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The Interaction of Lanthanide and Nitrate Ions in Solution. I. Inner- and Outer-Sphere Coordination in Aqueous Solutions

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The inner-sphere coordination of nitrate ions to lanthanide ions, in particular erbium, has been explored from studies of the density and molar absorptivity of erbium nitrate solutions and the chemical shift of ^{17}O-enriched water in the presence of erbium and lithium nitrates. The dehydration of the erbium ion and replacement of water by nitrate in the inner coordination sphere are deduced from the data. The average ligand number in the inner sphere is lower than the total ligand number, so that some outer-sphere coordination also occurs, for all the lanthanides in nitrate solutions.

Lanthanides, *i.e.*, the elements of atomic number Z from 57 to 72, are known to form both inner-sphere and outer-sphere complexes with suitable ligands. Carboxylate ligands supposedly form complexes of the first kind,[3] while chloride ions in aqueous solutions are reluctant to form any but outer-sphere complexes.[4] On the other hand, sulfate ions form both inner- and outer-sphere complexes in dilute solutions,[5] while thiocyanate ions seem to form outer-sphere complexes in dilute solutions, and inner-sphere complexes under sufficiently dehydrating conditions.[6] Recent spectral evidence on lanthanide covalent binding to nitrate ions[7] shows that here too inner-sphere complexes are formed, although in that study tributyl phosphate (TBP) was used as a solvent. In dilute aqueous solutions (up to about 1 M nitrate) only outer-sphere complexing with nitrate has been found,[8] although there is some spectral evidence that also in aqueous solutions at appropriate concentrations inner-sphere complexes may be formed.[9-11]

It is the purpose of this series of papers to show that, depending on the solvent and on the concentrations, both inner- and outer-sphere nitrate complexes of the lanthanides are indeed formed in solutions. The present paper deals with aqueous solutions of erbium and some other lanthanides containing nitrate. Spectrophotometric, nuclear magnetic resonance, and density measurements are applied to these solutions in order to investigate the interaction of the lanthanide and nitrate ions. The formation of inner-sphere nitrate complexes in sufficiently concentrated aqueous solutions, *i.e.*, the replacement of coordinated water of hydration by nitrate ions, has been demonstrated.

Experimental Section

Materials.—The aqueous solutions of the lanthanide nitrates and perchlorates were prepared from their oxides (99.9%, American Potash Chemical Corp.) and corresponding acids. The solutions were 0.0001–0.001 M in acids in order to avoid hydrolysis of the lanthanide ions. The concentrations of the lanthanides were checked by gravimetry or by complexometric titration in the case of very dilute solutions. The promethium nitrate solution was prepared from a $^{147}PmCl_3$ solution in 0.5 M HCl (Oak Ridge National Laboratory).

The erbium nitrate solution used in nmr measurements was prepared by dissolving $Er(ClO_4)_3 \cdot H_2O$ in water containing 1.7% ^{17}O to a concentration of 0.7 m. Dried lithium nitrate was added to this solution as required.

Method.—Spectra were measured on a Cary Model 14 recording spectrophotometer. In the case of erbium, the molar absorptivity ϵ at 5215 A was determined as a function of the nitrate ion concentration from measurements made in a thermostated flow system at 25°.

The nmr experiments were performed on a Varian DP 60 apparatus. The solutions were placed in a spherical container to eliminate the need for paramagnetic corrections. The peak of ^{17}O was observed.

The density was measured using 25-ml pycnometers with a ground-glass head, making the required buoyancy correction.

Results

The spectrum of erbium nitrate at low concentration of salt resembles that of erbium perchlorate solutions, but increasing concentrations of nitrate ions cause a hypsochromic shift of all the peaks of 20–30 A. The dependence of the molar absorptivity of erbium nitrate solutions at 5215 A, ϵ_{5215}, on the erbium concentration, c_{Er}, can be described by the empirical equation

$$\epsilon_{5215} = a + bc_{Er} \qquad (1)$$

where $a = 2.20 \pm 0.05$ and $b = 1.4 \pm 0.1$. The nonzero value of b shows that Beer's law is not obeyed. When lithium nitrate is added to solutions at constant erbium concentrations, ϵ_{5215} varies nearly linearly with the nitrate concentration, the slope of the lines being smaller, the higher the erbium concentration (Figure 1). When lithium perchlorate is added, the molar absorptivity does not change from the value it has in the absence of added salt.

