Structures of Nitrate Complexes of Erbium in Aqueous Solutions

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The coordination around Er^{3+} in aqueous erbium nitrate solutions has been derived
from large-angle X-ray scattering measurements on isostructural erbium and yttrium
solutions. The nitrate ion forms inner-sphere complexes in which it acts as a bidentate
ligand, which is symmetrically bonded to Er^{3+}. The $Er–O(NO_3)$ bonds are longer
than the $Er–O(H_2O)$ bonds in the inner coordination sphere. The total coordination
number is close to 8.0.

The lanthanide ions form weak complexes with nitrate ions in aqueous solutions. For the predominant complex, $LnNO_3^{2+}$, formation constants, β_1, have been determined to be around 2 M^{-1}.[1] Several methods have been used in attempts to characterize these complexes in terms of outer- or inner-sphere complexes, but their structures in solution are not known. Direct structural information can be obtained from large-angle X-ray scattering measurements, but the metal–ligand interactions cannot always be distinguished among the many intra- and intermolecular distances that contribute to the scattering. Since the nitrate group contains only light atoms and the metal–nitrate interactions occur in a region of the radial distribution functions (RDFs) which is dominated by intermolecular contributions, primarily from $H_2O–H_2O$ interactions, unique structure determinations of metal–nitrate complexes are usually difficult to obtain.

It has been shown in previous papers[2,3] that the close similarity between yttrium(III) and erbium(III) leads to isostructural solutions. For two solutions having the same compositions, one containing Y^{3+} and the other Er^{3+}, interactions, which do not involve the metal ions, are the same and give identical contributions to the scattering. By using the difference between the normalized diffraction curves of yttrium(III) and erbium(III) solutions these interactions can be eliminated. The radial distribution functions, calculated from the difference intensity functions, contain contributions only from interactions involving the metal ion and give information on the coordination around the metal ion, which is not obscured by other interactions in the solution.

For erbium halide,[4] perchlorate[2,4] and selenate[2] solutions it has been possible by this method to determine the struc-

tures of the inner- and outer-sphere complexes in aqueous solutions of different concentrations and anion/metal ratios. In the present paper the same method has been used for an investigation of the structures of erbium nitrate complexes in solution.

Experimental

The solutions were prepared by dissolving Y_2O_3 or Er_2O_3 (Johnson-Matthey 99.9 %) in nitric acid. To increase the NO_3^-/Ln^{3+} ratio in some of the solutions lithium nitrate was added. In order to avoid hydrolysis a slight excess of HNO_3 was maintained. Pairs of yttrium and erbium solutions of the same compositions were prepared.

Yttrium and erbium were determined by titration with EDTA at pH 5.0 with xylenol orange as indicator. Checks were also made by evaporating a weighed sample to dryness, heating and weighing the residue as Y_2O_3 or Er_2O_3. Nitrate was determined by passing a portion of the solution through an ion-exchange resin titrating the eluate with NaOH. Densities were determined by an Anton-Paar digital density meter, model DMA35.

The compositions of the three pairs of solutions investigated are given in Table 1.

The X-ray scattering was measured in a Rigaku θ–θ diffractometer with Ag $K\alpha$ radiation (λ = 0.5608 Å), as described in a previous paper.[4] Intensities were collected for 2 < 2θ < 140° (where 2θ is the scattering angle) at intervals in θ of 0.1° for θ < 25° and 0.25° in the remaining region. For each point at least 10^5 counts were collected and each solution was scanned twice, which corresponds to a statistical error in the measured intensities of about 0.2 %. Corrections to the data and the derivation of the reduced intensity functions, $i(s)$, (s = 4π sin θ/λ) were carried out as described previously.[4] Each data set was normalized to a stoichiometric unit of volume containing one metal ion (Table 1).

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Table 1. Compositions of solutions.

Solu-tion	C mol dm^{-3}		Unit volume, $V/Å^3$	No. per unit volume				
	[Er^{3+}]	[Y^{3+}]		M^{3+}	NO$_3^-$	H$^+$	Li$^+$	H$_2$O
A	0.992		1674	1	3.28	0.27	–	52.4
		0.996	1667	1	3.30	0.30	–	51.9
B	0.970		1712	1	9.49	0.30	6.19	41.5
		0.970	1712	1	9.49	0.30	6.19	41.3
C	2.896		573.4	1	3.24	0.24	–	14.7
		2.880	576.7	1	3.21	0.21	–	14.9

The reduced intensity functions, $si(s)$, for the yttrium and the erbium solutions for one of the pairs (C) investigated, are shown in Fig. 1.

