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X-ray Investigation of the Coordination and Complex Formation of Lanthanoid Ions in Aqueous Perchlorate and Selenate Solutions

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The coordination and complex formation of some three-valent lanthanoids (Er, Tb, Sm, La) in aqueous perchlorate and selenate solutions have been determined from X-ray scattering measurements. Isomorphous substitution with yttrium as the substituent was used for the analysis of the data for Er^{3+} and Tb^{3+}, which have ionic radii close to that of Y^{3+}. Inner-sphere complexes are formed with the selenate ion. The Ln–O–Se angle is about 140°, which corresponds to monodentate bonding. No indication of inner-sphere complex formation is found in the perchlorate solutions. The data are consistent with a coordination number of 8 in the solutions. The root-mean-square variations in the corresponding Ln–H_2O distances, as determined from comparisons with calculated peaks, are 0.09 and 0.11 Å for the perchlorate and the selenate solutions, respectively. A second coordination sphere is clearly indicated in the RDFs.

The coordination of the lanthanoid ions in solution has been the subject of a large number of investigations, but the results have often been contradictory. Values obtained for hydration numbers in aqueous solution seem to depend on the method used,[1,2] and studies of complex formation by thermodynamic and transport properties and by spectroscopic methods often lead to different results as to the formation of inner- or outer-sphere complexes.[3] Diffraction methods, which can give direct information on interatomic distances and their frequencies in solution, have been used in some investigations of the hydration numbers but hardly at all for the study of complex formation.

In an early X-ray diffraction study of erbium chloride and iodide solutions Brady[4] estimated the hydration number for Er^{3+} to be about 6. Wertz and co-workers[5-7] found a value of 8.0 throughout the series in concentrated chloride and bromide solutions. Habenschuss and Spedding[8] determined from X-ray scattering measurements in 3 M chloride solutions that the ions La^{3+} through Nd^{3+} are nine-coordinated and those from Tb^{3+} to Lu^{3+} are eight-coordinated, while those between Nd^{3+} and Tb^{3+} have intermediate values. A neutron diffraction investigation of neodymium chloride solutions with use of isotopic substitution led to 8.5 ± 0.2 water molecules in the first coordination sphere.[9]

The X-ray data in these investigations were analyzed from the radial distribution functions by using the first peak for an estimation of the hydration number, assuming that no inner-sphere complex formation with the halide ions took place. Even if this is true, the peak is partly overlapped by contributions from H_2O–H_2O interactions, particularly for the first elements in the series, where Ln–H_2O distances are the longest and approach the hydrogen bond distances between water molecules. The method used to separate the peaks involves assumptions about the water structure, which may influence the results. In an investigation of a cerium(III) nitrate solution Caminiti et al. showed that equally good agreement between calculated and observed correlation functions could be obtained for coordination numbers of 7.5 and 8 for slightly different assumptions about other interactions in the solutions.[10]

The ambiguities involved in the interpretation of the X-ray data should be possible to avoid by utilizing isomorphous substitution. Yttrium is chemically closely related to the lanthanoids and has an ionic radius close to that found for the elements at the end of the series (Er 1.00 Å, Y 1.015 Å, and Tb 1.04 Å, for coordination numbers of 8[11]), and in crystals yttrium compounds are isomorphous with those of the lanthanoids. Assuming an isomorphous replacement also in solution, the difference between a radial distribution function for an Er or Tb solution and an Y solution of the same composition would show interactions involving only the Ln^{3+} ions, as all other interactions would cancel out. The resulting difference curve should give the surroundings of an average Ln^{3+} ion not obscured by other types of interactions.

Table I. Composition of Solutions (mol/L)

solution					
no.	Ln	$[Ln^{3+}]$	$[ClO_4^-]$	$[SeO_4^{2-}]$	$[H_2O]$
A1	Y	1.094	5.30		43.7
A2	Tb	1.093	5.30		43.4
A3	Y	2.91	8.85		36.1
A4	Er	2.96	9.08		35.8
A5	Tb	2.68	8.90		36.6
A6	Sm	2.53	8.07		38.4
A7	La	2.88	9.16		34.6
B1	Y	0.77		1.54	53.3
B2	Er	0.78		1.55	53.6
B3	Y	0.89		1.85	51.8
B4	Er	0.95		2.06	50.4
B5	Tb	1.15		1.86	50.9
B6	La	0.70		1.16	53.8

In the present work we have used this method in an attempt to determine the coordination and complex formation of the lanthanoid ions in a series of aqueous perchlorate and selenate solutions. The selenates have been chosen rather than the sulfates as they are slightly more soluble and Se has a higher atomic number, making it a stronger contributor to the scattering.

Experimental Section

Preparation and Analysis of Solutions. The solutions were prepared from rare-earth-metal oxides or carbonates, perchloric acid, and selenic acid. The metal concentration was determined by an EDTA titration at pH 4.7 with xylenol orange as indicator. The perchlorate or selenate concentration was determined by passing the solution through a cation exchanger and titrating the hydrogen ions in the eluate by sodium hydroxide. Densities were determined by an Anton PAAR digital density meter, Model DMA35. The compositions of the solutions are given in Table I.

