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Structural Parameters of the Nearest Surrounding of Lanthanide Ions in Aqueous Solutions of Their Salts

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Abstract—Published data on the structural characteristics of the local surrounding of lanthanide ions in aqueous solutions of respective salts obtained by different research methods under standard conditions are reviewed. Structural parameters like the coordination number, interparticle distance, parameters of the second coordination sphere, and types of ionic association are discussed.

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Study of the structure of aqueous solutions of electrolytes is an important task of the modern chemistry. This is due both to the need to address the challenges faced by the basic science, and to the use of a variety of solutions in versatile branches of industry and economy. For a number of ions the structural parameters of the nearest surrounding in solution have already been found with sufficient reliability. Reviews [1, 2] summarize the studies carried out before 1986 and 1993, respectively. But with respect to some ions there is still a significant uncertainty. This concerns the lanthanide ions. Despite the fact that these cations are considered to manifestat in aqueous solutions the so-called *gadolinium effect*, namely, the change of coordination number from nine to eight in the middle of the series, currently neither clarity in this issue, nor uniquely defined characteristics of the ions themselves were reached. This article, while continuing a series of studies on the structure of aqueous solutions of electrolytes under standard conditions [3–5], is aimed at generalization of the available literature data on the structural parameters of lanthanide hydration like coordination number, interparticle distances, the characteristics of ion pairs, and refinement of the above parameters on the basis of the material published to the date.

First we reviewed the studies on the structure of the local surrounding of the La^{3+} ion, because the structures of the hydrated complexes of the other cations could be understood easier when the parameters of the ions of the first row are known. Then, in order to identify the problems, we give a brief review of the studies of the lanthanide ions solutions as a whole. Then we analyze the results for each specific ion, to focus on the characteristics interesting to us in each case, to estimate the volume of work concerning the discussed system, and to estimate the accuracy of the found parameters. The main objective of this work is to tabulate the best quantitative parameters of the local surrounding of lanthanide ions. This will contribute to further development of models of the electrolyte solutions and to rapid assessment of the structural properties of hydrated complexes of lanthanide ions.

Structure of the closest surrounding of the La^{3+} ion. The La^{3+} ion is the first element of the lanthanide series, therefore numerous studies of coordination properties were performed with this cation. In the trifluoromethanesulfonate, ethyl sulfate, and bromate crystal hydrates the La^{3+} ion coordinates nine water molecules in the form of three-cap trigonal prism with the average distances to the nearest molecules 0.2515 nm, and to distant ones, 0.2614 nm [6–8]. Determining the parameters of the coordination spheres of the cation in solution is much more complicated. A rather long time ago the aqueous solution of lanthanum perchlorate was investigated by NMR spectroscopy, and the cation coordination number was estimated as equal to six [9], the value was clearly underestimated. Pioneering X-ray diffraction (XRD) studies included the study by Smith and Wertz of aqueous solutions of lanthanum chloride in a concentration range from 1.54 to

2.67 mol kg^{-1} with and without the hydrochloric acid additives [10]. It was found that the cation was surrounded by eight water molecules located at a distance of 0.248 nm. Later on, the same group investigated concentrated aqueous solutions of lanthanum bromide [11]. The La^{3+} was found to coordinate 8.0±0.2 water molecules at an average distance of 0.248 nm. Based on the XRD data on the the isomorphous substitution of aqueous solutions of lanthanum selenate (0.70 M) and perchlorate (2.88 M) the cation coordination number was determined equal to eight [12]. The distance to the coordinated water molecules is 0.256 nm in the selenate solution and 0.257 nm in the solution of lanthanum perchlorate. The La^{3+} ion forms the second coordination sphere located at an average distance of 0.470 nm and consisting of 11 water molecules in selenate and 13 in perchlorate solutions. However, more recent studies suggest the lanthanum coordination number to be *CN* = 9. Indeed, XRD research on the $LaCl_3$ 3.8 M aqueous solution showed that the basic structural unit of the system was the complex $[La(H_2O)_9Cl_2]^+$ hydrated additionally in the second coordination sphere. The cation is surroundded by nine water molecules at a distance of La^{3+}–OH_2 0.255 nm forming a three-cap trigonal prism. The distance to about six molecules of water in the second coordination sphere, La^{3+}– H_2O_{II}, is 0.460 nm. In addition, the second coordination sphere includes two chloride ions [13].

In a molecular dynamics study of aqueous solutions of lanthanum chloride a high value of the cation coordination number was unexpectedly found [14]. In an infinitely dilute solution, the *CN* was found to equal twelve. Water molecules surround the La^{3+} ion to form an icosahedron (20 facets) at a distance of 0.264 nm. With increasing concentration up to 2 mol kg^{-1} the cation *CN* decreases to 10.2, while the distance La^{3+}–OH_2, to 0.255 nm. The same high value of *CN* = 12 was confirmed by the Extended X-Ray Absorption Fine Structure (EXAFS) method for the dilute aqueous solutions of lanthanum chloride (0.05, 0.1 and 0.2 M, pH = 1) [15]. The La^{3+}–OH_2 distance was determined to be equal to 0.256 nm. Despite the relatively high accuracy of the EXAFS method in determining the distances from the cation to the first coordination sphere, the coordination number is not always possible to find precisely, particularly with regard to large strongly hydrated cations that can distort the resulting spectrum due to the effect of multielectron excitation and the presence of hydrogen atoms. We believe that the *CN* value equal to twelve is highly overestimated. Using the same method, the distance La^{3+}–OH_2 in 0.8 M aqueous solution of lanthanum perchlorate was determined to be equal to 0.2545 nm (at a fixed coordination number equal to nine) [16]. 0.1 M aqueous solution of lanthanum chloride was studied by EXAFS in the presence of 0.2 M HCl (low content of chloride ions) and in the presence of 14 M LiCl (high content of chloride ions). In the first case for the La^{3+} ion *CN* = 9.2 was found and the distance to the coordination sphere, 0.254 nm. In the case of high concentration of chloride ions the La^{3+} ion forms an inner-sphere complex with the chloride ions with the simultaneous loss of water molecules in the coordination sphere. The average number of the anions in the complex and the distance La^{3+}–Cl are, respectively, $N = 2.1$, $R = 0.292$ nm [17].

The investigation of the hydration structure of ions La^{3+} in 0.662 M solution of lanthanum perchlorate by XRD and EXAFS showed that the cation coordinated nine water molecules arranged around it in a three-cap trigonal prism. The distance to the nearest six water molecules is equal to 0.252 ± 0.002 nm, and to three more distant, 0.265 ± 0.003 nm. The results of XRD indicate the presence of the second coordination sphere around the La^{3+} ion consisting of eighteen water molecules at a distance of 0.463 ± 0.002 nm [18, 19]. A similar shape of the first coordination shell was obtained by XRD and EXAFS for the lanthanum chloride and bromide aqueous solutions in a wide concentration range (from 0.51 to 3.40 m for chloride and from 0.46 to 3.17 m for the bromide) [20]. Nine water molecules in the first coordination sphere of lanthanum ions are at an average distance 0.259 ± 0.002 nm and arranged in a three-cap trigonal prism, were found by EXAFS also elsewhere (in 0.007 M aqueous solution of La^{3+} ion) [21]. Monte Carlo calculation of the $La^{3+}(H_2O)_n$ clusters to $n = 9$ showed the predominant formation of the [7+1] and [7+2] structures [22]. From the results of the molecular dynamics it was concluded that in solution hydrated complexes with *CN* = 9 and *CN* = 10 co-existed [23]. They mutually transform into each other in a nanosecond time range as a result of dissociation. The average coordination number is determined as equal to 9.6, while the distance La^{3+}–OH_2, 0.265 nm. Also the presence was found of the second coordination shell, located at an average distance of 0.50 nm, and comprising, on the average, 23.4 molecules of water. We think that the number of water molecules in the second coordination sphere and the distance to them are overestimated. Using the same method it was shown that for the ions La^{3+} $CN = 9.2$ and the distance La^{3+}–O was equal to 0.252 nm, and it was indicated that the complex $La(H_2O)_9{}^{3+}$ was slightly distorted by the [6+3] type, while its structure was a three-cap trigonal prism with D_{3h} symmetry [24, 25]. More recently Duvail et al. have refined the parameters of the first coordination sphere: the distance to 5.31 water molecules arranged as a prism is 0.250 nm, and to 3.69 more distant molecules, is 0.258 nm [26]. The second coordination sphere consists on the average of 18.8 water molecules located at a distance of 0.465 nm. The molecular dynamics study of the structure of the coordination sphere of this ion in highly concentrated aqueous solution of lithium chloride (14 M) [27] showed that the geometry of the coordination sphere is a square antiprism. It consists of two chloride ion at a distance of 0.288 nm and six water molecules at a distance of 0.255 nm.

