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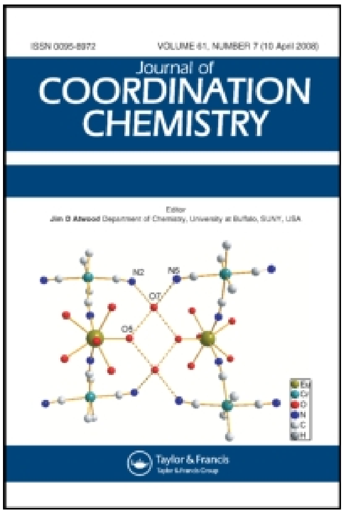

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THERMODYNAMICS OF KOJATE COMPLEXES OF THE LANTHANIDES

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THERMODYNAMICS OF KOJATE COMPLEXES OF THE LANTHANIDES

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The thermodynamic parameters have been determined for the formation of the lanthanide monokojate complexes at 25° C in aqueous solutions of 2.00 *M* and 0.10 *M* ionic strength ($NaClO_4$). The stabilities are comparable to those of the analogous acetylacetonates. The variation of the enthalpies and entropies of formation as a function of lanthanide atomic number are discussed in terms of possible hydration and bonding effects.

INTRODUCTION

A previous publication reported the stability constants for the formation of the complexes of the trivalent lanthanide ions and kojate in a solution of 2.00 *M* ($NaClO_4$) ionic strength.[1] These measurements have been repeated and extended in solutions of both 2.00 *M* and 0.10 *M* ($NaClO_4$) ionic strength. Moreover, a calorimetric titration technique was used to obtain enthalpy values for complexation in these systems.

EXPERIMENTAL

Reagents and Apparatus

Stock solutions of lanthanide perchlorates were prepared as described previously.[2] Final solutions were made by diluting the stock solutions to ~5*mM*. Stock solution of $HClO_4$ and $NaClO_4$ were used, respectively, to adjust the *p*H and the final ionic strength of 3.3 and 0.10 *M* in one case and 3.5 and 2.00 *M* in the other. The solutions were analyzed for the concentration of the lanthanide ions by titrating with standard ethylenediaminetetraacetate solution, using xylenol-orange as indicator and hexamethylenetetramine as buffer. Kojic acid (Eastman Organic Chemicals) was purified by the method of McBryde and Atkinson[3] and the buffer solution was made and standardized following the method used earlier.[2] The *p*H and calorimetric titrations in the 2.00 *M* ionic strength solutions have been performed with the equipment described previously.[4] The measurements in the solutions of 0.10 *M* ionic strength have been made with a calorimeter which was designed in this laboratory and is to be described elsewhere.[5] The *p*H-measuring system consisted of a Beckman Research *p*H meter, model 1019, a glass electrode (Beckman) and a calomel reference electrode.

Procedure and Calculations

The pK_a and enthalpy of protonation of kojic acid were measured by adding several increments of $HClO_4$, ~0.1 *N*, to a solution of ~0.025 *N* half-neutralized kojic acid adjusted to a total ionic strength of 0.10 *M* with sodium perchlorate. The millivolt readings were converted to *p*H by using buffer solutions to calibrate the *p*H meter. These hydrogen ion activities were finally converted to concentrations using the Davies equation.[6] Log K_1 and ΔH_1 values for complex formation between the langhanides and kojate ions were determined by titrating the metal solution with the kojate buffer solution. Heat of dilution data for the buffer titrant, determined by titration into a 0.10 *M* $NaClO_4$ solution, were found to be negligible. The values of pK_a and log K_1 and the concentration of the different species were calculated in a straightforward manner from mass balance and electroneutrality expressions. The heat data ($Q_{(corr)}$ corrected for the heat of protonation, and the corresponding number of moles of complex formed were used to calculate the enthalpy change for each step in the complex formation. A least-square treatment of the data was used to calculate the standard deviations. The procedures and treatment of the data for the 2.00 *M* ionic strength solutions have already been described.[4] All computations were performed with a CDC 6400 computer.

