

tion, the optical activity of the *trans*-[Co(*l*-chn)<sub>2</sub>X<sub>2</sub>]<sup>+</sup> ions is independent of X. However, a closer examination of the rotational strengths reveals some trends. In the series X<sup>-</sup> = F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> for the transition <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>E<sub>g</sub><sup>a</sup> there is an increase and for <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>A<sub>2g</sub> a decrease in *R*. Of the theoretical treatments proposed to date, neither the crystal field<sup>5a</sup> nor the molecular orbital<sup>4</sup> model explicitly provides for the effect of the *trans* ligands. A more complete molecular orbital model mixing halogen and metal orbitals would be necessary.

While it is interesting that the trends noted above for the rotational strength are also found for the dipole

strength, nothing more than a qualitative correlation exists. This is because the absorption band intensity results from odd vibrational states<sup>5a,12c,d</sup> whereas the CD band involves even vibrations.<sup>16</sup>

**Acknowledgments.**—The author is indebted to Professor B. Douglas and Dr. I. Legg of the University of Pittsburgh for measurements of the CD spectra in the 600–700-mμ range. Helpful suggestions of Professors T. L. Brown, R. L. Belford, and R. G. Denning are acknowledged. This research was partly supported by an August Kocks Fellowship.

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## Complexes of Trivalent Lanthanide Ions. III. Bidentate Chelates<sup>1</sup>

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Received February 3, 1966

The enthalpy and entropy of complexation are reported in an ionic strength of 2.00 *M* (NaClO<sub>4</sub>) for lanthanide ions with glycolate, lactate, and α-hydroxyisobutyrate ligands. The complexes are found to be stabilized by both the enthalpy (exothermic) and the entropy (positive). Interpretations of these thermodynamic values are offered in terms of (a) the increasing basicity of the α-hydroxyl group and (b) the inclusion of a water molecule in the chelate ring between the metal ion and the α-hydroxyl group.

The two previous publications of this series<sup>2,3</sup> have reported the thermodynamic parameters for the formation of complexes of lanthanide ions with inorganic anions and with monodentate organic anions. In this paper, we report the extension of this study to bidentate anions. We also describe the calorimetric apparatus used both in this study and in the previous one.<sup>3</sup>

### Experimental Section

**Reagents.**—A carbonate-free solution of NaOH was made up and standardized against potassium hydrogen phthalate, primary standard grade.

A stock solution of HClO<sub>4</sub> was diluted from the 9 *M* reagent grade solution obtained from G. F. Smith Co. and standardized by titration against the standard NaOH. The solution for the standard cell was prepared by diluting this stock solution. Anhydrous reagent grade NaClO<sub>4</sub> from G. F. Smith Co. was used to make the final ionic strength 2.00 *M*.

Stock solutions of lanthanide perchlorates were made and standardized as described previously.<sup>4</sup> Final solutions were made by diluting the stock solution to ~25 mM. If necessary, stock HClO<sub>4</sub> solution was added to maintain a maximum pH of ~3.5, which was considered necessary to prevent hydrolysis of the trivalent lanthanide ions. Solid NaClO<sub>4</sub> was used to make the final ionic strength 2.00 *M*.

Glycolate, lactate, and α-hydroxyisobutyrate buffer solutions were made and standardized as described previously.<sup>4</sup>

Quinhydrone of potentiometric quality was used as obtained from Fisher Scientific Co.

**Calorimeter.**<sup>5</sup>—The calorimeter used in these studies was similar to that described by Schlyter.<sup>6</sup> The calorimeter initially contained 50.00 ml of lanthanide perchlorate solution at 25.00°. Ligand solution at the same temperature was added from a thermostated buret. This arrangement requires far less work per experimental point than the conventional ampoule-breaking method, with only a slight decrease in accuracy.<sup>6</sup> The calorimeter was provided with a heater and a cooler for adjusting its internal temperature prior to adding an increment of titrant. The sensitivity of the calorimeter was approximately 10<sup>-4</sup>°.

The calorimeter heater was a length of no. 32 nichrome wire wound into a spiral on a glass rod. Copper leads were silver-soldered to the ends of the nichrome wire, which was then given a thin coating of epoxy resin. The resistance of the wire was measured using a potentiometer with a constant current source and standard resistor (each accurate to ±0.01%).