Results

Treatment of the data. The radial distribution functions (RDFs) were calculated from the $si(s)$ values according to eqn. (1).

$$D(r) = 4\pi r^2 \varrho_0 + 2r\pi^{-1} \int_0^{s_{max}} si(s)M(s)\sin(rs)ds \qquad (1)$$

ϱ_0 is the average scattering density, $(\Sigma n_i Z_i)^2/V$, in e^2 Å^{-1}, n_i is the number of i atoms per stoichiometric unit of volume (V in Å^3) and Z_i is the atomic number. The modification function, $M(s)$, was chosen to be the same as used previously:[4] $M(s) = f_o^2 (0)f_o^{-2}(s)\exp(-0.01s^2)$. An upper integration limit of $s_{max} = 20.0$ Å^{-1} was used for all Fourier inversions. The scattering factors, $f_i(s)$, for the neutral atoms, corrected for anomalous dispersion, were taken from Ref. 5. Values for incoherent scattering were taken from Cromer and Mann[6] and were corrected for the Breit–Dirac effect.
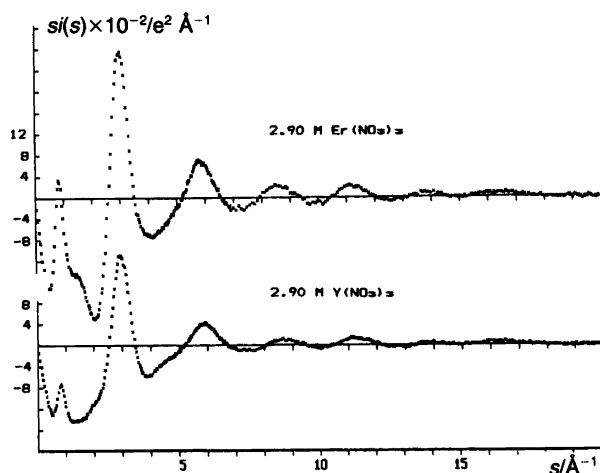
For the C solutions the RDFs, derived from the reduced intensities $si(s)$ (Fig. 1), are compared in Fig. 2.

The intensity difference functions, $s\Delta i(s)$, obtained as the difference between the normalized $si(s)$ values for the erbium and the yttrium solutions for each of the three pairs of solutions, are shown in Fig. 3. The corresponding RDFs, $D^{Er}(r)$, were calculated according to eqn. (2).

$$D^{Er}(s) = 4\pi r^2 \varrho_0^{Er}$$

$$+ 2r\pi^{-1} \int_0^{s_{max}} s\Delta i(s)\sin(rs)M(s)f_{Er}(s)[f_{Er}(s) - f_Y(s)]^{-1} ds \qquad (2)$$

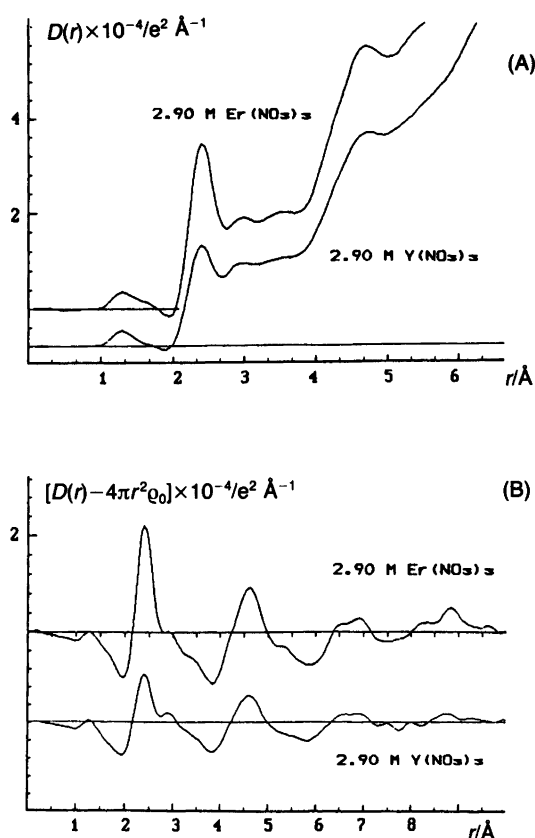*Fig. 1.* Reduced intensities, $si(s)$, for a 2.90 M Er(NO$_3$)$_3$ solution and an Y(NO$_3$)$_3$ solution of the same composition.