With regard to ion association, we should note the following results. For the lanthanum chloride aqueous solutions in the concentration range 0.5–3.5 mol kg^{-1} it was found by the method of Raman spectroscopy that in concentrated solutions there were mainly the outer-sphere complexes [28]. The XRD analysis showed that in aqueous solutions of lanthanum chloride in a concentration range from 1.54 to 2.67 mol kg^{-1} with and without addition of hydrochloric acid formed non-contact ion pairs with the La^{3+}–Cl^- distance equal to 0.47 nm (Smith and Wertz [10]). The same group found, while studying by XRD the concentrated aqueous solutions of lanthanum bromide, that hydrate-separated ion pairs formed with the characteristic La^{3+}–Br^- distance equal to 0.48 nm [11]. The hydrate-separated associate with two chloride ions per one cation located at an average distance of 0.500 nm was detected by X-ray investigation in 3.8 M aqueous solution of lanthanum chloride. The value of the La^{3+}–Cl^- distance indicates either a trigonal orientation of the inner-sphere water molecules and the hydrogen bond angle 170°, or orientation at a 30° angle to the plane of water molecules and the linear hydrogen bonds [13]. The same method for aqueous solutions of selenate (0.70 M) and perchlorate (2.88 M) of lanthanum showed the presence of contact ion pairs with the selenate ions at the La^{3+}–O–Se bond angle 140°, which, according to Johansson and Wakita, suggested the monodentate nature of bonding. The La^{3+}–Se distance in the ion pair is 0.393 nm. The inner-sphere complexes with perchlorate ions in the investigated solutions were not detected [12]. The Raman spectroscopy showed that the average amount of nitrate ions associated with one La^{3+} ion in aqueous solution at the molar ratio 1:20 is equal to 1.4 [29]. This, as Kanno and Hiraishi believe, indicates the system of two types of complexes, $[La\ (NO_3)_2]^+$ and $[La(NO_3)]^{2+}$. The investigation of aqueous solutions of lanthanum nitrate, chloride, and perchlorate (pH 4.0–6.5) by NMR spectroscopy showed the presence in all solutions of contact ion pairs $(LaX)^{2+}$ [30]. But in 0.1 M aqueous solutions of lanthanum trifluoromethane-sulfonate (pH = 2) the contact ion pairs were not detected by the same method [31].

From the foregoing it is evident that the most probable coordination numbers of La^{3+} ion are in the range of eight to nine. In our opinion the *CN* equal to eight found in the early X-ray studies does not reflect the actual structure and is somewhat underestimated. This is probably due to the impossibility of correct determination of *CN* of ions at the early stage of development of the XRD method for the study of solutions. We believe that the results of recent studies more accurately reflect the actual structure. Accordingly, we conclude that the *CN* of La^{3+} ion is nine, with the first coordination shell shaped as a three-cap trigonal prism. The average distance to the nearest six water molecules is equal to 0.252 nm, and three molecules are more distant, 0.265 nm. As for the second coordination sphere, the number of molecules in it, on the basis of the published information, is in the range from 6 to 23.4, with the distance from 0.460 to 0.500 nm. Obviously, the lanthanum ion, having a high charge, forms the second coordination sphere. In assessing the number of water molecules in it, we adhere to the assumption that it probably consists of eighteen water molecules (two water molecules in the second shell, which interact with one molecule of the first sphere). It is known that in aqueous electrolyte solutions the interaction of three water molecules in the second shell with one molecule of the first sphere is also possible, but in this case the steric factor prevents such interaction. The distance to the second sphere is probably in the range 0.460–0.465 nm [2, 18]. The discussed cation forms ionic associates with counterions. It can be both contact and noncontact ion pairs, depending on the chemical nature and the anion concentration.

Structure of the local surrounding of lanthanide ions. Lanthanide ions comprise a long series of chemically similar metal ions. Along the series occurs sequential filling of 4*f* orbitals from the La^{3+} ion to ion Lu^{3+}, and the contraction of the ions, that is, a decrease in their ionic radii, due to the increase in the electrostatic field of the nucleus. Rather long ago, it was suggested on the basis of structural studies that the *CN* of the ions in solution changed in the middle of the series from nine to six [32], which was known as the *gadolinium effect*. Based on the measurements of the apparent molar volumes of aqueous solutions of the lanthanide chlorides, nitrates and perchlorates [33, 34], of heat capacity [35] and viscosity [36] of lanthanide chlorides solutions a change was reported in the coordination number from nine in the light to eight in the heavy lanthanide ions. Then, it was noted that the structure of near surrounding of these ions and consequently their coordination number remained unchanged in going from dilute solutions up to saturation [37]. By measurements of laser-stimulated luminescence the change was determined in the coordination number from 10 for ions La^{3+}–Nd^{3+} to 9 in the ions Tb^{3+}–Lu^{3+} [38]. In an early work carried out by XRD, 3.2–3.6 M aqueous solutions of the heavy lanthanide ions chlorides were studied, namely, of $TbCl_3$, $DyCl_3$, $ErCl_3$, $TmCl_3$ and $LuCl_3$ [39]. The *CN* of each of the studied ions was found to be equal to eight. The assumption on the change the *CN* of lanthanide ions in aqueous solutions from nine to eight in the middle of the series was confirmed by XRD study of aqueous solutions of the chlorides at the concentration of 3.2–3.6 mol kg^{-1} [40, 41]. The vast majority of studies by a variety of methods have shown a decrease in *CN* of the lanthanide ions in going from light to heavy ions. For example, this fact was proved by Raman spectroscopy for aqueous solutions of chlorides and nitrates of lanthanides in liquid and in the glass state [29, 42] and by infrared spectroscopy of aqueous solutions of the lanthanide ethyl sulfates [43]. The preference for this change was shown by a theoretical calculation using a simple electrostatic model [44]. The problem is, whether this change occurs sharply in going to some next ion, e.g., gadolinium, or it occurs gradually. Thus, by EXAFS of aqueous solutions of perchlorates of the rare earth elements in molar ratio 1:28 it was found that *CN* of ions changes from nine to eight, and this transition occurs between the ion Sm^{3+}–Ga^{3+} [45]. By using the method of neutron diffraction for aqueous solutions of lanthanide perchlorates in the concentration of 2 M it was established that the change in the *CN* of the cations occurred from 10 to 8 [46]. In another study, also performed using neutron diffraction to study the acidified aqueous solutions of 0.3–1.0 M $Nd(ClO_4)_3$ and 1.0 M $Sm(ClO_4)_3$ the *CN* was found to change from 9 to 8.5 in the case of Sm^{3+} ion [47]. By NMR method it was found that in 1 M aqueous solutions of lanthanide trifluoromethanesulfonate the number of water molecules in the first coordination sphere of the cations varied from 9 in La^{3+}–Sm^{3+} series to 8 in heavier ions, the change occurred at the Eu^{3+} [31]. The change in *CN* from nine to eight was confirmed by the Monte Carlo method [48]. The generalization of the publications confirming these effects is given in [49]. However, based on the results of neutron diffraction analysis it was indicated that this effect is not of a jumping mode, but the change in *CN* occurred gradually, depending on the relative stability of the structures consisting of either eight or nine water molecules in the coordination sphere [50]. As a system where an equilibrium exists between eight- and nine-coordinated hydrate complexes the solution of Eu^{3+} is stated. It is also noteworthy that, at the *CN* of a lanthanide ion equal to nine, the geometry of three-cap trigonal prism was attributed to the coordination sphere, which was found both in crystal and solutions [51, 52]. In the case of *CN* equal to eight the geometry of a two-cap trigonal prism and a square antiprism is possible.

The change in the coordination number in the series of lanthanide ions was also confirmed by the molecular dynamics calculation [53, 54]. Besides, based on the results of this method it was suggested that the change in *CN* from 9 to 8 occurred at the Sm^{3+} ion. In the case of this cation the mechanism of exchange of the ninth water molecule between the first coordination sphere and the solvent bulk is so intense that the equilibrium between the two forms of hydrated complexes $[Sm\ (H_2O)_8]^{3+}$ and $[Sm\ (H_2O)_9]^{3+}$ is maintained [55]. The point of view about the change in *CN* in aqueous solutions of salts of lanthanides in the middle of the series was recognized for some time that was reflected in the survey article [56].

It should be noted that for aqueous solutions of lanthanides the so-called tetrad-effect was discovered expressed as a periodic change in the properties of rare earth elements due to the formation of complex compounds in the aquatic surrounding [57, 58]. According to some studies the nonmonotonic change in the properties can be explained only by quantum effects [59].

There are also some publications including a fundamentally opposite assessment of coordination of the lanthanide ions. Based on the results of IR spectroscopy of dilute aqueous solutions of lanthanide perchlorates the following set of hydration numbers of these ions was suggested: 7.8 ± 0.6 for La^{3+}, 8.0 ± 0.6 for Nd^{3+}, 8.7 ± 0.6 for Dy^{3+} and 8.8 ± 0.6 for Yb^{3+} [60]. The study of the structure of the local surrounding of the ions Nd^{3+}, Gd^{3+} and Yb^{3+} (light, medium, and heavy ion series) in the systems with the molar ratio of 1:342 by the molecular dynamics method showed no change in the coordination number [61]. In all studied ions it was determined to be nine. A modern work carried out using the methods of EXAFS and crystallography to study both crystals and 0.2 M aqueous solutions of lanthanide trifluoromethane-sulfonate has refuted the hypothesis of the *gadolinium effect* [62]. The coordination sphere configuration is suggested to be a trigonal prism with three additional water molecules located at somewhat longer distance, the length and the strength of the bond to three water molecules varying along the series of lanthanide ions. For larger ions (La–Nd) the molecules are equidistant. Starting with the Sm^{3+} ion, a noticeable distortion of the symmetry arises, and it increases in going to the Dy^{3+} ion. For the smallest lanthanide ions (Ho^{3+}–Lu^{3+}), only one of the discussed molecules remains tightly bound to the cation and the remaining two may leave their sites in the coordination sphere. The structure of the hydrated Lu^{3+} ion can be described as consisting of seven water molecules, namely, the six molecules arranged in a prism and a single molecule located at a slightly greater distance. Two other molecules are removed at a distance, which is difficult to determine by the method used. Person et al. argue that there is no abrupt change in the coordination number in the series of lanthanide ions, and the most noticeable change in the coordination sphere occurs in the Ho^{3+} ion. Another explanation of the decrease in the coordination number in a series of lanthanide ions is given in [63]. The coordination of nine water molecules includes six water molecules forming a prism and three molecule in the equatorial position, which eventually leads to the geometry of a three-cap trigonal prism. With increasing atomic number of lanthanide ions, the three separated water molecules become more mobile, and one of them leaves the coordination sphere. All this does not happen abruptly but gradually. Structures with $CN = 9$ and $CN = 8$ are in equilibrium, the geometry is varied between a two-cap trigonal prism and a square antiprism. The equilibrium in going to the heavier lanthanides shifts to the state with eight water molecules in the nearest surrounding of the ion arranged as a square antiprism.

