

Review

Structures of Hydrated Metal Ions in Solid State and Aqueous Solution

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Abstract: This review article summarizes the reported crystallographically determined structures of compounds containing a hydrated metal ion and the reported structures of hydrated metal ions in aqueous solution. A short overview of the methods available to study structures of metal complexes in solution is given.

Keywords: review; hydrated metal ions; structure; solid state; aqueous solution

1. Introduction

Structures of hydrated and solvated metal ions and complexes in solution are of utmost importance in order to understand the chemical behavior in their reaction medium. It is common that structures of metal ion complexes determined in the solid state are extrapolated to have the same or similar structure in solution. This paper gives an overview of reported structures of hydrated metal ions in the solid state and aqueous solution and discusses some cases where the structure in aqueous solution differs from the observations in the solid state or where the results are under scientific discussion. A short presentation of the available methods for accurate structure determination in solution is given. Hydrated metal ions are used as examples as they have simple composition and are of general great importance and interest. Metal ions with low charge density, such as the heavier alkali metal ions and thallium(I), are weakly hydrated and solvated and crystallize in most cases without a complete first hydration or solvation shell. A second hydration shell can only be studied in aqueous solution, as no hydrated metal ion has been reported to crystallize with a second hydration sphere. Symmetry plays an important role in crystallization, and high-symmetry complexes may crystallize from a solution dominated by complexes with low symmetry. Another aspect is the random structural disorder in the solid state. The outcome of a crystallographic investigation is the mean of all irradiated unit cells. If a low-symmetry complex is randomly oriented in a crystal, the mean structure may have a higher symmetry than the individual complexes. This is discussed in detail for some hydrated metal ions with low symmetry in aqueous solution, but with normally higher symmetry in the solid state. In the supporting material section, the structures of all reported crystal structures containing hydrated metal ions with full hydration shell, reported through 2021, are summarized in Supplementary Tables S1–S16.

2. Methods to Investigate the Coordination Chemistry in Solution

The structural information, concerning bond distances and basic configurations of hydrated and solvated metal ions and complexes in solution, is obtained with Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, Large Angle X-ray Scattering (LAXS), and Large Angle Neutron Scattering (LANS). These methods give structural information in one dimension as a Fourier transform (EXAFS) or a radial distribution function (RDF) (LAXS and LANS) of the studied sample. It is important to stress that the obtained information is a mean value of the irradiated sample. It is therefore a great advantage, if



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possible, to study solutions with only one chemical species except the solvent and a counter ion with known structure. The data collection of an EXAFS spectrum requires very high X-ray intensity in a wide energy range, at least 700 eV, ideally 1600 eV (wavelength in Å = 12,398.4/energy in eV). Therefore, synchrotron light is required for accurate EXAFS measurements. EXAFS gives only structure information around the absorbing atom through back-scattering of the outgoing photoelectron wave of the excited atom. [1–4]. Furthermore, dilute solutions down to sub-millimolar concentrations can be studied.

LAXS, also known as WAXS (wide angle X-ray scattering), can be performed in two ways: reflection mode, scattering from a planar liquid surface in a Θ - Θ goniometer, and transmission mode, the scattering of the sample in a capillary. The scattering is determined as a function of the scattering angle, 2Θ , in the angle range of 0–140 degrees. LAXS in reflection mode is formed by an X-ray tube as the X-ray source, as both the X-ray source and detector have to be moved synchronically. LAXS in transmission mode is preferably performed by synchrotron light as a higher X-ray intensity can be obtained. LAXS in reflection mode has been found to superior, as a large scattering angle range can be applied without advanced absorption corrections. On the other hand, LAXS in transmission mode required advanced absorption corrections, especially at scattering angles above 90 degrees.