Fig. 2. Radial distribution functions (A) and reduced RDFs (B) for a 2.90 M Er(NO$_3$)$_3$ solution and an Y(NO$_3$)$_3$ solution with the same composition.

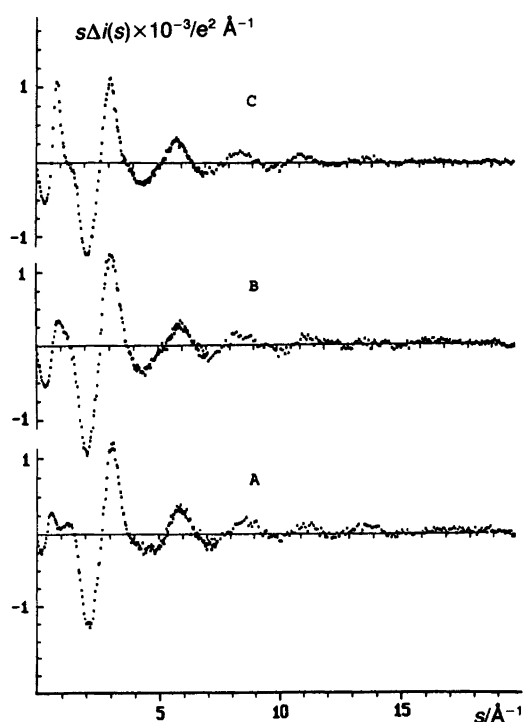*Fig. 3.* Intensity difference functions, $s\Delta i(s)$, for the three pairs of solutions investigated.

Analysis of the RDFs. The $D^{Er}(r)$ functions in Fig. 4 and the corresponding reduced RDFs (curves b in Fig. 5) show peaks at about 2.35 and 4.6 Å corresponding to a first and a second coordination sphere around the Er^{3+} ion. In the reduced RDFs (curves c in Fig. 5), which contain non-metal interactions only, peaks occur at 1.3 and 2.2 Å, which are the expected N–O and O–O distances in the NO_3^- ion, at about 2.8 Å, corresponding to H_2O–H_2O interactions, and at about 3.5 Å, which probably result from the hydration of the NO_3^- ion. Li–O distances in the hydrated Li^+ ion contribute in the region around 2 Å in solution B.

In the previously investigated 1 M erbium chloride, bromide and perchlorate solutions[2,4] peaks in $D^{Er}(r)$, corresponding to the first coordination sphere, were nearly identical and were independent of the anion present. They could all be described by an Er–H_2O distance of 2.35 Å, a root mean-square variation (r.m.s.) in the distance of 0.09 Å and a coordination number of 8.0. For the 1 M nitrate solution, A, the first coordination peak is similar but occurs at a slightly longer distance, 2.38 Å, and is slightly broadened towards longer distances. This asymmetry is much more pronounced for solution B, which has a large excess of NO_3^-, and also for the concentrated solution C (Fig. 4). A theoretical Er–O peak adjusted to the left-hand side of the experimental peak does not fully reproduce the right-hand side of the peak. The position of the peak maximum changes towards longer distances from 2.38 Å in solution A to 2.41 Å in C. It seems reasonable to assume that these effects are caused by the bonding of nitrate ions in the inner coordination sphere of the erbium ion.

