served that upon irradiating the Co(III) acidopentaammine complexes at wave lengths where electron-transfer and d–d bands partially overlap, both photoreactions occur. Since with irradiation of the Co(III)–amino acid complexes in pure d–d bands (λ 546 mμ) no appreciable reaction occurs, it is thought that the d–d excitation does not contribute to quantum yields at every wave length. Therefore the photodecomposition following the irradiations at 313 and 365 mμ can be attributed to the partial electron-transfer character of the absorption. Thus the overlap between the electron-transfer and d–d bands is probably more accentuated in α-tris(valinato)cobalt(III),[5b] in accordance with the quantum yields obtained for this complex.

Finally, according to the proposed mechanism, which regards the photodecomposition as a direct consequence of the radial redistribution of the electronic charge caused by the excitation, the quantum yield is wholly independent of the H^+ concentration and is also almost independent of the temperature, the type of coordinated amino acid, and the steric arrangement of the complex.

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Complexes of Trivalent Lanthanide and Actinide Ions. I. Outer-Sphere Ion Pairs

BY GREGORY R. CHOPPIN AND WILLIAM F. STRAZIK

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Stability constants have been measured for the mononitrato complexes of Ce(III), Pm(III), Eu(III), Tb(III), Tm(III), and Am(III) by a solvent-extraction technique. These stability constants as well as the enthalpy and entropy data for MNO_3^{2+} indicate that these are outer-sphere ion pairs. It is proposed that these data can be interpreted in terms of a general model of lanthanide complexing in which the effect on the hydration sphere about the cation is the dominant effect.

Introduction

The sequence of stabilities of lanthanide complexes as a function of atomic number has been of interest for a number of years. Attempts to correlate this sequence with various properties of the lanthanide ions have been less than successful. A major reason for this difficulty has been the lack of sufficiently complete thermodynamic data. Although values of the enthalpy and entropy of complexation have been published in the past few years,[1–6] considerable disagreement exists in interpretation of the observed data. This is to be attributed partially to the relative complexity of the chelate systems studied. We have begun examination of simpler systems to minimize this difficulty. In previous publications[7,8] the thermodynamic values for the formation of MCl^{2+} and $MSCN^{2+}$ have been reported. In this paper the results of a study of the nitrate complexes are reported. In the next paper, we report the thermodynamic parameters for the formation of propionate and isobutyrate systems.[9]

Peppard and his co-workers[10] have measured the first stability constants for several trivalent lanthanide nitrates and obtained values only half as large as those reported by Russian chemists.[11] Recently Bansal, Patil, and Sharma[12] have reported first stability constants for Eu(III) and Am(III) nitrates which were smaller than Peppard's. Second step constants for these same ions were also given in this last paper. However, thus far no data have been reported on the enthalpy and entropy changes in formation of these complexes.

Experimental

Materials.—Ce^{144}, Pm^{147}, $Eu^{152-154}$, and Am^{241} were obtained from the Oak Ridge National Laboratory as carrier-free isotopes. Tb^{160} and Tm^{170} were obtained by the neutron irradiation of Tb_3O_4 and Tm_2O_3 at the University of Florida reactor. All isotopes were dissolved in 1 M $HClO_4$.

The extractant, dinonylnaphthalenesulfonic acid (referred to as HD), was obtained from the R. T. Vanderbilt Co., Inc., as a 38.2% solution in *n*-heptane. It was analyzed according to the procedure described previously[7] and found to be approximately 0.8 M.

All acids were reagent grade, diluted to volume, and standardized to a phenolphthalein end point with standard NaOH. The aqueous and organic solutions were pre-equilibrated with each other prior to use.

Procedure.—The procedure followed that of the earlier report.[7] Whenever possible, the aqueous phase was prepared to contain at least 7000 counts/min. per ml. for each radioisotope. The concentration of HD was varied from approximately 10^{-2} M to 6×10^{-5} M. The total ionic strength of the aqueous phase

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[2] T. Moeller and R. Ferrus, *J. Inorg. Nucl. Chem.*, **20**, 261 (1961).

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[5] I. Grenthe, *Acta Chem. Scand.*, **17**, 2487 (1963).

[6] I. Grenthe, *ibid.*, **18**, 283 (1964).