In contrast to EXAFS, LAXS detects all distances in the sample. The scattered intensity from a pair of atoms, independent of if they are bound or not, is proportional to the number of electrons in the atom pair. This means in practice that the required concentration to distinguish the compound or complex under study from the contribution increases with atom numbers in the complex under study. As a rule of thumb, complexes with a first row transition metal ion require a 0.3–0.5 mol·dm⁻³ solution for accurate measurement.

The EXAFS and LAXS methods are complementary as they give partly different information. EXAFS gives very accurate information of well-defined distances up to 4–5 Å from the absorbing atom, while in principle no information is obtained about longer distances. The reason is that the EXAFS signal is highly damped by increasing distance, R_j , and the Debye–Waller coefficient, σ , accounting for the thermal and configurational disorder. The EXAFS equation in its most simple form is expressed in the following way:

$$\chi(k) = \sum \frac{N_j S_0^2}{kR^2} \cdot |f_{eff}(k)| \cdot \exp\left(-\frac{2R_j}{\Lambda_j(k)}\right) \cdot \exp(-2k^2\sigma^2) \cdot \sin[2kR_j + \phi_j(k)] \quad (1)$$

where $\chi(k)$ is the EXAFS function, k is the photoelectron wavenumber or wave vector, N_j the number of distances, S_0^2 is the amplitude reduction factor, R is the distance between the absorbing atom and the back-scattering in single scattering and total distance divided by two in multiple scattering, f_{eff} is the effective amplitude function for the scattering path, $\exp(-2k^2\sigma^2)$ is the Debye–Waller factor in harmonic approximation including the Debye–Waller parameter accounting for the thermal and configurational disorder, $\Lambda(k)$ is the photoelectron mean free path and $2kR + \Phi(k)$ the total phase. The theory of the EXAFS method and how it can be applied in different areas of science are given in refs. [1–4].

LAXS detects all distances in the sample, but the angular range is smaller, causing the resolution for short distances to be smaller compared to EXAFS. On the other hand, the damping of the LAXS signal for long distances is much smaller compared to EXAFS. This makes it possible to observe very long distances, as the general bulk order, with LAXS giving structural information out to 15–20 Å. As an example, LAXS can accurately detect a second, and possibly a third hydration shell around a metal ion, while they are hardly detectable by EXAFS. The X-ray scattering of liquids and non-crystalline solids is described by the following equation:

$$i(s) = \sum \sum \left\{ f_i(s) \cdot f_j(s) + \Delta f_i'' \cdot \Delta f_j'' \right\} \cdot \frac{\sin(s \cdot R_{ij})}{s \cdot R_{ij}} \cdot \exp\left(-\frac{l_j^2}{2}\right) + del(s) \left(\frac{\lambda}{\lambda'}\right)^2 I_{m, incoh}(s) \quad (2)$$

where $i(s)$ is the reduced intensity, s is the scattering vector expressed as $s = 4\pi\sin\Theta/\lambda$, where Θ is the scattering angle divided by two, and λ is the wavelength of the X-ray radiation, f is the scattering factors, including a correction for anomalous dispersions (f'), where the $\Delta f''$ is the imaginary part, R is the distance between two atoms, and, in the root-mean-square variation assuming Gaussian distribution, l^2 , and $del(s)$ describe the fraction of incoherent scattering passing the monochromator, where λ is the wavelength of X-ray radiation and λ' is the wavelength measured in the X-ray spectrum of the X-ray source, giving $del(s)$ for the scattering angle 2Θ , and where $\lambda' = \lambda + 0.02426(1 - \cos 2\Theta)$. For a more detailed description of the LAXS method and the theory of scattering of liquids and amorphous compounds, refs. [5,6] are recommended.

