Observations on the Rare Earths. LXXX.[1] The Thermodynamic Stabilities of Ethylenediamine Chelates of the Tripositive Lanthanide Ions in Anhydrous Acetonitrile

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Four distinct enthalpy changes characterize the calorimetric titration of a lanthanide(III) perchlorate solution in acetonitrile with ethylenediamine under rigorously anhydrous conditions. The calculated enthalpies of formation of the species $Ln(en)_n{}^{3+}$ ($n = 1-4$) demonstrate the remarkable thermodynamic stabilities of these ions in acetonitrile. With nitrate as the anion, only the first two enthalpy changes can be evaluated, and the continuing evolution of heat even beyond a 6:1 ligand to cation mole ratio indicates competition between nitrate ion and ethylenediamine for additional coordination sites. Variations in thermodynamic stability in the lanthanide series are discussed. The ethylenediamine complexes formed under these conditions are enthalpy stabilized.

The isolation of both tris- and tetrakis-ethylenediamine chelates of the tripositive lanthanide ions as solid salts of considerable thermal but limited hydrolytic stability and as products of reactions in anhydrous acetonitrile[1,2] raises a question as to the real existence of the ions $Ln(en)_{3,4}{}^{3+}$ in acetonitrile solution as opposed to their formation solely to satisfy the demands of crystal stability. The purpose of the present investigation was to provide quantitative evidence that these complex ions do indeed possess considerable thermodynamic stability in this solvent and thus exemplify lanthanide complex ions based solely upon nitrogen coordination.

Although thermodynamic stability is commonly measured in terms of formation constant data, the usual methods of evaluating formation constants are inapplicable to nonaqueous systems. We have chosen, therefore, to evaluate calorimetrically the stepwise enthalpies of formation of the species $Ln(en)_n{}^{3+}$ ($n = 1-4$) for the reactions of ethylenediamine with the ions $Ln(CH_3CN)_x{}^{3+}$ in anhydrous acetonitrile. No calorimetric determinations of enthalpies of complexation of the lanthanide ions in nonaqueous media have been reported previously, and only a limited number have been described for aqueous systems.[3-6] Most of the enthalpy data reported for aqueous systems have been calculated from the temperature dependence of formation constant data.[7] The values so obtained are small and sometimes positive,[8, 9] probably as a consequence

of the need to displace strongly bound water molecules in the complexation reaction, and are of little utility in determining the existence or stability of complex species in solution.

In a nonaqueous solvent of reduced coordinating strength toward a lanthanide ion, the enthalpy of complexation could be sufficiently negative (exothermic process) to be of value in establishing the existence of species in solution. Furthermore, since it has been shown[10] that in certain favorable cases enthalpy data can be used to evaluate formation constants, reasonable free energy and entropy values may also be obtainable. This approach has proved to be of value in determining the thermodynamic stabilities of the ethylenediamine chelates of the tripositive lanthanides and in showing that these species are enthalpy stabilized.

Experimental Section

Materials.—All materials were prepared and handled under anhydrous conditions as described previously.[1]

Calorimeter.—The calorimeter used was constructed after the basic design of Arnett and coworkers.[11] Temperature changes in the calorimeter were detected by means of a 100-kilohm Fenwal thermistor, as one arm of a Wheatstone bridge, in conjunction with a Sargent Model SR recorder utilizing a 1.25-mV range plug. The sensitivity of the instrument was such that 3.5 cal of heat added to 225 ml of acetonitrile produced a pen deflection of 100 mm. The heater used for calibration of the instrument was a 100-ohm, wire-wound resistor coated with sealing wax. The calorimeter calibration was checked by measuring the enthalpy of neutralization of aqueous hydrochloric acid solution with aqueous sodium hydroxide solution (literature, 13.36 kcal mol^{-1} at infinite dilution; found, 13.5 kcal mol^{-1} corrected for heat of solution to 0.0025 M). The dewar flask of the calorimeter was contained in a nitrogen-flushed dry bag to protect the system from moisture.

Enthalpy Measurements.—The calorimetric determination of an enthalpy of complexation was effected by incremental addition of anhydrous ethylenediamine to a solution of an anhydrous lanthanide perchlorate in anhydrous acetonitrile. All additions

(1) Part LXXIX: J. H. Forsberg and T. Moeller, *Inorg. Chem.*, **8**, 883 (1969).