With regard to ion association, we can note the following. Previously, using various methods it has been established that the formation of ion associates depends on the chemical nature of anions. The investigation of the absorption spectra of lanthanide nitrate solutions showed that they form contact ion associates with the nitrate ions [64]. By NMR it was revealed that lanthanide ions do not form contact ion pairs with perchlorate ion, whereas they are formed from the nitrate and acetate ions [65]. The Raman spectroscopy demonstrated that in aqueous solutions of $Ln(SCN)_3$ (Ln, a lanthanide ion) with molar ratio of 1:20 the ion pairs formed through attaching the anion to the cation at the side of the nitrogen atom [66]. An interesting work studying the structure of aqueous solutions of lanthanides (from Nd^{3+} to Lu^{3+} with a cation concentration 1 M) chlorides (HCl content 0 to 6 M) and nitrates (0 to 13 M) was carried out using EXAFS [67]. It was concluded that nitrate ion forms inner-sphere complex with lanthanide ion even at moderate concentrations (~2 M HNO_3), while the chloride ion does not produce it even at relatively high concentrations (~6 M HCl). The oxygen atom of the nitrate ion is located by 0.01 nm further from the cation than the oxygen atoms of water molecules. These findings are in good agreement with the results of a study performed by the method of fluorescent spectroscopy [68]. According to these results, the nitrate ion forms inner-sphere complexes with ions Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} in concentrated aqueous solution, whereas the chloride and perchlorate ions do not form such complexes. In [17] also by EXAFS, on the contrary, was found that lanthanide ions form inner-sphere complexes with chloride ions. Maybe it does not contradict the conclusions of the study [67], because the concentration of Cl^- ions in the said work is very high.

We now consider the structural information about the parameters of the nearest surrounding specific to each lanthanide ion. While tabulating the parameters of the local surrounding of the ions, we were guided by the following approximations:

– The distance from the cation to the first coordination sphere is reduced along the series;

– every light lanthanide ion (the ions at the beginning of the series) coordinates the nine water molecules arranged around it to form a three-cap trigonal prism;

– each heavy lanthanide ion (ions at the end of the series) coordinates eight water molecules arranged around it to form a square antiprism,

– in a solution of intermediate ions there is an equilibrium between nine- and eight-coordinated complexes, which leads to a fractional value of the coordination number. This equilibrium is shifted toward the formation of the coordination sphere of eight water molecules in going to the heavier cations.

Ce^{3+}. The information available to date on the structure of the local surrounding of the ion Ce^{3+} is rather scarce. The XRD study of aqueous cerium nitrate with the molar ratio of 1:25.4 [69] showed that the cation coordinates on the average 7.5 water molecules at a distance of 0.2552 nm. Also it was noted that the Ce^{3+} ion formed the second coordination sphere at a distance of 0.456 nm, consisting on the average of 15.5 water molecules. The XRD study revealed also the presence of the second coordination sphere in aqueous solution of cerium perchlorate with the molar ratio of 1:38 [70]: The second coordination sphere was located at a distance of 0,436 nm and comprised 19.5 water molecules. By EXAFS it was determined that the coordination number of cerium ions in dilute aqueous solutions of cerium chloride (0.05, 0.1 and 0.2 M, pH = 1) was equal to twelve, and the distance Ce^{3+}–OH_2 was 0.253 nm [15]. Using the same method the distance Ce^{3+}–OH_2 in 0.81 M aqueous solution of cerium perchlorate was determined to be 0.2538 nm (at a fixed coordination number equal to nine) [16]. 0.1 M aqueous solution of cerium chloride was studied by EXAFS in the presence of 0.2 M HCl (low content of chloride ions) and in the presence of 14 m LiCl (high content of chloride ions) [17]. In the first case it was found that the coordination number of the Ce^{3+} was 9.3, and the distance to the coordination sphere was 0.252 nm. In the case of high concentration of chloride ions, the Ce^{3+} ion forms inner-sphere complex with the chloride ions with the simultaneous loss of water molecules in the coordination sphere. The average number of anions in the complex and the distance Ce^{3+}–Cl are, respectively, Ce^{3+}, $N = 1.8$, $R = 0.289$ nm. It should be noted that no contact ion pair was detected by NMR in 0.1 M aqueous solution of cerium trifluoromethanesulfonate (pH = 2) [31]. These two facts confirm that the ionic association in solutions of cerium salts depends on the concentration and chemical nature of the anion. Based on studies of aqueous solutions of cerium chloride in a concentration range from 1 M to 2.8 M using XRD and Raman spectroscopy it was concluded that in concentrated solutions there was an "intermediate" order (up to 1.0 nm) [71]. The hydrated complexes $Ce(H_2O)_8^{3+}$ and $Ce(H_2O)_9^{3+}$ were analyzed by varying the density functionals [72]. It is noted that when the second coordination sphere was included in the calculation, in the first case the optimal complex contained 14 water molecules in the second sphere, and in the second case 12 water molecules.

In an advanced study with EXAFS of 0.2 M aqueous solutions of lanthanide trifluoromethanesulfonate it was found that the coordination number of Ce^{3+} ion was 9 with an average distance to the coordinated water molecules 0.254 nm [62]. The molecular dynamics gave similar results: $CN = 9$, $r =$ 0.250 nm [26, 63]. For the two spheres model the following parameters were obtained: $r = 0.248$ nm ($CN = 5.1$), $r = 0.256$ nm ($CN = 3.9$). The second coordination sphere, consisting on an average of 19.3 water molecules, is located at a distance of 0.465 nm.

Ion association depends, as noted above, on the nature of the counterion. In [73] by measuring stability constants the existence was established of the outer-sphere cerium complexes with nitrate ions. However, the Raman spectroscopy revealed the presence of contact ion associates in aqueous solutions of cerium nitrate in a wide range of concentrations [74]. According to this study, the NO_3^- ions may be associated with the cation in both mono- and a bidentate forms. The ion forms contact ion pairs with sulfate ion, whereas with the chloride ion the outer-sphere associates are formed [75]. In solutions with nitrate ion both these types of ion pairs can be formed.

We regard the distances to water molecules as only slightly shorter than those for the lanthanum ion (in accordance with decreasing ionic radius of the cation), namely, 0.250 and 0.263 nm, respectively. Since the parameters of the first sphere of the cerium ion differ little from that of the lanthanum ion, it seems appropriate to make the assumption that the parameters of the second shell of the ions will also be similar. The phenomenon of ionic association is inherent to the cation, therewith the form of ion associates depends on the chemical nature of counterions and the concentration.

Pr^{3+}. The studies determining the structural parameters of hydration of the ion Pr^{3+} are also relatively rare. In the crystal hydrate, the $[Pr(OH_2)_9]I_3$ cation coordinates nine water molecules to form a three-cap trigonal prism with distances of 0.2520 and 0.2541 nm

[76]. By XRD 3.4 and 3.8 M aqueous solutions of praseodymium chloride were studied [40]. The cation coordination number was determined to be nine, with an average distance of Pr^{3+}–$O(H_2O)$ equal to 0.2539 nm. The ion pairs formed with the Pr^{3+}–Cl^- distance equal to 0.50 nm. By neutron diffraction study of 2 M aqueous solutions of praseodymium perchlorate it was found that the cation coordination number was 10 and the distance to the coordinated water molecules was 0.248 nm [46]. By EXAFS of Pr^{3+} ion in dilute aqueous solutions of its chloride (0.05, 0.1 and 0.2 M, pH = 1) its *CN* was determined to be equal to twelve, the Pr^{3+}–OH_2 distance, 0.252 nm [15]. Using the same method the Pr^{3+}–OH_2 distance in 1.4 M aqueous solution of praseodymium perchlorate was determined to be 0.2503 nm (at a fixed coordination number equal to nine) [16]. In a modern study by EXAFS the average coordination number of Pr^{3+} ions in 0.2 M aqueous solution of praseodymium trifluoromethanesulfonate was found as equal to 9 with at an average distance to the coordinated water molecules 0.250 nm [62]. By molecular dynamics similar results were obtained: $CN = 9$, $r = 0.249$ nm [26, 63]. For the model of two spheres the following parameters were obtained: $r = 0.246$ nm ($CN = 5.25$), $r = 0.255$ nm ($CN = 3.75$). The second coordination sphere consisting on an average of 19.3 water molecules is located at a distance of 0.464 nm. The outer-sphere complexes with nitrate ions were revealed [73] by measuring the stability constants.