The titrant solution was delivered by a buret system consisting of a fine buret tip, a 50-ml reservoir, and a piston buret. The reservoir was immersed in the water bath. Its purpose was to ensure that the titrant delivered was at the temperature of the water bath.<sup>6</sup>

The temperature was measured by a Sargent S-81620 thermistor, rated at 0–90°. The thermistor formed one arm of a Wheatstone bridge. The unbalance voltage of the bridge was amplified and used to indicate temperature change. The output of the linear amplifier was recorded on a strip-chart recorder.

The pH in the calorimeter was measured in one of two ways. In the earlier experiments, the calorimeter solution was saturated

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(2) G. R. Choppin and W. F. Strazik, *Inorg. Chem.*, **4**, 1250 (1965).

(3) G. R. Choppin and A. J. Graffeo, *ibid.*, **4**, 1254 (1965).

(4) G. R. Choppin and J. A. Chopoorian, *J. Inorg. Nucl. Chem.*, **22**, 97 (1961).

(5) A detailed description of the calorimeter and its use may be found in the dissertation of H. G. F., which may be obtained from University Microfilms, Inc.

(6) K. Schlyter, *Trans. Roy. Inst. Technol., Stockholm*, **132**, 1 (1959).

with quinhydrone, and a potentiometer was used to measure the emf between platinum electrodes in the calorimeter and a standard cell. The standard cell contained a solution of known hydrogen ion concentration, with a total ionic strength of 2.00 *M*. Quinhydrone was added in excess of the amount required to saturate the solution. The cell was thermostated in the bath near the calorimeter vessel. A salt bridge, using 2.00 *M* NaClO<sub>4</sub> solution as electrolyte, was used to connect the standard cell to the calorimeter vessel. In the later experiments, the pH was measured on a Beckman Model G pH meter, using glass and silver-silver chloride electrodes.

The calorimeter was checked by running an acid-base titration. The results substantiated the electrical calibration with the heater.

### Calculations

The treatment of the calorimetric data to determine heats of complex formation was similar to that described by Schlyter.<sup>7</sup> Let  $l$  represent the total relative enthalpy per liter of the solution in the calorimeter and define  $\bar{l} = l/C_M$ , where  $\bar{l}$  is the average relative partial molar enthalpy of M-containing species, where M stands for a trivalent lanthanide ion and  $C_M$  is the total (stoichiometric) concentration of M. Then it can be shown<sup>7</sup> that

$$\bar{l} = \frac{\sum_{n=1}^N \beta_n [L]^n \Delta H_n}{\sum_{n=0}^N \beta_n [L]^n}$$

where  $\beta_n$  and  $\Delta H_n$  are the over-all stability constant and over-all enthalpy of complex formation, respectively, of the  $n$ th complex,  $[L]$  is the free-ligand concentration, and  $N$  is the maximum number of ligands that can be coordinated to the metal ion (in this case, 4).

Most of the stability constants needed have been previously determined.<sup>4</sup> However, in the course of this study, they were recalculated, using the original data. The new calculations were done on a larger computer (an IBM 709), thus allowing the use of a more sophisticated program.<sup>8</sup> One advantage of this program is that it calculates the probable error of the results. The new values are only slightly different from those reported earlier<sup>4</sup> and are reported here as  $\Delta G$  values. A few stability constants were needed which had not previously been determined. These were determined by the same method used in the earlier work.

Values of  $[L]$  were determined as described for the stability constants from the pH data.<sup>4</sup> Values of  $\bar{l}$  were determined from the calorimetric data as follows.

At each point in the titration, an unknown heat,  $Q_x$ , is evolved within the calorimeter. Subsequently, the heater is used to evolve a known heat,  $Q_c$ . Neither the heat capacity of the calorimeter nor the actual temperature change need be actually calculated. Let  $D_x$  and  $D_c$  be the recorder deflections corresponding to  $Q_x$  and  $Q_c$ . The deflections are proportional to the corresponding heats. Since the resistance of the heater,

the emf across it, and the length of time it was turned on were all measured,  $Q_c$  (and thus  $Q_x$ ) can be calculated.

