in Table IV. At the same time, the entropy change is negative due to the ordering of ionic charges without a compensatory disordering due to extensive disruption of the hydration sphere. The more negative entropy for $NdSCN^{2+}$ formation is probably due to loss of rotational entropy by the thiocyanate ion.

In the inner-sphere complexes, the hydration zone is disrupted to a greater extent which results in a net endothermic enthalpy term. The elimination of water molecules from the inner hydration zone to the thawed middle zone also results in a net positive entropy effect.

A test of the suggestion that the outer-sphere complexes involve little disruption in the inner hydration zone is possible. We would expect that the free energy changes upon ion-pair formation would reflect changes in ionic attraction and, hence, vary linearly as the radius of hydrated ions. While such radii are unknown, it is possible to assume that the ionic conductances, Λ^+, at infinite dilution are proportional to these hydrated radii. These conductances have been calculated previously[24] from data of Spedding and coworkers (values for Pm and Tb were interpolated). Figure 2 shows the expected linear relationship between log K_1 and $\Lambda+$ except for cerium. We can offer no explanation for the behavior of cerium but it seems unlikely that either log K_1 or the $\Lambda+$ value could be sufficiently in error to account for this.

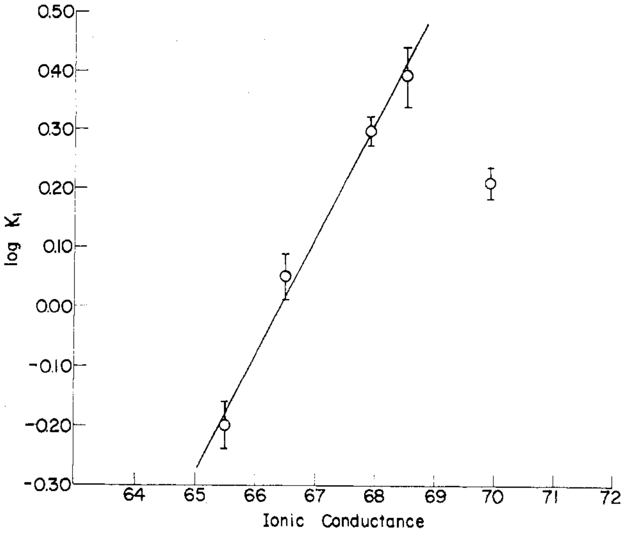

Figure 2.—The relation between log K_1 for MNO_3^{2+} and the ionic conductance at infinite dilution of M^{3+}.

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Complexes of Trivalent Lanthanide and Actinide Ions. II. Inner-Sphere Complexes[1]

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The stability constants and thermodynamic parameters for the first and second steps in the formation of the lanthanide propionate and isobutyrate complexes have been determined at 25.0° and an ionic strength of 2.00 *M* $NaClO_4$. The stability constants were obtained by direct pH titrations and the enthalpy changes by calorimetric titrations. An interpretation of the data is offered in terms of the effect of complexing on the hydration sphere about the cation.

Introduction

In the preceding publication, the thermodynamic parameters for the formation of complexes between lanthanide ions and inorganic anions were reported.[2] In this paper, we report on a study of the complexes between lanthanide ions and simple organic anions. Previous reports (see ref. 1–6 of the preceding paper) have been concerned with polydentate organic ligands with the exception of a recent paper by Grenthe[3] in which data on acetate and thioglycolate are presented.

Experimental

Reagents and Apparatus.—Stock solutions of the lanthanide perchlorates were prepared as described earlier.[4] The working solutions were prepared from these by dilution. Buffer solutions were prepared from the acids by the "half-neutralization" method also described in the previous publication. The ionic strength of all solutions was adjusted to 2.00 *M* by the addition of solid sodium perchlorate (anhydrous reagent grade).

The calorimeter used in these determinations was designed in our laboratories and is similar to that used by Schlyter.[5] It contained a pH measuring system, a heater, and a thermistor making possible the simultaneous determination of both the stability

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(1) Abstracted in part from a Master's Thesis by A. J. G., Florida State University, 1964.

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

(3) I. Grenthe, *Acta Chem. Scand.*, **18**, 283 (1964).

