with polydentate anions. The entropy data suggest the presence of different desolvation processes for these cations.

The different orders of stability constants are an interesting problem in the study of alkaline-earth metal complexes in aqueous media. In fact it is well-known that, according to the ligand nature, the  $\log K$  order for Mg, Ca, Sr, and Ba may vary greatly.

In general, these  $\log K$  series can be divided into the following three fundamental types.

(a)  $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$ . I.e., the stabilities decrease with the increase of the crystalline radii of cations. Such sequences are mainly due to small or highly charged anions and to certain mono- or bidentate ligands.<sup>1</sup>

(b)  $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$ . This series is opposite to the preceding one; it is defined "in accordance with the hydrated radii" of cations. The corresponding ligands have well-defined characteristics. They are, in general, anions of oxygenated inorganic acids, of large dimensions, such as iodate, nitrate, sulfate, or thiosulfate.

(c)  $\text{Mg} < \text{Ca} > \text{Sr} > \text{Ba}$ . The position of magnesium in this series was previously defined as "irregular".<sup>2</sup> The ligands in this case are the anions of some hydroxycarboxylic and polycarboxylic ligands and particularly polyaminopolycarboxylic ligands.

In most of the previous papers on the alkaline-earth metal complexes only the stability constants were considered, while in a few works the enthalpy and entropy of association were determined. The calorimetric values available in literature refer, almost exclusively, to the complexes of polyaminopolycarboxylic ligands.<sup>1</sup> Knowledge of the  $\Delta H^\circ$  and  $\Delta S^\circ$  values appears to be very useful in the present case, in order to clarify the processes determining one or the other of the above sequences. Therefore, it was thought to be of interest to determine, by means of direct calorimetry, the  $\Delta H^\circ$  and  $\Delta S^\circ$  of reaction between the above four alkaline-earth metals and malate ion, for which the series of stabilities is irregular (type c). The present results refer to the aqueous medium, at 25 °C and  $I = 1$  M.

### Experimental Section

**Reagents.** The nitrates of Mg(II), Ca(II), Sr(II), and Ba(II) were used (C. Erba RPE). The concentrations of the solutions were determined by complexometric titration with EDTA (0.1 M solution, C. Erba RPE). Ligand solutions were prepared by DL-malic acid (C. Erba RPE, >99%). Inert electrolyte was sodium nitrate (C. Erba RPE).

**Equipment.** Calorimetric measurements were performed at 25.00 °C by an LKB 8700-2 Precision Calorimetry System and an LKB 8726-1 100-mL titration vessel, provided with a standard resistor (50  $\Omega$ ) and a thermistor (2000  $\Omega$ ). The accuracy of the instrument was checked by measuring the molar enthalpy of the reaction between tris(hydroxymethyl)methylamine and HCl in aqueous solution. The

Table I. Experimental Data for the Mixing of Metal and Malate Ion Solutions,<sup>a</sup> at 25 °C and  $I = 1$  M

metal	$C_M$ , M	$\Sigma V_T$ , mL	$10^3 C_{ML}$ , M	$10^3 C_L$ , M	$\Sigma Q_c$ , cal
Mg	0.0799	2.507	6.12	3.29	-0.549 <sup>b</sup>
		5.014	11.5	6.87	-1.057
		7.521	16.0	10.7	-1.483
		10.028	20.0	14.8	-1.887
Ca	0.0799	2.507	7.23	2.18	0.230
		5.014	13.6	4.68	0.495
		7.521	19.2	7.53	0.863
		10.028	24.0	10.7	1.097
Sr	0.0799	2.507	5.67	3.75	0.042
		5.014	10.6	7.75	0.111
		7.521	14.8	12.0	0.198
		10.028	18.4	16.4	0.284
Ba	0.0800	2.507	4.92	4.50	-0.179
		5.014	9.15	9.17	-0.350
		7.521	12.8	14.0	-0.488
		10.028	15.9	18.9	-0.611

<sup>a</sup> Initial concentration of malate in the titrant solution 0.340 M.

<sup>b</sup> The negative sign of  $\Sigma Q_c$  means endothermic.

temperature of the titrant was kept at the temperature of the calorimeter by immersing (at least 12 h before the measure) the Teflon reservoir of the titrant in the same thermostatic bath containing the calorimetric cell. The calorimeter was also equipped with a Radiometer ABU 12b autoburet for the titrant addition. The calorimetric experiments were performed in a room whose temperature was kept constant within  $\pm 0.3$  °C.