X-ray Scattering Data. The diffraction data were obtained with Mo Kα radiation (λ = 0.7107 Å) by measuring the scattering from the free surface of the solution in a θ–θ diffractometer described in previous papers.[12,13] A focusing single-crystal LiF monochromator was placed

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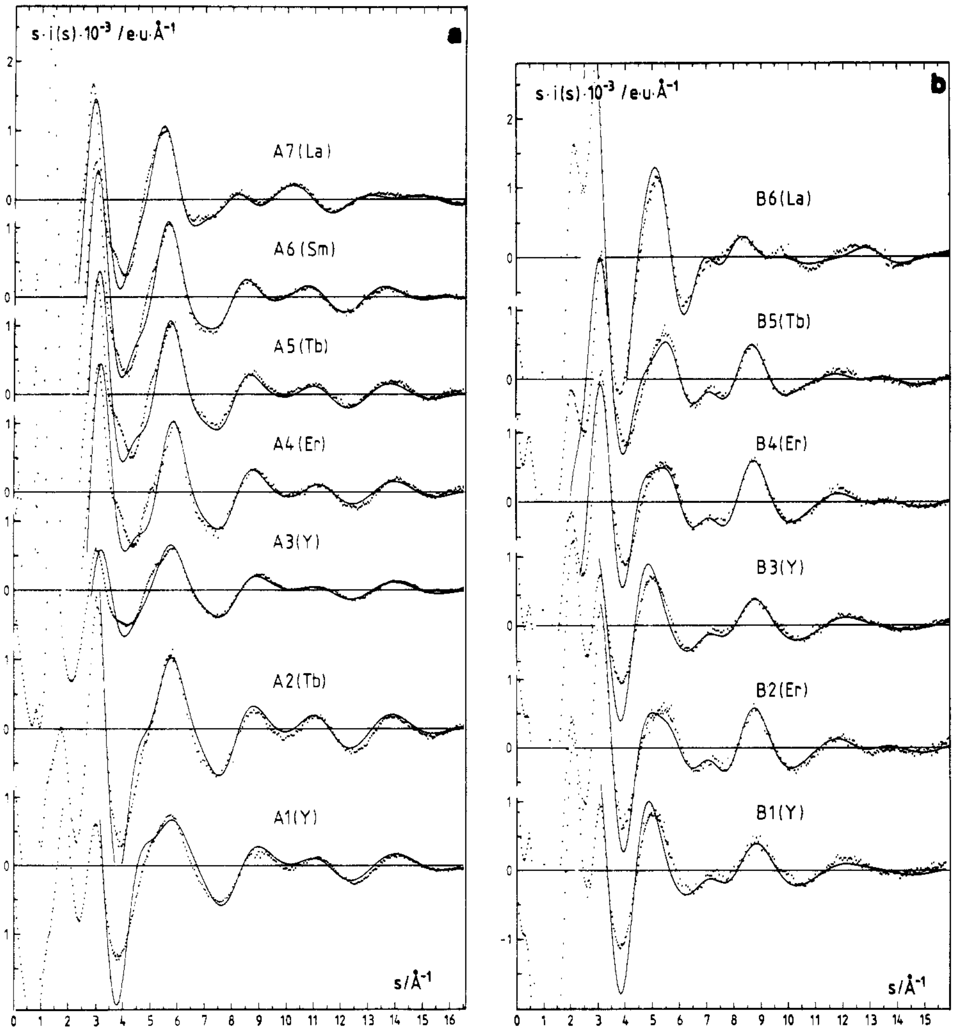

Figure 1. Observed intensity values, $s\ i(s)$, given as dots, compared with theoretical values (solid lines) calculated with the parameters in Table II: (a) perchlorate solutions; (b) selenate solutions.

on the receiving side of the goniometer, and the scintillation counter was equipped with a pulse-height analyzer and discriminator. The θ range covered (2θ is the scattering angle) was $0.8° < \theta < 70°$, with opening slits of $^1/_{12}$, $^1/_4$ and 1° being used. Intensities were measured at intervals of 0.1° for $\theta < 20°$ and 0.25° for $\theta > 20°$. The number of counts collected at each position was 10^5, and each scattering curve was scanned twice, resulting in a statistical error of 0.22% in the number of counts for each point. The amount of Compton scattering reaching the counter was estimated from the spectrum of the X-ray tube and was checked by comparing measurements at large θ angles with a Zr filter placed either before or after the sample.

Data Treatment

The scattering data were corrected for polarization in the sample and in the monochromator, Compton scattering, absorption, and multiple scattering and were normalized to a stoichiometric unit of volume containing one metal ion. The K absorption edge of yttrium is close to the wavelength used, and a correction for fluorescence radiation was made for the concentrated yttrium perchlorate solution by subtracting a constant intensity from the scattering curve. No correction was needed for the 1 M yttrium solutions.