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

(5) K. Schlyter, *Trans. Roy. Inst. Technol., Stockholm*, No. 132 (1959).

constants and the heats of formation of a given complex. The pH measuring system consisted of a Beckman Model G pH meter, a Beckman Type "42" glass electrode, and a silver–silver chloride reference electrode. The remainder of the apparatus was used for the determination of the heats of complexation. The calorimeter was calibrated by a heater circuit consisting of an epoxy-coated nichrome heater and a Leeds and Northrup Type K-3 potentiometer. The detection system was composed of a Sargeant thermistor (S-81620), a Sargeant thermistor bridge, a Leeds and Northrup microvolt amplifier, and a Sargeant variable range potentiometric recorder. This system translated heat changes in the calorimeter to measurable recorder deflections. A more complete description of the calorimeter is to be published in a future paper from this laboratory in which data from chelate complexes of lanthanide ions will be presented.[6]

Calculations.—The method of Bjerrum[7] was used to calculate the stability constants. Values of $\bar{n}$, the average ligand number, and [L], the free ligand concentration, are used to calculate values of the functions $\bar{n}/(1-\bar{n})[\mathrm{L}]$ and $(2-\bar{n})[\mathrm{L}]/(1-\bar{n})$. A graph with these functions as the axes yields a straight line when the ligand concentration is such that no third complex is formed. The intercept of this straight line is β_1, the first stability constant, and the limiting slope is β_2, the second over-all stability constant.[8]

Values of $\bar{n}$ and [L] were determined by direct pH titration and treatment of the pH data in a manner similar to that described previously.[4]

The treatment of the calorimetric data to determine heats of complex formation essentially followed that of Schlyter.[5] A nonlinear least-squares treatment was applied to the equation

$$\bar{l} = \frac{\sum_{i=1}^{N} \beta_i[\mathrm{L}]^i \Delta H_i}{\sum_{i=0}^{N} \beta_i[\mathrm{L}]^i} \tag{1}$$

where β_i is the over-all stability constant determined separately by the pH titration and ΔH_i is the over-all heat of formation of the ith complex. $\bar{l}$ is defined by

$$\bar{l} = l/C_\mathrm{M} \tag{2}$$

with l representing the total relative molal enthalpy of the solution in the calorimeter and C_M the total metal ion concentration of this solution. The method of treatment of the raw data to obtain $\bar{l}$ will be described elsewhere.[6] All computations were performed using an IBM 709 computer.

Data and Results

All studies were carried out in an ionic medium consisting primarily of 2.00 M sodium perchlorate and dilute with respect to the reacting species. The values obtained in this way are related to those at infinite dilution by the equations

$$\Delta F = \Delta F^\circ + RT\Sigma\gamma_i \ln \gamma_i \tag{3a}$$

$$\Delta H = \Delta H^\circ - RT^2\Sigma\gamma_i\partial\,(\ln \gamma_i)/\partial T \tag{3b}$$

$$\Delta S = \Delta S^\circ - R[T\Sigma\gamma_i\partial\,(\ln \gamma_i)/\partial T - \Sigma\gamma_i \ln \gamma_i] \tag{3c}$$

where the thermodynamic changes at infinite dilution are denoted by the superscript degree sign. By maintaining a high concentration of neutral salt the activity coefficients remain approximately constant for small changes in the solution composition. The activity-dependent terms in the above equations are thus constant and changes in the "concentration" constants reflect the same trends as do the true thermodynamic constants.

Sample sets of data for the pH and enthalpy titrations are given in Tables I and II.[9] The logarithms of the stability constants are listed in Table III. The enthalpy and entropy values are shown in Table IV. Since it is not possible to determine the change in the number of interacting particles we cannot assess the relative magnitudes of the unitary and cratic parts of the ΔF and ΔS values.[10]

TABLE I

PRASEODYMIUM–PROPIONATE SYSTEM pH DATA[a]

Vol. of titrant, ml.	pH	[L], m	$\bar{n}$
1.50	3.820	5.449×10^{-3}	0.276
1.75	3.810	6.148×10^{-3}	0.305
2.00	3.870	8.162×10^{-3}	0.382
2.25	3.890	9.373×10^{-3}	0.426
2.50	3.900	1.061×10^{-2}	0.467
2.75	3.930	1.270×10^{-2}	0.531
3.00	3.980	1.547×10^{-2}	0.608
3.25	4.020	1.829×10^{-2}	0.677
3.50	4.070	2.201×10^{-2}	0.758
4.00	4.070	2.491×10^{-2}	0.813

[a] $C_\mathrm{M}{}^0 = 28.29$ mM, $C_\mathrm{H}{}^0 = 0.6041$ mM, $C_\mathrm{L}{}^0 = 1002.8$ mM, $C_\mathrm{HL}{}^0 = 1002.8$ mM, initial volume = 50.00 ml., $T = 25.0°$, pH′ 4.550.