**Procedure.** For each metal, several sets of measurements of the reaction and dilution heats were carried out, each set being performed in the following manner. Successive amounts of  $2.507 \pm 0.002$  mL of sodium malate solution (about 0.3–0.4 M) were added to 88.00 mL of metal nitrate solution (0.08 M), and the heat for each addition was measured. The pH of all solutions had been previously brought to  $8.0 \pm 0.1$  and the ionic strength to 1 M by  $\text{NaNO}_3$ . The corresponding heat of dilution was measured by adding the same amounts of ligand solution to 88.00 mL of 1 M  $\text{NaNO}_3$ , at pH 8.0. Under these conditions the interaction between proton and malate was negligible ( $\text{p}K_2$  of malic acid<sup>2</sup> 4.68).

**Treatment of the Experimental Data.** Table I collects the experimental data for some measurements: initial concentration of metal in the calorimetric vessel ( $C_M$ ); cumulative volume of titrant added ( $\Sigma V_T$ ); complex and free-ligand concentrations after each addition ( $C_{ML}$ ,  $C_L$ ); cumulative heat corrected for the dilution ( $\Sigma Q_c$ ).

The molar enthalpies of complex formation were determined from the experimental heats ( $\Sigma Q_c$ ) and the complex species concentrations. The latter were obtained by means of the corresponding stability constants,<sup>2</sup> previously corrected to  $I = 1$  M by Davies' equation:  $-\log f = Az^2[I^{1/2}/(1 + I^{1/2}) - 0.2I]$ . The calculations of  $\Delta H^\circ$  and its standard deviation were made by two different methods, reported previously: (a) the numerical method<sup>3</sup> of minimization of the error square sum and (b) the graphical method<sup>4</sup> derived from the equations

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**Table II.** Thermodynamic Parameters for the Complex Formation Reaction  $M^{2+} + L^{2-} \rightarrow ML$  ( $L^{2-}$  = Malate Ion), in Aqueous Solution, at 25 °C and  $I = 1$  M

$M^{2+}$	log $K$	$-\Delta G^\circ$ , kcal mol <sup>-1</sup>	$\Delta H^\circ$ , kcal mol <sup>-1</sup>	$\Delta S^\circ$ , gibbs mol <sup>-1</sup>	$\frac{\Delta S^\circ_0 + \bar{S}^\circ(M^{2+},aq)}{d}$ , gibbs mol <sup>-1</sup>
Mg <sup>2+</sup>	1.42	1.94	0.97 ± 0.01 <sup>c</sup>	9.8	-13.2
Ca <sup>2+</sup>	1.67 <sup>a</sup>	2.28	-0.44 ± 0.02	6.2	3.4
Sr <sup>2+</sup>	1.32	1.80	-0.10 ± 0.04	5.7	7.1
Ba <sup>2+</sup>	1.17	1.59	0.39 ± 0.01	6.6	17.6

<sup>a</sup> For Ca<sup>2+</sup> with L<sup>2-</sup> a log  $K$  value of 3.02 was also obtained, by solubility measurements, by Das and Nair,<sup>5</sup> at 25 °C. <sup>b</sup> The results are expressed by means of the thermochemical calorie, equal to 4.1840 abs J. <sup>c</sup> The uncertainty in each case is given as the estimated standard deviation. <sup>d</sup> The quantity  $\Delta S^\circ_0 + \bar{S}^\circ(M^{2+},aq)$  refers to  $I = 0$ .  $\Delta S^\circ_0$  is the entropy variation corrected to  $I = 0$  by means of the equation  $\Delta S^\circ_0 = \Delta S^\circ + R [T \sum \nu_i \partial (\ln \gamma_i) / \partial T - \sum \nu_i \ln \gamma_i]$ , reported by J. M. Austin, R. A. Matheson, and H. N. Parton, in "The Structure of Electrolytic Solutions", W. J. Hamer, Ed., Wiley, New York, 1959, pp 370, 375. For the values used in this calculation see also H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold, New York, 1950, pp 116, 118. For the  $\bar{S}^\circ(M^{2+},aq)$  values see ref 6.

of Leden and Fronaeus for the overall formation constants. These methods gave results in good accordance. The entropy values were obtained in gibbs mol<sup>-1</sup> by  $\Delta S^\circ = 10^3(\Delta H^\circ - \Delta G^\circ)/T$ .

### Results

The molar thermodynamic quantities are listed in Table II. The only possible comparison with previous literature data regards the reaction of calcium.<sup>5</sup> By the method of the log  $K$  variation with temperature a  $\Delta H^\circ$  of  $8.608 \pm 0.002$  kcal mol<sup>-1</sup> was obtained. This value is in complete disagreement with that of Table II. As previously observed,<sup>1</sup> the  $\Delta H^\circ$  values obtained by this method within a too narrow temperature range are less reliable than those found by direct calorimetry.