Scattering factors, $f_i(s)$, for neutral atoms corrected for anomalous dispersion were used. Values for incoherent scattering were corrected for the Breit–Dirac effect.[14]

The data treatment was done as described in a previous paper.[15] Electronic radial distribution functions were calculated from the reduced intensities, $i(s) = I_{\mathrm{obsd}}(s) - \sum n_i f_i^2(s)$, where $s = 4\pi\lambda^{-1} \sin \theta$, according to the expression

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{s_{\max}} s\ i(s) \sin (rs)\ M(s)\ ds$$

Here $\rho_0 = (\sum n_i Z_i)^2/V$, with Z_i being the atomic number of atom "i", V is the stoichiometric unit of volume chosen, and the modification function $M(s) = f_0^2(0) f_0^{-2}(s) \exp(-0.01 s^2)$. Theoretical intensities for a discrete interaction were calculated as

$$f_p(s) f_q(s) \sin (s r_{pq}) / ((s r_{pq}) \exp(-b_{pq} s^2))$$

r_{pq} is the distance between the two atoms involved, and b is related to the root-mean-square variation in the distance: $l_{pq} = (2 b_{pq})^{1/2}$. Corresponding theoretical peaks were calculated by a Fourier inversion in the same way as for the experimental curves with the same modification function and integration limits.

The experimental intensity curves were corrected for low-frequency contributions resulting in peaks below 1.0 Å in the RDFs, not related to interatomic distances (O–H in H_2O).

All calculations were carried out by means of the KURVLR program.[15]

Discussion of the Results

Experimental $s\ i(s)$ functions and corresponding $D(r)$ and $D(r) - 4\pi r^2 \rho_0$ functions are shown in Figures 1–3.

The first peak (~1.5 Å) in the distribution curves (Figure 2) corresponds to Cl–O (Se–O) distances within the tetrahedral ClO_4^- (SeO_4^{2-}) groups. The second peak (~2.5 Å) includes contributions from Ln–H_2O interactions in the hydrated Ln^{3+} ions and from O–O interactions in the ClO_4^- (SeO_4^{2-}) groups. The third peak (~2.9 Å) is due to H_2O–H_2O (O) interactions. In the selenate solutions a peak at ~3.7 Å has no correspondence in the perchlorate solutions (Figure 3). It occurs at a distance that would

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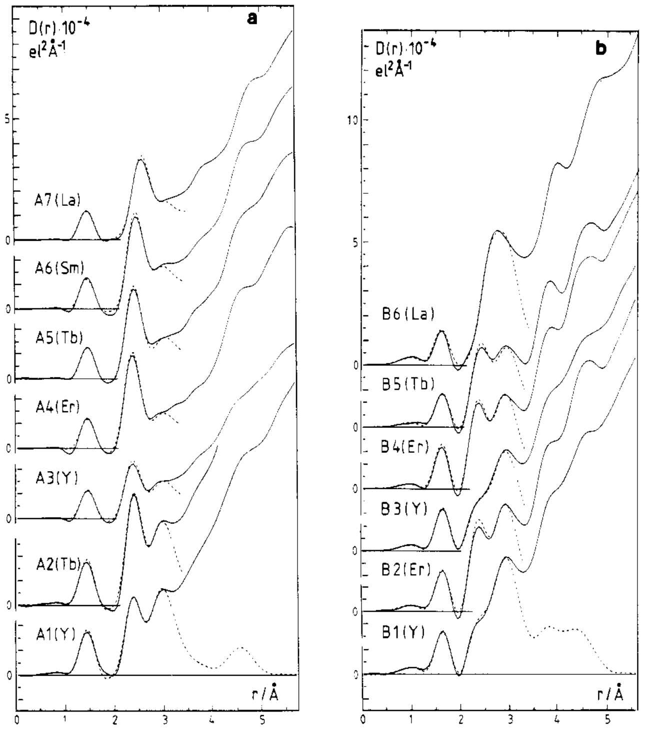

Figure 2. $D(r)$ functions (solid lines) compared with theoretical peaks (dashed lines) calculated with parameters given in Table II: (a) perchlorate solutions; (b) selenate solutions.

be expected for an Ln–Se interaction in an inner-sphere complex. It may also contain contributions from Se–H_2O distances in a hydrated SeO_4^{2-} ion. The 4.5-Å peak in each solution probably corresponds largely to Ln–H_2O interactions in a second coordination sphere.

For the anions, ClO_4^- and SeO_4^{2-}, structural parameters (i.e. distances, d, and rms variations, l) were determined from the well-resolved Cl–O and Se–O peaks at about 1.5 Å (Figure 2). The results are given in Table II. The Ln–H_2O distances in the 1st coordination sphere, which are needed for the following analysis of the difference curves, were then determined. This was done by matching calculated Ln–H_2O peaks with peaks in the $D(r)$ functions that remain after subtracting the known intramolecular ClO_4^- and SeO_4^{2-} interactions. In this procedure approximate values for the coordination number, n, and the rms variation, l, were also obtained. Water–water interactions at ~2.9 Å were included since they partly overlap the Ln–H_2O interactions. The values obtained for the Ln–H_2O distances are given in Table II. They are not affected by small variations in the other parameters, which were not precisely known at this stage. This was confirmed by later repeating the calculations with the parameter values finally determined from the substitution difference curves.

Within each pair of "isomorphous" solutions (A1–A2, A3–A4, B1–B2 and B3–B4 in Table I) the RDFs are closely similar except for an expected reduction in size of peaks in which yttrium is involved (Figure 3). This supports the assumption of an isomorphous substitution causing no structural change in the solution.