A bidentate NO_3^- ion, which is symmetrically bonded to Er^{3+} with an Er–O bonding distance of 2.36 Å, would be expected to have an Er–N distance of 2.73 Å, if the N–O distance in NO_3^- is 1.25 Å (Fig. 6). If the theoretical Er–O peak, which gives the best fit to the left-hand part of the asymmetric experimental peak for solution B (Fig. 4), is subtracted, a rather broad peak remains with a maximum at about 2.7 Å, in approximate agreement with an Er–N distance expected for a symmetric bidentate bonding. The
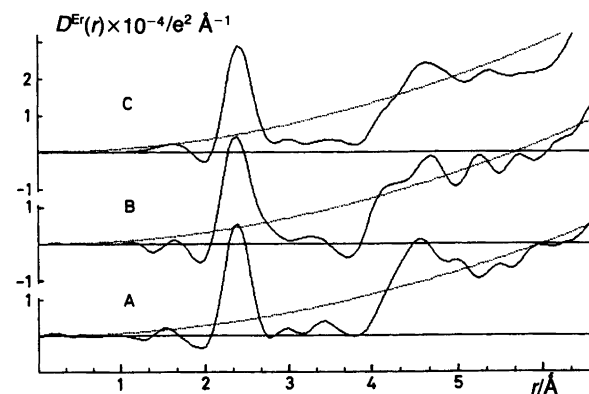
$\varrho_0^{Er} = (\Sigma n_i Z_i)^2/V$ includes terms involving the erbium ion only. This expression has been derived in a previous paper.[3] In $D^{Er}(r)$ the non-metal interactions, which are assumed to be the same in the erbium and the yttrium solutions, are eliminated, and only contributions from interactions involving the Er^{3+} ions remain.

Theoretical peaks, $P_{pq}(r)$, corresponding to a specific pair interaction between two atoms p and q, which were used for the analysis of the $D^{Er}(r)$ function, were calculated from the Debye expression for the theoretical intensities, eqn. (3), by a Fourier transformation analogous to the one used for the experimental intensities, eqn. (4).

$$i_{pq}(s) = n_p n_q f_p(s) f_q(s) \sin(rs) (rs)^{-1} \exp(-\tfrac{1}{2} l^2_{pq} s^2) \qquad (3)$$

$$P_{pq}(r) = 2r\pi^{-1} \int_0^{s_{max}} s i_{pq}(s) \sin(rs) M(s) \, ds \qquad (4)$$

The $D^{Er}(r)$ functions for the three pairs of solutions investigated are shown in Fig. 4. The corresponding reduced RDFs are given in Fig. 5, which shows the reduced RDF for each erbium solution (curve a), and its separation into the RDF involving only the metal ion interactions (curve b) and the remaining part involving only the non-metal interactions (curve c).

Fig. 4. The separated radial distribution functions, $D^{Er}(r)$ (solid line) and $4\pi r^2 \varrho_0^{Er}$ (dotted line), which include metal ion interactions only.
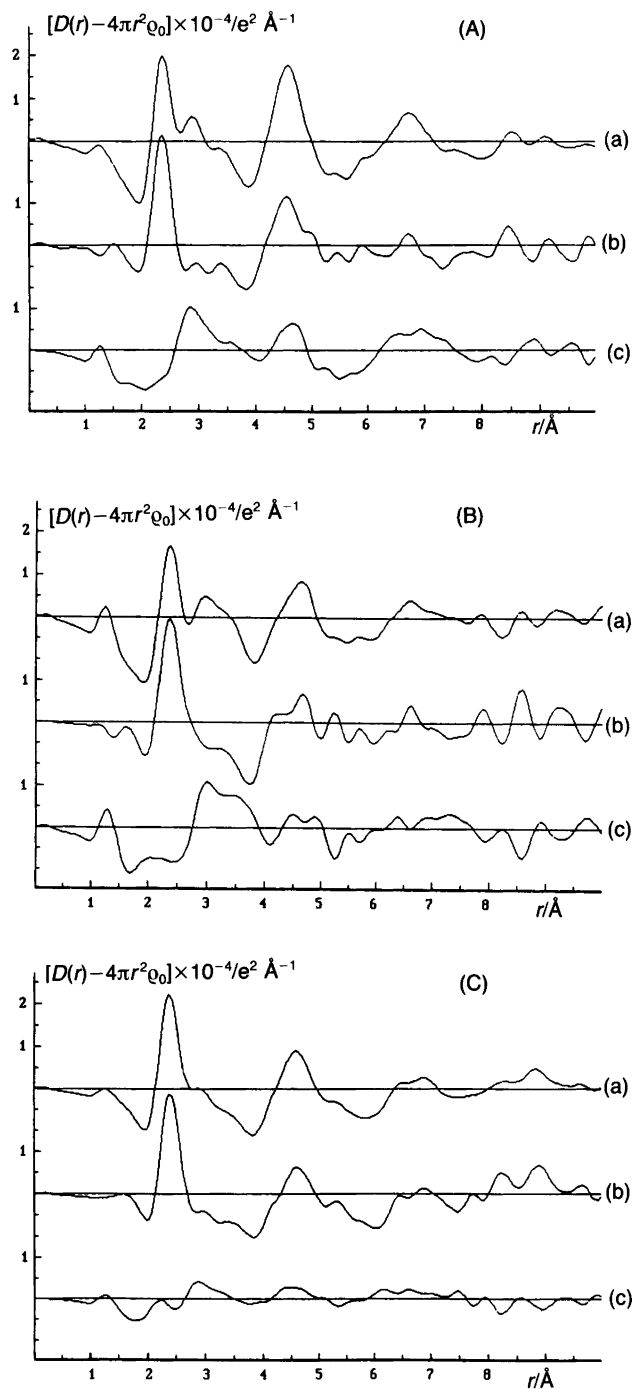
Fig. 5. The reduced radial distribution function for the erbium solution (curve a), the separated function involving only erbium ion interactions (curve b) and the part involving only non-metal interactions (curve c). (A) Solution A, (B) solution B and (C) solution C.