This heat,  $Q_x$ , evolved on adding an increment of titrant to the calorimeter solution, is also given<sup>7</sup> by

$$Q_x = V^I l^I - V^F l^F$$

where  $V$  is the volume of solution in the calorimeter, in liters, and  $l$  is the total relative enthalpy per liter of solution. The superscripts I and F refer to the initial and final states of the solution in the calorimeter, respectively. Using the definition of  $\bar{l}$ , this can be transformed into

$$Q_x = V^I C_M^I \bar{l}^I - V^F C_M^F \bar{l}^F$$

However, the total number of moles,  $m$ , of metal ion in the calorimeter did not change; *i.e.*,  $V^I C_M^I = V^F C_M^F = m = \text{constant}$ . Therefore

$$\bar{l}^F = \bar{l}^I - \frac{Q_x}{m}$$

At the first titration point, there is initially no ligand in the calorimeter, and  $[ML_n]^I = 0$ . Therefore,  $\bar{l}^I = 0$  and  $\bar{l}^F = -Q_x/m$  at the first titration point. However, the titration is so arranged that  $\bar{l}^F$  for one point becomes  $\bar{l}^I$  for the next point. Therefore,  $\bar{l}^F$  can be found at each titration point after the first by adding  $-Q_x/m$  to  $\bar{l}^F$  for the preceding point. This is the required value of  $\bar{l}$ .

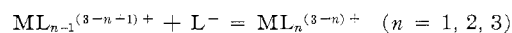
The calculations were performed on the IBM 709 at Florida State University and on the IBM 7094 at the University of Illinois.

### Data and Results

The experiments were carried out in solutions of total ionic strength of 2.00 *M* with NaClO<sub>4</sub> as the inert electrolyte. Since the concentrations of reacting species were always small ( $\leq 30$  mM) compared to the total ionic strength, it was assumed that activity coefficients remained constant. Consequently, the standard state for the solute species is the hypothetical ideal 1 *M* solution in the solvent 2.00 *M* sodium perchlorate.

A sample set of data is given in Table I. In this table, pH is the pH in the calorimeter vessel, and pH' is the pH in a similar vessel containing the same volume of titrant, but no metal ions.<sup>9</sup>

In Tables II-IV the thermodynamic parameters for the stepwise reactions



are listed. The error limits were calculated from the least-squares fit of the data by the methods described by Sullivan, *et al.*<sup>8</sup> Previous investigations<sup>4,10,11</sup> have shown that it is possible to form the complexes  $ML^{2+}$ ,  $ML_2^+$ ,  $ML_3$ ,  $ML_4^-$  in these systems. However, in the

(9) The data supplementary to this article have been deposited as Document No. 8956 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be obtained by citing the document number and by remitting \$6.25 for photoprints or \$2.50 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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TABLE I  
 DATA ON THE LANTHANUM-LACTATE SYSTEM<sup>a</sup>

Vol of titrant, ml	pH	pH'	$D_x$	$D_e$	Emf, v (heater + leads)	Calibration time, sec
0.400	2.46	3.50	132.5	136.9	0.94072	35.15
0.900	2.61	3.50	107.6	136.0	0.94070	35.74
1.600	2.72	3.50	138.0	199.0	0.94073	50.30
2.400	2.81	3.50	143.3	73.7	0.94073	46.34
3.300	2.91	3.49	140.0	171.4	0.94074	47.06
4.400	2.99	3.49	144.0	182.2	0.94075	50.31
5.600	3.03	3.49	138.9	155.3	0.94072	44.09
6.900	3.10	3.49	123.5	149.2	0.94072	43.63
8.600	3.18	3.49	129.0	155.4	0.94070	46.11
11.500	3.22	3.49	129.6	185.6	0.94078	57.49

<sup>a</sup> Initial concentrations: Metal solution: [metal ion] = 0.282 M; [H<sup>+</sup>] = 0.00526 M. Titrant solution: [ligand ion] = 0.836 M; [ligand acid (HL)] = 0.852 M. Volume of metal solution 50.0 ml. Resistance of calorimeter heater 16.73 ohms; resistance of heater + leads 16.91 ohms.

