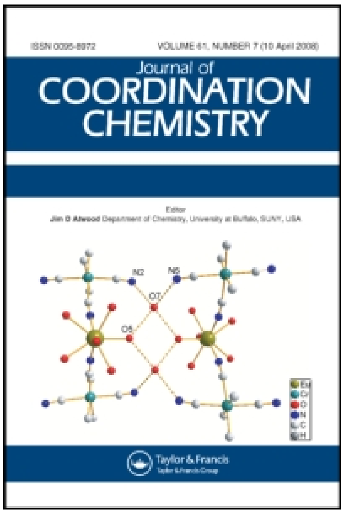

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THE THERMODYNAMIC PARAMETERS OF FORMATION OF LANTHANIDE SQUARATE COMPLEXES

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The thermodynamic parameters of complexation of the lanthanide ions by squarate anions have been measured by potentiometric and calorimetric titrations. The design and operation of the calorimeter is described as it has some unique features. The complexes are weaker than analogous complexes with other hydroxy-keto ligands due to a more endothermic enthalpy of complexation.

INTRODUCTION

The thermodynamic parameters of complexation in aqueous solution between lanthanide ions and hydroxy-keto ligands have been reported for several ligands[1,2,3]. Similar data have been obtained for complexation with the dibasic ligands malonate and maleate[4,5,6,7] anions. These systems were studied to obtain insight into the role of such factors as ligand basicity, chelate ring size, and steric effects on the enthalpies and entropies of complexation. To extend such studies, we have investigated the formation of the complexes of the lanthanide cations with the oxocarbon ligand of squaric acid. This ligand forms a relatively strong diprotic acid whose anion is known to have considerable resonance stabilization. From these properties, as well as the probability that the complex should have a 5-membered chelate ring with different bond angles and distances than in the ligands previously studied, we hoped to gain further understanding of the factors affecting complexation of the lanthanides in aqueous systems.

We have determined the free energy change by potentiometry and, then, using these values, calculated the enthalpy change from calorimetry. In order to ascertain the validity of the calorimetric data, we have also calculated the values of ΔG, ΔH, and ΔS from a calorimetric titration. This method assumes that the integral heat change in the calorimetric titration is a function of both the free energy and the enthalpy changes. Mathematical analysis of the heat curve provides most probable values for both ΔG and ΔH. Since the calorimeter is quite sensitive yet relatively simple to use, we describe it in the Experimental Section.

EXPERIMENTAL

Chemicals

Lanthanide perchlorate stock solutions were prepared from reagent grade oxides or from carbonates by reaction with insufficient perchloric acid. Filtration produced an aqueous stock solution with a pH of 4–5. Appropriate quantities of the lanthanide stock and 2 M $NaC1O_4$ solutions were diluted with deionized water to produce a working solution ca. 5 mM in Ln(III) and 70 mM in Na(I). Each working solution was analyzed for both lanthanide and total cation concentration in order that the ionic strength could be precisely evaluated. The lanthanides were assayed by EDTA complexometric titration employing xylenol-orange as indicator while the total cation concentrations were determined by cation exchange.

Potentiometric Procedure

A Beckman Research pH meter (Model 1019), modified by the addition of a zenor diode stabilized reference voltage supply, was used in conjunction with a Sargent–Welsh combination Thalamide glass electrode (Model-5–30072–15). Suzuki[8] has reported that the problem of erratic response in perchlorate solutions is eliminated if an electrolyte of 4.16 M NH_4Cl is substituted for the usual saturated KCl solution. In this work, both electrolytes (KCl and NH_4Cl) were used in the potentiometry of the lanthanide squarate systems without any apparent difficulties with either.

In the potentiometric titration, identical volumes (usually 40 ml) of blank solution (0.1 M $NaClO_4$) and lanthanide solution (0.1 M ionic strength) were titrated individually with identical incremental volumes of ligand buffer. In order to assure comparable conditions the blank solution was adjusted to the same initial potential (pH) as the lanthanide solution to which it was to be compared. The potential of the reference phthalate buffer (pH = 4.009, 25° C) which was determined before and after each titration was used as a criterion for compatability of different titrations. For instance, if the phthalate buffer potential was within 0.5 mv, two or more lanthanide titrations could be combined in a single data set for the computations. This was desirable with the light lanthanides where precipitation prevented the accumulation of many data points during a single titration. Naturally the phthalate potential during the blank run also had to agree with that obtained during the lanthanide titration. The use of additional reference buffer solutions was not considered necessary since the response of the electrode was found to agree with the Nernst Equation and the maximum range of the potential readings was small.