The addition of lithium nitrate to promethium and holmium nitrate solutions also causes a nearly linear dependence of the molar absorptivity of the prominent

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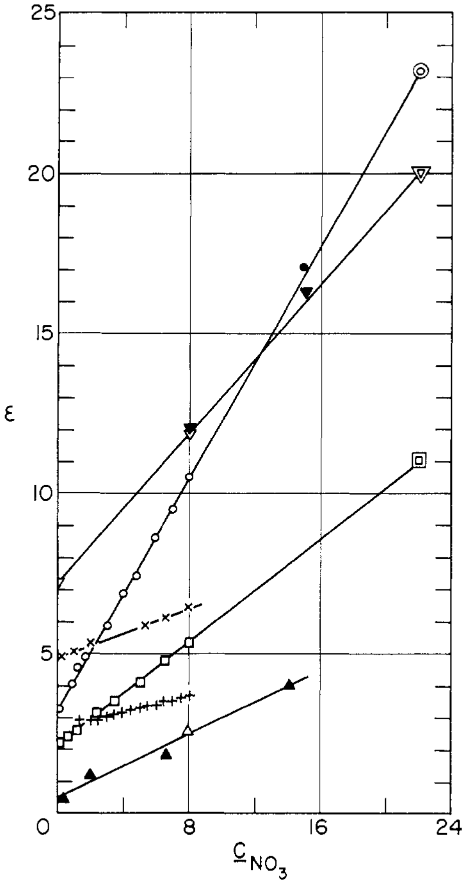

Figure 1.—Molar absorptivity ε of lanthanides in nitrate solutions: ▽, Nd peak at 579 mμ [data for nitric acid from W. J. Maeck, M. E. Kussy, and J. E. Resin, *Anal. Chem.*, **37**, 103 (1965)]; ○, Ho peak at 498 mμ; □, Er peak at 521.5 mμ; △, Eu peak at 464 mμ (ε × 5) [P. K. Gallagher, *J. Chem. Phys.*, **41**, 3061 (1964)]; ×, Pm peak at 568 mμ (all ≤0.1 *M* lanthanides); +, Er peak at 521.5 mμ, 0.47 *m* Er. Open symbols, lithium nitrate added; filled symbols, nitric acid added; double symbol, in $NaNO_3$–KNO_3 eutectic at 250° [W. T. Carnall, *Anal. Chem.*, **34**, 786 (1962)].

peaks on the nitrate ion concentration. The curves for holmium, neodymium, and erbium can be extrapolated linearly beyond the highest molarity of aqueous lithium nitrate attainable, the curves for holmium and neodymium passing through the point for 15 *M* nitric acid and all of them meeting the experimental absorptivities for molten sodium–potassium nitrate solvent, which is 22 *M* in nitrate (Figure 1). This apparent agreement may be fortuitous, since the incomplete dissociation of the nitric acid, the variation of the erbium absorptivity with the erbium concentration, and the temperature effect on the absorptivity are ignored. The latter quantity, though small, is not negligible: $\Delta\epsilon_{5215} = f(t - 25°)$, where $f = 0.0025$ for perchlorate solutions, but as much as 0.0080 for a 3 *M* erbium nitrate solution, even without correction for the change in molarity with temperature.

The changes in the spectra of those lanthanides which absorb in the visible region—praseodymium, neodymium, promethium, samarium, europium, terbium, dysprosium, holmium, erbium, and thulium—when 8 *M* lithium nitrate is added to their dilute aqueous solutions, have been measured.[12] (Only those peaks which show major changes in intensity are recorded.)

The nmr measurements on erbium solutions are presented in Figure 2. Erbium perchlorate causes a shift of δ 100 ppm toward low field as compared to pure water. The addition of lithium perchlorate to the erbium solution does not change the chemical shift caused by the erbium. The addition of lithium nitrate, on the other hand, causes a shift back toward high field. No shift was observed in solutions of lithium nitrate and perchlorate without erbium. The effect of the nitrate becomes considerable at a concentration of 1.5 *m* lithium nitrate, when the nitrate to erbium ratio is 2:1. In 7 *m* lithium nitrate the shift is 20% less than that caused by erbium in the absence of lithium nitrate.