[7] G. R. Choppin and P. J. Unrein, *J. Inorg. Nucl. Chem.*, **25**, 387 (1963).

[8] G. R. Choppin and J. Ketels, *ibid.*, **27**, 1335 (1965).

[9] G. R. Choppin and A. J. Graffeo, *Inorg. Chem.*, **4**, 1254 (1965).

[10] D. F. Peppard, G. W. Mason, and I. Hucher, *J. Inorg. Nucl. Chem.*, **24**, 881 (1962).

[11] I. A. Lebedev, S. V. Pirozhkov, and G. N. Yakovlev, Akad. Nauk. SSSR, Ordena Lenina Institut Atomnoi Energii. United States Atomic Energy Commission Translation, AEC-Tr-4275.

[12] B. M. L. Bansal, S. K. Patil, and H. D. Sharma, *J. Inorg. Nucl. Chem.*, **26**, 993 (1964).

was adjusted to the desired values for mixture of the necessary concentrations of $HClO_4$ and HNO_3. All tubes were mixed for 12–24 hr.

Duplicate 1-ml. aliquots from both phases were taken for counting samples. Radionuclides whose decay is accompanied by sufficiently energetic γ emission were counted directly as liquid aliquots using a NaI(Tl) well scintillation counter. The other nuclides were counted as solid samples for either α or β emission in a windowless 2π gas flow proportional counter. Because of the corrosive effect of the acids on metal, the aqueous samples were prepared on glass planchets and evaporated to dryness under a heat lamp. The organic samples were prepared on metal planchets, evaporated to dryness, and ignited in the flame of a Fischer burner to ensure removal of the organic residue. Correction was made for the difference in backscattering between the two types of planchets. It was demonstrated that no correction was necessary in either case for sample self-absorption.

Results

The equations describing the equilibria in this system have been discussed by White, *et al.*,[13] and Choppin and Unrein.[7] The extraction of the metal ion by HD is described by the equation

$$M_A{}^{3+} + ((HD)_x)_O = M(H_{x-3}D_x)_O + 3H_A{}^+ \qquad (1)$$

where the subscripts A and O denote the aqueous and organic phases, respectively. In the presence of nitrate ion in the aqueous phase, competing reactions exist, such as

$$M^{3+} + NO_3^- = MNO_3^{2+} \qquad (2a)$$

$$MNO_3^{2+} + NO_3^- = M(NO_3)_2^+ \qquad (2b)$$

The distribution ratio is defined as

$$K_d = \frac{\Sigma(M)_O}{\Sigma(M)_A} \qquad (3)$$

If we assume that the variation of anionic composition at constant ionic strength does not change the activity coefficients, and the concentration of H^+ and HD are kept constant, the relation between the distribution ratio and the stability constant of the complex species is

$$\frac{K_d^0}{K_d} = 1 + K_1[NO_3^-] + K_1K_2[NO_3^-]^2 + \ldots K_n[NO_3^-]^n \qquad (4)$$

where K_1, K_2. . . . .K_n are the step stability constants for the formation of the species MNO_3^{2+}. . . . . .$M(NO_3)_n{}^{3-n}$ and K_d^0 is the distribution ratio in the absence of complexing ligand. If only the first complex is formed, a plot of $1/K_d$ *vs.* $[NO_3^-]$ gives a straight line whose slope is equal to K_1/K_d^0 and whose intercept is equal to $1/K_d^0$. If the second complex in the series is also formed, the above line will curve upward as the relative amount of the second complex becomes important. For the majority of our runs, the data could be fitted quite well with a straight line (Figure 1). The values of K_1 were obtained from a least-squares analysis of the $1/K_d$ *vs.* $[NO_3^-]$ data using an I.B.M. 709 computer. The error limits were obtained by compounding the standard deviations of the slope and intercept for each graph. Table I gives a typical set of data, while Figure 1 shows other sets of data.[14] The values of K_1 averaged from several runs in most cases are listed with the compounded error limits in Table II for solutions at 25°.