TABLE II

PRASEODYMIUM–PROPIONATE SYSTEM CALORIMETRIC DATA[a]

$D_\mathrm{x}{}^b$	$D_\mathrm{cal}{}^c$	Time, sec.	$10^{-2}Q$,[d] cal.	10^2[L],[e] m	$10^{-2}\bar{l}$,[f] cal./mole
−627.8	320.1	25.10	−55.80	0.5449	4.050
−44.47	315.1	25.03	−4.004	0.6147	4.334
−95.45	309.8	24.77	−8.652	0.8162	4.945
−38.61	298.6	23.65	−3.467	0.9373	5.190
−28.81	275.0	20.51	−2.436	1.061	5.363
−25.40	266.6	18.50	−1.998	1.270	5.504
7.18	250.1	16.23	5.283	1.547	5.466
50.33	244.3	14.01	3.272	1.829	5.235
112.6	240.6	13.56	7.191	2.201	4.727
105.2	252.1	15.14	7.158	2.491	4.221

[a] $\mu = 2.00$ M NaClO$_4$, $C_\mathrm{M}{}^0 = 0.00142$ M, heater resistance = 17.09 ohms, heater e.m.f. = 0.9006 v., $T = 25.0°$. [b] Recorder deflection caused by the complexation. [c] Recorder deflection caused by calorimeter heater. [d] The heat change upon complexation. [e] The molal concentration of the ligand. [f] Defined as $1/C_\mathrm{M}$.

An analysis of the determinate errors present in the experimental methods used leads to an expected maximum deviation of ±2% and ±5% in the first and second over-all stability constants and corresponding deviations of ±3% and ±8% in the over-all enthalpy changes reported. Calculation of the standard deviations of a number of the systems studied bears out

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(6) G. R. Choppin and H. G. Friedman, to be published.

(7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(8) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1166 (1955).

(9) The data supplementary to this article have been deposited as Document No. 8480 with the A.D.I. 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 $7.50 for photoprints or $2.75 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(10) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953.

TABLE III

STEPWISE STABILITY CONSTANTS OF THE PROPIONATE AND ISOBUTYRATE COMPLEXES

25° and μ = 2.00 *M*

	Propionates		Isobutyrates	
Ion	log K_1	log K_2	log K_1	log K_2
La	1.53	0.89	1.57	0.90
Ce	1.67	1.00	1.62	1.10
Pr	1.78	1.08	1.80	1.11
Nd	1.93	1.15	1.91	1.18
Sm	2.02	1.22	2.00	1.25
Eu	1.98	1.30	1.98	1.31
Gd	1.84	1.33	1.86	1.34
Tb	1.73	1.37	1.73	1.39
Dy	1.63	1.34	1.65	1.32
Ho	1.62	1.23	1.63	1.21
Er	1.60	1.12	1.61	1.11
Tm	1.61	1.05	1.61	1.06
Yb	1.63	1.07	1.62	1.05
Lu	1.66	1.12	1.65	1.12
Y	1.61	1.20	1.64	1.15