Fig. 6. A bidentate nitrate group symmetrically bonded to Er^{3+}.

corresponds to the expected Er-O_3 distance (Fig. 6) for a symmetrically bonded bidentate nitrate ion. No support for a monodentate bonding or an asymmetric bidentate bonding of the nitrate ion is given by the RDFs in Fig. 4.

An analysis of the RDFs was made by a trial-and-error procedure using five theoretical peaks: one Er-$O(H_2O)_{1st}$ peak, three Er-NO_3 peaks, Er-$O(O_1$ and $O_2)$, Er-N and Er-O_3 (Fig. 6) with the relative frequencies 2:1:1, and one Er-O peak for Er-H_2O and Er-NO_3 interactions in the second coordination sphere around 4.6 Å. The distance and the r.m.s. variation for the Er-$O(H_2O)_{1st}$ peak were determined from the position and the shape of the left-hand side of the experimental 2.4 Å peak. The remaining parameter values were varied until the best fit to the experimental curve was obtained. The dimension of the NO_3^- ion was not explicitly used in this analysis, but the derived parameter values are in approximate agreement with a regular triangular NO_3^- ion with N–O distances of about 1.25 Å (Fig. 6). The parameter values corresponding to the

Table 2. Derived parameter values.[a]

Interaction	Parameter	Solution		
		A	B	C
Er-$O(H_2O)_{1st}$	r	2.35	2.32	2.37
	l	0.06	0.06	0.06
	n	5.8	4.0	3.3
Er-$O_1(O_2)$	r	2.45	2.45	2.45
	l	0.10	0.08	0.10
	n	1.8	3.9	4.4
Er-N	r	2.86	2.78	2.86
	l	0.14	0.08	0.14
	n	0.9	2.0	2.2
Er-O_3	r	4.12	4.10	4.12
	l	0.10	0.06	0.10
	n	0.9	2.0	2.2
Er-O(2nd sphere)[b]	r	4.58	4.64	4.62
	l	0.32	0.35	0.28
	n	17.0	17.5	14.6
Coordination number (1st sphere)		7.6	7.9	7.7

[a]r = distance in Å, l = r.m.s. variation in Å, n = number of interactions per Er atom. [b]Oxygen atoms of H_2O and NO_3^- in the second sphere. The analyses were made without including Er-$H(H_2O)_{2nd}$ interactions.

peak corresponding to the second coordination sphere has its maximum at about 4.6 Å, which is close to 4.5–4.6 Å found for the Er-H_2O distances for the second sphere in the previously investigated halide and perchlorate solutions,[4] but in the nitrate solutions, B and C (Fig. 4) there is a pronounced shoulder on this peak at about 4.1 Å. This
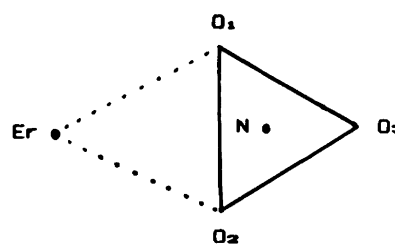
(A)