The Calorimetric System

The Peltier cooling calorimeter used in this work was designed to nullify steady state thermal effects such as the heat of stirring and to provide a means of rapidly returning the calorimeter vessel and its contents to exactly the titrant temperature before each titration increment. The negligible temperature off-set allowed the observation of dilution heats which may be required as a corrective parameter. In this work, corrections for dilution heats were made negligible by keeping the ionic strength differences between all the solutions small. Though the calorimeter was operated in the adiabatic mode, the high thermal conductivity of the Peltier cooling vessel (relative to dewar type vessels) limits the reaction time to a few seconds for accurate results. This requirement presented no problems for the fast ionic reactions encountered in this work.

The 40–60 ml calorimeter vessel consisted of a thin pyrex glass shell which had been silver and copper plated on the outside to provide a very conductive heat path between the contents of the vessel and the Peltier cooler. The cooler was indium-soldered to both the copper plated vessel and to the copper heat sink. The annulus was air filled and sealed by silicone sealant.

Other components of the calorimeter were modifications of earlier designs. The use of 4 Swagelok fittings in the calorimeter head had proven to be a useful means by which the heater, thermistor, buret tip and even a 1/4″ OD combination glass electrode could be quickly replaced or adjusted. The titrant was delivered with high accuracy by a 10 ml Metrohm piston buret whose cylinder was immersed directly in the 25°C water bath. Thermal equilibrium of the titrant was attained in less than 30 minutes for a working temperature of 25°C.

The electrical components of the calorimeter consisted of the signal handling, calibration and Peltier subsystems. The temperature change (sensitivity $\sim 1 \times 10^{-5}$ ° C) was sensed by a 100 K ohm thermistor which was interfaced by a thermostated bridge to a Model 150B Keithly amplifier and Sargent recorder. The calibration system included a precision power supply and relays controlled by a digital electronic timer. The 40 ohm calibration heater was an epoxy coated Manganin alloy wire (Temple Electrical Co., Ltd.) loosely coiled on a glass support for fast response. The voltage drop across the calibration heater and a precision 1.00000 ohm resistor, measured by an Eldorado Digital Voltmeter, provided the precise measure of the power dissipation by the calibration heater. The Peltier cooler was driven by a precision power supply in series with easily switchable resistances which allowed momentary changes in the cooling power.

Calorimetric Procedure

The calorimetric titration procedure was nearly the same as the potentiometric titration except that the reaction heat was observed rather than the equilibrium pH. A standard volume of 40 ml of the 5 mM lanthanide solution was reacted incrementally with up to 20 ml of the ligand solution. Increasing titrant increments were taken throughout the titrations in order to maintain a more uniform precision in the observed heats.

CALCULATIONS AND RESULTS

The equilibria and associated thermodynamic parameters of interest are:

$$\mathrm{Ln}^{+3}_{(aq)} + \mathrm{Sq}^{-2}_{(aq)} \xrightleftharpoons{\beta_1,\ \Delta\psi_1,\ \Delta\zeta_1} \mathrm{LnSq}^{+1}_{(aq)} \tag{1}$$

$$\mathrm{Ln}^{+3}_{(aq)} + 2\mathrm{Sq}^{-2}_{(aq)} \xrightleftharpoons{\beta_2,\ \Delta\psi_2,\ \Delta\zeta_2} \mathrm{LnSq}^{-1}_{(aq)} \tag{2}$$

$$\mathrm{HSq}^{-1}_{(aq)} \xrightleftharpoons{K_{A2},\ \Delta H_{A2}} \mathrm{Sq}^{-2}_{(aq)} + \mathrm{H}^{+}_{(aq)} \tag{3}$$

Only the 1:1 and 1:2 complexes were considered as under the conditions of our investigation, there was