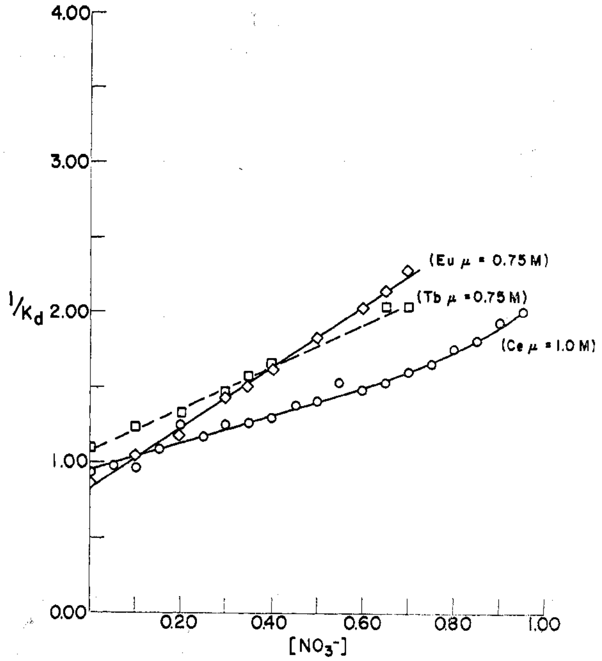

Figure 1.—Extraction of Ce (O, μ = 1.0 *M*), Eu (◇, μ = 0.75 *M*), and Tb (□, μ = 0.75 *M*) as a function of $[NO_3^-]$ by 0.009 *M* HD.

TABLE I

DETERMINATION OF STABILITY CONSTANTS FOR Eu(III) COMPLEXES WITH NITRATE IONS[a]

Initial concn. of HNO_3, *M*	Activity Aqueous phase	Activity Organic phase	$1/K_d$
1.00	4792	1524	3.145
0.95	4641	1641	2.828
0.90	4626	1655	2.795
0.85	4561	1712	2.664
0.80	4361	1921	2.270
0.75	4310	1925	2.239
0.70	4402	1871	2.353
0.65	4271	2054	2.079
0.60	4226	2075	2.037
0.55	4054	2177	1.862
0.50	4097	2162	1.895
0.45	3981	2203	1.807
0.40	4000	2299	1.740
0.35	3835	2655	1.444
0.30	3768	2596	1.451
0.25	3655	2584	1.414
0.20	3560	2615	1.361
0.15	3345	2900	1.153
0.10	3446	3038	1.134
0.05	3269	3038	1.076
0.00	. . .	. . .	0.95[b]

[a] $T = 25.0 \pm 0.02°$. Initial volume of both phases = 3.0 ml. Volume of aliquots taken = 1.0 ml. Tracer used = $Eu^{152-154}$. Initial concentration of HD 0.009 *M*. μ = 1.00 *M* (initial concentration of $HClO_4$ = 1.00 − concentration of HNO_3). [b] Determined independently in other experiments.

In some cases, a definite upward curvature was

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(13) J. M. White, P. Kelly, and N. C. Li, *J. Inorg. Nucl. Chem.*, **16**, 337 (1961).

(14) The data supplementary to this article have been deposited as Document No. 8479 with the A.D.I. Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $5.00 for photoprints or $2.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table II

Stability Constants for the Nitrate Complexes at 25.0°

Trivalent metal ion	Ionic strength, μ	K_1
Ce	1.00	1.63 ± 0.10
Pm	1.00	2.48 ± 0.29
Eu	1.00	2.04 ± 0.05
	0.75	2.43 ± 0.08
	0.50	2.73 ± 0.15
	0.30	2.89 ± 0.12
	0.20	2.68 ± 0.44
	0.00	17.0[a]
Tb	1.00	1.13 ± 0.05
	0.75	1.32 ± 0.04
	0.50	1.27 ± 0.03
	0.40	1.30 ± 0.04
	0.30	1.34 ± 0.13
	0.00	7.5[a]
Tm	1.00	0.56 ± 0.10
Am	1.00	1.80 ± 0.10

[a] Value extrapolated using eq. 7.

noticeable in the $1/K_d$ curve at the highest nitrate concentrations consistent with the formation of a second complex. However, in these cases the data were neither sufficiently accurate nor numerous to define the curve well enough to allow simultaneous calculation of K_1 and K_2 by a least-squares fit for the quadratic equation. Irving and Khopkar have discussed this same problem recently for the quite similar Eu^{+3}–Cl^- system.[15] The value of K_2 for the formation of $M(NO_3)_2^+$ could be estimated to be roughly 0.3–0.6. In these cases of curvature in the $1/K_d$ plots, only the data below 0.6–0.7 M HNO_3 were used to calculate K_1 as this always fitted a straight line within the error limits.