RESULTS

In solutions of 0.10 *M* ionic strength values of 7.61 ± 0.02 for the pK_a and 3.47 ± 0.05 kcal/mole for the enthalpy of ionization were found for kojic acid. This pK_a value is in fair agreement with the one (7.68) reported by Murakami[7] for measurements with a 0.10 *M* potassium nitrate medium at 25°.

Table I presents a sample set of data while the thermodynamic parameters and their standard deviations for the reaction

$$Ln^{3+}_{(aq)} + X^{-}_{(aq)} = LnX^{2+}_{(aq)}$$

are listed in Tables II and III.

TABLE I

Data for Ytterbium-Kojic acid titration

$T = 25°$ C, $\mu = 0.10M$ $(NaClO^4)$

Volume (ml)	pH	$Q_{(corr)}$
0.25	3.358	−0.004964
0.50	3.378	−0.005448
0.75	3.395	−0.005085
1.00	3.412	−0.005638
1.25	3.428	−0.005376
1.50	3.442	−0.006031
1.75	3.457	−0.005073
2.00	3.471	−0.005200
2.25	3.484	−0.005073
2.50	3.497	−0.005553
2.75	3.510	−0.005276
3.00	3.524	−0.006386

Initial volume = 50.00 *ml*, Initial *p*H = 3.337
$[Yb(ClO_4)_3]$ = 0.005008 *M*, [HL) = 0.02516 *M*
[L] = 0.02524 *M*, $Q_{dilution}$ = 0.0

DISCUSSION

In keeping with the hard acid character of the lanthanide cations, the stability of the kojate complexes is determined predominantly by the entropy changes. Even the enhanced stability in the 0.10 *M* solutions is a result of the larger ΔS values in 0.10 *M* compared to those in 2.00 *M* solution. In fact, the enthalpy values in the 2.00 *M* solutions are more exothermic than those in the 0.10 *M* system. It is common for the ΔS values to be more sensitive to the ionic strength. The trends in the thermodynamic values as a function of lanthanide atomic number are very similar for the two ionic strengths.

Several authors have compared the stability constants of divalent metal chelates of kojate with those of two ligands which have related structures, tropolonate and acetylacetonate.[7–12] The formal structures of the three ligands are shown in Figure 1. Since thermodynamic data are available on the formation of the lanthanide complexes with tropolonate[13, 14] and acetylacetonate,[12] our kojate data can be compared. Figures 2 and 3 show the enthalpy and entropy values for the three systems. All these data were obtained at 25° C in an ionic medium of 0.10 *M* by potentiometry and calorimetry. The −ΔG values are in the order tropolonate (8.5–10.5 kcal/mole) > kojate (7.2–8.8 kcal/mole) > acetylacetonate (6.7–8.4 kcal/mole). This is the same order observed for the divalent transition metal ions and is reversed from the order expected from simple consideration of acidity since tropolonate is the strongest and acetylacetonate the weakest acid. It has been suggested that this reflects the greater stability associated with 5-mem-