TABLE I
Calorimetric titration data for samarium-squarate system

titer vol. (ml)	Q_i obs. (mcal.)	Q_i calc. (mcal.)	[L] ($\times 10^3$)	$\bar{\eta}$	μ ($\times 10^2$)
0.50	17.5	16.94	0.1436	0.085	10.01
1.00	33.6	33.24	0.2845	0.159	9.85
1.50	49.3	48.77	0.4250	0.224	9.71
2.00	63.9	63.56	0.5656	0.282	9.58
2.50	77.6	77.62	0.7100	0.335	9.47
3.00	90.7	90.96	0.8559	0.383	9.37
3.50	103.5	103.58	1.0045	0.426	9.28
4.00	115.3	115.50	1.1559	0.466	9.21
5.00	137.1	137.33	1.4671	0.537	9.07
6.00	156.1	156.63	1.7885	0.597	8.97
7.00	173.0	173.63	2.1182	0.648	8.89
8.00	188.6	188.59	2.4539	0.692	8.83
9.00	201.9	201.76	2.7932	0.730	8.79
10.00	213.7	213.37	3.1339	0.764	8.75
12.00	233.2	232.78	3.8127	0.820	8.71
14.00	248.9	248.22	4.4785	0.865	8.70
16.00	261.3	260.71	5.1234	0.901	8.69
18.00	270.9	271.01	5.7459	0.932	8.70

Experimental Conditions

metal solution: [Sm] = 0.00460 M
[Na] = 0.0742 M
pH = 3.51
volume = 40.0 ml

titer: total ligand = 0.057 M
stochiometric (HL) = 0.0252
ionic strength = 0.10 M
temperature = 25.00°C

Computed Overall Thermodynamic Parameters

$\beta_1 = 647.$ $\Delta\mathcal{H}_1 = 2.00$ Kcal
$\beta_2 = 15200.$ $\Delta\mathcal{H}_2 = 2.97$ Kcal

no evidence for either the 1:3 complex or the protonated complex, $LnHSq^{+2}$. The H_2Sq species was absent at the pH values of the titrations.

The stability constants for the lanthanide squarates were determined by potentiometric and computational techniques suggested by Bjerrum.[9] The computational procedures were modified to allow for the changes in ionic strength brought on by the multicharged reacting species. The stability constants were calculated and corrected to a standard state of 0.1 M ionic strength by an iterative procedure which took into account the changing ionic strength during the titration.

The calorimetric data alone could be used to compute the thermodynamic parameters. Although either continuous or incremental titration can be used, we performed only the latter using a buffer solution of the squarate ligand as titrant. An iterative calculational procedure[10] was developed in which the observed heats and the known stoichiometric quantities of ligand, lanthanide ion and hydrogen ion served as input. In theory the observed heat curve could be matched by a non-linear least squares fitting procedure to yield all of the thermodynamic parameters of Eq. 1, 2, and 3. However, the precision of the data proved insufficient to define both the protonation and the complexation parameters simultaneously. A separate acid-base calorimetric titration allowed us to calculate the protonation heat, ΔH_{A2}, to be 1.75 ± 0.05 kcal/mole.(10) Using this protonation heat and the second dissociation constant for squaric acid given by Schwartz and Howard[11] ($K_{A2} = 8.91 \times 10^{-4}$; $\mu = 0.10$) as constants, the complexation parameters $\beta_1, \beta_2, \Delta\mathcal{H}_1, \Delta\mathcal{H}_2$, were calculated.

The enthalpy values were also calculated separately using the values of β_1 and β_2 obtained from the potentiometric titrations. In all the calorimetric calculations, corrections were applied to take into account the significant deviations during the titration from the standard state of 0.1 M ionic strength. All computations were performed on a CDC 6400 computer.