 TABLE II  
 STEPWISE THERMODYNAMIC PARAMETERS  
 OF COMPLEXES OF GLYCOLATE AT 25°

Sample	$\Delta G_1$ , kcal/mole	$\Delta G_2$ , kcal/mole	$\Delta G_3$ , kcal/mole	Data source
Y	-3.22 ± 0.02	-2.72 ± 0.02	-1.68 ± 0.02	a
La	-2.92 ± 0.04	-2.45 ± 0.06		b
Ce	-3.07 ± 0.01	-2.42 ± 0.01	-1.42 ± 0.02	a
Nd	-3.28 ± 0.01	-2.68 ± 0.02	-1.30 ± 0.03	b
Sm	-3.27 ± 0.01	-2.83 ± 0.02	-1.71 ± 0.02	a
Eu	-3.25 ± 0.03	-2.84 ± 0.04	-1.66 ± 0.05	a
Gd	-3.25 ± 0.06	-2.74 ± 0.08		a
Tb	-3.27 ± 0.06	-2.80 ± 0.09		a
Dy	-3.38 ± 0.01	-2.68 ± 0.01	-1.57 ± 0.02	b
Ho	-3.30 ± 0.03	-2.90 ± 0.04	-1.67 ± 0.05	a
Er	-3.60 ± 0.03	-2.57 ± 0.06		b
Tm	-3.58 ± 0.05	-2.77 ± 0.08	-1.99 ± 0.01	b
Yb	-3.53 ± 0.03	-2.97 ± 0.04	-1.95 ± 0.05	a
Lu	-3.64 ± 0.05	-2.85 ± 0.01		b
	$\Delta H_1$ , kcal/mole	$\Delta H_2$ , kcal/mole	$\Delta H_3$ , kcal/mole	
Y	-0.15 ± 0.04	-0.25 ± 0.10	-1.22 ± 0.28	
La	-0.85 ± 0.07	-0.23 ± 0.13		
Nd	-0.96 ± 0.04	-0.48 ± 0.08		
Sm	-0.93 ± 0.04	-0.80 ± 0.08		
Eu	-0.84 ± 0.06	-0.90 ± 0.11		
Gd	-0.62 ± 0.06	-1.19 ± 0.13		
Tb	-0.09 ± 0.07	-0.83 ± 0.10		
Dy	-0.08 ± 0.02	-0.97 ± 0.08		
Ho	-0.08 ± 0.03	-0.40 ± 0.08	-2.40 ± 0.36	
Er	-0.09 ± 0.01	-0.39 ± 0.05		
Tm	-0.29 ± 0.01	-0.57 ± 0.03	-0.84 ± 0.08	
Yb	-0.36 ± 0.06	-0.75 ± 0.18	-1.15 ± 0.62	
Lu	-0.65 ± 0.02	-0.59 ± 0.06		
	$\Delta S_1$ , cal/deg mole	$\Delta S_2$ , cal/deg mole	$\Delta S_3$ , cal/deg mole	
Y	10.3 ± 0.1	8.3 ± 0.3	1.5 ± 0.9	
La	7.0 ± 0.3	9.0 ± 0.5		
Nd	7.8 ± 0.1	7.4 ± 0.3		
Sm	7.9 ± 0.1	6.8 ± 0.3		
Eu	8.1 ± 0.2	6.5 ± 0.4		
Gd	8.8 ± 0.3	5.2 ± 0.5		
Tb	10.7 ± 0.3	6.6 ± 0.4		
Dy	11.1 ± 0.1	5.8 ± 0.3		
Ho	10.8 ± 0.1	8.4 ± 0.3	-2.5 ± 1.2	
Er	11.8 ± 0.1	7.3 ± 0.3		
Tm	11.1 ± 0.1	7.4 ± 0.1	3.9 ± 0.3	
Yb	10.6 ± 0.2	7.4 ± 0.6	2.7 ± 2.1	
Lu	10.0 ± 0.1	7.6 ± 0.2		

<sup>a</sup> Data from Choppin and Chopoorian, ref 4. <sup>b</sup> Data from this work.