The $D(r)$ functions for the four pairs of solution and the corresponding difference curves are shown in Figure 4. In the difference curves, which for an isomorphous substitution should contain contributions from interactions involving the metal ions only, the first coordination sphere is clearly indicated by the peak at ~2.5 Å. A second coordination sphere appears as a peak at ~4.5 Å, which is well-defined toward the Ln^{3+} ion but rather diffuse toward longer distances. In the selenate solutions the peak at ~3.7 Å is still present, which confirms that it represents an Er–Se distance in an inner-sphere complex.

Theoretical (Ln–Y) difference peaks, calculated with the use of the distances in Table II and by taking into account the minor deviations in concentration for some of the solutions (Table I), were now compared with peaks in the $D(r)$ difference curves (Figure 4), and values for the coordination numbers, n, and the rms variations, l, were determined (Table II). None of the observed peaks showed significant deviations from theoretical peaks calculated for $n = 8.0$. From a comparison with peaks calculated

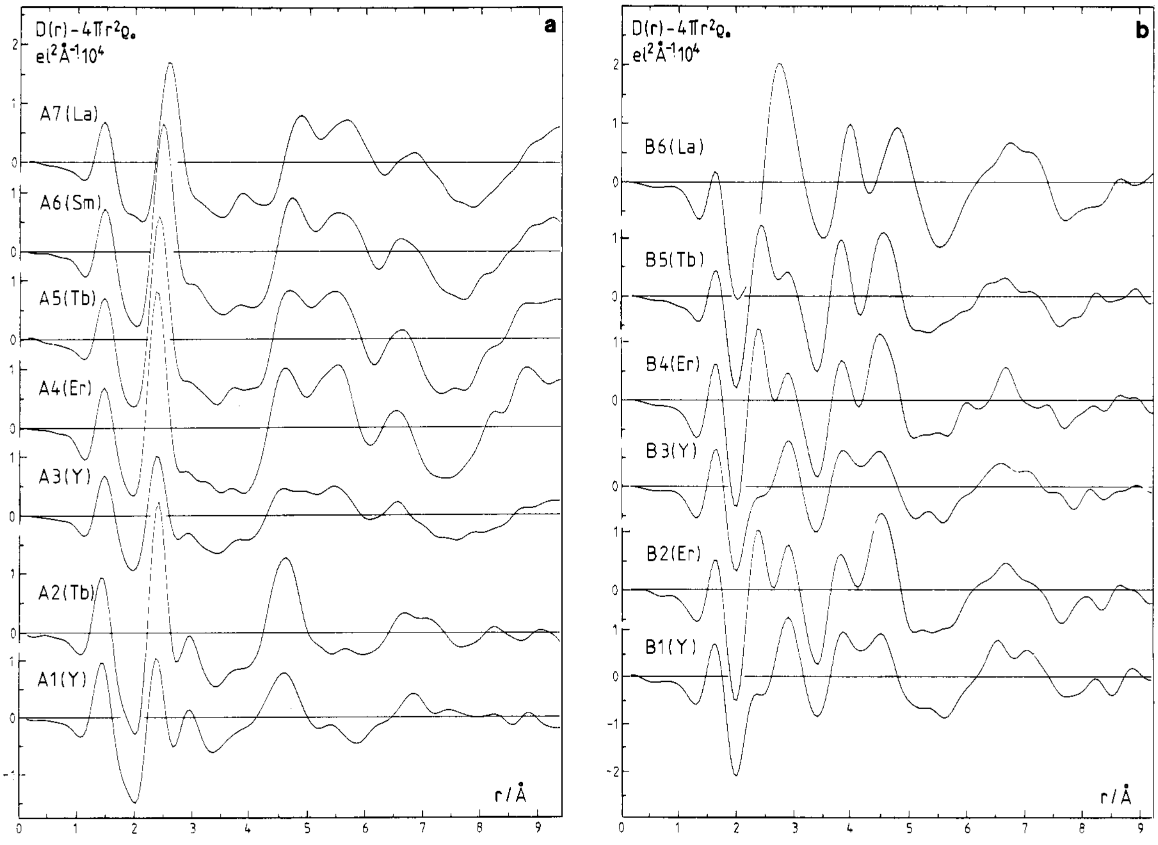

Figure 3. $D(r) - 4\pi r^2\rho_0$ functions for the solutions investigated, normalized to a stoichiometric unit of volume containing one Ln ion: (a) perchlorate solutions; (b) selenate solutions.