A comparison of Equations (1) and (2) shows that the amplitude of the structure-dependent intensity contributions decreases more rapidly in the EXAFS equation, $\exp(-2\cdot R_{ij}/\lambda(k))$, than in the LAXS one, $\sin(s\cdot R_{ij})/s\cdot R_{ij}$, and this difference increases significantly with increasing interatomic distances. EXAFS and LAXS give different information about the local structure of metal complexes, EXAFS solely from the absorbing atom and LAXS as part of all distances in the sample. The great advantage of EXAFS is that it can be applied on very dilute solutions, down to sub-millimolar concentrations, and it gives accurate information about short distances around the absorbing atom. Furthermore, the contribution from multiple scattering in EXAFS may give information bond angles around the absorbing atom, e.g., M–O–C bond angles, and high-symmetric coordination geometry. The advantage of LAXS is that long distances, such as, e.g., second hydration spheres and bulk order, can be determined with high accuracy.

Large angle neutron scattering (LANS) of liquids is complementary to LAXS. The main difference is that the scattering ability (scattering factors) of the elements are different. X-rays are scattered by the electrons of an atom, while neutrons are scattered by the nucleus of the atom. This means that light atoms, similarly to hydrogen, can hardly be detected by X-rays, while the scattering ability of, e.g., deuterium is large and can be detected in a LANS experiment. As different isotopes of the same element have different neutron scattering abilities, isotopically pure solutions with only one isotope of each element are required. The main limitation for the extensive application of LANS is the radiation source, as a nuclear reactor or a neutron spallation source is required. A comprehensive description of the LANS method is given in ref. [7].

The scope of this review is the structure of hydrated metal ions in aqueous solution and a solid state. Information such as water exchange kinetics and the number of ligands bound to metal ions can be obtained by NMR spectroscopy [8], and information about the strength of the hydrogen bonds in hydrated metal ions is obtained by double-difference infrared spectroscopy [9] and will not be further discussed in this survey.

3. Structures of Hydrated Metal Ions in Solid State and Aqueous Solution

3.1. Alkali Metal Ions

3.1.1. Lithium

The tetrahedral tetraaqualithium ion, $[\text{Li}(\text{H}_2\text{O})_4]^+$, is by far the most common form of hydrated lithium ions in the solid state with a mean Li–O bond distance of 1.941 Å (a mean of 53 reported crystal structures) (Supplementary Table S1a). Tetrahedral coordination around lithium is also present in the dimeric $[\text{Li}_2(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Li}_2(\text{H}_2\text{O})_7]^{2+}$ ions, as well as in the polymeric $[\text{Li}_3(\text{H}_2\text{O})_6]_n^{3n+}$ and $[\text{Li}_3(\text{H}_2\text{O})_8]_n^{3n+}$ ions (Supplementary Table S1a). The dimeric lithium hydrate complexes have either a single ($[\text{Li}_2(\text{H}_2\text{O})_7]^{2+}$) or double ($[\text{Li}_2(\text{H}_2\text{O})_6]^{2+}$) aqua bridge with mean Li–O bond distances of 1.962 and 1.988 Å, respectively. In the polymeric $[\text{Li}_3(\text{H}_2\text{O})_6]_n^{3n+}$ complex, all water molecules are bridged with a mean Li–O bond distance of 2.001 Å. The bridging Li–O bond distances are significantly longer than the terminal ones, explaining the difference in the mean Li–O bond distances of mono-, di- and polynuclear hydrated lithium ions (Supplementary Table S1a). Mähler and Persson have reported an analysis of Li–O bond distances of reported crystal structures of monomeric lithium complexes with oxygen donor ligands in four- and

six-coordination [10]. The mean Li–O bond distances were found to be 1.942 and 2.132 Å, respectively, where the former is in excellent agreement with the mean value of all structures containing a $[\text{Li}(\text{H}_2\text{O})_4]^+$ ion reported up to date, and the latter is in reasonable agreement with the only reported solid-state structure containing a $[\text{Li}(\text{H}_2\text{O})_6]^+$ ion, 2.144 Å (Supplementary Table S1a). By extrapolation, the mean Li–O bond distance in a $[\text{Li}(\text{H}_2\text{O})_5]^+$ ion should be close to 2.04 Å [10]. The structure of the square pyramidal $[\text{Li}(\text{H}_2\text{O})_5]^+$ ion has been reported in a couple of studies, but only one of these is close to the expected Li–O bond distance, 2.044 Å, while the other reported Li–O bond distances are much longer than expected for this configuration (Supplementary Table S1a).