 TABLE III  
 STEPWISE THERMODYNAMIC PARAMETERS OF  
 COMPLEXES OF LACTATE AT 25°

Sample	$\Delta G_1$ , kcal/mole	$\Delta G_2$ , kcal/mole	$\Delta G_3$ , kcal/mole	Data source
Y	-3.49 ± 0.04	-2.87 ± 0.05	-2.10 ± 0.05	a
La	-3.09 ± 0.03	-2.29 ± 0.10	-1.51 ± 0.29	b
Ce	-3.12 ± 0.01	-2.44 ± 0.01	-1.38 ± 0.02	a
Nd	-3.37 ± 0.01	-2.58 ± 0.01		a
Sm	-3.51 ± 0.01	-2.74 ± 0.01	-1.85 ± 0.03	a
Eu	-3.46 ± 0.01	-2.77 ± 0.02	-1.86 ± 0.02	a
Gd	-3.54 ± 0.05	-2.58 ± 0.09	-2.29 ± 0.09	a
Tb	-3.62 ± 0.06	-2.66 ± 0.08	-2.38 ± 0.08	a
Dy	-3.70 ± 0.06	-2.79 ± 0.08	-2.72 ± 0.08	a
Ho	-3.77 ± 0.03	-2.87 ± 0.05	-2.51 ± 0.05	a
Er	-3.89 ± 0.03	-2.89 ± 0.05	-2.66 ± 0.05	a
Yb	-3.94 ± 0.07	-3.13 ± 0.10	-2.59 ± 0.10	a
	$\Delta H_1$ , kcal/mole	$\Delta H_2$ , kcal/mole	$\Delta H_3$ , kcal/mole	
La	-1.58 ± 0.26	-1.1 ± 1.3	-2.3 ± 4.8	
Ce	-1.69 ± 0.19	0.6 ± 0.5	-5.3 ± 1.6	
Nd	-3.23 ± 0.34	1.5 ± 1.1		
Sm	-2.33 ± 0.36	0.45 ± 1.0	-7.2 ± 2.6	
Eu	-1.94 ± 0.25	0.8 ± 0.6	-4.4 ± 1.4	
Gd	-1.97 ± 0.21	-0.2 ± 0.6	-2.8 ± 1.1	
Tb	-1.64 ± 0.30			
Dy	-2.16 ± 0.46			
Er	-1.91 ± 0.25	1.0 ± 0.9	-4.2 ± 1.2	
Yb	-2.19 ± 0.39	-1.4 ± 1.4	1.4 ± 3.0	
	$\Delta S_1$ , cal/deg mole	$\Delta S_2$ , cal/deg mole	$\Delta S_3$ , cal/deg mole	
La	5.1 ± 0.9	4.0 ± 4.5	-2.6 ± 16	
Ce	4.8 ± 0.6	10.1 ± 1.7	-13.0 ± 5.5	
Nd	0.5 ± 1.1	13.7 ± 3.7		
Sm	4.0 ± 1.2	10.7 ± 3.4	-17.8 ± 8.6	
Eu	5.1 ± 0.8	12.1 ± 2.1	-8.6 ± 4.7	
Gd	5.3 ± 0.7	7.9 ± 2.1	-1.7 ± 3.8	
Tb	6.6 ± 1.0			
Dy	5.2 ± 1.5			
Er	6.6 ± 0.8	12.9 ± 3.0	-5.1 ± 4.2	
Yb	5.9 ± 1.3	5.9 ± 4.6	3.9 ± 10	

<sup>a</sup> Data from Choppin and Chopoorian, ref 4. <sup>b</sup> Data from this work.

calorimetric titrations, it was not possible to continue beyond the point where the average ligand number was 2.5-3, since the heat evolved,  $Q_x$ , became too small to be measured. The thermodynamic constants for  $ML_3$  formation are reported only for those experiments in which the average ligand number exceeded 2.5, while constants for  $ML_4^-$  are not reported.

### Discussion

Comparison of the thermodynamic data for formation of  $LnL^{2+}$ , where L is an  $\alpha$ -hydroxycarboxylate ligand, with similar data for the analogous simple carboxylate ligands shows several interesting facts. In Figures 1 and 2, the order in both  $\Delta H_1$  and  $\Delta S_1$  is acetate<sup>12</sup> < propionate < isobutyrate for the simple ligands, whereas it is lactate <  $\alpha$ -hydroxyisobutyrate < glycolate for the  $\alpha$ -hydroxycarboxylate ligands. Moreover, the enthalpy of complexation is exothermic for the  $\alpha$ -hydroxy ligands while it is endothermic for their simpler analogs. The entropy of complexation, though still positive, is smaller for the  $\alpha$ -hydroxy ligands. For the simple carboxylates, the complexation

TABLE IV  
STEPWISE THERMODYNAMIC PARAMETERS OF COMPLEXES  
OF  $\alpha$ -HYDROXYISOBUTYRATE AT 25°

Sample	$\Delta G_1$ , kcal/mole	$\Delta G_2$ , kcal/mole	$\Delta G_3$ , kcal/mole	Data source
Y	$-3.85 \pm 0.02$	$-3.59 \pm 0.02$	$-2.45 \pm 0.02$	a
La	$-3.11 \pm 0.01$	$-2.31 \pm 0.01$	$-1.64 \pm 0.02$	b
Ce	$-3.28 \pm 0.02$	$-2.63 \pm 0.03$	$-1.22 \pm 0.04$	a
Nd	$-3.52 \pm 0.01$	$-2.71 \pm 0.01$	$-1.73 \pm 0.02$	b
Sm	$-3.65 \pm 0.03$	$-3.02 \pm 0.04$		a
Eu	$-3.73 \pm 0.02$	$-2.94 \pm 0.03$	$-2.31 \pm 0.03$	a
Gd	$-3.66 \pm 0.05$	$-3.40 \pm 0.06$	$-1.83 \pm 0.09$	a
Tb	$-3.87 \pm 0.01$	$-3.26 \pm 0.02$	$-2.47 \pm 0.02$	a
Ho	$-4.00 \pm 0.05$	$-3.77 \pm 0.06$	$-2.42 \pm 0.07$	a
Er	$-4.27 \pm 0.04$	$-3.45 \pm 0.05$	$-3.06 \pm 0.05$	a
Tm	$-4.16 \pm 0.03$	$-2.86 \pm 0.08$		a
Yb	$-4.15 \pm 0.03$	$-3.87 \pm 0.04$	$-2.92 \pm 0.04$	a