Table II. Parameter Values Determined from the Solution Diffraction Data[a]

	coord sphere										
	first			second			Ln-Se			XO_4	
solution	*d*	*l*	*n*	*d*	*l*	*n*	*d*	*l*	*n*	*d*	*l*
A1 (Y)	2.370	0.063	8.0	4.52	0.20	9				1.429	0.045
A2 (Tb)	2.400	0.077	8.0	4.56	0.20	9				1.429	0.042
A3 (Y)	2.365	0.084	8.0	4.52	0.27	15				1.450	0.045
A4 (Er)	2.360	0.100	8.0	4.52	0.27	15				1.446	0.040
A5 (Tb)	2.400	0.100	8.0	4.60	0.26	14				1.450	0.040
A6 (Sm)	2.455	0.089	8.0	4.63	0.24	12				1.448	0.037
A7 (La)	2.570	0.089	8.0	4.70	0.26	13				1.448	0.042
B1 (Y)	2.330	0.100	8.0	4.47	0.21	11	3.75	0.08	0.35	1.628	0.040
B2 (Er)	2.345	0.100	8.0	4.47	0.21	11	3.75	0.08	0.35	1.633	0.040
B3 (Y)	2.325	0.100	8.0	4.47	0.22	11	3.75	0.12	0.60	1.640	0.040
B4 (Er)	2.340	0.100	8.0	4.47	0.22	11	3.75	0.12	0.60	1.630	0.040
B5 (Tb)	2.380	0.110	8.0	4.50	0.22	11	3.78	0.12	0.60	1.635	0.040
B6 (La)	2.560	0.110	8.0	4.70	0.22	11	3.93	0.12	0.60	1.621	0.040

[a] For each interaction the distance, *d* (Å), its rms variation, *l* (Å), and its frequency, *n* (per Ln^{3+}), are given. The ClO_4^- and the SeO_4^{2-} groups are assumed to form regular tetrahedra, and only the Cl–O or Se–O distances are given. Parameters determined for H_2O–H_2O (O) interactions are approximately equal and are not given separately for each solution. Values used were $d = 2.91$–2.95 Å, $l = 0.18$–0.21 Å, and $n = 2.4$–2.7 (per O). Hydration of the ClO_4^- and the SeO_4^{2-} groups were included as Cl(Se)–H_2O interactions at $d = 3.80$ Å (ClO_4^-) or 3.95 Å (SeO_4^{2-}), $l = 0.3$ Å, and $n = 8$.

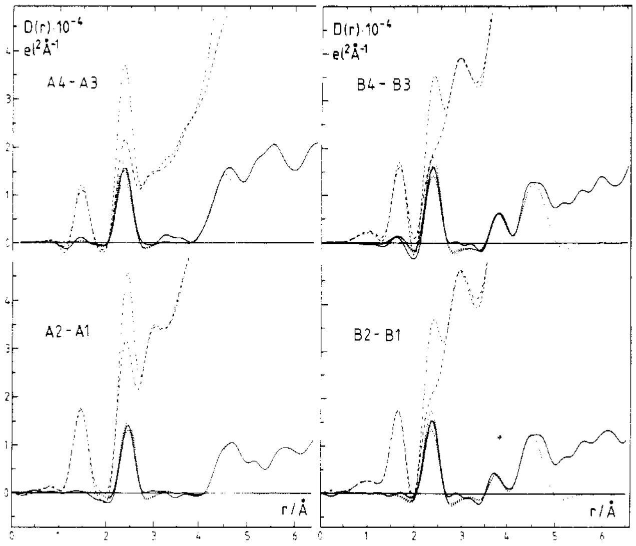

Figure 4. Radial distribution curves for the four pairs of "isomorphous" solutions (dashed lines), the corresponding differences curves (solid lines), and calculated curves (dotted lines) obtained with the use of the parameters in Table II. For comparison purposes, theoretical peaks, assuming coordination numbers of 7.0 and 9.0, are also included (dotted lines).

for different *n* values (Figure 4) the uncertainty was estimated not to exceed ± 0.3. A more precise estimate did not seem justified, and the coordination number is thus determined to be 8.0 ± 0.3 for all of the solutions. Within the accuracy of the determination the coordination number thus seems to be independent of both the concentration and the anion. For the selenate solutions the Ln–H_2O distance is slightly shorter and the rms value is slightly higher than for the perchlorate solutions (Table II). No obvious asymmetry in the peaks is observed. If differences between Ln–H_2O distances within the first coordination sphere do occur, as has been found in many crystal structures, they are contained within the rms value of ~0.10 Å and cannot be distinguished by the solution scattering data.

The peak corresponding to the second coordination sphere differs in shape between the solutions and cannot be fully reproduced by a single interaction peak. The parameters used for the theoretical peaks in Figure 4 are those given in Table II.

By combining the Ln–Se distance of 3.75 Å with the Ln–H_2O and the Se–O distances in the selenate solutions (Table II) a value of ~140° can be calculated for the Ln–O–Se angle in the Ln–SeO_4 complex. Similar values have been found in crystal structures when selenate (or sulfate) groups are bonded directly to the Ln^{3+} ion. Rotation of the SeO_4^{2-} group around the Ln–O bond can take place with no change in the Ln–O–Se angle. If a preferred orientation occurs, it cannot, however, be determined from the scattering data since contributions from the Ln–O(SeO_4) interactions to the second coordination sphere are too weak to be distinguished. The shortest possible Ln–O(SeO_4) distance for an Ln–O–Se angle of 140°, excepting the O belonging to the first coordinations sphere, is 4.0 Å, and the theoretical peak for the Ln–SeO_4 complex in Figure 4 has been calculated for an orientation that leads to that conformation. The average number of SeO_4^{2-} groups bonded to Er^{3+} (Y^{3+}) is found to be about 0.35 for B1 and B2 and about 0.6 for the nearly saturated solutions B3 and B4, which also have a slightly higher SeO_4/Er(Y) ratio.