Thus, the first coordination sphere of the Pr^{3+} ions consists of nine water molecules surrounding the cation in the form of three-cap trigonal prism. Based on the above experimental data and taking into account the decrease in the ionic radius of the cation compared with the previous lanthanide ions, we assume that the distance to the six neighboring and three more distant water molecules is 0.248 and 0.260 nm, respectively. We can also assume that the parameters of the second coordination sphere are only slightly different from those for the second sphere of the ion Ce^{3+}. In our view, the distance interval 0.460–0.465 nm would be suitable as an estimated distance to the second shell of the praseodymium ion. For the cation the ion association is characteristic.

Nd^{3+}. In the crystal hydrate of the neodymium trifluoromethanesulfonate the cation coordinates nine water molecules in the form of a three-cap trigonal prism with distances of 0.2451 and 0.2568 nm [77]. In the crystal hydrate $[Nd(OH_2)_9]I_3$ the corresponding distances are somewhat different: 0.2507 and 0.2519 nm [78]. An interesting finding was obtained in the early studies of the structure of aqueous solutions of lanthanides by spectrophotometric method. According to Karraker, the *CN* of Nd^{3+} ion varies from nine to eight in going from a dilute solution of neodymium chloride to a concentrated one [79]. This is one of a few studies on the effect of concentration on the structure of solutions of lanthanide salts. The studyof the structure of 1.73 M aqueous solution of neodymium chloride carried out by XRD fairly long ago showed that the cation coordination number was eight, the distance to the coordinated water molecules was 0.241 nm, and to the chloride ion present in the solution in contact ion pairs, 0.278 nm [80]. The XRD study of 3.4 and 3.8 M aqueous solutions of neodymium chloride [40] showed that the rare earth cation formed hydrated complexes $[Nd(H_2O)_9]^{3+}$ in each investigated solution. The Nd^{3+}–$O(H_2O)$ distance is 0.2513 nm. The Nd^{3+}–Cl^- distance in the formed ion pairs is 0.50 nm. The coordination of nine water molecules by the Nd^{3+} ion in dilute aqueous solutions of neodymium chloride in both frozen and in liquid states was confirmed on the basis of analysis of the light absorption spectra [81]. In more recent study of $NdCl_3$ 2.85 M solution in D_2O [82, 83] using neutron diffraction it was found that each Nd^{3+} ion was surrounded by 8.6 O atoms and 16.7 D atoms at distances 0.248 and 0.313 nm, respectively. These results indicate the existence of a pronounced hydration sphere consisting of 8.5 ± 0.2 molecules of D_2O, whose D atoms are drawn from the cation at an inclination of 55 ± 2°. Later on, this result was confirmed also by Hahn et al. [84]. In another study of the anion hydration by neutron diffraction of the same solution (2.85 M solution of $NdCl_3$ in D_2O) it was noted that no evidence was found of the formation of contact ion pairs [85]. Using EXAFS spectroscopy the aqueous solution of neodymium perchlorate with the molar ratio of salt:water = 1:28 was investigated, and it was established that the cation coordination number was equal to 9.5, and the distance to the coordinated water molecules was 0.251 nm [45]. In a study using neutron diffraction of 2 M aqueous solution of neodymium perchlorate [46] it was found that the cation coordination number was 10 and the distance to the coordinated water molecules was 0.248 nm. The same value of *CN* (10 ± 0.9) was found in a modern work using XAS in an aqueous solution of neodymium chloride, 0.07 M Nd/0.16 M HNO_3 [86]. However, in most studies, the *CN* of the considered ion is found as equal to nine. Such a value of *CN* was found by the neutron diffraction in acidified 0.3 and 1.0 M aqueous solutions of neodymium perchlorate, with the distance to the first coordination sphere 0.251 nm [47]. The *CN* of Nd^{3+} ion was determined by the molecular dynamics as equal to nine, the Nd^{3+}–OH_2 distance 0.243 nm [53]. Kowall et al. also found that the geometry of the first coordination sphere of this cation is a trigonal prism with three additional water molecules [54]. By EXAFS, the *CN* of Nd^{3+} ion in dilute aqueous solutions of neodymium chloride (0.05, 0.1 and 0.2 M, pH = 1) was determined as equal to twelve, and the distance Nd^{3+}–OH_2 0.248 nm [15]. Using the same method the distance Nd^{3+}–OH_2 in 0.86 M aqueous solution of neodymium perchlorate was determined to be 0.2488 nm (at a fixed coordination number equal to nine) [16].

The 0.1 M aqueous solution of neodymium chloride with low and high content of chloride ions was investigated by EXAFS. In the first case it was found that the coordination number of Nd^{3+} was equal to 9.5, and the distance to the coordination sphere was 0.249 nm. In the second case, the Nd^{3+} ion formed inner-sphere complex with the chloride ions with the simultaneous loss of water molecules in the coordination sphere. The average number of anions in the Nd^{3+}complex and the Nd^{3+}–Cl distance are, respectively, $N = 1.9$, $R = 0.285$ nm [17]. The *ab initio* calculations gave the following parameters of the first coordination sphere of the discussed ion: $CN = 9$, $r(Nd^{3+}–H_2O) = 0.256$ nm [87]. According to molecular dynamics, the *CN* of Nd^{3+} ion in infinitely dilute solution is nine, and the distance to the coordinated water molecules is 0.253 nm [61]. In addition, the cation forms a second coordination sphere consisting of 15 ± 3 water molecules at a distance of 0.458 nm. The next by chronology study was carried out by EXAFS with 0.1 M aqueous solution of neodymium nitrate [88]. The cation coordination number was found equal to 9.1 ± 0.4, and the distance to the coordinated water molecules, 0.2517 ± 0.0004 nm. A Monte Carlo study of the $Nd(H_2O)_n^{3+}$ clusters with different numbers of water molecules [89] showed that only at a large number of solvent molecules ($n = 128$) included in the calculations, the cation coordination number begins to approach the experimentally established value ($CN = 8.6$). The calculated distance Nd^{3+}–H_2O was clearly overestimated (r 0.277 nm), which, according to Hughes et al., was due to the lack of the anion influence. In the work carried out by the EXAFS, the coordination number of Nd^{3+} in 0.2 M aqueous solution of neodymium trifluoromethanesulfonate was found equal to 9 with an average distance to the coordinated water molecules 0.249 nm [62]. The molecular dynamics method showed the same value ($CN = 9$) at a shorter distance (0.248 nm) [26, 63]. For the model of two spheres the following parameters were obtained: $r = 0.246$ nm ($CN = 5.1$), 0.254 nm ($CN = 3.9$); the second coordination sphere consisted on the average of 19.2 water molecules located at a distance of 0.463 nm. In a recent research carried out by molecular dynamics it was found that the discussed ion coordinated 8.9 water molecules, which were located around it to form a trigonal three-cap prism at an average distance of 0.263 nm [90]. The second coordination sphere consisted on the average of 18.8 water molecules at a distance of 0.483 nm, which was slightly greater than the number of water molecules (17.6) determined in [53]. In the modern study by XANES of 0.2 M aqueous solution of neodymium trifluoromethanesulfonate it was found that six water molecules were located around the cation in the form of a prism at a distance of 0.244 nm, and three others, at a longer distance of 0.256 nm [91]. The existence of a second coordination sphere of the cation was confirmed.

It was shown spectroscopically that the formation of ionic associates in the case of aqueous solutions of neodymium salts was strongly dependent on the chemical nature of the cation [92]. From the data on UV spectroscopy, the discussed cation is not prone to form ion associates with the perchlorate ions [93]. As noted above, it was found by EXAFS that the nitrate ion formed with lanthanide ions the inner-sphere complexes even at moderate concentrations (~2 M HNO_3), while the chloride ion does not produce them, even at relatively high concentrations (~6 M HCl) [67]. The formation of contact ion pairs $NdNO_3^{2+}$ in solutions of neodymium nitrate was found in a spectrophotometric study [94]. An NMR study of 0.1 M aqueous solution of neodymium trifluoromethanesulfonate did not reveal the existence of contact ion pairs [31]. The cation forms only non-contact associates also with the SCN^- anions [95].

We suggest that the results of recent studies [91] most accurately reflect the parameters of the first coordination sphere of the Nd^{3+} ion (see the table). The cation forms the second coordination sphere of about eighteen water molecules located at an average distance of 0.460 nm. Ion association occurs primarily with the nitrate ions and is negligible in the case of chloride and perchlorate ions.