(2) J. H. Forsberg, Doctoral Dissertation, University of Illinois, 1968.

(3) J. L. Mackey, J. E. Powell, and F. H. Spedding, *J. Am. Chem. Soc.*, **84**, 2047 (1962).

(4) I. Grenthe, *Acta Chem. Scand.*, **17**, 2487 (1963).

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

(6) L. A. Staveley, D. R. Markham, and M. R. Jones, *ibid.*, **30**, 231 (1968).

(7) F. J. C. Rossotti in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, Chapter 1.

(8) T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrús, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965).

(9) T. Moeller, E. R. Birnbaum, J. H. Forsberg, and R. B. Gayhart in "Progress in the Science and Technology of the Rare Earths," Vol. 3, L. Eyring, Ed., Pergamon Press, New York, N. Y., 1968, pp 61–128.

(10) A. Brenner, *J. Electrochem. Soc.*, **112**, 611 (1965).

(11) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

of ethylenediamine were made in a drybag. The perchlorates were used because of the poor coordinating ability of this anion.[1] A few nitrates were investigated for comparison.

A 6-mmol quantity of the lanthanide perchlorate was dissolved in 225 ml of acetonitrile (0.026 M solution) contained in the calorimeter. To minimize heat loss from the calorimeter, the solution was then cooled to slightly below room temperature by immersing in it an 8-mm glass tube containing Dry Ice. The solution was allowed to equilibrate until a base line of constant slope was obtained. Because the contents of the calorimeter were below room temperature, the slope was positive, indicating a constant gain of heat from the surroundings. The temperature of the contents of the calorimeter was maintained between 22 and 23° throughout each run.

Ethylenediamine was added in 0.30-mmol increments (0.02 ml), using a 50-μl Hamilton syringe fitted with a Chaney adapter. The heat released upon complexation of the 0.30-mmol increment gave a pen deflection of 100–150 mm. At ligand:metal ion mole ratios larger than 3.5, the increments of ethylenediamine were increased to 0.60 mmol to compensate for decrease in heat quantities released. No measurable quantities of heat were observed at ligand:metal ion mole ratios larger than 4.5. Approximately 80 increments of ethylenediamine were added in each run, thus giving about 80 independent measurements of the heat evolved upon complexation. The heat of solution of ethylenediamine was determined independently by measuring the heat evolved upon addition of a 0.05-ml volume of ethylenediamine to 225 ml of acetonitrile containing no Ln^{3+} ion. The heat of solution so obtained, 0.8 ± 0.5 kcal mole^{-1}, was used to correct the measured heats of complexation.

The molar enthalpy of complexation for each increment of ethylenediamine was calculated by dividing this corrected value by the number of moles of ethylenediamine added per increment. This procedure assumes that the increment in question reacted completely to form a single complex species. The complex formed is characteristic of the ligand:metal ion mole ratio at which the increment was added; i.e., an increment added at a mole ratio of 1.5 reacted completely to form the 2:1 complex. That this assumption is valid is borne out by the stability constants calculated from the enthalpy data. These enthalpy values were used to construct for each Ln^{3+} ion a graph of the molar enthalpy of complexation vs. ligand to metal ion mole ratio.

Calibrations of the calorimeter before and after the addition of ethylenediamine were the same, indicating negligible changes in the heat capacity of the system upon complexation. No further corrections were applied.