(B)

(C)

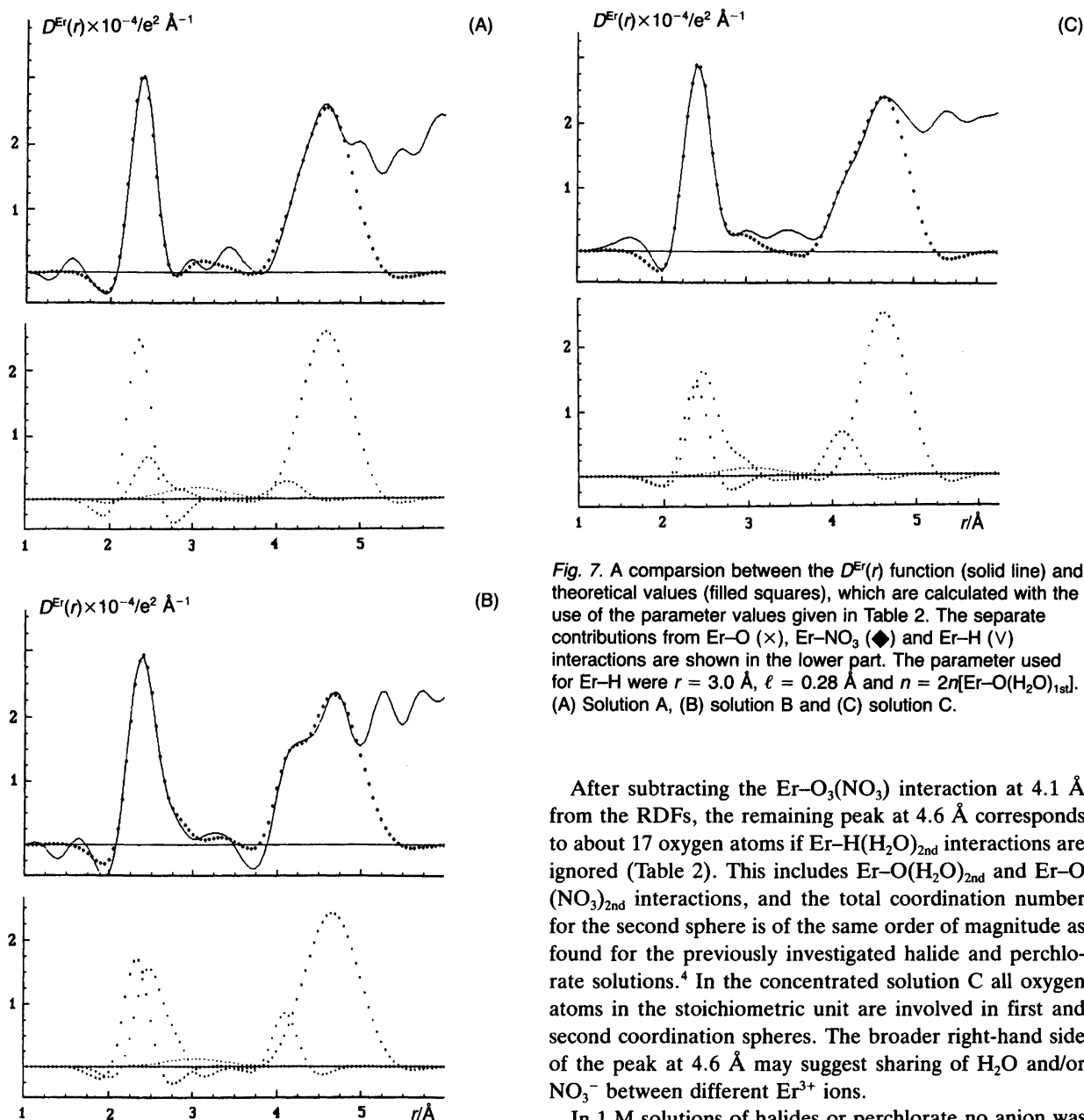*Fig. 7.* A comparsion between the $D^{Er}(r)$ function (solid line) and theoretical values (filled squares), which are calculated with the use of the parameter values given in Table 2. The separate contributions from Er–O (×), Er–NO$_3$ (◆) and Er–H (V) interactions are shown in the lower part. The parameter used for Er–H were $r = 3.0$ Å, $\ell = 0.28$ Å and $n = 2n[\text{Er–O(H}_2\text{O)}_{1\text{st}}]$. (A) Solution A, (B) solution B and (C) solution C.

