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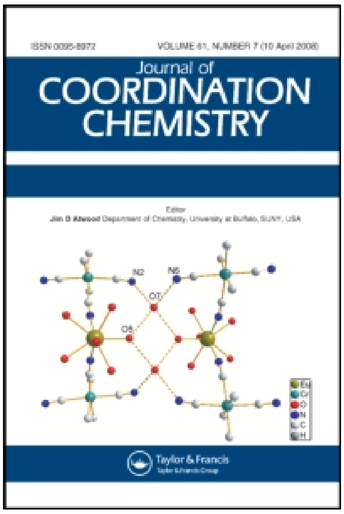

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THE THERMODYNAMICS OF LANTHANIDE COMPLEXING BY ACETYLACETONATE

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The thermodynamic parameters for the formation of the 1 : 1 complex between lanthanide ions and acetylacetonate in an aqueous medium of 0.10 M ($NaClO_4$) are reported. These complexes are less stable than the analogous tropolonate complexes due to less exothermic enthalpies of chelation.

A variety of ligands have been studied for complex formation with trivalent lanthanide ions[2,3] but these studies have differed widely in technique, ionic media and nature of the ligand. The simple carboxylates, the hydroxycarboxylate and the aminopolycarboxylate have been investigated. The stability constants of the acetylacetonates have been reported[4,5] and for Ce(III) the enthalpy and entropy of complexation has been measured.[6] In the latter case, a temperature coefficient technique was used. In this paper we report the measurements of the thermodynamic parameters for acetylacetonate complexes of the lanthanides obtained by potentiometry and calorimetry.

EXPERIMENTAL

Chemicals

Stock solutions of the lanthanide perchlorates were prepared as described in an earlier publication.[7] The lanthanide perchlorate solutions used in this work were prepared by diluting the stock metal perchlorates with distilled water. The acidity of these solutions was adjusted with 0.1 M $HClO_4$ to around *p*H 3.5. The exact concentration of the metal ions was determined by an EDTA titration, using xylenol orange as indicator and hexamethylenetetramine as buffer. Sodium perchlorate solutions were prepared using analytical grade reagent. The concentration was determined by running a known volume of the solution through a cation exchanger in the hydrogen form and titrating the eluent hydrogen ions with standard sodium hydroxide. Standard sodium hydroxide solution was prepared by diluting a standard acculute solution with distilled CO_2-free water. This solution was standardized against potassium hydrogen phthalate. Acetylacetone (Eastman Kodak Co.) was purified by distillation. Standard solutions of acetylacetone were prepared by direct weighing of the distilled sample since the latter was 98.7% pure.[8] Buffer solutions of *p*H 2.075, 4.008 and 7.413 were prepared by following NBS methods. Standard solutions of $HClO_4$ were prepared by diluting analytical grade 62% $HClO_4$ with distilled water and standardizing it against sodium hydroxide.

Calorimeter

The calorimeter used was designed in this laboratory and is described[9] elsewhere.

CALCULATIONS

Stability Constants

The reactions between lanthanide ions and acetylacetonate as well as the dissociation of acetylacetone are given below and for the sake of brevity the actual charges are omitted:

$$M + L = ML \qquad K_1$$

$$HL = H + L \qquad K_A$$

The millivolt readings, corresponding to the hydrogen ion activity obtained from the *p*H meter, were converted to *p*H values using buffer solutions of *p*H 2.075, 4.008 and 7.413. The *p*H readings were converted to hydrogen ion concentrations using the Davies equation.[10] Since the ionic strength was kept constant at 0.1 M, it was assumed that the concentration did not change appreciably and hence, no correction was made for the activity coefficient of the species involved.

The concentration of [ML], [M], [L] and [HL] were calculated from mass balance and electroneutrality expressions.[11] The values of pK_A and $\log K_1$ were calculated according to the methods described previously.[12]

In a typical run the solution in the calorimeter vessel consisted of 10 to 12 mM metal ions, 8 mM sodium hydroxide, 18 mM acetylacetone, and enough sodium perchlorate to give a final ionic strength of 0.10 M. Distilled water was added to make up the total volume before the start of titration, to 50.00 ml. Prior to adding each increment of titrant, the internal temperature of the calorimeter was adjusted to 25° C by means of a heater and a cooler which were built in the calorimeter system. The resistance of the heater was measured potentiometrically.

At each titration point, an unknown heat, Q_x, is evolved within the calorimeter. The recorder deflection corresponding to Q_x is called SQ_x in Table I. In order to convert the recorder deflection after each addition of the titrant it was necessary to have a reference deflection curve. This was obtained by using the heater to evolve a known heat, Q_c, during time t. The resistance of the heater, the time t and the current I (measured using 1 ohm standard resistor) were all measured and since the deflections were proportional to the corresponding heats, Q_c and Q_x were calculated.