Results and Discussion

A plot of molar enthalpy of complexation, in terms of the general equation

$$Ln(en)_{n-1}(CH_3CN)_x{}^{3+} + en \rightleftharpoons Ln(en)_n(CH_3CN)_y{}^{3+} + (x - y)CH_3CN$$
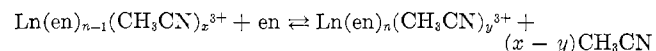
is given in Figure 1 for the gadolinium perchlorate–ethylenediamine system. Results for the other lanthanide perchlorates were similar, and each curve was characterized by four distinct plateaus, indicating the formation of four $Ln(en)_n{}^{3+}$ species in solution. The stoichiometries of these species are given by the whole-number ligand:metal ion mole ratios at the breaks in the curves. Inasmuch as these ratios were clearly and exactly established, simple stepwise formation of the ions $Ln(en)_n{}^{3+}$ ($n = 1$–4) was established. This characteristic is common to thermodynamically stable species. The four distinct breaks also indicate that the ClO_4^- ion does not compete effectively with ethylenediamine as a ligand for the Ln^{3+} ion. However,
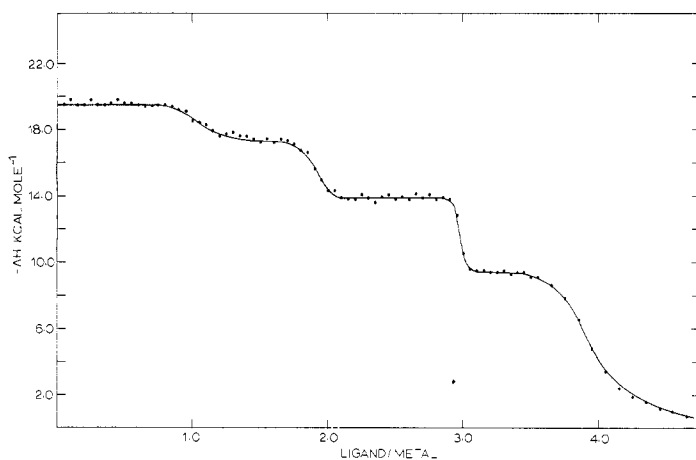

Figure 1.—Enthalpy curve for the formation of $Gd(en)_n(ClO_4)_3$.

ion pairing or weak coordination by the ClO_4^- ion cannot be completely precluded by these data.

The stepwise enthalpy of complexation, ΔH_n, was obtained from the enthalpy at a plateau on the titration curve. Where the plateau was not completely horizontal, ΔH_n was obtained by extrapolating along the observed slope of the plateau to the $n-1$ mole ratio. Deviation from the horizontal is a consequence of the formation of a mixture of higher order species. In most instances, these deviations were very small, indicating that the successive formation constants are both large and well separated, and extrapolations gave fairly accurate values of ΔH_n. The values obtained for the perchlorates are summarized in Table I.

A typical enthalpy of complexation curve characteristic of the lanthanide nitrates is given in Figure 2. Only two plateaus, corresponding to ΔH_1 and ΔH_2, were observable for each nitrate. The measured values of these two enthalpy changes are summarized in Table II.

Table I

ENTHALPIES OF COMPLEXATION OF LANTHANIDE PERCHLORATES AT 23°

Ln^{3+}	Enthalpy change,[a] kcal mol^{-1}			
	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$	$-\Delta H_4$
La^{3+}	17.3	15.5	13.8	11.0
Pr^{3+}	18.7	16.8	13.6	10.8
Nd^{3+}	18.8	16.9	13.8	10.9
Sm^{3+}	19.3	18.0	13.5	9.9
Eu^{3+}	19.8	18.3	13.9	9.7
Gd^{3+}	19.5	18.0	13.9	9.5
Tb^{3+}	19.9	18.6	13.1	9.0
Dy^{3+}	19.9	18.4	12.6	9.2
Ho^{3+}	19.9	18.2	12.7	10.0
Er^{3+}	20.1	18.7	13.1	11.5
Yb^{3+}	20.1	18.8	14.4	12.8
Lu^{3+}	20.0	18.6	14.3	12.8
Y^{3+}	20.0	18.7	12.9	10.5

[a] ±0.3 kcal mol^{-1}, reflecting errors in both calorimetry and extrapolation. All enthalpy data were corrected for heat of solution of ethylenediamine.
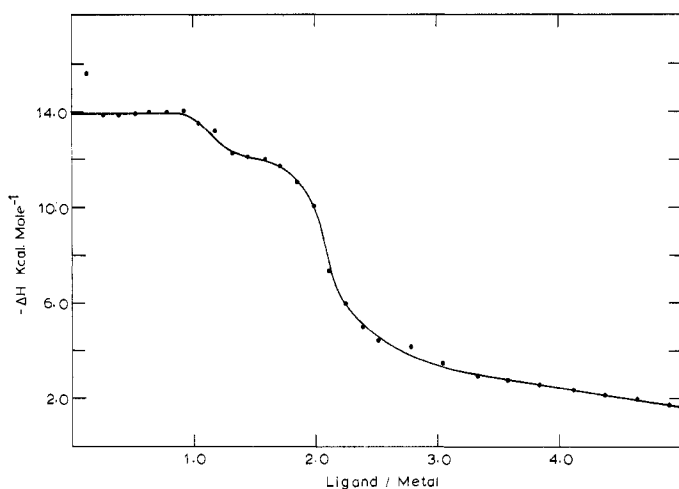
Figure 2.—Enthalpy curve for the formation of $La(en)_n(NO_3)_3$.