The hydrated lithium ion has been studied extensively in aqueous solution by X-ray methods, in spite of the severe difficulties, *vide ultra*. Smirnov and Trostin reviewed available experimental data for the lithium ion until 2006 [11], and later studies are summarized in later general studies and reviews [10,12–15]. As lithium is a very weak scatterer of X-rays, it is not possible to unambiguously determine the coordination number of the hydrated lithium ion in aqueous solution from present X-ray-based experimental data. The results of the reported simulation studies on the hydrated lithium ion in aqueous solution scatter, and no conclusive picture is obtained. However, four-coordination in the tetrahedral configuration is mainly proposed. A neutron scattering study on the hydrated lithium ion in heavy water has reported a mean Li–O bond distance of 1.96 Å [16] with mean coordination numbers of 4.3–5.0, depending on the concentration. However, the reported mean Li–O bond distance correlates well with four-coordination in tetrahedral fashion, *vide ultra*. Simulation studies of the hydrated lithium ion in tetrahedral configuration have reported Li–O bond distances of 1.95 [17], 1.97 [18], 1.971 [19], and 2.03 Å [20]. None of the dimeric or polymeric complexes in the solid state have been observed in aqueous solution independent of concentration. As lithium scatters X-rays very weakly, studies in aqueous solution using X-ray techniques will give results with limited accuracy. The most reliable data seem to be crystallographic ones, and four-coordination in a tetrahedral fashion is by far the most common configuration of the hydrated lithium ion. It seems, therefore, most likely that the hydrated lithium ion is four-coordinated in a tetrahedral fashion in aqueous solution with a mean Li–O bond distance of 1.94 Å.

3.1.2. Sodium

The octahedral hexaaquasodium ion, $[\text{Na}(\text{H}_2\text{O})_6]^+$, is the most common sodium hydrate complex in the solid state with a mean Na–O bond distance of 2.417 Å (28 structures) (Supplementary Table S1b). However, other configurations, including monomeric $[\text{Na}(\text{H}_2\text{O})_2]^+$, $[\text{Na}(\text{H}_2\text{O})_4]^+$, $[\text{Na}(\text{H}_2\text{O})_5]^+$, and $[\text{Na}(\text{H}_2\text{O})_8]^+$ ions, and a large number of di-, tetra-, and octameric hydrated sodium ions, $[\text{Na}_2(\text{H}_2\text{O})_6]^{2+}$, $[\text{Na}_2(\text{H}_2\text{O})_7]^{2+}$, $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$, $[\text{Na}_2(\text{H}_2\text{O})_9]^{2+}$, $[\text{Na}_2(\text{H}_2\text{O})_{10}]^{2+}$, $[\text{Na}_4(\text{H}_2\text{O})_{14}]^{4+}$, $[\text{Na}_4(\text{H}_2\text{O})_{16}]^{4+}$, and $[\text{Na}_4(\text{H}_2\text{O})_{18}]^{4+}$ ions, as well as the polymeric $[\text{Na}_4(\text{H}_2\text{O})_{14}]_n^{4n+}$, $[\text{Na}_4(\text{H}_2\text{O})_{18}]_n^{4n+}$, and $[\text{Na}_8(\text{H}_2\text{O})_{24}]_n^{8n+}$ chains have also been reported (Supplementary Table S1b). An analysis of the Na–O bond distances of reported crystal structures of sodium complexes with oxygen donor ligands in five- and six-coordination has been reported [10]. The mean Na–O bond distances are 2.358 and 2.412 Å, respectively, which are in excellent agreement with the mean values of the hydrated sodium ion in five- and six-coordination, 2.366 and 2.417 Å, respectively (Supplementary Table S1b).