### Discussion

Before examining the values in Table II, it may be useful to discuss briefly the thermodynamics for some ligands giving regular orders of log  $K$ . For this purpose, previous values for iminodiacetate ion<sup>7</sup> (crystalline-radii order of log  $K$ ) and for sulfate<sup>8</sup> and thiosulfate<sup>9</sup> ions (hydrated-radii order) are listed in Table III. For reasons of solubility, calorimetric data of the last two ligands are available only for the reactions with magnesium and calcium ions.

The entropies in Table III for iminodiacetate follow the same order as the log  $K$  values, while the enthalpy order is reversed. Therefore the stability order of the complexes appears to be determined by the entropy factor. The positive values of  $\Delta S^\circ$  are related to the solvent-destructuring processes accompanying the charge neutralization between metal and ligand. The smaller in size the crystalline radius of cation, the stronger the solvent-destructuring process. Therefore, it can be concluded that the log  $K$  order is determined, through a destructuring action, by the crystalline radius.

Also in the case of sulfate and thiosulfate the stability sequence is due to the entropy variation, at least for magnesium

**Table III.** Thermodynamics for the Reaction  $M^{2+} + L^{2-} \rightarrow ML$ , in Aqueous Solution

$M^{2+}$	$L^{2-}$	log $K$	$\Delta H^\circ$ , <sup>a</sup> kcal mol <sup>-1</sup>	$\Delta S^\circ$ , gibbs mol <sup>-1</sup>	$T$ , °C	$I$ , M
Mg <sup>2+</sup>	IMDA <sup>2-</sup> <sup>b</sup>	2.94	2.94	23.5	20	0.1
Ca <sup>2+</sup>	IMDA <sup>2-</sup>	2.59	0.3	12.7	20	0.1
Sr <sup>2+</sup>	IMDA <sup>2-</sup>	2.23	0.1	10.5	20	0.1
Ba <sup>2+</sup>	IMDA <sup>2-</sup>	1.67	0.1	8.0	20	0.1
Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	2.23	0.51	12.0	25	0.0
Ca <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	2.43	0.81	13.7	25	0.0
Mg <sup>2+</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	0.56	0.40	3.9	25	0.5
Ca <sup>2+</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	0.70	0.64	5.3	25	0.5

<sup>a</sup>  $\Delta H^\circ$  were all determined by direct calorimetry. <sup>b</sup> Iminodiacetate ion.

and calcium. In previous papers<sup>9,10</sup> the formation of outer-sphere pairs was demonstrated for magnesium, while for calcium the entropy data showed fairly clearly the formation of contact ion pairs with the probable displacement of two water molecules from the cationic hydration sphere. These different desolvation processes may justify the  $\Delta S^\circ$  series for Mg and Ca with the above two anions, and consequently they seem to be the determining factor of the stability order for this type of ligand. It must also be noted that the correlation previously proposed<sup>11</sup> between this log  $K$  order and the radii of the hydrated cations may have only a formal significance and does not seem to reflect the real course of these processes.

The data of Table II for malate show that, unlike the preceding cases, the log  $K$  order is now in agreement with that of  $\Delta H^\circ$ , being, for both log  $K$  and  $-\Delta H^\circ$ , Mg < Ca > Sr > Ba. No similar sequence is observed for  $\Delta S^\circ$ . The  $\Delta H^\circ$  for calcium is exothermic, while for magnesium it remains considerably endothermic. The same was observed, even more markedly, for polyaminopolycarboxylic ligands.<sup>1</sup> Therefore it must be thought that the inversion of the stabilities between Ca and Mg is related, for these ligands, to the metal-anion bond strength. It is probable that magnesium, owing to its small dimensions, has some difficulties in forming stable bonds with certain polydentate anions.

In the last column of Table II the quantity  $\Delta S^\circ_0 + \bar{S}^\circ(M^{2+},aq)$  is reported. It is equal to  $\bar{S}^\circ(ML,aq) - \bar{S}^\circ(L^{2-},aq)$ , so it is the difference between the standard partial molar entropy of the complex (enclosing the water molecules displaced from the cationic sphere) and of the free ligand. Supposing that (a) the contribution of  $\bar{S}^\circ(L^{2-},aq)$  is constant for all cations and (b) the influence of the cation dimension on  $\bar{S}^\circ(ML,aq)$  is negligible if the complex is electrically neutral,<sup>10</sup> it can be concluded that the different values in the last column of Table II are mainly determined by the different numbers of water molecules displaced from the metals. Taking into consideration the conclusions of previous papers<sup>9,10</sup> and the value of about 7.3 gibbs for the displacement of 1 mol of water from a cation, the data in Table II agree with the displacement of two water molecules in the reaction of calcium in comparison with that of magnesium. For strontium and especially for barium the above desolvation processes appear to be even more marked.

**Registry No.** MgL, 74096-72-3; CaL, 74096-73-4; SrL, 74096-74-5; BaL, 74096-75-6.

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