TABLE II

ENTHALPIES OF COMPLEXATION OF CERTAIN
LANTHANIDE NITRATES AT 23°

| Ln^{3+} | —Enthalpy change,[a] kcal mol^{-1}— | |
	$-\Delta H_1$	$-\Delta H_2$
La^{3+}	13.9	12.6
Pr^{3+}	14.3	12.8
Nd^{3+}	14.7	13.1

[a] The deviation is ± 0.3 kcal mol^{-1}. Data were corrected for heat of solution of ethylenediamine.

TABLE III

FORMATION CONSTANT AND ENTROPY DATA FOR CERTAIN
LANTHANIDE PERCHLORATES AT 23°

| | —Formation constant[a]— | | | | Entropy change,[b] cal mol^{-1} deg^{-1} | | | |
	Log K_1	Log K_2	Log K_3	Log K_4	ΔS_1	ΔS_2	ΔS_3	ΔS_4
La^{3+}	9.5	7.5	6.2	3.3	−15.1	−18.2	−18.4	−22.1
Tb^{3+}	10.4	8.4	6.2	3.2	−19.8	−24.5	−16.0	−15.8
Yb^{3+}	11.5	9.3	6.5	3.8	−15.4	−21.1	−19.0	−25.9

[a] The deviation is ± 0.5. [b] The deviation is ± 3.0 cal mol^{-1} deg^{-1}.

As suggested by the procedure of Brenner,[10] log K_n values (K_n is the formation constant of the *n*th species) were obtained as functions of the total metal ion concentration, ΔH_n, and the slope of the enthalpy curve near the ligand : metal ion mole ratio equal to *n*. Inasmuch as measurement of the slope of the curve is subject to considerable error, the values of log K_n so obtained are not sufficiently accurate to reflect the relatively small variations across the series as a function of changing crystal radius of the Ln^{3+} ion. However, these log K_n values are of the correct orders of magnitude and are useful for establishing thermodynamic stability. Values for log K_n for the lanthanum, terbium, and ytterbium chelates are given in Table III.

From the measured ΔH_n values and the ΔG_n values calculated from the formation constants, values of ΔS_n can be calculated. Those obtained for the lanthanum,

terbium, and ytterbium complexes are summarized in Table III. The calculated values of log K_n and ΔS_n for the other lanthanide chelates lie between those for the lanthanum and ytterbium species.

The formation in solution of a thermodynamically stable complex species is favored by a negative enthalpy change and a positive entropy change. The enthalpy change associated with the complexation reaction is a measure of the difference in bond energy toward the metal ion between the ligand and the coordinated molecules of the solvent. Thus complexation is favored in a poorly coordinating solvent by the resulting larger negative enthalpy change. The relatively large negative stepwise enthalpy changes observed for the lanthanide ion–ethylenediamine reactions in acetonitrile (Tables I and II) indicate that this solvent is weakly coordinating and that the resulting ethylenediamine complexes are stable in this medium.

The entropy change upon complexation is a composite of a negative contribution due to the conversion of translational entropy of the free ligand,[7] and positive contributions due to release of coordinated solvent molecules[7] and a smaller degree of ion pairing. The negative stepwise entropy changes observed for the ethylenediamine–lanthanide perchlorate reactions in acetonitrile (Table III) emphasize the predominance of the coordination process.

It is apparent, therefore, that the sizable thermodynamic stabilities indicated by the log K_n values (Table III) result from the substantial enthalpy changes upon complexation. In the ethylenediamine–lanthanide ion system, therefore, acetonitrile is a useful solvent for the formation of enthalpy-stabilized complex ions.

Available data show that, generally, the formation of thermodynamically stable lanthanide complexes in aqueous solution is characterized by small negative or positive enthalpy changes and large positive entropy changes.[8,9] Entropy stabilization of complexes formed under these conditions is a consequence of the lack of lability of coordinated water molecules (large enthalpy of solvation). The difference between the ΔH values measured in acetonitrile and aqueous systems emphasizes the extreme importance of the solvent in determining the thermodynamic stability measured for a lanthanide complex.