	$\Delta H_1$ , kcal/mole	$\Delta H_2$ , kcal/mole	$\Delta H_3$ , kcal/mole
Y	$-1.23 \pm 0.21$	$-2.9 \pm 0.4$	$-0.4 \pm 0.7$
La	$-1.96 \pm 0.09$	$-0.4 \pm 0.3$	$-3.5 \pm 0.6$
Ce	$-1.48 \pm 0.10$	$-0.4 \pm 0.3$	$-5.7 \pm 1.4$
Nd	$-1.60 \pm 0.05$	$-1.7 \pm 0.2$	$-0.7 \pm 0.4$
Eu	$-1.51 \pm 0.10$	$-1.8 \pm 0.3$	$-1.6 \pm 0.4$
Tb	$-1.47 \pm 0.21$	$-3.2 \pm 0.5$	$1.0 \pm 0.8$
Er	$-0.98 \pm 0.20$	$-4.3 \pm 0.7$	$1.6 \pm 0.8$
Yb	$-1.11 \pm 0.27$	$-5.2 \pm 0.7$	$1.0 \pm 1.1$

	$\Delta S_1$ , cal/deg mole	$\Delta S_2$ , cal/deg mole	$\Delta S_3$ , cal/deg mole
Y	$8.8 \pm 0.7$	$2.3 \pm 1.3$	$6.8 \pm 2.4$
La	$3.9 \pm 0.3$	$6.4 \pm 1.0$	$-6.3 \pm 2.2$
Ce	$6.0 \pm 0.3$	$7.3 \pm 0.8$	$-14.9 \pm 4.8$
Nd	$6.5 \pm 0.2$	$3.5 \pm 0.5$	$3.4 \pm 1.3$
Eu	$7.5 \pm 0.3$	$3.8 \pm 0.8$	$2.4 \pm 1.3$
Tb	$8.1 \pm 0.7$	$0.14 \pm 1.7$	$11.5 \pm 2.5$
Er	$11.0 \pm 0.7$	$-2.8 \pm 2.2$	$15.7 \pm 2.8$
Yb	$10.2 \pm 0.9$	$-4.5 \pm 2.2$	$13.1 \pm 3.5$

<sup>a</sup> Data from Choppin and Chopoorian, ref 4. <sup>b</sup> Data from this work.

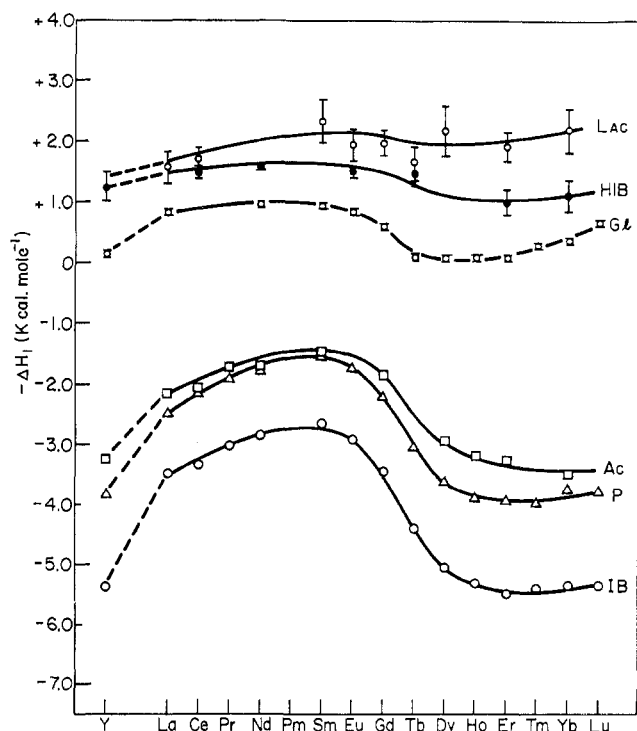


Figure 1.—The variation with lanthanide ion in the enthalpy of formation of  $\text{LnL}^{2+}$  for lactate,  $\alpha$ -hydroxyisobutyrate, glycolate, acetate,<sup>11</sup> propionate,<sup>3</sup> and isobutyrate<sup>3</sup> ligands.