TABLE II

Thermodynamic parameters for kojate complexing

$T = 25°$ C, $\mu = 0.1M$ $(NaClO_4)$

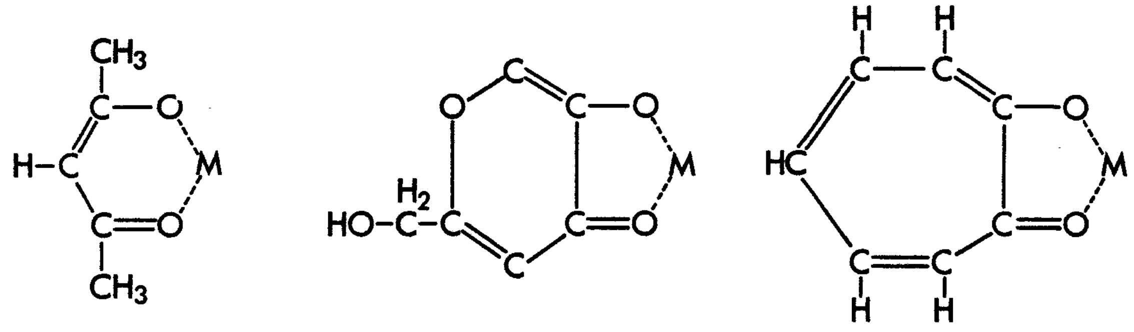
Ion	Log K_1	$-\Delta G_1$ (Kcal/mole)	$-\Delta H_1$ (Kcal/mole)	ΔS_1 (cal/deg/mole)
La	5.30 ± 0.08	7.22 ± 0.11	0.57 ± 0.27	22.3 ± 1.0
Pr	5.69 ± 0.05	7.76 ± 0.07	0.90 ± 0.12	23.0 ± 0.5
Nd	5.75 ± 0.05	7.84 ± 0.07	0.55 ± 0.19	24.4 ± 0.7
Sm	6.00 ± 0.04	8.19 ± 0.05	0.51 ± 0.23	25.8 ± 0.8
Eu	6.12 ± 0.03	8.35 ± 0.04	0.34 ± 0.20	26.9 ± 0.7
Gd	6.09 ± 0.03	8.30 ± 0.04	0.34 ± 0.14	26.7 ± 0.5
Tb	6.25 ± 0.02	8.52 ± 0.02	0.28 ± 0.16	27.6 ± 0.5
Dy	6.34 ± 0.02	8.65 ± 0.02	0.36 ± 0.17	27.9 ± 0.6
Ho	6.35 ± 0.02	8.66 ± 0.02	0.46 ± 0.11	27.5 ± 0.4
Er	6.39 ± 0.02	8.71 ± 0.02	0.20 ± 0.12	28.5 ± 0.4
Tm	6.46 ± 0.02	8.81 ± 0.02	0.30 ± 0.13	28.6 ± 0.5
Yb	6.53 ± 0.02	8.90 ± 0.02	0.60 ± 0.10	27.9 ± 0.3
Lu	6.50 ± 0.02	8.86 ± 0.02	0.19 ± 0.11	29.1 ± 0.4

TABLE III

Thermodynamic parameters for kojate complexing

$T = 25°\text{ C}, \mu = 2.00M\ (NaClO_4)$

Ion	Log K_1	$-\Delta G_1$ (kcal/mole)	$-\Delta H_1$ (kcal/mole)	ΔS_1 (cal/deg/mole)
La	5.11 ± 0.02	6.97 ± 0.03	1.37 ± 0.07	18.8 ± 0.3
Ce	5.28 ± 0.03	7.20 ± 0.04	1.52 ± 0.08	19.1 ± 0.3
Pr	5.41 ± 0.02	7.38 ± 0.03	1.44 ± 0.05	19.9 ± 0.2
Nd	5.42 ± 0.03	7.39 ± 0.04	1.43 ± 0.11	20.0 ± 0.4
Sm	5.66 ± 0.03	7.73 ± 0.04	1.19 ± 0.15	21.9 ± 0.5
Eu	5.72 ± 0.03	7.80 ± 0.04	1.22 ± 0.09	22.1 ± 0.3
Gd	5.72 ± 0.03	7.80 ± 0.04	1.08 ± 0.10	22.5 ± 0.4
Tb	5.88 ± 0.03	8.02 ± 0.04	1.07 ± 0.12	23.3 ± 0.4
Dy	5.97 ± 0.03	8.14 ± 0.04	1.12 ± 0.10	23.5 ± 0.4
Ho	5.94 ± 0.03	8.10 ± 0.04	1.08 ± 0.11	23.5 ± 0.4
Er	6.00 ± 0.03	8.18 ± 0.04	1.02 ± 0.09	24.0 ± 0.3
Tm	6.01 ± 0.04	8.20 ± 0.05	1.01 ± 0.08	24.1 ± 0.3
Yb	6.09 ± 0.04	8.30 ± 0.05	0.75 ± 0.11	25.3 ± 0.4
Lu	6.00 ± 0.05	8.19 ± 0.06	0.46 ± 0.16	25.9 ± 0.6
Y	5.84 ± 0.03	7.97 ± 0.04	1.04 ± 0.09	23.2 ± 0.3



a) Acetylacetonate b) Kojate c) Tropolonate

FIGURE 1 Structure of the metal acetylacetonate (a), metal kojate (b) and metal tropolonate (c) chelates.

bered compared to 6-membered chelate rings. With the more extensive thermodynamic data we can reinvestigate this question more thoroughly.