best fit are given in Table 2. For each solution a comparison between observed and calculated peaks is shown in Fig. 7, which also gives the individual contributions from the Er–O (H$_2$O)$_{1\text{st}}$, the Er–NO$_3$ (1st) and the Er–O(H$_2$O and NO$_3$)$_{2\text{nd}}$ interactions.

Since the peaks of Er–O(H$_2$O), Er–O$_1$(NO$_3$), Er–O$_2$ (NO$_3$) and Er–N interactions in the first coordination sphere are not separated, the uncertainties in the derived parameter values become relatively large. The derived distances, given in Table 2 for the Er–NO$_3$ interactions in the first sphere, are all, however, within ± 0.04 Å from the distances expected for a symmetrically bonded, bidentate, regular NO$_3^-$ group with an N–O distance of 1.25 Å and an Er–N distance of 2.82 Å as shown in Fig. 6.

After subtracting the Er–O$_3$(NO$_3$) interaction at 4.1 Å from the RDFs, the remaining peak at 4.6 Å corresponds to about 17 oxygen atoms if Er–H(H$_2$O)$_{2\text{nd}}$ interactions are ignored (Table 2). This includes Er–O(H$_2$O)$_{2\text{nd}}$ and Er–O (NO$_3$)$_{2\text{nd}}$ interactions, and the total coordination number for the second sphere is of the same order of magnitude as found for the previously investigated halide and perchlorate solutions.[4] In the concentrated solution C all oxygen atoms in the stoichiometric unit are involved in first and second coordination spheres. The broader right-hand side of the peak at 4.6 Å may suggest sharing of H$_2$O and/or NO$_3^-$ between different Er^{3+} ions.

In 1 M solutions of halides or perchlorate no anion was coordinated in the first sphere of Er^{3+}, but about two anions were in the second sphere.[4] Also in the 1 M solution of nitrate, one or two nitrate ions are probably coodinated in the second sphere. The small peak around 5.0 Å (Figs. 4A and 7A) may be due to Er–N(NO$_3$)$_{2\text{nd}}$ interactions. The strong peak at 5.25 Å in solution B (Figs. 4B and 7B) suggests the presence of several nitrate ions in the second coordination sphere, similar to the halide solutions containing excess anions.[4] If in the second coordination sphere the nitrate ions are symmetrically orientated in a similar way to that shown in Fig. 6 and their two oxygen atoms are situated at 4.6 Å, the distance between Er and N(NO$_3$) should be 5.1 Å, which is close to the observed peak position. However, it is difficult to estimate a reliable number of Er–N(NO$_3$)$_{2\text{nd}}$ interactions because of overlapping by other interactions such as Er–O(H$_2$O)$_{3\text{rd}}$, and because the

nitrate ion may have different orientations in the second sphere.

Discussion

The elimination of non-metal interactions by using diffraction data from isostructural yttrium and erbium solutions makes it possible to separate the contributions to the scattering from interactions involving the erbium ion from those of other interactions. The radial distribution functions obtained from the intensity difference functions reveal the coordination around the erbium ion, and its bonding to the surrounding water and ligand molecules can be determined. The RDFs for the investigated nitrate solutions (Fig. 4) show conclusively that inner-sphere complexes are formed.