Structural parameters of the lanthanide ions hydrate complexes in aqueous solutions of their salts

Cation	Coordination number	$r(\mathrm{Ln}^{3+}–\mathrm{OH}_2)$, nm	Second coordination sphere	$r[\mathrm{Ln}^{3+}–\mathrm{OH}_2(\mathrm{II})]$, nm
La^{3+}	6+3	0.252 0.265	18	0.465
Ce^{3+}	6+3	0.250 0.263	18	0.465
Pr^{3+}	6+3	0.248 0.260	18	0.463
Nd^{3+}	6+3	0.246 0.258	18	0.460
Pm^{3+}	6+3	0.244 0.256	18	0.458
Sm^{3+}	6+3	0.242 0.254	18	0.456
Eu^{3+}	8.8	0.244	18	0.454
Gd^{3+}	8.7	0.242	18	0.453
Tb^{3+}	8.6	0.239	16–18	0.452
Dy^{3+}	8.5	0.238	14–16	0.451
Ho^{3+}	8.4	0.236	14–16	0.450
Er^{3+}	8.3	0.235	14–16	0.449
Tm^{3+}	8.2	0.234	14–16	0.448
Yb^{3+}	8.1	0.233	14–16	0.446
Lu^{3+}	8.0	0.232	14–16	0.445

Pm^{3+}. The local surrounding of the promethium(III) ion was studied using calculation methods and described only in a few works. By quantum-chemical method, the Pm^{3+} ion coordination number was found to be 8.76 [96]. By molecular dynamics the average coordination number of this ion is determined as equal to 8.95, and the distance to the coordinated water molecules, as 0.244 nm [63]. Duvail et al. also refined later the parameters for the model of one sphere, r = 0.246 nm (CN = 9). The second coordination sphere consisting on the average of 18.5 water molecules, was found to be located at a distance of 0.464 nm [26]. We believe that the distance to the second coordination sphere is overestimated.

The average distances to the water molecules listed in the table are 0.244 and 0.256 nm. The second shell consists of approximately 18 water molecules at the distance 0.458 nm. Ion association in aqueous solutions of promethium salts also occurs and is found to depend on the chemical nature of anions.

Sm^{3+}. The XRD study of 3.23 M aqueous solution of samarium perchlorate [41] showed that the Sm^{3+} ion coordination number was 8.8. Water molecules in the first coordination shell are located at a distance of 0.2474 nm. More recently, 2.53 M aqueous solution of samarium perchlorate was investigated by XRD [12], and it was established that the cation coordinated eight water molecules at an average distance of 0.2455 nm. The Sm^{3+} ion forms the second coordination sphere consisting of 12 water molecules located at a distance of 0.463 nm. No formation of ion pairs of cation with perchlorate ions was detected. By quantum-chemical method, the CN of Sm^{3+} ion was obtained as equal to 8.53 [96]. In a study of the aqueous solution of samarium perchlorate with the salt:water molar ratio 1:28 using EXAFS spectroscopy [45] it was found that the cation coordination number was equal to 9.3, and the distance to the coordinated water molecules was 0.245 nm. By the method of neutron diffraction the cation CN in acidified 1.0 M aqueous solution of samarium perchlorate was found to be equal to 8.5

with the distance to the first coordination sphere of 0.247 nm [47]. The same value of the *CN* of Sm^{3+} ion, but with a much smaller Sm^{3+}–OH_2 distance of 0.233 nm, was determined by the molecular dynamics [53]. Kowall et al. consider that such value of *CN* is explainable by an equilibrium in the system of eight- and nine-coordinated hydrate complexes of Sm^{3+} ion [55]. Based on the study of aqueous samarium bromate by the method of luminescent analysis, the cation coordination number was determined to be 9.0 ± 0.5 [97]. By EXAFS, the Sm^{3+}–OH_2 distance in 0.66 M aqueous solution of samarium perchlorate was determined as equal to 0.2455 nm (at a fixed coordination number equal to nine) [16]. The study by EXAFS of 0.2 M aqueous solution of samarium trifluoromethanesulfonate [62] showed that *CN* of the Sm^{3+} ion was 9 with an average distance to the coordinated water molecules of 0.246 nm. The molecular dynamics gave similar structural parameters: $CN = 9$, $r = 0.246$ nm [26, 63]. For the model of two spheres the following parameters were obatined: $r = 0.244$ nm ($CN = 5.36$), $r = 0.253$ nm ($CN = 3.64$). The second coordination sphere consisting on the average of 19.1 water molecules is located at a distance of 0.460 nm.

We assume that the geometry of the first coordination sphere of the Sm^{3+} ion is also a three-cap trigonal prism with a slight decrease in the distances to water molecules to 0.242 and 0.254 nm. The second shell consists of approximately 18 water molecules at a distance of 0.456 nm. For this cation the contact ion association is characteristic, at least with the nitrate ions [67].

Eu^{3+}. The ionic radius of Eu^{3+} is 0.1066 nm [98]. The XRD investigation of 3.23 M aqueous solution of europium(III) chloride [41] revealed the following parameters of the first coordination sphere of Eu^{3+} ion: $CN = 8.3$, the average distance of Eu^{3+}–OH_2 = 0.245 nm. The next study by EXAFS spectroscopy of aqueous europium(III) perchlorate with the molar ratio of salt:water = 1:28 [45] established that the cation coordination number was 8.6, and the distance to the coordinated water molecules was 0.243 nm. By quantum-chemical method the *CN* of Eu^{3+} ion was computed equal to 8.33 [96]. By EXAFS, the *CN* of Eu^{3+} ion in dilute aqueous solutions of europium chloride (0.05, 0.1, and 0.2 M, pH = 1) was estimated at twelve, and the distance Eu^{3+}–OH_2, at 0.241 nm [15]. By molecular dynamics the structural parameters of hydration of the Eu^{3+} ion in a very dilute solution of $EuCl_3$ ($EuCl_3$:225 H_2O) were examined [99, 100]: eight molecules of the first coordination sphere of the cation were arranged in a square antiprism at a distance of 0.245 nm.

By EXAFS the distance of Eu^{3+}–OH_2 in 0.62 M aqueous solution of europium perchlorate was determined to be equal to 0.2424 nm (at a fixed coordination number equal to eight) [16]. The study by EXAFS of 0.1 M aqueous solution of europium(III) chloride of either low or high content of chloride ions showed that at low concentrations of anions the *CN* of Eu^{3+} ion was equal to 9.3, and the distance to the coordination sphere was 0.243 nm. In the case of high concentration of anions the Eu^{3+} ion forms an inner-sphere complex with the chloride ions with the simultaneous loss of water molecules in the coordination sphere. The average number of anions in the complex and the distance Eu^{3+}–Cl are, respectively, $N = 1.1$, $r = 0.281$ nm [17]. It was determined by EXAFS that the cation *CN* in 0.1 M. aqueous solution of europium nitrate was 8.7 ± 0.4, and the distance to the coordinated water molecules, 0.2479 ± 0.0004 nm [88]. In [101] on the basis of XAFS analysis it was revealed that in 0.15 M aqueous solution of europium trifluoromethanesulfonate an equilibrium existed between hydrated complexes $[Eu(H_2O)_8]^{3+}$ and $[Eu(H_2O)_9]^{3+}$. The same conclusion was obtained in the study of a system of Eu^{3+}:60 H_2O by the molecular dynamics method [102]. Note that in the system there is an equilibrium between the hydrated complexes with $CN = 8$ (63.2%) and $CN = 9$ (36.8%). The average coordination number of the cation was determined to be equal to 8.4, the distance to the coordinated water molecules was 0.244 nm. Approximately 15.7 water molecules are in the second coordination sphere at a distance of 0.464 nm. The average coordination number obtained by EXAFS of Eu^{3+} ion in 0.2 M aqueous solution of europium trifluoromethanesulfonate was equal to 9, the average distance to the coordinated water molecules, 0.2425 nm [62]. By the molecular dynamics slightly lower values of structural parameters were obtained: $CN = 8.90$, $r = 0.241$ nm [26, 63]. With the model of two spheres the following parameters were calculated: $r = 0.240$ nm ($CN = 5.48$), $r = 0.249$ nm ($CN = 3.42$). The second coordination sphere consisting on the average of 17.6 water molecules, is located at a distance of 0.461 nm.

The outer-sphere complexes with nitrate ions were revealed by measuring the stability constants in [73]. The formation of ion associates with the nitrate and chloride ions is confirmed in [103]. By the method of luminescent analysis the inner-sphere complexes with nitrate ions were identified [104]. The Eu^{3+} ion was found to form outer-sphere complexes with perchlorate ions. The formation of associates with the perchlorate ions (without establishing the type of ion pair), even at low concentrations, was proved by fluorescence analysis in [105]. In [106], by the ultrasound absorption the absence of contact ion associates with the perchlorate ions was proven, while the presence of contact ion associates with the nitrate ions was noted. The method of luminescent analysis revealed the formation of contact ion associates in aqueous solutions of europium chloride, thiocyanate, and nitrate [107]. The inner-sphere ion pairs were revealed by the thermodynamic studies of europium sulfate in aqueous solutions [108, 109]. The measurements of the fluorescence lifetime of Eu^{3+} ion did not reveal contact ion pairs in dilute aqueous solutions of europium chloride and perchlorate, while they were found in sulfate and nitrate solutions [110]. XRD of 3.23 M aqueous solution of europium chloride proved the existence in it of non-contact ion pairs with a Eu^{3+}–Cl^- distance equal to 0.490 nm [41]. A 0.1 M chloride solution of europium with a high content of chloride ions, as shown above, by contrast, consists of contact ion associates [17]. Therefore we can conclude that in solutions of europium nitrate and sulfate the preferred form is contact ion pairs, while the chloride and perchlorate ions form with the cation predominantly the non-contact ion pairs.