TABLE IV

Thermodynamic values for protonation of tropolonate, kojate and acetylacetonate

$T = 25°\text{ C}; \mu = 0.1$

Ligand	pK_a	$-\Delta G_1$ kcal/mole	$-\Delta H_1$ kcal/mole	ΔS_1 e.u.
tropolonate	6.69	9.13	2.79	21.3
kojate	7.61	10.38	3.47	23.2
acetylacetonate	8.86	12.08	3.43	29.0

The thermodynamic values for the protonation of these ligands are listed in Table IV. Earlier authors have noted that the acidity of acetylacetonate may be too low since the total concentration rather than only that of the enol form was used in the calculation. Considering only ionization of the enol, it would seem likely that acetylacetone and kojate would have similar acid strengths.

Figure 2 shows that on a comparative basis, the stability of tropolonate is due to the enthalpy. The enthalpy order is tropolonate > acetylacetonate $\gtrsim$ kojate. The differences in entropy between the three systems are smaller than the differences in enthalpy. The entropy order is kojate > acetylacetonate $\geqslant$

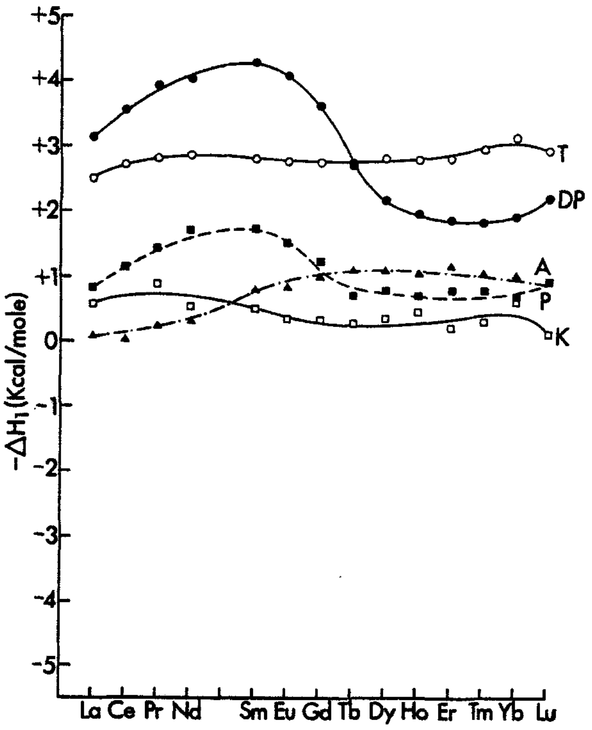


FIGURE 2 The variation of the enthalpy of formation of ML in the lanthanide series where L = α-picolinate (P), dipicolinate (DP), kojate (K), acetylacetonate (A) and tropolonate (T).

tropolonate. The similarity of the entropy values would seem to indicate that the size of the ring is not a predominant factor in the relative stabilities. Therefore, if we wish to understand the relative stabilities, we must turn to the enthalpies. The similarity of the enthalpy values for kojate and acetylacetonate is understandable if kojate and acetylacetonate enolate have comparable basicity which is reasonable as we have discussed. The question of the relative stabilities, then, is primarily one of why tropolonate complexes have such relatively large enthalpies. Calvin has proposed that tropolonate's acidity is unusually high rather than its complexes being unusually stable.[9] He attributes this unusual acidity to the unfavorable distance between the oxygen atoms which results in weak hydrogen bonding. In a chelate, the metal ion more easily bridges the oxygen–oxygen distance and the inherent strongly basic nature of tropolonate is observed. Support for the view that the stability of the tropolonate complexes is due to the strongly basic nature of the tropolonate ligand is found in the fact that the enthalpies are very similar to those for the formation of the lanthanide complexes of the dicarboxylate ligands malonate[15] and dipicolinate.[16] By contrast, the enthalpy values for the kojate and acetylacetonate complexing are comparable to those for complexation with α-picolinate.[17]