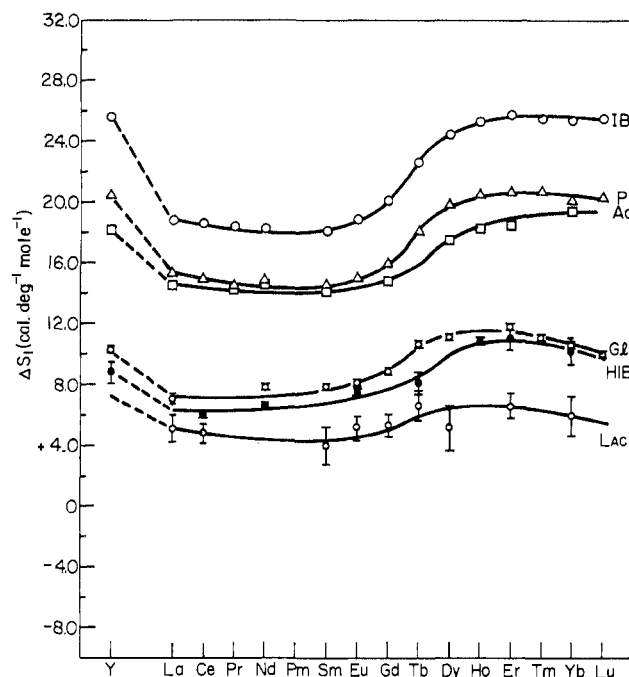


Figure 2.—The variation with lanthanide ion in the entropy of formation of  $\text{LnL}^{2+}$  for isobutyrate,<sup>3</sup> propionate,<sup>3</sup> acetate,<sup>11</sup> glycolate,  $\alpha$ -hydroxyisobutyrate, and lactate ligands.

was stabilized by the favorable entropy factor predominating over the unfavorable enthalpy effect. In the case of the  $\alpha$ -hydroxycarboxylates, both entropy and enthalpy favor complexation.

In Figures 1 and 2, it would be possible to draw a straight line for the lactate and  $\alpha$ -hydroxyisobutyrate systems because of the relatively large error limits. However, the similarity between the glycolate curve and the acetate, propionate, and isobutyrate curves would indicate a good probability that the lactate and  $\alpha$ -hydroxyisobutyrate curves also have that shape. Moreover, this shape in the  $\alpha$ -hydroxycarboxylate systems is very likely to be due to the same cause as in the simple systems, *i.e.*, a difference in hydration number between the lighter and the heavier lanthanide ions.<sup>3,13,14</sup> Grenthe's values of  $\Delta H$  and  $\Delta S$  for nine of the lanthanide-glycolate systems under identical conditions<sup>12</sup> differ from our values by 0.1 kcal, or less, which is roughly within the error limits. The ligand order in both  $\Delta H_1$  and  $\Delta S_1$  for the simple carboxylate ligands is that expected if the increasing size of the ligand serves to cause increased disruption of the hydration sphere of the cation upon complexation. The order for the  $\alpha$ -hydroxy ligands follows no such simple pattern. It is, however, instructive to consider the difference in enthalpy and entropy values between analogous ligands in Figures 1 and 2. Defining  $\Delta(\Delta N) = \Delta N_{\text{OH acid}} - \Delta N_{\text{simple}}$ , we find for the Sm complexes

	$\Delta(\Delta H)$ , kcal/mole	$\Delta(\Delta S)$ , cal/deg mole
Glycolate-acetate	-2.5	-6.2
Lactate-propionate	-3.7	-10.4
$\alpha$ -Hydroxyisobutyrate-isobutyrate	-4.5	-11.6

(13) I. Grenthe, *Acta. Chem. Scand.*, **18**, 293 (1964).

(14) P. L. E. de la Praudiere and L. A. K. Staveley, *J. Inorg. Nucl. Chem.*, **26**, 1713 (1964).

We now can see that there is a regularity in the order for the ligands when analogs are compared.