In the perchlorate solutions no inner-sphere complex formation is indicated (Figure 4). In the concentrated solutions, however, several peaks appear beyond the second coordination sphere at 4.7 Å (Figure 3a), which may be related to an ordering of the perchlorate groups outside the first coordination sphere.

Derivation of the Coordination of Other Ions in the Series

With use of the parameter values determined from the difference curves for the intramolecular interactions in the yttrium solutions (Se(Cl)–O and O–O in SeO_4^{2-} (ClO_4^-), Y–H_2O in the first and, in part, in the second coordination spheres, and Y–SeO_4), we can subtract the corresponding theoretical peaks from the distribution curves. The remaining curves will then represent contributions from all other interactions in the solution, and up to about 4.7 Å, they will contain only interactions that do not involve yttrium or intramolecular SeO_4^{2-} (ClO_4^-) distances. If we assume these remaining curves to be approximately unchanged if yttrium is replaced by other lanthanoid ions, we can apply them to the distribution curves of these ions and derive the interactions involving the lanthanoid ions only (up to ~4.7 Å). The resulting curves for the 3 M perchlorate solutions and the 1 M selenate solutions are shown in Figures 5 and 6. They have the same characteristics as the difference curves in Figure 4, although scaled up as they are now "Ln" and not "Ln–Y" peaks. The peak positions reflect the differences in ionic radii of the Ln^{3+} ions. Theoretical peaks, calculated with the use of the parameters given in Table II, are compared in Figure 5 with those observed. Among the selenate solutions in Table I the only pair precisely matched is B1–B2. The other solutions were prepared in order to achieve as strong Ln–Se interactions as possible and were all saturated or nearly saturated. For the derivation of the curves in Figure 6 the light-atom interactions were estimated in the following way: In order to compensate for the different Ln^{3+} concentrations, the stoichiometric unit of volume for the Y^{3+} solution was chosen to contain the same number of oxygen atoms as for the comparison solution. From the distribution curve the known intramolecular interactions were then subtracted, and the remaining curve was

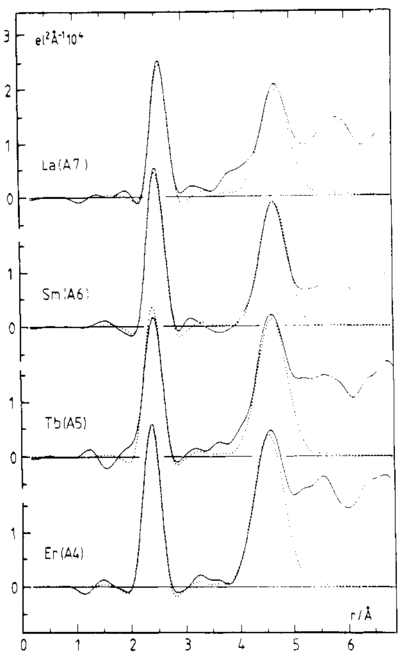

Figure 5. Distribution curves (solid lines) for the perchlorate solutions after subtraction of light-atom interactions compared with theoretical peaks (dotted lines) calculated for Ln–H_2O interactions in the first and second coordination spheres by using the parameter values in Table II.

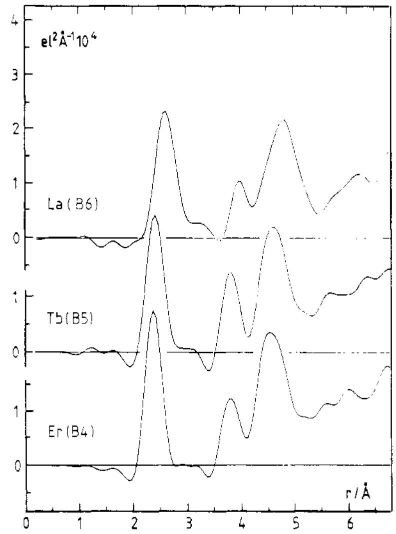

Figure 6. Distribution curves for the selenate solutions after subtraction of light-atom interactions.

used as an approximation for the light-atom interactions in the comparison solution. This seems to be a satisfactory approximation in the distance region up to the first coordination sphere. It is probably less satisfactory at longer distances, where the peak sizes may be less reliable. For that reason no quantitative evaluation of the curves in Figure 6 is made by comparing them with theoretical peaks. The general features of the curves are not expected to be affected by this, however. They indicate the same type of complex formation throughout the series.