The major uncertainty in evaluation of these stability constants is the validity of the assumption that the activity coefficients do not change as the anionic composition is varied at constant ionic strength. From eq. 1 and 3 it can be shown when no complexing occurs that

$$K_d \propto \gamma_M/\gamma_H{}^3 \qquad (5)$$

where γ_M and γ_H are the activity coefficients of the trivalent metal ion and the hydrogen ion in the aqueous phase. Unfortunately, insufficient data exist to attempt to apply Harned's rule for these mixed electrolyte systems. However, estimates of the effect on the activity coefficients (and, hence, on K_d) can be obtained by assuming that the changes in the activity coefficients are linear with concentration, using values for $\mu = 1$ M nitrate and $\mu = 1$ M perchlorate as the limits. This approach was given an experimental test by measuring the extraction of Na^{22} in $\mu = 1.0$ M (H^+) for perchlorate–chloride[7] and for perchlorate–nitrate solutions. Sodium ion was chosen as no complexing is expected and activity coefficient data are readily available.[16] The expected ratio $K_d(1\ M\ HClO_4)/K_d(1\ M\ HCl)$ for Na^{22} was calculated to be 0.93, which compared well with the experimental value of 0.90.[7] A value of unity was calculated for the expected ratio $K_d(1\ M\ HClO_4)/K_d(1\ M\ HNO_3)$ and experimentally no change was observed in K_d within experimental error as the nitrate concentration was varied from 0 to 1.0 M.

The lack of proper activity coefficient data for the trivalent lanthanide ions does not allow direct calculation of the expected K_d ratio in 1 M $HClO_4$ and 1 M HNO_3. The calculated ratios for Li^+, Ca^{2+}, Mg^{2+}, and Na^+ were used to arrive at an estimated $K_d(1\ M\ HClO_4)/K_d(1\ M\ HNO_3)$ ratio of 1.0–1.2 for the lanthanide ions. The ions Li^+ and Ca^{2+} have similar ionic charge densities as M^{3+} and their ratios were both 1.05. Since the experimental ratio for M^{3+} is 2.5–3.0, even this crude treatment seems to justify the interpretation that the change in K_d can be attributed to complexing.

If it is assumed that $MNO_3{}^{2+}$ does form, eq. 4 can be rewritten to show the influence of activity coefficients

$$\frac{1}{K_d} = \frac{1}{K_x}\frac{\gamma_H{}^3}{\gamma_M} + \frac{K_1}{K_x}\frac{\gamma_H{}^3}{\gamma_M}\gamma_{NO_3}[NO_3{}^-] \qquad (6)$$

where K_x is the equilibrium constant for eq. 1. Estimations based on Harned's rule (for γ_{NO_3}) and on the preceding arguments lead to an estimate that the "correct" values for K_1 in $\mu = 1.0$ M HNO_3 are roughly 10% larger than the values given in Table II.

To determine the $\Delta H°$ of formation for the species $EuNO_3{}^{2+}$, a series of experiments was carried out with Eu(III) at various temperatures and at constant ionic strength of 1.00 M. The resulting data are tabulated in Table III. The Van't Hoff relationship was used to calculate the enthalpy change at 25°. The change in entropy, $\Delta S°$, was then determined by application of the Gibbs–Helmholtz equation. These thermodynamic constants, which relate to a standard state of $\mu = 1.00$ M $(HClO_4 + HNO_3)$, are summarized in Table IV.

Table III

Stability Constants for Europium(III) Nitrate Complex at $\mu = 1.0$ M

	0°	25°	40°	55°
K_1	2.10 ± 0.05	1.99 ± 0.12	1.8 ± 0.05	1.76 ± 0.06

Since all the species involved are charged, it was decided to follow the suggestion of Rossotti and Rossotti[17] in determining the thermodynamic stability constant at $\mu = 0$ of the species $MNO_3{}^{2+}$. Accordingly, the stability constants for $EuNO_3{}^{2+}$ and $TbNO_3{}^{2+}$ were determined at various ionic strengths. These constants (Table II) were then used in an extended form of the Debye–Hückel equation

$$\log {}^TK_1 = \log K_1 - \frac{\Delta Z^2 A\sqrt{\Gamma}}{1 + B\mathring{a}\sqrt{\Gamma}} - Cc - Dc^2 \qquad (7)$$

where ${}^TK_1$ and K_1 are the first stability constants for $\mu = 0$ and $\mu > 0$, respectively; A, B, C, and D are the constants used in the Debye–Hückel equation and depend on the dielectric constant of the solvent and the temperature; Γ is the ional concentration (*i.e.*, 2μ); c is the concentration ($= \mu$); and $\mathring{a}$ is the mean distance of closest approach (in Ångstroms). The quantity