Interpreted in view of the model proposed previously, the negative values of  $\Delta(\Delta H)$  and  $\Delta(\Delta S)$  would indicate that the  $\alpha$ -hydroxy ligands do not disrupt the hydration layer about the lanthanide ion to any greater extent than the analogous simple ligands. Moreover, the increasingly negative trend from glycolate to  $\alpha$ -hydroxyisobutyrate is consistent with the postulate in an earlier paper<sup>4</sup> that the increasing basicity of the hydroxyl group due to addition of methyl groups to the  $\alpha$ -carbons results in increased stability of the chelate. This could also explain the trend in the  $\Delta(\Delta S)$  values since stronger bonding would result in a large decrease in configurational entropy of the chelating ligand.

Grenthe has proposed an alternate explanation for the lower  $\Delta S$  for the glycolate system compared to the acetate system.<sup>12</sup> He suggests that the chelate may be formed *via* a water molecule between the  $\alpha$ -hydroxy group and the cation. Larsson has also offered evidence that a water molecule is present between the hydroxy group and the gadolinium ion in the glycolate chelate.<sup>15</sup> Consequently, the retention of a water molecule in the chelate ring would make the  $\Delta H$  more exothermic and

(15) R. Larsson, *Acta Chem. Scand.*, **19**, 783 (1965).

the  $\Delta S$  more negative than might be expected, which is in agreement with the experimental data. The decrease in  $\Delta S$ , then, between simple and chelate complexing could be due to both the decrease in configurational entropy and the inclusion of a water molecule in the chelate ring. It should be noted that Powell and Farrell report that the lanthanide triglycolates separate from solution as anhydrous complexes from La(III) to Gd(III) and as dihydrates from Gd(III) to Lu(III).<sup>16</sup>

Unfortunately, the values of  $\Delta H_2$ ,  $\Delta H_3$ ,  $\Delta S_2$ , and  $\Delta S_3$  are not sufficiently accurate to permit much discussion of their implications. Generally,  $\Delta H_2$  is more exothermic than  $\Delta H_1$  while  $\Delta S_2$  is smaller than  $\Delta S_1$ . These orders are also present for the simple carboxylate systems and reflect the decreasing importance of the disruption of hydration layer of the cation to the overall enthalpies and entropies of complexation.<sup>3</sup>

**Acknowledgment.**—This research was supported by the U. S. Atomic Energy Commission. The National Science Foundation also contributed support through grants to the Florida State University Computer Center and the University of Illinois Department of Computer Science.

(16) J. E. Powell and J. L. Farrell, "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, p 26.

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## Polarographic Reduction of Copper Chelates of 1,3-Diketones. IV. Chelate Stability and Electron-Transfer Mechanism<sup>1</sup>

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Received March 7, 1966

The polarograms of 23 1,3-diketone copper(II) chelates were recorded in aqueous 75% dioxane solution, using potassium nitrate as supporting electrolyte. When the series of chelates is separated into three homogeneous series (aliphatic substituted, aromatic substituted, and chelates in which both aliphatic and aromatic groups are substituted), good correlations between half-wave potentials and stabilities are observed within each of these divisions. The chelates of 1,3-diketones which have aromatic substituents reduce at much more positive potentials than would be expected in view of their stabilities. The relative ease of reduction of the aromatic-substituted chelates, as compared to the aliphatic-substituted chelates, leads to the conclusion that the aromatic groups provide a low-energy path for electron transfer through the  $\pi$ -electron system.

### Introduction

Inasmuch as the polarographic reduction of 1,3-diketone copper(II) chelates in dioxane-water mixtures takes place irreversibly, no simple calculation of the stability constants from half-wave potential data can be made. However, the reduction potential should be a function of the electronic density on and around the copper atom. Assuming that the stability of the chelate increases with increasing electron density near the copper ion, the reduction potential ought to become more negative as the chelate becomes more stable.

(1) For the previous paper in this series see: E. R. Nightingale, Jr., and H. F. Holtzclaw, Jr., *J. Am. Chem. Soc.*, **81**, 3523 (1959).

This relationship presupposes that the mechanism of electron transfer is the same in all chelates for which the half-wave potentials and stability are compared.

### Experimental Section

**A. Apparatus and Polarographic Procedures.**—Each sample solution was  $10^{-3}$  M with respect to chelate, weighed to the nearest 0.1 mg. The solutions were 0.1 M with respect to potassium nitrate as supporting electrolyte. The chelate and supporting electrolyte were dissolved in aqueous 75% dioxane. The resistance of the system, measured through the saturated calomel electrode, a fine frit, and the dropping-mercury electrode (the circuit used in conjunction with the IR compensator), was about 6000 ohms. The resistance of the system, measured through the mercury pool and the dropping-mercury electrode