The use of the light-atom interactions derived from the yttrium solutions assumes that they do not change when Y^{3+} is replaced by a larger Ln^{3+} ion. This is probably a good approximation for most of the interactions but is obviously not true for the H_2O–H_2O interactions within the first coordination sphere. As these distances are relatively close to the Ln–H_2O distances, a change may affect the peak of the first coordination sphere. This effect should be most pronounced for the lanthanum ion, which differs most in size from the yttrium ion. Assuming a regular cubic coordination around the metal ion, the shortest H_2O–H_2O distance, from the Y^{3+}–H_2O and La^{3+}–H_2O distances in Table II, should increase from 2.72 Å for Y^{3+} to 2.97 Å for La^{3+}. The influence this would have on the La–H_2O peak in the derived curves (Figure 5) can be estimated by including them in the calculations. Since the H_2O–H_2O distance is shorter in the Y solution, a subtraction of these H_2O–H_2O contributions would tend to increase the size of the La–H_2O peak in the derived curve, which is not balanced by including the corresponding distances in the theoretical peak for La^{3+}. The magnitude of the difference will depend on the assumptions made about the coordination and, to some extent, on the sharpening used in the Fourier inversion. For a very low rms value, l, for the H_2O–H_2O distances, i.e. for small variations in the distances and, therefore, a rather sharp H_2O–H_2O peak, calculations show that the increase can amount to almost one La–H_2O interaction but would be smaller for the smaller lanthanoid ions. For a larger and more likely rms value the increase would be negligible. If, on the other hand, we assumed a coordination number of 9 for La^{3+} and 8 for Y^{3+}, the H_2O–H_2O distances around La^{3+} would be expected to be smaller ($\sim 8/9)^{1/2}$ $2.97 = 2.80$ Å) and the effect would not arise. The theoretical peaks shown in Figure 5 have been calculated without including H_2O–H_2O interactions within the coordination spheres of the Y^{3+} and the Ln^{3+} ions.

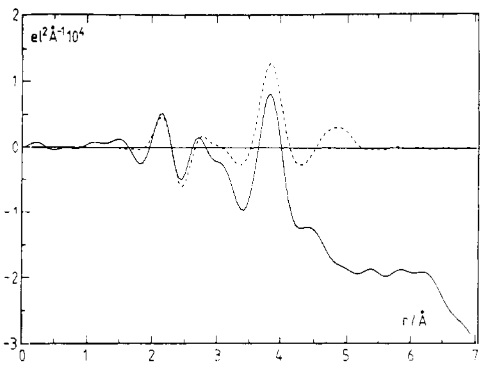

Figure 7. Difference (solid line) between the $D(r)$ functions for the 1 M terbium selenate and perchlorate solutions compared with a difference curve (dashed line) calculated by using the parameters in Table II.

The discussion shows that the results do not seem to give support for different coordination numbers within the lanthanoid series, but this conclusion is subject to the assumptions made about the coordination polyhedra.

Selenate–Perchlorate Difference Curves

In a chemical system of some complexity the separate intermolecular interactions can never be derived from the distribution curves alone. They usually appear as a rather diffuse background curve on which the much more well-defined intramolecular interactions are superimposed. This is brought out by the direct comparison between a selenate and a perchlorate solution shown in Figure 7. It is given as the difference between the distribution curves, after subtraction of the intramolecular SeO_4^{2-} and ClO_4^- interactions, and it is compared with a theoretical curve obtained as the difference between peaks for the first coordination spheres calculated with the parameters in Table II, including the Tb–SeO_4 interactions for the selenate solution.

The theoretical curve reproduces very closely the experimental one. The gradient at $\sim$2.4 Å results from the slight difference in d and l values for the Tb–H_2O interactions between the selenate and the perchlorate solutions (Table II), and the sharp peak at 3.7 Å corresponds primarily to the Tb–Se interaction. Thus all significant details in the difference curve can be derived from the intramolecular interactions. Despite the rather pronounced difference in composition between the two solutions, the intermolecular interactions thus appear mainly as a diffuse background curve without sharp peaks that can hide the contributions from the intramolecular interactions.

Concluding Remarks

A summary of parameter values determined from the scattering data is given in Table II. The agreement between observed and calculated $s\ i(s)$ and $D(r)$ functions for the individual solutions is shown in Figures 1 and 2.

The bond lengths in the ClO_4^- and the SeO_4^{2-} ions are close to values found in crystal structures (1.44 Å for Cl–O and 1.65 Å for Se–O[16]), and variations between the different solutions can probably be taken as a measure of the uncertainty in the determinations.

For the first coordination sphere probable errors can be estimated to about ±0.005 Å for the Ln–H_2O distances and about ±0.3 for the coordination numbers. For all of the solutions a coordination number of 8.0 is consistent with the data. The Ln–H_2O distances in the perchlorate solutions are all about 0.010 Å shorter than those determined by Habenschuss and Spedding for concentrated chloride solutions.[8] Their values are 2.580 Å for La^{3+}, 2.474 Å for Sm^{3+}, 2.409 Å for Tb^{3+}, and 2.369 Å for Er^{3+}. For the selenate solutions our values are about 0.02 Å shorter than for the corresponding perchlorate solutions. The rms variation of the Ln–H_2O distances are about 0.09 Å for the perchlorate solutions and are slightly higher, about 0.11 Å, for the selenate solutions (Table II).

Marcus[17] has given least-squares-fitted values of the radii of lanthanide aqua ions based on solution diffraction data and molecular dynamics calculations. From these radii and his value of 1.393 Å for the average radius of a molecule of water in the first hydration shell, the expected Ln–H_2O distances can be calculated to be 2.51 Å for La^{3+}, 2.45 Å for Sm^{3+}, 2.41 Å for Tb^{3+}, and 2.37 Å for Er^{3+}. Within the limits of error given, these values are fully consistent with those found here for the hydrated ions in the perchlorate solutions (Table II).