The heat Q_x, evolved on adding an increment of titrant to the calorimeter solution, is given by the following equation:

$$Q_x = Q_{H_2O} + Q_{HL}$$

Therefore,

$$Q_{ML} = Q_{HL} - Q_x + Q_{H_2O}$$

where:

$$Q_{H_2O} = \Delta H_{H_2O} \times [OH] = 13.490 \text{ Kcal mole}^{-1} \times \Delta[OH]$$

$$Q_{HL} = \Delta H_{HL} \times \Delta[HL] = -3.430 \text{ Kcal mole}^{-1} \times \Delta[HL]$$

$$Q_{ML} = \Delta H_{ML} \times \Delta[M]$$

$\Delta[OH]$, $\Delta[HL]$ and $\Delta[M]$ are the changes in the number of moles of free hydroxide ions, protonated ligand and free metal ions respectively. The heat of neutralization of acetylacetone, ΔH_{HL}, was calculated by a procedure analogous to that of complexation. Knowing the values for $\log K_1$ and ΔH, ΔG and ΔS can be calculated from standard thermodynamic relationships.

All the calculations were performed on the CDC–6400 computer of Florida State University.

RESULTS

A sample set of data is given in Table I. Thermodynamic functions for the 1 : 1 complex are given

TABLE I

Data of the Dysprosium-Acetylacetonate[a]

($\mu = 0.10$ M; T = 25.0° C)

Volume of titrant, ml	pH meter reading, mv	I amp	t sec	SQ_x mm	SQ_c mm	FSQ cal/mm
0.30	18.98	0.053422	13.84	54.0	58.3	0.0012860
0.60	24.85	0.053422	13.84	54.2	58.3	0.0012860
0.90	31.50	0.053444	13.80	55.2	60.6	0.0012347
1.20	37.72	0.053444	13.80	57.4	60.6	0.0012347
1.50	43.90	0.053450	13.82	56.6	60.5	0.0012388
1.80	50.63	0.053450	13.82	58.2	60.5	0.0012388
2.10	57.80	0.053450	13.59	56.5	56.0	0.0013160
2.40	65.60	0.053450	13.59	56.2	56.0	0.0013160

[a] Initial concentrations: Metal solution: [Metal ions] = 0.01126 M; [Ligand acid (HL)] = 0.01002 M; [Ligand ions] = 0.008 M. Titrant solution: $[HClO_4] = 0.1011$ M; Volume of metal solution = 50.00 ml. Resistance of calorimeter heater 7.94 ohms. $FSQ = I^2Rt/4.184 \times SQ_c$ cal/mm.

in Table II. The pKA of acetylacetone and the enthalpy of protonation at 25° C were determined to be 8.86 ± 0.02 and −3.43 ± 0.02 Kcal/mole respectively. The error limits were calculated subjecting the data to a least squares analysis and represent a standard deviation of an individual run.

TABLE II

Thermodynamic parameters of the formation of Lanthanide-Monoacetylacetonate

(μ = 0.10 M; T = 25.0° C)

Lanthanide	log K_1[a]	ΔG[b] (kcal/mole)	ΔH[c] (kcal/mole)	ΔS[d] (cal/mole/deg)
La	4.92	−6.72	−0.07	22.4
Ce	5.20	−7.09	−0.02	23.8
Pr	5.43	−7.41	−0.23	24.1
Nd	5.41	−7.38	−0.30	23.8
Sm	5.74	−7.83	−0.79	23.6
Eu	5.99	−8.17	−0.85	24.6
Gd	5.90	−8.05	−0.99	23.6
Tb	6.02	−8.22	−1.10	23.9
Dy	6.08	−8.29	−1.08	24.2
Ho	6.07	−8.28	−1.05	24.3
Er	6.16	−8.40	−1.15	24.3
Tm	6.18	−8.43	−1.04	24.8
Yb	6.18	−8.43	−1.01	24.9
Lu	6.14	−8.38	−0.88	25.2
Y	5.90	−8.05	−0.86	24.1

[a] ±0.03
[b] ±0.04 kcal/mole
[c] ±0.05 kcal/mole
[d] ±0.30 cal/mole/deg

DISCUSSION

Our stability constants measured at 25° C in a medium of 0.10 M ($NaClO_4$) ionic strength compare well with those reported by Grenthe and Fernelius for 30° C and a 0.10 M ($NaNO_3$) medium.[4] The constants for the 0.10 M ionic strength solutions are approximately twice as large as those measured in solutions of 2.0 M ($NaClO_4$) ionic strength.[5] The agreement of the enthalpy and entropy of complexation of cerium with the earlier values is excellent.[6]