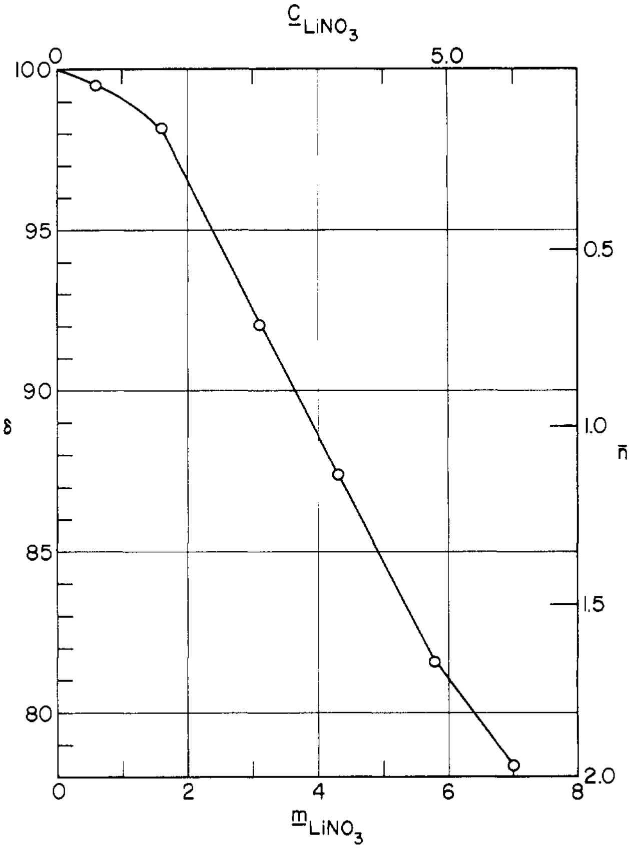

Figure 2.—The chemical shift δ in ppm of the ^{17}O peak in water containing 1.7% ^{17}O and 0.7 *m* erbium perchlorate, as a function of the added lithium nitrate concentration.

The densities of erbium nitrate solutions, *d*, in the range 0.6–4.0 *M* (up to near saturation) were measured at 25.0 ± 0.1° to a precision of 1×10^{-4} g/cm³ (Table I). Apparent molar volumes

$$\phi_v = [M_{Er} - 1000(d - d_0)/c_{Er}]/d_0 \qquad (2)$$

where M_{Er} is the formula weight of erbium nitrate and d_0 is the density of water, were calculated from the data.

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[12] These data have been deposited as Document No. 9560 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE I

DENSITIES OF ERBIUM NITRATE SOLUTIONS AT 25°

c	d^{25}_4	ϕ_V	c	d^{25}_4	ϕ_V
0.6178	1.1844	50.2	1.791	1.5148	64.5
0.6219	1.2198	51.3	2.593	1.7261	72.3
0.9073	1.2670	56.0	3.021	1.8443	73.0
1.035	1.3042	56.7	3.319	1.9199	75.4
1.379	1.4023	59.6	3.937	2.0886	76.3
1.630	1.4734	61.2			

They were fitted to the empirical equation $\phi_v = a_0 + a_1m^{1/2} + a_2m + a_3m^{3/2}$, which Spedding, *et al.*,[13] recently fitted to results from dilute erbium nitrate solutions. The parameters $a_0 = 45.59$, $a_1 = 20.28$, $a_2 = -11.9$, and $a_3 = 4.0$ give a fit within the experimental error with both the present results and those reported by Spedding, *et al.* Of these parameters, a_0 and a_1 are those used by these authors, but their $a_2 = -19.95$ and $a_3 = 13.35$ do not fit the present results, obtained at higher concentrations, where the terms involving these parameters predominate.

Discussion

The experimental results were used to study the interaction of nitrate and lanthanide ions both in pure aqueous erbium nitrate solutions and in solutions of lanthanide perchlorate or nitrate, to which lithium nitrate is added.

Consider the most concentrated erbium nitrate solution studied, which is 4.0 *M* or 5.9 *m*, *i.e.*, contains 9.45 moles of water per mole of erbium nitrate. According to the equation[14]