In summary, it seems that the basicity of acetylacetonate is smaller and that of tropolonate larger than the measured acidities would indicate. Of the three ligands, kojate seems to be the only one whose acidity can be used to correlate with complex stability.

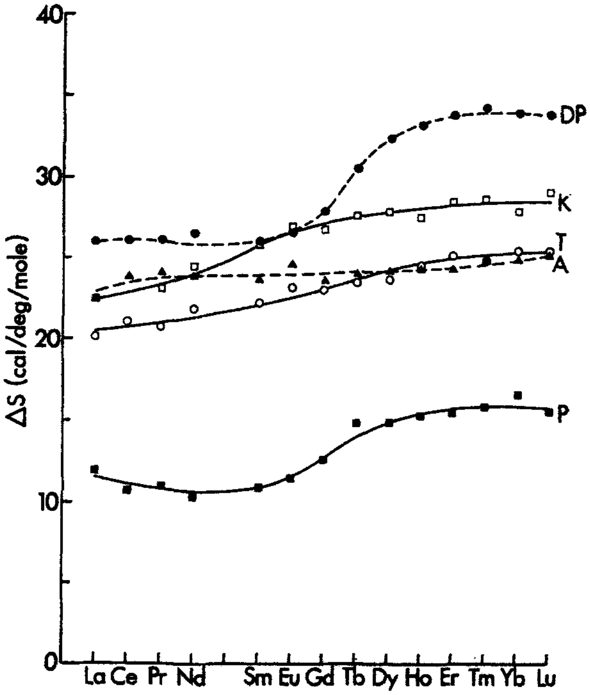


FIGURE 3 The variation of the entropy of formation of ML in the lanthanide series where L = α-picolinate (P), dipicolinate (DP), kojate (K), acetylacetonate (A) and tropolonate (T).

Moeller and Campbell[14] have pointed out that the variation of the thermodynamic parameters for tropolonate complexing with lanthanide atomic number does not follow the pattern observed with other carboxylate ligands. We can see in Figures 2 and 3 that kojate and acetylacetonate also fail to show the "normal" trends as exhibited by picolinate and dipicolinate. This "normal" pattern has been interpreted as reflecting different numbers of waters of hydration released upon complexation for the light (La–Nd) and heavy (Dy–Lu) lanthanides. Such an effect is most easily observed in the entropy term. For the tropolonate and kojate complexing, the variation in ΔS from La to Lu is 5–6 cal/deg/mole in comparison to values of 5 and 8 cal/deg/mole for picolinate and dipicolinate respectively. So, while the net change in the ΔS values are comparable, there is much less obvious separation of the lanthanides into two groups. This may be a reflection that the monoligand complex of kojate and tropolonate consists of several species of different hydration in solutions. A similar explanation was offered to account for the fact that the ΔS values changed gradually between Sm and Dy in the "normal" pattern.[18] In the kojate and tropolonate complexes, the equilibrium mixture of hydrates covers a wider range of lanthanides. The variations in ΔH are more difficult to account for since the variation of ionic radii for these rather rigid ligands may result in variations in bonding energies which balance the hydration effects.

For the acetylacetonate complexing there is almost no variation in ΔS values indicating a similar degree of dehydration upon complex formation for all the cations. However, the curve for the ΔH values shows an opposite trend to the "normal". If this curve reflects the pattern of change in bonding energy, it has approximately the correct shape and magnitude to support the proposal that the flatness of the ΔH curves for the tropoloate and kojate complexing result from a balance between bonding and dehydration.

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