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(15) H. M. N. H. Irving and P. K. Khopkar, *J. Inorg. Nucl. Chem.*, **26**, 1561 (1964).

(16) K. S. Pitzer and L. Brewer, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1961, Appendix 4.

(17) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961, p. 32.

TABLE IV

THERMODYNAMIC PARAMETERS FOR LANTHANIDE COMPLEXES AT 25°

Complex	Ionic strength, M	$\Delta F_1°$, kcal./mole	$\Delta H_1°$, kcal./mole	$\Delta S_1°$, e.u.	Ref.
$EuNO_3^{2+}$	1.00	-0.41 ± 0.02	-0.57 ± 0.06	-0.54 ± 0.20	...
$EuCl^{2+}$	1.00	-0.07 ± 0.03	-0.05 ± 0.03	-0.41 ± 0.20	7
$NdSCN^{2+}$	1.00	-1.10 ± 0.01	-5.47 ± 0.20	-14.7 ± 0.7	8
$Nd(OAc)^{2+}$	2.00	-2.64	1.71	14.6	6
$Eu(propionate)^{2+}$	2.00	-2.70	1.76	15.0	9
$TlCl^{2+}$	3.00	-9.8	-5.5 ± 0.6	14.5	a

[a] Sr. M. J. M. Woods, O. P., P. K. Gallagher, Z Z. Hugus, and E. L. King, *Inorg. Chem.*, **3**, 1313 (1964).

ΔZ^2 is the difference in the square of the ionic charge of MNO_3^{2+} and the sum of the squares of the charges of M^{3+} and NO_3^-; it has a value of -6 in this case. Equation 7 may be rewritten[18] for reaction 2a as

$$\log {}^{T}K_1 = \log K_1 + \frac{2.16\sqrt{\Gamma}}{1 + 0.232å\sqrt{\Gamma}} - 2.206 \times 10^{-3}å^3M \quad (8)$$

(a final term, $2.627 \times 10^{-6}å^6M^2$, is small enough to permit its omission).

The right-hand side of eq. 8 was evaluated as a function of ional concentration. The slope of the straight line resulting from the plot of the resulting values *vs.* Γ was minimized by varying $å$ and then extrapolated to $\Gamma = 0$ to obtain $\log {}^{T}K_1$. The mean distances of closest approach were calculated as 5.0 ± 0.2 Å. for both $EuNO_3^{2+}$ and $TbNO_3^{2+}$. The values of ${}^{T}K_1$ were calculated to be 17 for formation of $EuNO_3^{2+}$ and 7.5 for that of $TbNO_3^{2+}$.

Discussion

Our values for the stability constants for the formation of MNO_3^{2+} agree more closely with those of the Argonne group[10] than with other reports.[11,12] They also show that the stability of MNO_3^{2+} is intermediate between that of MCl^{2+} and that of $MSCN^{2+}$. In Table IV, the thermodynamic parameters of the nitrate, chloride, and thiocyanate complexes also reflect this intermediate character of the nitrate complexes. As in the case of the chloride and thiocyanate complexes, the negative values for both $\Delta S_1°$ and $\Delta H_1°$ are interpreted as indicating that the lanthanide cations retain most of their primary hydration sphere and form outer-sphere ion pairs with the nitrate anions. Data for the europium monopropionate, europium monisobutyrate, and thallium(III) monochloride complexes are included in Table IV for comparison. It is assumed that the propionate and the isobutyrate ligands form inner-sphere complexes with the trivalent metal ions. The positive entropy change for $TlCl^{2+}$ formation is further evidence for this difference in lanthanide complexes since $TlCl^{2+}$ is believed to be an inner-sphere complex (Tl^{3+} has the same crystal radius as Eu^{3+}).