$$h/h^0 = 1 + S_K c_{Er}{}^{1/2}/\phi_K{}^0 \qquad (3)$$

where h is the hydration number of erbium nitrate, superscript zero refers to infinite dilution, $\phi_K{}^0$, the apparent molal compressibility, is -1.2935×10^{-2} cm^3/bar mole, and $S_K = d\phi_K/dc_{Er}{}^{1/2} = 0.2971 \times 10^{-2}$ bar mole$^{3/2}$ cm$^{-9/2}$;[15] the hydration relative to infinite dilution at the highest concentration is $h/h^0 = 0.536$, increasing to 0.838 at 0.5 *M* salt (Figure 3). No quantitative estimate of the separate hydration numbers of the ions in the concentrated solutions can be made, but from $h_{Er}{}^0 = 8$,[13] and $h_{NO_3}{}^0 = 1$[16a] or 2,[16b] any reasonable assumption concerning the dehydration of the nitrate ion leads to $h_{Er} \sim 5$ at the highest concentrations. This figure may be compared with the fact that the pentahydrate crystallizes out from the saturated solution[17] and that $h_{Er} = 6.3$ has been found for a half as concentrated solution (3.05 *m*) of erbium chloride from an X-ray diffraction study on the solution.[18] In this solution two chloride ions were found to be coordinated to the erbium ion beyond the first coordination sphere, and the solution showed an absorption spectrum identical with those of dilute solutions of hydrated erbium. In the present study, where more dehydration occurs at the higher concentrations, it is reasonable to conclude that some inner-sphere coordination of nitrate occurs to make the total number of ligands up to a constant coordination number, which may be most probably eight.

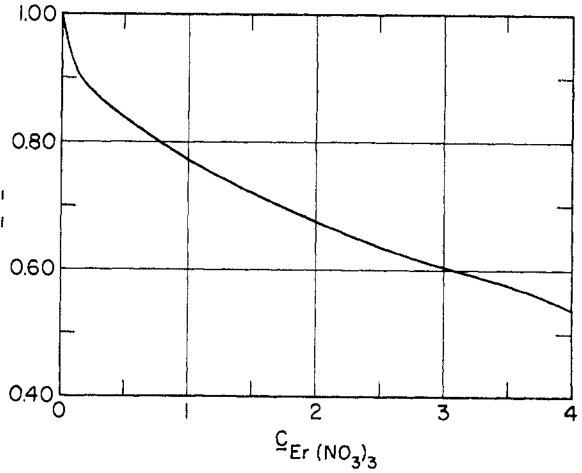

Figure 3.—Relative hydration numbers h/h^0 in erbium nitrate solutions obtained from density and compressibility data.

That nitrate enters the inner coordination sphere at higher concentration, contrary to the behavior of chloride or iodide,[18,19] is confirmed by the observation of the deviation from Beer's law (eq 1).

The intensity of the Laporte-forbidden band $I_{15/2} \rightarrow {}^2H_{11/2}$ at 5215 A would increase somewhat if the microsymmetry around the erbium ions is decreased,[19] as would result from the partial replacement of water by nitrate ligands in the immediate vicinity of the erbium, in the inner coordination sphere. In other words, this "hypersensitive"[20] transition of the erbium is affected when the more polarizable nitrate ion replaces some of the water in an asymmetric fashion around the erbium ion.

The nmr results can be interpreted in a more definite manner. The chemical shift δ^0 of 100 ppm in the completely hydrated erbium solutions is ascribed to the bonding of the ^{17}O water to the paramagnetic ion. A decrease of this shift is interpreted as a partial release of the bound water back to the bulk of the solution.[21] Rapid exchange between free and bound water prevents the observation of separate peaks for the two kinds and leads to the observed shift δ in the single peak. It is assumed that the chemical shift per water molecule left bound to the erbium is independent of the number of ligands of each kind[22] and that each nitrate ion entering the inner coordination sphere replaces just one water molecule; *i.e.*, it is monodentate. Then the ligand number of nitrate ions in the inner coordination sphere, $\bar{n}_i$, is given by the relationship

$$\bar{n}_i = h_{Er}{}^0(\delta^0 - \delta)/\delta^0 \qquad (4)$$

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Assuming again the value $h_{Er}^0 = 8^{13}$ leads to the values of $\bar{n}_i$ on the right-hand ordinate in Figure 2, ranging up to $\bar{n}_i = 1.7$ at 7.0 *m* (5.8 *M*) lithium nitrate in the solution.