The reported experimental studies on the hydrated sodium ion in aqueous solution do not give a conclusive picture with Na–O bond distances in the range of 2.34–2.50 Å and coordination numbers in the range of 4.6–8 [21,22]. The reported theoretical simulation studies of the hydrated sodium ion in aqueous solution propose a mean Na–O bond distance of 2.35–2.40 Å in an octahedral fashion [23–25]. By summarizing the available information on the hydrated sodium ion including LAXS studies, solid-state structures containing hydrated sodium ions, vibration spectroscopic studies, and reported theoretical simulations, the hydrated sodium ion seems to bind six water molecules in an octahedral fashion with a mean bond distance of 2.43 Å in aqueous solution [10]. It has not been

possible with the available experimental techniques to determine whether the hydrated sodium has a second hydration sphere or not [10].

None of the di- or polymeric complexes reported in solid structures have been detected in aqueous solution independent of concentration. Sodium scatters X-rays weakly, and studies in aqueous solution using X-ray techniques will give results with limited accuracy. The most reliable data seem to be the crystallographic data, and six-coordination in an octahedral fashion is the most common configuration of the hydrated sodium ion. It seems therefore most likely that the hydrated sodium ion is a six-coordinated octahedral fashion in aqueous solution with a mean Na–O bond distance of ca. 2.42 Å.

3.1.3. Potassium

Only a limited number of crystal structures with a full hydration shell around the potassium ion have been reported, including $[\text{K}(\text{H}_2\text{O})_6]^+$, $[\text{K}(\text{H}_2\text{O})_7]^+$, and $[\text{K}(\text{H}_2\text{O})_8]^+$ (Supplementary Table S1c). However, the reported K–O bond distances are very scattered and not close to the K–O bond distances obtained by X-ray techniques in aqueous solution, nor the sum of the ionic radii of potassium in coordination numbers 6–8 proposed by Shannon [26] and the atomic radius of oxygen in the coordinated water molecule, 1.34 Å [27]. It is not possible to draw any conclusion about the structure of the hydrated potassium ion from the reported crystal structures.

The reported mean K–O bond distance in the hydrated potassium ion in aqueous solution from experimental studies is uncertain, 2.65–2.97 Å [10,28–30]. Theoretical simulation studies propose a K–O distance of ca. 2.80 Å and a coordination number close to seven in aqueous solution [23,24,31]. An EXAFS study on an aqueous potassium chloride solution reports a mean K–O bond distance of 2.73 Å and a coordination number of 6–7 [32], and a LAXS study on an aqueous solution of potassium iodide reports a mean K–O bond distance of 2.81(2) Å in seven-coordination [10]. It was not possible to detect any second hydration shell around the potassium ion from LAXS, and an infrared study showed that the water molecules bound to the potassium ion are less affected than the water molecules in the aqueous bulk [10]. This strongly indicates that there are no water molecules with significant order outside the first hydration shell.

3.1.4. Rubidium

Only two crystal structures with a full hydration shell around the rubidium ion, $[\text{Rb}(\text{H}_2\text{O})_9]^+$, have been reported (Supplementary Table S1d). However, the reported Rb–O bond distances are much longer than the ones obtained in aqueous solution, *vide infra*, the sum of the proposed ionic radii in coordination numbers 6–8 [26], and the atomic radius of oxygen in coordinated water molecules [27]. The reported Rb–O bond distances in the hydrated rubidium ion in aqueous solution are in a wide range, 2.83–3.05 Å, mean ca. 2.95 Å, with coordination numbers in the range 5.6–8.0 (Table 1 in ref. [33]). A combined LAXS and EXAFS study of aqueous rubidium iodide solutions reported a mean Rb–O bond distance in the hydrated rubidium ion of 2.98 Å [34]. Only one structure of a solid rubidium compound with water molecules in the coordination sphere, $[\text{Y}(\text{C}_2\text{O}_4)_2\text{Rb}(\text{H}_2\text{O})_4]_n$, has been reported. The mean Rb–O bond distance in this compound is 2.95 Å [35]. According to the reported results on the hydrated rubidium ion in aqueous solution, it is most likely eight-coordinated in a square antiprismatic fashion with a mean Rb–O bond distance of ca. 2.95 Å. As expected from LAXS and infrared spectroscopic studies, no well-ordered water molecules are present outside the first hydration shell of the hydrated rubidium ion in aqueous solution.