From the foregoing it is evident that experimental methods indicated a slight decrease in the *CN* ion in the case of Eu^{3+}. It is difficult to judge unambiguously which among existing theories explains this effect most accurately. But probably, the averaging over the observation period, namely, the consideration of the so-called diffusion-averaged structure, really reflects the change in *CN*. Therefore, in the final table as an average coordination number 8.8 is taken and the distance to the coordinated water molecules, 0.244 nm. The distance to the second coordination shell, obtained by calculation methods, is assumed to be overstimated, and we suggest that on the average it equals 0.454 nm. In our opinion, the number of molecules in the second coordination sphere must not decrease significantly and is still about 18 molecules.

Gd^{3+}. Pioneering study on XRD of the structure of 1.55 and 2.66 M aqueous solutions of gadolinium chloride with and without addition of hydrochloric acid revealed that the cation was surrounded by eight water molecules located at a distance of 0.237 ± 0.002 nm [111]. In solutions with a large excess of chloride ions, the predominant species in the solution are $Cl_2Gd(H_2O)_6^+$. The Gd^{3+}–Cl^- distance in the contact ion pair is 0.28 nm, in non-contact ion pairs 0.48 nm in a solution without the addition of acid and 0.50 nm in a solution with the acid. It was concluded that gadolinium ion was more prone to association with chloride ions than the La^{3+} ion. By quantum-chemical method the *CN* of the Gd^{3+} ion was obtained to be equal to 8.33 [96]. By EXAFS spectroscopy, in the study of aqueous solution of gadolinium perchlorate at a molar ratio of salt:water 1:28 [45] it was established that the cation coordination number was equal to 7.6, and the distance to the coordinated water molecules was 0.241 nm. By EXAFS, the Gd^{3+}–OH_2 distance in 0.52 M aqueous solution of gadolinium perchlorate was estimated at 0.2415 nm (at a fixed coordination number equal to eight) [16]. According to the molecular dynamics, the *CN* of Gd^{3+} ion in infinitely dilute solution is nine, and the distance to the coordinated water molecules, 0.246 nm. In addition, the cation forms a second coordination sphere consisting of 14 ± 2 water molecules at a distance of 0.450 nm [61]. The Gd^{3+} ion coordination sphere, according to the molecular dynamics, consists of eight water molecules surrounding the ion as a square antiprism, on an average distance of 0.237 nm [112]. Besides, the presence of a well-determined second coordination sphere was noted. In another study, also performed by the molecular dynamics method, the distance Gd^{3+}–OH_2 is somewhat larger, 0.244 nm for *CN* equal to 8.6 [113]. Clavaguéra et al. also noted the existence of the second coordination sphere at an average distance of 0.465 nm, consisting of approximately eighteen water molecules. By XAFS study of the structure of dilute aqueous solutions of nitrate (0.006 M Ga^{3+}/0.16 M HNO_3) and chloride (0.006 m and 0.1 m) of gadolinium [114] the cation *CN* was determined as equal to 9 ± 0.5, and the distance Gd^{3+}–OH_2, 0.2416 ± 0.0006 nm. By EXAFS, in 0.2 M aqueous solution of gadolinium trifluoromethanesulfonate [62] the *CN* of the Gd^{3+} ion was found to be equal to 9 with an average distance to the coordinated water molecules 0.243 nm. The molecular dynamics provided slightly lower values of the structural parameters: *CN* = 8.7, r = 0.238 nm [26, 63]. For the model of two spheres the following results were obtained: r = 0.238 nm (*CN* = 5.38), r = 0.247 nm (*CN* = 3.34). The second coordination sphere consists on the average of 19.2 water molecules located at a distance of 0.461 nm. In a recent study by molecular dynamics it was found that the discussed ion coordinates, on the average, 8.4 water molecules, arranged around it at a distance of 0.255 nm [90]. Villa et al. believe that there is an equilibrium between the hydrated cation complexes, comprising eight water molecules as a square antiprism, and with nine water molecules in the form of three-cap trigonal prism. This effect is due to the fast exchange of water molecules of the first coordination sphere with the surrounding solvent, which leads to a distortion of the ideal geometry of the coordination sphere. The second coordination sphere consists on the average of 18.8 water molecules at a distance of 0.475 nm. In the modern study by XANES of 0.2 M aqueous solution of gadolinium trifluoromethanesulfonate it was found that six water molecules were arranged around the cation to form a prism at a distance of 0.237 nm, and three others at greater distances, from 0.247 nm to 0.253 nm [91]. The existence of the second coordination sphere of the cation was confirmed.

The association of the discussed ion with nitrate ions was revealed long ago using IR and Raman spectroscopy [115]. According to this study, the NO_3^- ions may be associated with the cation in both single- and bidentate forms. By Raman spectroscopy for aqueous solutions of gadolinium chloride in the concentration range 0.5–3.5 mol kg^{-1} it was found that in concentrated solutions mainly outer-sphere complexes were formed [28].

Gadolinium ion is precisely the cation which gave the name to the effect of changing the *CN* value in a series of lanthanide ions. Therefore, precise knowledge of the *CN* of this ion is very important. Nevertheless, at present, as seen from the above material, the statement on this point cannot be unambiguous. We believe that in aqueous solutions of the gadolinium salts besides the hydrate complexes $Gd(H_2O)_9^{3+}$ there are the complexes $Gd(H_2O)_8^{3+}$, which affects the average coordination number value making it fractional, namely, 8.7. The second coordination sphere, consisting on the average of eighteen water molecules at a distance of 0.453 nm is formed. The Gd^{3+} ion is prone to both contact and non-contact types of association with counterions.

Tb^{3+}. The aqueous solution of terbium chloride with molar ratio of 1:11 was investigated by XRD in [39]. It was established that the cation coordinates eight water molecules at an average distance 0.241 nm. The average distance in the ion pair of $Tb^{3+}\cdots Cl^-$ type was estimated at 0.480 nm. Later on, by the same method aqueous solutions of terbium perchlorate (1.093 M and 2.68 M) and selenate (1.15 M) were studied [12]. The coordination number of cations in all investigated solutions was also found to be eight with a minor correction of the Tb^{3+}–$O(H_2O)$ distance, to 0.240 nm. The Tb^{3+} ion forms the second coordination sphere consisting of 9 water molecules at a distance of 0.456 nm [1.093 M solution of $Tb(ClO_4)_3$], or 14 water molecules at a distance of 0.460 nm [2.68 M solution of $Tb(ClO_4)_3$], or 11 water molecules at a distance of 0.450 nm [1.15 M solution of $Tb(SeO_4)_3$]. The cation forms contact ion pairs with selenate ions with the Tb^{3+}–O–Se bond angle 140° and the Tb^{3+}–Se distance 0.378 nm. Contact ion pairs of the Tb^{3+} with perchlorate ions are absent. Later in the study by EXAFS of aqueous solution of terbium perchlorate with the molar ratio of salt:water 1:28 [45] it was established that the cation coordination number was 7.5, and the distance to the coordinated water molecules was 0.239 nm. Then, the neutron diffraction study of 2 M aqueous solutions of terbium perchlorate [46] showed that the cation coordination number was 9, and the distance to the coordinated water molecules was 0.239 nm. By EXAFS, the Tb^{3+}–OH_2 distance in the 0.52 M aqueous solution of terbium perchlorate was found to be 0.2390 nm (at a fixed coordination number equal to eight) [16]. Using the same method, the average coordination number of Tb^{3+} ion in 0.2 M aqueous solution of terbium trifluoromethanesulfonate was found equal to nine with the average distance to the coordinated water molecules 0.241 nm [62]. The molecular dynamics method resulted in a slightly smaller values of structural parameters: $CN = 8.59$, $r = 0.237$ nm [26, 63]. The number of water molecules in the second coordination sphere varies from 16.3 to 18.9, while the distance, from 0.455 to 0.460 nm, depending on the models used in the calculations. The outer-sphere complexes with nitrate ions were revealed by measuring the stability constants in [73].

The average distance to the first coordination sphere is 0.239 nm, as established in [45, 46]. The second coordination sphere at an average distance of 0.452 nm comprises 16 to 18 water molecules. Tb^{3+} ion is prone to association with counterions, the association type depends on the type and concentration of the latter.

Dy^{3+}. The neutronography of 2.38 M solution of $DyCl_3$ [116] showed that each Dy^{3+} ion is surrounded by 7.4 ± 0.5 water molecules, with the distances Dy^{3+}–O =

0.237 nm and Dy^{3+}–D = 0.304 nm. In the study by the same method of the solutions of 1 M $DyCl_3$, 1.0 M $Dy(ClO_4)_3$, and 0.3 M $Dy(ClO_4)_3$ in D_2O [117] it was found that *CN* of Dy^{3+} ion is eight regardless of the concentration or the counterion type. The distance Dy^{3+}–O = 0.239 ± 0.002 nm and Dy^{3+}–D = 0.303 ± 0.002 nm. The study by EXAFS of the aqueous solution of dysprosium perchlorate with the salt:water molar ratio of 1:28 [45] showed that the coordination number of the cation was equal to 8.1, and the distance to the coordinated water molecules was 0.237 nm. In the investigation by neutron diffraction of 2M aqueous solution of dysprosium perchlorate [46] it was determined that the coordination number of the cation was 9, and the distance to the coordinated water molecules was 0.239 nm. By EXAFS the coordination number of Dy^{3+} ion in dilute aqueous solutions of dysprosium chloride (0.05, 0.1 and 0.2 M, pH 1) was estimated at 12, the distance Dy^{3+}–OH_2 = 0.237 nm [15]. This value of the coordination number is clearly overestimated. By the same method the Dy^{3+}–OH_2 distance in 0.5 M aqueous solution of dysprosium perchlorate was found to be 0.2373 nm (at a fixed coordination number equal to 8) [16]. In the study of the dysprosium bromate aqueous solution by the method of luminescent analysis the cation coordination number was found to be 8.4 ± 0.4 [97]. By NMR, the coordination number of the cation in aqueous solutions of dysprosium trifluoromethanesulfonate was found to be equal to 8 [118]. As noted, the CF_3SO^{3-} anions are in the second coordination sphere.