Campbell and Moeller[13] have reported the thermodynamic parameters of lanthanide complexation by tropolone (α-hyroxycycloheptatrienone) in a 0.10 M (KNO_3) medium.[13] The obvious similarity in the nature of the bonding groups in bidentate chelation by tropolone and acetylacetone (Figure 1) suggest a comparison of the thermodynamic parameters for complexation. The acid strengths [pKA(tropolonate) = 6.7; pKA(acetylacetonate) = 8.9] would lead to the expectation that acetylacetonate should form the more stable complexes whereas, in fact, the reverse is true. From Figure 1 we see that the greater stability of the tropolonate complexes results from the more exothermic enthalpy values since the entropy values of complexation are quite similar for the two ligands.

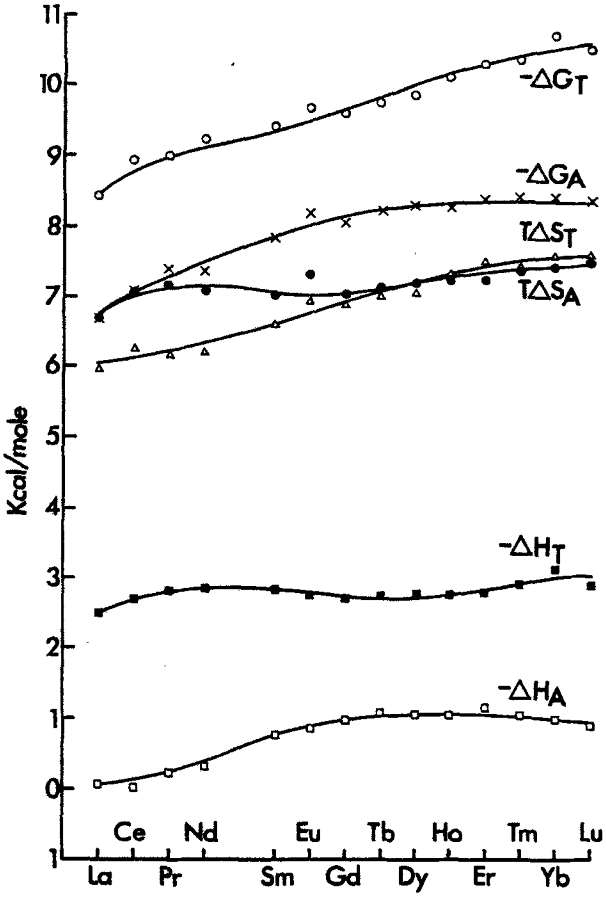

FIGURE 1 Variation of the thermodynamic parameters for formation of the monoligand complex with acetylacetonate and tropolonate.

It has been possible to relate thermodynamic stability for a number of ligand systems to lanthanide ion dehydration upon complexation.[3] If there are differences in the dehydration of the lanthanide ions or of the ligand anions upon complexation in the tropolonate and acetylacetonate systems, the differences must be canceled more or less by the hydration of the resultant complexes since no entropy difference is observed. Consequently, the greater stability of the tropolonate complexes must be attributable to a greater bonding attraction between the cations and this ligand. Since lanthanide complexes are predominantly ionic, such an enhanced attraction could be due to shorter metal-oxygen bond distances in the 5-membered tropolonate ring than in the 6-membered acetylacetonate ring. Alternately, the negative character of the tropolonate oxygens could be greater than that of the acetylacetonate oxygens. Inasmuch as tropolone is the stronger acid, it seems unlikely that the hydroxy oxygen is more negative than the enolic oxygen of acetylacetone. Therefore, it seems possible that the greater stability of the tropolonate complexes may be due to a greater negative character of the ketonic oxygen in the tropolonate complexes. This might be a result of the pi electron system of the tropolone ring.

Campbell and Moeller have called attention to the smooth variation of the thermodynamic parameters with lanthanide atomic number. This is in sharp contrast to other complexing systems such as acetate[14] and glycolate[15, 16] in which the curves show a distinct variation between the lighter and heavier lanthanide ions. This pattern in the curves has been attributed to different degrees of dehydration of the cations upon complexation. The amount of the variation in entropy between lanthanum and lutetium is almost the same for tropolonate and acetate. The implication, then, of the linear tropolonate curve is that the dehydration is a smooth function of the lanthanide ion whereas for acetate, there is a more abrupt change between gadolinium and holmium. For acetylacetonate, the entropy of the light (La to Eu) lanthanides is higher and the enthalpy more endothermic than the tropolonate pattern. This would imply slightly more dehydration by acetylacetonate than by tropolonate. However, it is necessary to study more analogous ligand systems before these possibilities can be evaluated properly.

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