Table I reports a sample data set with the computed free ligand concentrations and ionic strength which were the most important variables in the computations. This table also lists the computed complexation heats and the experimental values. Table II gives the thermodynamic values obtained by the combination of potentiometric and calorimetric

TABLE II

Thermodynamic parameters for lanthanide squarate complexation determined by potentiometric and calorimetric titrations

T = 25.0°C, $\mu = 0.10\text{M}(\text{NaClO}_4)$

Lanthanide	β_1	$\Delta\mathcal{G}_1$ *	$\Delta\mathcal{H}_1$ *	$\Delta\mathcal{S}_1$ ‡	β_2 x10^{-3}	$\Delta\mathcal{G}_2$ *	$\Delta\mathcal{H}_2$ *	$\Delta\mathcal{S}_2$ ‡
La	516	−3.70	1.51	17.6				
Ce	525	−3.71	1.78	18.4				
Pr	533	−3.72	1.89	18.8				
Nd	543	−3.73	1.99	19.3				
Sm	643	−3.83	2.02	19.6	12.1	−5.57	3.04	28.9
Eu	699	−3.88	2.00	19.7	13.2	−5.62	4.31	33.3
Gd	735	−3.91	2.01	19.9	14.6	−5.68	3.79	31.8
Tb	748	−3.92	2.18	20.4	16.1	−5.74	3.44	30.8
Dy	735	−3.91	2.18	20.4	17.6	−5.79	4.08	33.1
Ho	711	−3.89	2.14	20.2	18.5	−5.82	3.83	30.9
Er	653	−3.84	2.42	21.0	17.9	−5.80	4.57	34.8
Tm	601	−3.79	2.33	20.5	16.4	−5.75	4.02	32.8
Yb	543	−3.73	2.42	20.6	14.1	−5.66	3.83	31.8
Lu	474	−3.65	2.47	20.5	10.8	−5.50	3.90	31.5
Y	533	−3.72	2.37	20.4	17.6	−5.79	3.33	30.6

*Kcal/mole ≠ cal/deg./mole

Errors (1σ): β_1 = ±10%; $\Delta\mathcal{G}_1$ = ±0.05; $\Delta\mathcal{H}_1$ = ±0.10, T$\Delta\mathcal{S}_1$ = ±0.10
β_2 = ±50%; $\Delta\mathcal{G}_2$ = ±0.20; $\Delta\mathcal{H}_2$ = ±0.25, T$\Delta\mathcal{S}_2$ = ±0.25

TABLE III

Thermodynamic parameters for lanthanide squarate complexation determined by calorimetric titrations

T = 25.0°C; $\mu = 0.10\text{M}(\text{NaClO}_4)$

Lanthanide	β_1	$\Delta\mathcal{G}_1$ *	$\Delta\mathcal{H}_1$ *	$\Delta\mathcal{S}_1$ ‡	β_2 x10^{-3}	$\Delta\mathcal{G}_2$ *	$\Delta\mathcal{H}_2$ *	$\Delta\mathcal{S}_2$ ‡
La	540	−3.72	1.51	17.6	15.1	−5.70	3.00	29.2
Ce	559	−3.74	1.69	18.2	13.6	−5.36	3.14	28.5
Pr	531	−3.71	1.84	18.6	8.5	−5.36	3.14	28.5
Nd	597	−3.78	1.87	18.9	16.4	−5.75	2.96	29.2
Sm	662	−3.84	2.00	19.6	15.4	−5.71	2.97	29.1
Eu	568	−3.75	2.12	19.7				
Gs	588	−3.77	2.22	20.1				
Tb	797	−3.95	2.12	20.4				
Dy	824	−3.97	2.10	20.3				
Ho	1044	−4.11	2.06	20.7				
Er	1027	−4.10	2.11	20.8				
Tm	448	−3.61	2.61	20.8	14.8	−5.69	3.24	29.
Yb	488	−3.66	2.53	20.8	9.8	−5.78	3.27	30.
Lu	448	−3.61	2.56	20.7	11.9	−5.56	3.48	30.
Y	598	−3.78	2.31	20.4	14.8	−5.69	3.67	31.

*Kcal/mole ≠ cal/deg./mole

Errors (1α): β_1 = ±10%; $\Delta\mathcal{G}_1$ = ±0.005; $\Delta\mathcal{H}_1$ = ±0.005; T$\Delta\mathcal{S}_1$ = ±0.05
β_2 = ±25%; $\Delta\mathcal{G}_2$ = ±0.13; $\Delta\mathcal{H}_2$ = ±0.15; T$\Delta\mathcal{S}_2$ = ±0.15

TABLE IV
Thermodynamic parameters of complexation of samarium
(μ = 0.10M, T = 25°C)