A modern study of the aqueous solutions of dysprosium chloride in a concentration range from very dilute to 3.36 mol kg^{-1} by UV spectroscopy, molecular dynamics, and EXAFS, showed that the distance to the eight coordinated water molecules in the first sphere is 0.237 nm [119]. The concentration does not affect the first coordination sphere. Chloride ion is not included in the first coordination sphere of the cation, even in a concentrated solution. The 18 water molecules in the second coordination sphere are at an average distance of 0.460 nm. The molecular dynamics calculation showed also that with increasing concentration the number of water molecules in the second shell was reduced from 17.5 to 10, while the number of chloride ions increased from 0.5 to 6.3 with the distance to them of 0.52 nm. In another investigation carried out by using the EXAFS for the study of 0.2 M aqueous solutions of lanthanide trifluoromethanesulfonate it was found that the average coordination number of Dy^{3+} ion is 9 with an average distance to the coordinated water molecules 0.239 nm [62]. By the molecular dynamics slightly lower values of structural parameters were obtained: *CN* = 8.36, *r* = 0.236 nm [26, 63]. The number of water molecules in the second coordination sphere varies from 16.6 to 18.7, while the distance, from 0.452 to 0.459 nm depending on the models used in the calculations.

We assume that the average coordination number is 8.5. The average distance of Dy^{3+}–O is equal to 0.238 nm. The cation forms the second coordination sphere. Analyzing a series of lanthanide ions and the known distance to the second coordination sphere of the ions, one can also assume that the distance to it is in the range of 0.445–0.455 nm. The ion association in aqueous solutions of salts of dysprosium does occur.

Ho^{3+}. In the holmium trifluoromethanesulfonate crystal hydrate the cation coordinates nine water molecules in the form of three-cap trigonal prism with the distances 0.2367 and 0.2526 nm [77]. We could find only three papers describing the structure of the hydrated complex ion Ho^{3+} in solution. By EXAFS the of Ho^{3+}–OH_2 distance in 0.5 M aqueous solution of holmium perchlorate was determined to be 0.2359 nm (at a fixed coordination number equal to eight) [16]. The study by EXAFS of 1 M aqueous solutions of the holmium chloride and nitrate with various concentrations of chloride and nitrate ions [67] showed that the distance to the coordinated water molecules was equal to 0.237 nm. The nitrate ion forms a contact ion pair with the cation with a Ho^{3+}–N distance of 0.288 nm. The cation is located in the same plane as the anion. No contact ion pair with chloride ion is formed. The investigation by EXAFS of 0.2 M aqueous solution of holmium trifluoromethanesulfonate [62] revealed that the average coordination number of Ho^{3+} ion is 8.91 with the distance to the coordinated water molecules 0.238 nm. By molecular dynamics slightly lower values of the structural parameters were obtained: *CN* = 8.24, *r* = 0.234 nm [26, 63]. The second coordination sphere, consisting on the average of 18.6 water molecules, is located at a distance of 0.452 nm.

We assume that the average coordination number found experimentally is 8.4. The average distance of Ho^{3+}–O is 0.236 nm. The ion forms the second coordination sphere. Reducing the number of molecules in the first coordination sphere should result in the corresponding decrease of their number in the second sphere. Therefore, we assume that in going to heavier lanthanide ions, the average number of water molecules in the second shell is reduced from 18 to 14–16. Analyzing the series of lanthanide ions and the known distances to the second coordination sphere of ions, we can also assume that the distance to it is in the range 0.445–0.455 nm. Ion association takes place in the aqueous solutions of holmium salts.

Er^{3+}. This ion was studied by X-ray diffraction in aqueous solutions of erbium chloride (molar ratios of 1:18.2, 1:37.7 and 1:58.5) and iodide (1:41.7) in an early work [120]. It was determined that the coordination sphere of the cation was an octahedron of water molecules. The presence in solution of ionic associates of the type Er^{3+}–Cl_2^- and Er^{3+}–I_2^- was established. Later on, by XRD of 3.2–3.6 M aqueous solution of erbium chloride [39] it was found that the coordination number of the cation was eight and the average Er^{3+}–O distance was 0.2369 nm. The average distance in the ion pairs of the $Er^{3+}\cdots Cl^-$ type was estimated at 0.480 nm. The analysis of the absorption spectrum of a dilute (0.044 M) frozen aqueous solution of erbium chloride showed that the eight water molecules are arranged around the cation in a square antiprism [121]. Then, it was found by XRD in the isomorphous substitution study of aqueous solutions of erbium selenate (0.78 and 0.95 M) and perchlorate (2.96 M) [12, 122] that the *CN* of the cation in all the solutions was equal to eight. The average Er^{3+}–O distance is equal to 0.236 nm in a solution of erbium perchlorate and 0.234 nm in a solutions of erbium selenate. The cation forms the second coordination sphere of 15 water molecules located at a distance of 0.452 nm in the perchlorate and 11 water molecules at a distance of 0.447 nm in the solutions of erbium selenate. The cation forms contact ion pairs with selenate ions with the bond angle Er^{3+}–O–Se 140° and the Er^{3+}–Se distance 0.375 nm. Contact ion pairs of Er^{3+} ions with the perchlorate ions are absent. In another study by XRD investigation of aqueous solutions of erbium halides and perchlorate [123] it was shown that the Er^{3+} ion coordinates 8.0 ± 0.3 water molecules in the first sphere at an average distance of 0.235 ± 0.001 nm. At very high concentrations, the halide and even the perchlorate ions can enter into this sphere, to form the contact ion pairs with the following characteristic distances: Er^{3+}–Cl^- = 0.27 ± 0.01 and Er^{3+}–Br^- = 0.287 ± 0.002 nm. It was noted that perchlorate ions can be introduced into the second coordination sphere. Yokoyama and Johansson studied the XRD of 0.99 and 2.89 M aqueous solutions of erbium nitrate [124], and noted the formation of ion pairs with an average distance Er^{3+}–N = 0.286 nm where the nitrate ion behaved as a bidentate ligand. The total coordination number of the cation is close to eight. The distance to the coordinated water molecules of the first sphere is 0.235 nm, and to the second sphere is 0.460 nm. Approximately 17 water molecules are included in the second sphere in a dilute solution and about 15 molecules in concentrated ones. The results of EXAFS of an aqueous solution of erbium perchlorate with the molar ratio of salt:water 1:28 give the *CN* of Er^{3+} ion equal to 7.8 at a distance of 0.234 nm [45]. The anomalous X-ray scattering study of 0.1, 0.5 and 1.0 M aqueous solutions of erbium chloride [125] showed that in a less concentrated solution the cation has an average coordination number equal to 8.2 ± 0.6 at the distance to the coordinated water molecules 0.240 ± 0.002 nm, in a more concentrated solution *CN* = 8.3 ± 0.8, and the distance Er^{3+}–OH_2 is 0.238 ± 0.002 nm. The same method was applied to determine the structural parameters of the local surrounding of the cation in 3 M aqueous solution of erbium bromide [126]. The cation *CN* was found to be equal to 8.9, and the distance to the coordinated water molecules, 0.239 nm. Beudert et al. note that in this system the contact ion pairs do not form, but there are associates with the bromide ion entering the second coordination sphere of the cation with the Er^{3+}–Br^- distance 0.51 nm. This leads to the overlap of the cation and anion coordination spheres. By EXAFS the Er^{3+}–OH_2 in 0.68 M aqueous solution of erbium perchlorate was determined to be equal to 0.235 nm (at a fixed coordination number equal to eight) [16]. Using the same method, the average coordination number of Er^{3+} ion in 0.2 M aqueous solution of erbium trifluoromethanesulfonate was determined to be equal to 8.95 with an average distance to the coordinated water molecules 0.238 nm [62]. By the molecular dynamics slightly lower values of the structural parameters were obtained: *CN* = 8.14, *r* = 0.233 nm [26, 63]. The second coordination sphere consisting on the average of 18.7 water molecules is located at a distance of 0.451 nm.

The inner-sphere coordination of the nitrate ion was revealed in [127] and confirmed by NMR for a wide range of concentrations of aqueous solution of erbium nitrate [128]. According to the UV spectroscopy, the discussed cation is not prone to form ion associates with the perchlorate ions [93].

In the final table we included the erbium *CN* equal to 8.3 and the distance Er^{3+}–OH_2 of 0.235 nm. In addition, as demonstrated experimentally, this cation forms the second coordination sphere. We presume that it includes 14–16 water molecules, located at an average distance of 0.449 nm. For solutions of erbium salts formation of ion pairs of both contact and noncontact types is characteristic.