3.1.5. Cesium

Only two crystal structures with a full hydration shell around the cesium ion, $[\text{Cs}(\text{H}_2\text{O})_{10}]^+$, have been reported (Supplementary Table S1e). However, the reported Cs–O bond distances are much longer than those obtained in aqueous solution, *vide infra*, and the sum of the proposed ionic radii of cesium in coordination number ten proposed by Shannon [26]

and the atomic radius of coordinated water molecules [27]. A survey of experimental and simulation studies of the hydrated cesium ion in aqueous solution reported before 2006 a broad range of mean Cs–O bond distances, 3.0–3.2 Å, mean ca. 3.1 Å, as well as proposed coordination numbers, 5.1–9.6 (Table 1 in ref. [33]). Recent LAXS studies on aqueous solutions of cesium hydroxide, iodide, fluoride, and chloride report mean Cs–O bond distances of 3.08, 3.08, 3.10, and 3.13 Å, respectively [10,36,37]. Summarizing, the reported results on the hydrated cesium ion in aqueous solution mean that the most likely structure is eight-coordination in a square antiprismatic fashion with a mean Cs–O bond distance of ca. 3.10 Å. No ordered water molecules outside the first hydration shell of the hydrated cesium ion have been detected [10]. This is expected as cesium is the most weakly hydrated alkali metal ion.

3.2. Alkaline Earth Metal Ions

3.2.1. Beryllium

The tetraaquaberyllium(II) ion, $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$, is the only reported hydrated beryllium ion in the solid state. Its structure has been determined in 20 crystal structures, giving a mean Be–O bond distance of 1.614 Å (Supplementary Table S2a). Due to the weak X-ray scattering ability of beryllium, the results of experimental studies using X-ray techniques in aqueous solution become uncertain. Only one study is reported in the literature [38], with a reported Be–O bond distance of 1.67 Å. This is significantly longer than the bond distances obtained in the solid state. As the only reported study in aqueous solution is uncertain, the most likely structure of the hydrated beryllium(II) ion in aqueous solution is a tetrahedral tetraaquaberyllium(II) ion with the mean Be–O bond distance found in the solid state to be 1.62 Å. Due to the high charge density of the beryllium(II) ion, it is strongly hydrated and certainly has a well-defined second hydration sphere.

3.2.2. Magnesium

A very large number of crystal structures (511) contain a hexaaquamagnesium ion, $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ (Supplementary Table S2b). The configuration of the hexaaquamagnesium ion is octahedral, and the mean Mg–O bond distance in these structures is 2.066 Å. No crystal structures containing a hydrated magnesium ion with another coordination number than six have been reported.

The reported studies of hydrated magnesium ions in aqueous solution are scattered concerning both Mg–O bond distance and coordination number [28,29]. The mean Mg–O bond of these studies is slightly longer than the distance found in the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ ions in the solid state. As in the case of the hydrated beryllium ion, the results from X-ray methods on magnesium in an aqueous solution are less accurate than crystallographic determinations. A number of theoretical simulation studies have shown that the hexaaquamagnesium ion is by far the most stable structure of the hydrated magnesium ion in aqueous solution [39–42]. The hydrated magnesium ion binds certainly six water molecules in an octahedral fashion in aqueous solution with a mean Mg–O bond distance of 2.07 Å and a well-defined second hydration sphere.