In previous investigations enthalpy and entropy data have been interpreted to indicate the formation of mainly outer–sphere ion-pairs,[7,8] but according to spectral data some inner-sphere complexes are also formed.[9,10] A comparison of formation constants, obtained from spectral and NMR data, which are expected to correspond primarily to inner-sphere coordination, with results from extraction and ion-exchange methods, which are assumed to measure the total complexing, shows the average ligand number in the inner sphere to be lower than the total ligand number, as expected if both inner- and outer-sphere complexes are formed.[11] Infrared and Raman spectra of aqueous lanthanum(III) nitrate solutions[12] and Raman spectra on aqueous gadolinium nitrate solutions[13] and on other rare-earth nitrate solutions[14] indicate the formation of inner-sphere complexes. Both bidentate and monodentate bonding have been suggested to occur.

Dilatometric measurements of molar volume changes, although they give no clear evidence, also indicate that both inner- and outer-sphere complexes may be present.[15,16] NMR measurements on ^{17}O and ^{139}La show the formation of stable inner-sphere complexes,[17,18] and proton magnetic resonance measurements on lanthanum nitrate solutions in water–acetone mixtures at low temperature indicate extensive formation of strong inner-sphere complexes.[19] Ultrasonic absorption spectroscopy[20,21] and luminescence excitation spectroscopy[22,23] give evidence for inner-sphere complexation of Eu(III) by the NO_3^- ion. Solution X-ray diffraction data on a 2 M $Ce(NO_3)_3$ solution have been interpreted by assuming a monodentate bonding of about one NO_3^- to each Ce^{3+}, with a Ce–N distance of 3.44 Å.[24]

In the present work the radial distribution functions have been shown to be consistent with a bidentate, symmetric bonding of the nitrate ion in the inner coordination sphere with an average Er–N distance of 2.82 Å. The average distance for the two nitrate oxygens, O_1 and O_2 in Fig. 6, which are bonded to erbium, is 2.45 Å (Table 2), and this distance is longer than the average $Er–O(H_2O)$ distance, which is 2.35 Å (Table 2). In the 1 M solution, A, with no excess of nitrate ions, an average of about 0.9 NO_3^- ions is

coordinated to each Er^{3+}. This number increases to about 2 for the more concentrated solutions (Table 2).

The O_3 atom (Fig. 6) of a nitrate ion bonded in the first coordination sphere has an Er–O distance of about 4.1 Å, which is close to the main Er–O distance of about 4.6 Å for oxygens in the second coordination sphere. The contribution from the $O_3(NO_3)_{1st}$ atom to the second coordination sphere can be determined (Table 2), while contributions from the NO_3^- ions in the second sphere to the peak at 4.6 Å are difficult to estimate. The probable presence of nitrate ions of different orientations and the resulting overlap of peaks lead to a poor separation of the peaks in the second coordination sphere. An analysis assuming the small peak at about 5.1 Å to correspond to $Er–N(NO_3)_{2nd}$ interactions indicates that most remaining NO_3^- ions are in the second coordination sphere. However, a precise estimate can not be made.

The bonding of the nitrate ion to the erbium ion in the first coordination sphere, as found here, is similar to that found in crystal structures, where nitrate ions are usually bidentate with an approximately symmetric bonding to the lanthanide ions. Yttrium nitrate trihydrate contains $Y(NO_3)_3(H_2O)_3$ units with three bindentate nitrate ions (Y–O: 2.396–2.450 Å; av. 2.432 Å) and three water molecules (Y–H_2O: 2.321–2.331 Å; av. 2.325 Å) bonded to yttrium, which gives a coordination number of nine.[25] In $K_2Er(NO_3)_5$ five bidentate nitrate groups (Er–O: 2.392–2.493 Å; av. 2.432 Å) are bonded to erbium, which therefore has a coordination number of ten.[26] A penta-[27] and a hexahydrate[28] of yttrium both contain $Y(NO_3)_3(H_2O)_4$ units with a coordination number of ten and with similar differences between $Y–O(H_2O)$ and $Y–O(NO_3)$ distances. The bond lengths found here in the solutions therefore do not differ significantly from those in known crystal structures. The coordination numbers, however, seem to be lower in solution. The values found (Table 2) are close to or slightly lower than eight. Although the uncertainties in these values are probably somewhat larger than those determined for halide[4] and perchlorate[2,4] solutions, because of the unresolved contributions from several different interactions, a conservative estimate of the error should not exceed about 0.5 oxygens. The smaller average number of nitrate ions bonded to erbium in solution thus does not seem to be sufficient to increase the coordination number.

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