The second coordination sphere appears as a distinct peak at about 4.6 Å, the distance being dependent on the size of the Ln^{3+} ion (Table II). Not surprisingly the peak is rather diffuse toward longer distances and cannot be fully reproduced by a single interaction peak. The distances given in Table II are those obtained when a theoretical peak is fitted to the well-defined inner side of the observed peak (Figures 4–6). The distances are of a magnitude expected for a second coordination sphere. In a neutron investigation of a concentrated $NdCl_3$ solution Narten and Hahn determined the orientation of the water molecules in the first coordination sphere and found the Nd–O and the Nd–H distances to be 2.48 and 3.13 Å, respectively.[9] If we assume a linear hydrogen bond of a normal length of 2.8 Å between H_2O in the first and the second coordination spheres, the latter will appear at a distance from Nd^{3+} of 4.7 Å. The value found here for samarium, which is close to neodymium in the series, is 4.63 Å (Table II).

A complex formation can be established by identifying intramolecular interactions in the complex, and this requires a structure with well-defined bond distances and angles. An inner-sphere complex formation must lead to Ln–Cl and Ln–Se distances shorter than about 4.0 Å and, therefore, well separated from the peak for the second coordination sphere (Figure 4). No Ln–Cl peak is present in that region for the perchlorate solutions, but for the selenate solutions a Ln–Se peak at 3.75 Å (for Er^{3+}) does occur. This leads to an Er–O–Se angle of 141° if combined with the distances 2.34 Å for Er–O and 1.63 Å for Se–O (Table II). If the selenate group is rotated around the Er–O bond, keeping the Er–O–Se angle and, therefore, the Er–Se distance constant, the shortest possible distance between Er and any of the other selenate oxygens will be 4.04 Å. The SeO_4^{2-} group thus forms an inner-sphere complex with a monodentate bonding to the Er^{3+} ion. Only about 0.5 SeO_4^{2-} groups are bonded to the average Er^{3+} ion in the solutions investigated (Table II). The weak complexing power of the ClO_4^- ion is well-known and is the reason for using it here for a comparison with a complex-forming anion. The analysis of the scattering data confirms that inner-sphere perchlorate complexes are not formed even in very concentrated solutions.

No investigation of complex formation between selenate and lanthanoid ions seems to have been reported in the literature. For the sulfato ligand stability constants, primarily for the monosulfate complex, have been reported.[18,19] If applied to the solutions used here, these constants would indicate a somewhat more extensive complex formation than that derived from the scattering data. Thermodynamic parameters[20] have been interpreted to indicate predominantly inner-sphere complex formation with sulfate in agreement with ultrasonic evidence.[21] Recently, thermodynamic and spectroscopic evidence has been interpreted in favor of a predominantly outer-sphere character for the $LaSO_4^+$ complex.[22] A recent study of the luminescence lifetimes in the Eu^{3+}–SO_4^{2-}–H_2O system indicates the formation of inner-sphere complexes over a wide concentration range.[23]

In crystal structures of rare-earth-metal selenates (and sulfates) the anions are usually bonded as inner-sphere complexes forming bridges between the cations. The Ln–O–Se angles show rather large variations but seem to be scattered around an average of about 140°. Values reported for $Ce_2(SeO_4)_3{\cdot}5H_2O$[24] are 148, 157, and 95°, for $Yb_2(SeO_4)_3{\cdot}8H_2O$,[25] which is isostructural with the sulfate, 150 and 128°, and for $La_2(SeO_4)_3{\cdot}12H_2O$ 109–152°.[26]

For the perchlorate solutions no inner-sphere complex formation is indicated. For the 3 M solutions, however, a number of peaks appear beyond about 5 Å in the RDFs, which are not present in the 1 M solutions (Figure 3a). This obviously results from an ordering of the structure when the number of H_2O per Ln^{3+} decreases. The peak positions occur at distances that seem possible to relate to ClO_4^- groups taking up ordered positions outside the first coordination sphere. By evaporation of the perchlorate solutions, crystals having the composition $Ln(H_2O)_6(ClO_4)_3$ can be obtained. A structure determination shows that the ClO_4^- groups, which are partly disordered, reside outside the first coordination sphere. The coordination of the Ln^{3+} ions is octahedral and is thus lower than found in the solutions, and as a consequence, the Ln–H_2O distances are shorter in the crystals than in the solutions.[27]

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Registry No. Er, 7440-52-0; Tb, 7440-27-9; La, 7439-91-0; Sm, 7440-19-9; $La(ClO_4)_3$, 14017-46-0; $Sm(ClO_4)_3$, 13569-60-3; $Tb(ClO_4)_3$, 14014-09-6; $Er(ClO_4)_3$, 14017-55-1; $La_2(SeO_3)_3$, 16354-21-5; $Er_2(SeO_3)_3$, 71935-43-8; $Tb_2(SeO_3)_3$, 71935-45-0; $Y_2(SeO_3)_3$, 21147-52-4; $Y(ClO_4)_3$, 14017-56-2.

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