TABLE IV

THERMODYNAMIC PARAMETERS FOR LANTHANIDE COMPLEXES AT 25° AND 2.00 *M* IONIC STRENGTH

	Propionates				Isobutyrates			
	ΔH_1, kcal.	ΔH_2, kcal.	ΔS_1, e.u.	ΔS_2, e.u.	ΔH_1, kcal.	ΔH_2, kcal.	ΔS_1, e.u.	ΔS_2, e.u.
La	2.47	1.66	15.3	9.6	3.47	2.50	18.8	12.5
Cc	2.16	1.77	14.9	10.5	3.33	2.55	18.6	13.6
Pr	1.89	1.68	14.5	10.6	3.02	2.51	18.4	13.5
Nd	1.78	1.47	14.8	10.2	2.84	2.36	18.3	13.3
Sm	1.56	1.33	14.5	10.0	2.66	2.08	18.1	12.7
Eu	1.76	0.99	15.0	9.3	2.91	1.85	18.8	12.2
Gd	2.22	0.86	15.9	8.9	3.45	1.66	20.1	11.7
Tb	3.03	0.65	18.1	8.5	4.38	1.46	22.6	11.3
Dy	3.67	0.83	19.8	8.9	5.04	1.79	24.5	12.0
Ho	3.90	1.63	20.5	11.1	5.31	2.55	25.3	14.1
Er	3.96	2.32	20.6	12.9	5.49	3.43	25.8	16.6
Tm	3.98	2.83	20.7	14.2	5.39	4.10	25.5	18.6
Yb	3.77	2.73	20.1	14.0	5.35	3.97	25.4	18.1
Lu	3.82	2.50	20.4	13.5	5.35	3.65	25.5	17.4
Y	3.88	2.02	20.4	12.2	5.36	3.22	25.5	16.0

these estimates. These errors lead to an estimated error of approximately 1 e.u. in the ΔS values. We have included a third significant figure as the relative errors in log K_1, ΔH, and ΔS between lanthanide ions are less than these estimates.

Discussion

The data in Table II show that the stability of the propionate and isobutyrate complexes of the lanthanides is due to the positive entropy change since the endothermic enthalpy opposes complexation. This is just the reverse situation from the outer-sphere complexes formed by these ions with chloride,[11] thiocyanate,[12] and nitrate anions.[2] As described in the preceding paper, we suggest that these trends can be explained in terms of the effects on the hydration sphere about the metal cation. The energy release in the combination of the cation and anion in the complex is less than the total energy loss in the disruption of water molecules from the ordered hydration structure about the cation. This decrease in the hydration sphere is a result of the steric effect of the placement of the anion immediately adjacent to the cation as well as the decrease in the net charge attracting the hydration sphere from +3 to +2. It would seem reasonable that the formation of the first complex would have a greater effect on the hydration sphere than would succeeding complexes. The fact that ΔH_2 is less endothermic than ΔH_1 is in agreement with this expectation.

The combination of the two ions causes a decrease in entropy while the release of water molecules from the ordered hydration zone causes an increase in entropy. The inner hydration zone about the lanthanide ions is large[13] so that these cations are order producers (*i.e.*, their solutions have more structure than the bulk solvent, 2.00 *M* $NaClO_4$). Upon complexation, the net entropy change is positive because the disruption of the large hydration zone is the more important factor. The larger positive values of ΔS and ΔH for the complex formation with the bulkier isobutyrate ion are in agreement with this model as this ligand should disrupt the hydration sphere more than propionate would. Also, the lower values of ΔS_2 compared to ΔS_1 for both ligands are consistent with the explanation of the difference between ΔH_1 and ΔH_2.

While this manuscript was in preparation, Grenthe[14] and de la Praudiere and Staveley[15] have proposed the same model to explain the thermodynamics of complex formation in chelate systems. We have abridged our discussion to minimize repetition with these authors. The ability to explain ΔH and ΔS values for outer-sphere as well as inner-sphere monodentate and chelate complexes in terms of the effect on the hydration layer adds considerable weight to this model.

Now let us consider the variation of the enthalpy and entropy values as a function of atomic number of the cation as shown in Table IV. We believe that these trends can be interpreted in terms of a relatively more rapid increase in the size of the hydration zone between Nd(III) and Dy(III). Data on such a change can be obtained from the trend in the ionic conductances at infinite dilution of the lanthanide ions as a function of the crystallographic radii. The conductances[16] have been calculated from data of Spedding and co-workers. The lanthanide ions seemingly fall into three groups: La to Nd, in which the conductance decreases slowly due to a slowly increasing size of the hydration zone; Pm to Tb, in which the conductance decreases rapidly, indicating more rapid increase in the size of the hydration sphere with atomic number; Dy to Lu, in which the conductance again decreases slowly and is smaller than for La to Nd, indicating a larger hydration sphere. In terms of the enthalpy changes on complex formation, the smaller hydration zone about La to Nd should result in a less endothermic effect than for

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[16] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press Inc., New York, N. Y., 1959, p. 463.

the Dy to Lu region with an intermediate effect between these two groups. This is precisely the effect observed in Table IV. MX^{2+} could be hydrated in a different trend through the lanthanide series than would M^{3+}, which would explain the shift of the minimum in the curves of ΔH_1 and ΔH_2 to higher Z.