Tm^{3+}. By XAFS method it was determined that the hydration number of the Tm^{3+} ion in crystalline $[Tm(H_2O)_9](CF_3SO_3)_3$ was 8.96(5) [129]. We managed to find only few studies on the structure of the thulium(III) ion hydrated complex. As a result of the X-ray study of aqueous solutions of thulium chloride in the molar ratio of 1:10.6 the cation *CN* was found to be equal to eight, and the Tm^{3+}–O distance, to 0.2358 nm [39]. The average distance in the ion pair $Tm^{3+}\cdots Cl^-$ was estimated at 0.480 nm. The results of EXAFS spectroscopy of an aqueous solution of thulium perchlorate at the molar ratio of salt: water 1:28 give the *CN* of the Tm^{3+} ion equal to 8.0 at a distance of 0.233 nm [45]. By neutron diffraction study of 2 M aqueous perchlorate thulium [46] it was found that the cation coordination number was 8, and the distance to the coordinated water molecules was 0.233 nm. Later on, in a study of dilute aqueous solutions of thulium chloride (0.05, 0.1 and 0.2 M, pH = 1) effected by EXAFS the *CN* was determined as equal to 12, and the distance to the coordinated water molecules, 0.232 nm [15]. This *CN* value of the discussed cation seems to be excessive. Using the same method, the distance Tm^{3+}–OH_2 in 0.55 M aqueous solution of thulium perchlorate was determined to be 0.2334 nm (at a fixed coordination number equal to eight) [16]. Study by EXAFS of 0.2 M aqueous solution of thulium trifluoromethanesulfonate [62] showed that the *CN* of the Tm^{3+} ion is equal to 8.8 with an average distance to the coordinated water molecules 0.235 nm. The molecular dynamics calculations gave slightly lower values of structural parameters: $CN = 8.06$, $r = 0.233$ nm [26, 63]. The second coordination sphere consists on the average of 18.3 water molecules located at a distance of 0.450 nm. The outer-sphere complexes with nitrate ions were revealed by measuring the stability constants in [73].

The summary table includes the following characteristics of the first coordination sphere of the thulium ion: $CN = 8.2$ and $r = 0.234$ nm. This cation obviously forms a second coordination sphere. We assume that, like that of the Er^{3+} ion, it includes on the average 14–16 water molecules located at an average distance of 0.445–0.450 nm. For thulium ion the ion association is typical.

Yb^{3+}. The structural parameters of the local surrounding of the Yb^{3+} ion studied by neutron diffraction with 1.0 M $Yb(ClO_4)_3$ solution in D_2O [117] showed that the cation coordination number was eight regardless of the concentration or the counterion type. The distances are: Yb^{3+}–O 0.233 ± 0.002 nm and Yb^{3+}–D 0.298 ± 0.002 nm. The study by neutron diffraction of 2 M aqueous perchlorate solutions of ytterbium [46] gave the cation coordination number 8, and the distance to the coordinated water molecules 0.233 nm. By the molecular dynamics the *CN* of Yb^{3+} ion was determined equal to nine, and the distance Yb^{3+}–OH_2, 0.221 nm [53]. Kowall et al. also determined the geometry of the first coordination sphere of the cation to be a square antiprism with three additional water molecules [54]. By EXAFS data, the Yb^{3+}–OH_2 distance in 0.73 M aqueous solution of ytterbium perchlorate is 0.2317 nm (at a fixed coordination number equal to eight) [16]. The study by EXAFS of 0.1 M aqueous solution of ytterbium chloride with low and high content of chloride ions [17] resulted in the *CN* of Yb^{3+} ion 9.3, the distance to the coordination sphere of 0.243 nm at the low content. According to the opinion of Allen et al. the complexation with chloride ions in a series of lanthanide ions decreases, and it is absent after reaching the Yb^{3+} ion. Therefore, even in the case of high concentration of chloride ions, the loss of water molecules does not occur. According to the molecular dynamics, the *CN* of Yb^{3+} ion in the infinitely dilute solution is equal to nine, and the distance to the coordinated water molecules is 0.237 nm. The cation forms a second coordination sphere consisting of 13 ± 2 water molecules at a distance of 0.441 nm [61]. By *ab initio* calculations the following parameters of the first coordination sphere of the discussed ion were obtained: $CN = 8$, $r(Yb^{3+}\text{–}H_2O) = 0.237$ nm [87].

A subsequent study by XAFS of aqueous solutions of ytterbium nitrate and chloride containing 0.006 M of Yb^{3+} ions showed that the *CN* of the ion under standard conditions is equal to 8.3 ± 0.6 [130]. In less dilute solutions the formation of ion pairs is non found. Monte Carlo study of $Yb(H_2O)_n^{3+}$ clusters with different number of water molecules [89] revealed that only at $n > 24$ the cation *CN* begins to approach the experimental value ($CN = 7.9$). The found Yb^{3+}–H_2O distance was clearly overestimated ($r = 0.264$ nm) and it was attributed to the lack of the influence of the anion. By EXAFS data, the average coordination number of Yb^{3+} ion in 0.2 M aqueous solution of ytterbium trifluoromethanesulfonate is 8.7 with an average distance to the coordinated water molecules of 0.232 nm [62]. By the molecular dynamics slightly lower values of structural parameters were obtained: $CN = 8.02$, $r = 0.232$ nm [26, 63]. The second coordination sphere consists on the average of 18.3 water molecules located at a distance of 0.449 nm. In a recent study by molecular dynamics it was determined that the discussed ion coordinates on the average 8.0 water molecules arranged around it to form a square antiprism at an average distance of 0,247 nm [90]. We presume that the resulting interparticle distance is considerably overestimated. The second coordination sphere consists on the average of 18.8 water molecules at a distance of 0.465 nm, which is slightly larger than the number of water molecules (16.7) determined in [53]. Using NMR it was found that in aqueous solution of ytterbium nitrate in a wide range of concentrations contact ion associates with the nitrate ions are formed [128].

The summary table includes the following characteristics of the first coordination sphere of the ytterbium ion: $CN = 8.1$, $r = 0.233$ nm. The cation forms likely the second coordination sphere consisting of 14–16 water molecules located at an average distance of 0.445–0.450 nm. For the ytterbium ion the ion association is characteristic.

Lu^{3+}. The lutetium ion coordination number equal to eight with the distance to the coordinated water molecules 0.2338 nm was determined long ago by XRD analysis of 3.6 M aqueous solution of lutetium chloride [39]. The existence was also determined of noncontact ion pairs with chloride ion with the distance Lu^{3+}–Cl^- of 0.480 nm. Later on, it was determined by NMR that CN of the Lu^{3+} ion in dilute aqueous acetone mixtures of lutetium perchlorate is more than or equal to nine [131]. The results of EXAFS spectroscopy study of aqueous lutetium perchlorate at the molar ratio salt: water 1:28 are as follows: CN of Lu^{3+} ion equal to 7.7 and the distance to the water molecules, 0.231 nm [45]. Using the same method the distance Lu^{3+}–OH_2 in 0.72 M aqueous solution of lutetium perchlorate was determined to be 0.231 nm (at a fixed coordination number equal to eight) [16]. On the basis of *ab initio* studies of the molecular geometry and stability of the $Lu(H_2O)_n^{3+}$ clusters ($n = 1$–9) it was concluded that the CN of Lu^{3+} ion in aqueous solutions was near eight and the distance to the coordinated water molecules was 0.232 ± 0.002 nm [132]. The study by EXAFS of 0.2 M aqueous solution of lutetium trifluoromethanesulfonate revealed that the average coordination number of the Lu^{3+} ion equaled 8.2, the distance to the coordinated water molecules was 0.232 nm [62]. The molecular dynamics found similar structural parameters: $CN = 8.01$, $r = 0.232$ nm [26, 63]. The second coordination sphere consists on the average of 18.3 water molecules located at a distance of 0.450 nm. The calculations carried out as a geometry optimization gave, in our opinion, somewhat overestimated distance to the first coordination sphere, 0.236 nm [133]. In the modern study by XANES of 0.2 M aqueous solution of lutetium trifluoromethanesulfonate it was found that six water molecules are arranged around the cation to form a prism at a distance of 0.227 nm, and two others at greater distances, 0.237 nm and 0.256 nm [91]. The existence of the second coordination sphere of the cation was confirmed.

By Raman spectroscopy for aqueous solutions of lutetium chloride in the concentration range 0.5–3.5 mol kg^{-1} it was found that in concentrated solutions mainly the outer-sphere complexes formed [28]. In another study by the same method it was found that in aqueous solution of lutetium nitrate at the molar ratio of 1:20 the main particles were the ions $[Lu(H_2O)_8]^{3+}$ and $[Lu(NO_3)]^{2+}$, e.g., the contact ion pairs were formed [29]. The formation of contact ion associates with the nitrate ions was also found by NMR in aqueous solutions of lutetium nitrate in a wide range of concentrations [128].

In the summary table are included the following characteristics of the first coordination sphere of the lutetium ion: $CN = 8.0$, $r = 0.232$ nm. The cation forms the second coordination sphere, consisting of 14–16 molecules of water located at an average distance of 0.445 nm. For the lutetium ion the ion association is characteristic.

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