Ligand	pK_a	$\log \beta_1$	$-\Delta G_1$ (kcal/mole)	$-\Delta H_1$ (kcal/mole)	ΔS_1 (cal/deg/mole)
Squarate	4.15*	2.81	3.84	−2.00	19.6
Tropolonate(1)	6.69	6.91	9.41	2.81	22.2
Kojate(2)	7.61	6.00	8.19	0.51	25.8
Acetylacetonate(3)	8.86	5.74	7.83	0.79	23.6

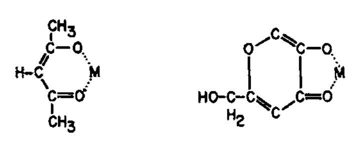
*$pK_a1 + pK_a2$

titrations. Table III lists the values obtained from the analysis of only the calorimetric titration procedure. The agreement between the values in Tables II and III indicates that the basic titration data as well as its mathematical analysis is reliable. Since the data in Table II was obtained by separate measurements of β_i and ΔH_i, it should be more accurate. In both Tables II and III, the values reflect the combination of several titrations for each metal ion.

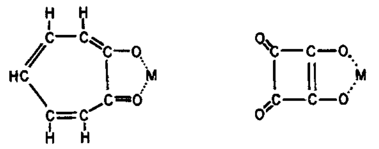
A rather thorough error analysis was applied to the data. The largest factor in the error in the potentiometrically determined stability constants was a small emf drift due to a junction potential. The errors quoted in the Tables reflect one standard deviation and are likely to be somewhat larger than they should be.

DISCUSSION

The values of the stability constants of the lanthanide square complexes are substantially lower than those of the complexes formed with acetylacetonate[3], kojate[2], and tropolonate[1] ions which is in agreement with the relative basicity of these ligands as measured by their pK_a values. The values of pK_a and of the thermodynamic parameters of complexation for the formation of the samarium complexes are compared in Table IV, the structures of the 1:1 complexes are shown in Figure 1. Much of the data on lanthanide complexation has demonstrated a "compensation effect" between ΔH and ΔS such that $\Delta H/\Delta S \approx 300°$. A positive increase in ΔS is associated with a compensatory endothermic change in ΔH. If we assume that such an effect is present in these complexes, the differences in ΔS can be used to estimate an expected ΔH value for the squarate complexes based on the values of the other ligand systems. For example, the difference in ΔS_1 values between the squarate and tropolonate complexes is –2600 cal which would lead us to predict a ΔH_1 value for $SmSq^{+}$ of 300 x 2600 or 0.8 kcal/mole more exothermic than for $SmTrop^{+2}$. Since the experimental value for $SmSq^{+1}$ is 4.8 kcal/mole more endothermic than that for $SmTrop^{+2}$, ΔH_1 for formation of $SmSq^{+}$ is calculated to be 5.6 kcal/mole more endothermic than would be expected from the tropolonate data. Inasmuch as the compensation effect is believed to be related to changes in hydration, this deviation of 5.6 kcal/mole must be due to other factors than hydration. Similarly, it can be calculated that the ΔH_1 value of $SmSq^{+}$ is more endothermic than expected from the compensation effect by 4.5 kcal/mole compared to $SmKoj^{+2}$ and by 4.0 kcal/mole compared to $SmAcac^{+2}$.



a) Acetylacetonate b) Kojate



c) Tropolonate d) Squarate

FIGURE 1 Structures of the lanthanide chelates of (a) acetylacetonate, (b) kojate, (c) tropolonate, and (d) squarate. Only one resonant structure is shown for each.

If we accept the validity of the compensation effect and its association with hydration effects, the simplest interpretation of the values of 5.6, 4.5, and 4.0 kcal/mole is that these values represent the difference in the bond energy between $SmSq^{+}$ and the $SmTrop^{+2}$, $SmKoj^{+2}$, and $SmAcac^{+2}$, respectively.

These values parallel the pK_a values of these ligands which also supports the interpretation that they reflect the differences in bond energies. The Sm-Sq bonding is weaker (less exothermic) than the bonding in the other complexes even though the squarate ligand is dinegative whereas the other three ligands are uninegative. This relative weakness must reflect the low partial negative charge on the oxygen atoms of squarate anion due to resonance effects.

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