The entropy changes in Table IV are in agreement with this idea of three groups of hydrated lanthanide ions. The ΔS_1 terms are lower for La to Nd than for Dy to Lu, reflecting a release of fewer water molecules from the smaller hydration sphere of the lighter lanthanides. Spedding, *et al.*,[17] first suggested such a model of different size hydration spheres for the lanthanide ions.

We have used the approach proposed by Nightingale[18] to estimate hydration numbers for the lanthanide ions from conductance data. Little reliance can be placed on such a technique in terms of the absolute values calculated, but the values should have a validity relative to each other. The ions from La(III) to Nd(III) have a value of 12.8 ± 0.1, those from Dy(III) to Yb(III) of 13.9 ± 0.1, while the other values are 13.1 (Sm), 13.3 (Eu), and 13.4 (Gd). In Figure 1, the relation between these ion hydration numbers and the ΔS_1 values for propionate complexing is shown. The grouping of La, Ce, Pr, and Nd ions and of Dy, Ho, Er, Tm, and Yb indicates that within each group there is a correlation between ΔS_1 and metal ion hydration. It has been suggested frequently that the heavier lanthanide ions have a lower coordination number than the lighter ions.[19] This is in contrast to the proposal that the heavier ions have a larger hydration number, but it seems probable that there is a direct correlation between these two trends.[20] The effect of this lower coordination number in formation of the MX^{2+} ion could be to cause a larger fraction of the total hydration sphere to be freed. This would account for the larger ΔS_1 value of the second (heavier) group.

There has also been speculation on the possibility of ligand field effects[21,22] and of covalent bonding effects (the nephelauxetic effect).[23-25] In lanthanide complexing the favored evidence for ligand field effects was the "gadolinium break" in many properties (such as stability constants) which were related to the free energy. That this is insufficient evidence has been discussed previously,[4,26] and comparison of enthalpy and entropy data shows that the "gadolinium break" is a result of addition of opposite trends. Although our enthalpy data do not provide evidence for the presence of either ligand field or nephelauxetic effects, neither do they necessarily provide evidence for the absence of such effects. Such effects would be relatively small, and we would only observe changes in these effects due to substitution of ligand for water molecules about the cation. Our data indicate that such effects must have a secondary role in the thermodynamic changes although they may have primary roles in the heats of hydration and of complex formation. It is not unlikely that the explanation of the trends in Figure 1 is associated with one or both of these effects.

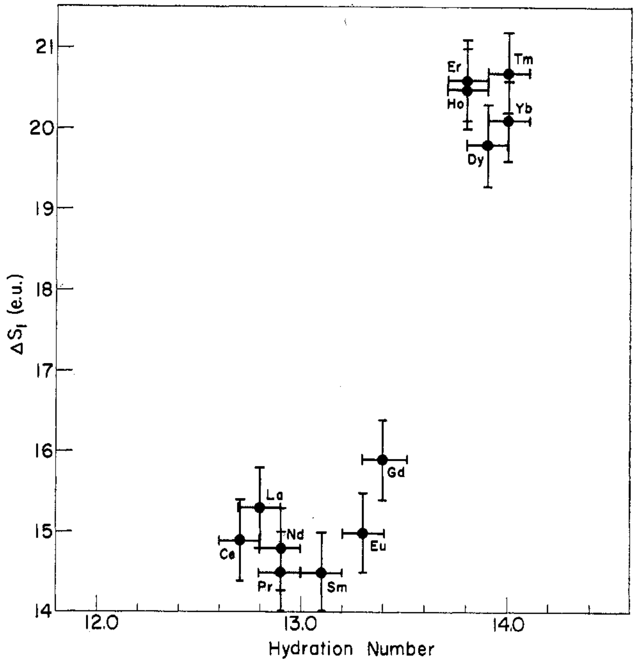

Figure 1.—Calculated hydration numbers of lanthanide ions as a function of the entropy of formation of lanthanide monopropionate.

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