An interpretation of the variations in ΔH_n values apparent from an examination of Table I must include consideration of both enthalpies of solvation and enthalpies of ligand–metal ion interactions. In general, increasingly exothermic complexation reactions may be expected to parallel decreasing crystal radius of the Ln^{3+} ion as a consequence of increasing electrostatic ligand–metal ion interactions. However, if the decrease in crystal radius reduces the solvation number of the cation, the resulting increase in energy of solvation can give a less exothermic reaction.[8,12]

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

For a given lanthanide ion, the decrease in ΔH_n as successive ethylenediamine molecules are added is best explained in terms of weaker ligand–metal ion interactions. Minimum values for ΔH_3 and ΔH_4 can be explained reasonably in terms of change in solvation number in the precursor bis and tris species, respectively. It is not unreasonable to assume that as the cationic radius decreases the number of molecules of acetonitrile directly coordinated decreases. This reduction need not, and probably does not, occur sharply at a particular cation. Rather it may occur as a displacement of an equilibrium between coordinated and free solvent molecules to an extent that reduces the *average* number of coordinated molecules. As the average solvation number is lowered, interaction between the cation and coordinated solvent molecules is increased, and the enthalpy change becomes decreasingly negative since addition of the next molecule of ethylenediamine can occur only by displacement of these more strongly bonded solvent molecules. As the cationic radius continues to decrease, steric repulsions among the remaining comparatively labile solvent molecules may become important. These repulsions will make at least one of the strongly coordinated solvent molecules more labile. The complexation reaction for the heavier lanthanides thus becomes increasingly exothermic because of the increased lability of one of the solvent molecules that the ethylenediamine molecule displaces. Change in solvation number has been suggested as a reason for similar variations in ΔH values for complexation reactions of the lanthanide ions in aqueous solution.[5,12]

Observed variations in ΔH_3 and ΔH_4 values cannot be accounted for in terms of ligand–metal ion bond enthalpies. These enthalpies can be expected to vary in one of three ways, namely, (1) an increase with decreasing radius of the Ln^{3+} ion, paralleling an increase in the polarizing power of the cation, (2) an increase in this way, followed by a decrease resulting from steric factors, or (3) a constant value irrespective of cationic size, resulting from a leveling effect on the polarizing powers of the cations by the coordinated ethylenediamine molecules. None of these variations provides an adequate explanation for the observed minima.

The stepwise enthalpy changes for the formation of the yttrium chelates (Table I) place the Y^{3+} ion in the Dy^{3+}–Ho^{3+} region, a position which is consistent with that predictable on the basis of size or size–charge effects and which supports the argument that the f orbitals are not primarily involved in the bonding.

Although the enthalpy curves for the nitrate systems indicate the definite formation of only 1:1 and 2:1 chelates, the continuous evolution of heat even beyond a 6:1 mole ratio indicates competition between the nitrate ion and ethylenediamine molecules for additional coordination sites. Nitrate ion does indeed bond to the lanthanide ions in acetonitrile, as indicated by the strong infrared bands at 1490 and 1300 cm^{-1} that show C_{2v} symmetry in the nitrate group. The addition of two molecules of ethylenediamine to the lanthanide ion without displacement of nitrate ion is consistent with the isolation of a bis chelate containing three coordinated nitrate groups.[1] Since the coordination of additional molecules of ethylenediamine can occur only by displacement of nitrate ions, competition between the two ligands in solution must occur. The absence of further breaks in the enthalpy curve indicates that the formation constants for nitrate coordination must be comparable to those for additional ethylenediamine coordination. At large ligand to metal ion mole ratios, complete displacement of nitrate groups is probable. The difference between this system and the perchlorate system indicates that the nitrate ion interacts more strongly than the perchlorate ion with a Ln^{3+} ion in acetonitrile.

The effect of the coordinated nitrate groups in reducing the effective positive charge on the metal ion is reflected in the smaller enthalpy changes (by *ca.* 3 kcal mol^{-1}) upon addition of the first two molecules of ethylenediamine. The observed decrease cannot be due to larger solvation enthalpy since the solvation enthalpy of a nitrato complex species should be less than that of the free lanthanide ion.