Our value of 5.0 Å. for the $å$ parameter in the Debye–Hückel equation is in reasonable agreement with that of 4.7 Å. reported by Spedding and Jaffe[19] from conductance data for $Nd(NO_3)_3$. Brady has calculated from X-ray diffraction data a value of 4.6 Å. as the average distance between Er(III) and Cl^- in concentrated $ErCl_3$ solutions,[20] which agrees with the sum of the radii of the lanthanide ion (0.9 Å.) plus the chloride ion (1.8 Å.) plus the diameter of a water molecule (2.8 Å.). However, the significance of correspondence between the value of the $å$ parameter and the physical distance expected for outer-sphere ion pairs is questionable due to the obscurity of the meaning of $å$ in eq. 7.

At the present time, the theory of ion-pair association seems to be expressed as well by the Bjerrum theory[17] as by any other. Using a value of 79 for the dielectric constant and of 5.0 Å. for $å$, the Bjerrum theory would predict a value of approximately 40 for the stability constant of $LnNO_3^{2+}$. Considering the inherent problems in applying the Bjerrum approach, the agreement between 40 and 17 (for $EuNO_3^{2+}$) is not unsatisfactory.

Comparison of the data in Table IV suggests a model for lanthanide complexes. For the outer-sphere complexes the enthalpy term is favorable whereas the entropy change is unfavorable. For the inner-sphere complexes, formed by the propionate and isobutyrate ligands, this situation is reversed, with unfavorable enthalpy and favorable entropy terms. To understand this, we must turn to the model of ionic solutions proposed by Frank and Evans[21] and Gurney[22] which considers three concentric zones of water about each ion. The inner first zone consists of one or more layers of water molecules oriented by ionic attraction; the outermost zone has the hydrogen-bonded structure of normal water (or, in this case, of 1 N $HClO_4$ solution). The middle zone is a "thawed" zone of less order than the bulk solution phase. In a previous study by infrared spectroscopy[23] it was shown that La(III) has a large inner zone and small middle zone. The lanthanide ions, consequently, are net structure promoters. The enthalpy and entropy terms in complex formation will reflect the disruption of this solvent structure as well as the combination of the ions. For the enthalpy the disruption of hydration structure is an endothermic contribution while the ionic combination is an exothermic one. In the outer-sphere complexes such as $EuNO_3^{2+}$, the hydration sphere is only partially disrupted and the net enthalpy is exothermic, in agreement with the data

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[18] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958, pp. 62, 508, 520, 522.

[19] J. H. Spedding and S. Jaffe, *J. Am. Chem. Soc.*, **76**, 884 (1954).

[20] G. W. Brady, *J. Chem. Phys.*, **33**, 1079 (1960).

[21] H. S. Frank and M. Evans, *ibid.*, **13**, 507 (1945).

[22] R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953.

[23] G. R. Choppin and K. Buijs, *J. Chem. Phys.*, **39**, 2042 (1963).

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.

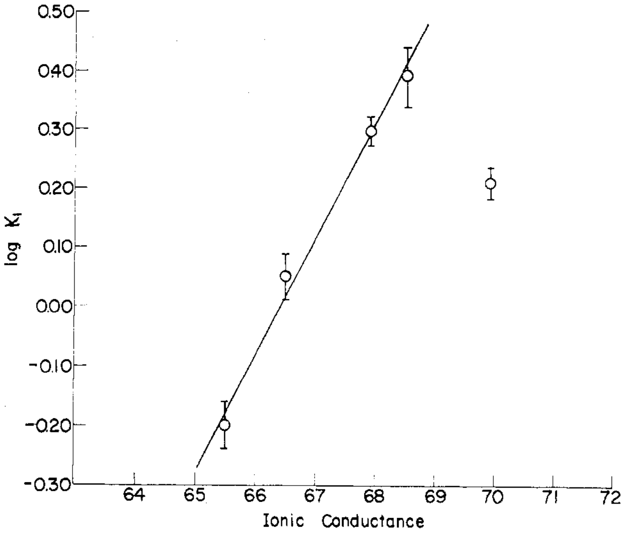

Figure 2.—The relation between log K_1 for MNO_3^{2+} and the ionic conductance at infinite dilution of M^{3+}.

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

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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.

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[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).