Turning to the spectrophotometric data (Figure 1), it is noted that the molar absorptivity can be written as the sum of the molar fractions α_n of the species $Er(NO_3)_n(H_2O)_{N-n}{}^{3-n}$ (where N is perhaps 8) times their molar absorptivities ϵ_n

$$\epsilon = \alpha_0\epsilon_0 + \alpha_1\epsilon_1 + \alpha_2\epsilon_2 + \ldots \qquad (5)$$

Similarly, the average ligand number $\bar{n}_i$ of the inner-sphere coordination complexes can be expressed as

$$\bar{n}_i = \alpha_1 + 2\alpha_2 + \ldots \qquad (6)$$

whether the law of mass action is obeyed in the solutions of varying high lithium concentration or not. In Figure 4 is plotted ϵ_{5215} for 0.47 *m* erbium nitrate solutions to which lithium nitrate has been added (data from Figure 1) against $\bar{n}_i$ obtained from the nmr data discussed above. It is seen that an approximately straight line results

$$\epsilon = \epsilon'_0 + \bar{n}_i\Delta\epsilon \qquad (7)$$

where $\epsilon'_0 = 2.90$ is the intercept and $\Delta\epsilon = 0.33$ is the slope. This expression is compatible with both eq 5 and 6, provided the relationships $\epsilon'_0 = \epsilon_0$ and $\epsilon_n = \epsilon_0 + n\Delta\epsilon$ hold. This means that the molar absorptivity increases by a constant increment of about 12% for each ligand nitrate ion replacing a water molecule in the inner coordination sphere. This result is reasonable, although, of course, not a proof that such replacement and such effects on the absorption intensity indeed occur.

Of the other lanthanides studied, only a few show appreciable changes in the absorption spectrum when concentrated lithium nitrate is added.[12] At 8 *M* lithium nitrate (*ca.* 11 *m*) there is very little free water available, and the lanthanide ions must exist in a partially dehydrated state, because of the competition of the lithium ions. Inner-sphere coordination with nitrate can, therefore, be assumed also for the other lanthanides. The results for the concentrated aqueous nitrate solutions[12] and the molten nitrate solutions[23,24] should be compared with the results for nitroethane solutions containing tetrabutylammonium nitrate[25] and with results for extracts with triisooctylammonium nitrate in xylene.[26]

A comparison of the results obtained from the spectral and nmr data, which are assumed to correspond to inner-sphere coordination, with those obtained from extraction or ion-exchange results, which correspond to total complexing, *i.e.*, both inner- and outer-sphere coordination, is instructive. In order to avoid the problem of the stability constants varying with the ionic medium, and the law of mass action not being obeyed in terms of concentrations, the average ligand number in 2.0 *M* nitrate solution has been calculated in every case, as far as possible from the original data. The values of $\bar{n} = \bar{n}_o + \bar{n}_i$ (o = outer, i = inner) range some 0.2 unit above $\bar{n}_i$.

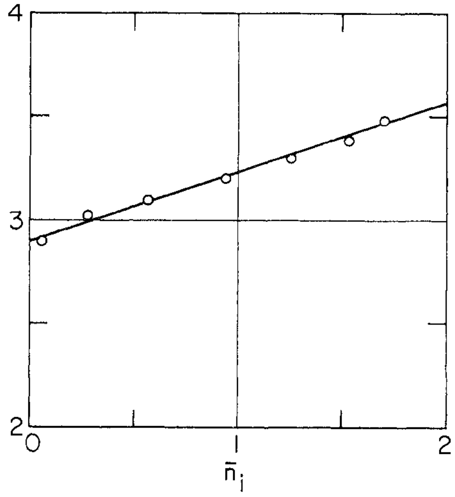

Figure 4.—Molar absorptivity ϵ_{5215} of 0.47 *m* erbium nitrate solution *vs.* the average ligand number $\bar{n}_i$ from nmr data.

Outer-sphere coordination of lanthanides to nitrate, although it explains the enthalpy and entropy changes found for europium,[8] is thus not the only mode of interaction.[11] The measured changes in the thermodynamic functions may also result from a combination of inner-sphere and outer-sphere coordination. Even at higher nitrate concentrations, both modes of interaction seem to occur. The present work suggests that $\bar{n}_i = 1.7$ for erbium at 7 *m* (5.5 *M*) lithium nitrate from the nmr results, and about $(5.5/22) \times N_{melt} = 1.5$ for neodymium, holmium, and erbium from the spectral data (Figure 1). This may be compared with electromigration results, which indicate $\bar{n} > 3$ (anodic migration) for cerium and europium[27] at 6 *m* lithium nitrate, and for lanthanum, praseodymium, and neodymium[28] at 23 *m* nitric acid, but $\bar{n} \sim 3$ for ytterbium at the same concentration of acid.[28] Thus both $\bar{n}_i$ and $\bar{n}$ seem to decrease with increasing Z, but $\bar{n}$ is, in all cases, only somewhat larger than $\bar{n}_i$.

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