3.2.3. Calcium

The hydrated calcium ion in solid compounds display different coordination numbers, $[\text{Ca}(\text{H}_2\text{O})_4]^{2+}$, $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ca}(\text{H}_2\text{O})_7]^{2+}$, and $[\text{Ca}(\text{H}_2\text{O})_8]^{2+}$ with mean Ca–O bond distances of 2.253, 2.324, 2.401, and 2.476 Å, respectively (Supplementary Table S2c). The $[\text{Ca}(\text{H}_2\text{O})_4]^{2+}$, $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$, and $[\text{Ca}(\text{H}_2\text{O})_8]^{2+}$ complexes have square-planar, octahedral, and square antiprismatic configuration, respectively, while the configuration of the $[\text{Ca}(\text{H}_2\text{O})_7]^{2+}$ complex is best described as monocapped octahedral. Furthermore, some solid state structures contain dimeric hydrated calcium ions where two or three water molecules bridge between two calcium ions, $[(\text{H}_2\text{O})_4\text{Ca}(\text{H}_2\text{O})_2\text{Ca}(\text{H}_2\text{O})_4]^{4+}$, $[(\text{H}_2\text{O})_4\text{Ca}(\text{H}_2\text{O})_3\text{Ca}(\text{H}_2\text{O})_4]^{4+}$, $[(\text{H}_2\text{O})_6\text{Ca}(\text{H}_2\text{O})_2\text{Ca}(\text{H}_2\text{O})_6]^{4+}$, and $[(\text{H}_2\text{O})_5\text{Ca}(\text{H}_2\text{O})_3\text{Ca}(\text{H}_2\text{O})_5]^{4+}$,

where the calcium ion is six-, seven-, eight-, and eight-coordinated, respectively (Supplementary Table S2c).

The structure of the hydrated calcium ion in aqueous solution has been reported in numerous experimental [28,29,43–52] and theoretical simulation [52–57] studies. The results are scattered with coordination numbers of 6–8 and Ca–O bond distances in the range of 2.35–2.48 Å. No dimeric hydrated calcium ions have been reported in aqueous solution. It seems most likely that the hydrated calcium ion in dilute aqueous solution is eight-coordinated in a square antiprismatic fashion with a mean Ca–O bond distance of ca. 2.48 Å, with a second hydration sphere, Ca(–O–H)···O, at ca. 4.58 Å [44]. Seven-coordination cannot completely be ruled out, but the reported Ca–O bond distances in experimental studies in aqueous solution are in most cases significantly longer than the mean Ca–O bond distance for seven-coordination in the solid state. Bond distances are much more accurately determined than the number of distances in LAXS and EXAFS experiments, and the strong correlation between the bond distance and the coordination number strongly indicates that the hydrated calcium ion is eight-coordinated in aqueous solution.

3.2.4. Strontium

The hydrated strontium ion is six- and eight-coordinated in octahedral and square antiprismatic fashions in the solid state with mean Sr–O bond distances of 2.496 and 2.613 Å, respectively (Supplementary Table S2d). A single solid-state structure has been reported to contain dimeric hydrated strontium ions, where four water molecules bridge two strontium ions, [(H₂O)₅Sr(H₂O)₄Sr(H₂O)₅]⁴⁺, where the strontium ion is nine-coordinated (Supplementary Table S2d).

The structure of the hydrated strontium ion in aqueous solution has been reported in several experimental [58–67] and theoretical simulation [68–74] studies. The results are consistent with a coordination number close to eight, and Sr–O bond distances in the range of 2.57–2.67 Å. The hydrated strontium ion is most likely eight-coordinated in a square antiprismatic fashion in aqueous solution with a mean Sr–O bond distance of ca. 2.62 Å. The hydrated strontium ion has a second hydration sphere, Sr(–O–H)···O, at ca. 4.78 Å [58].

3.2.5. Barium

The hydrated barium ion is eight- or nine-coordinated in the solid state with mean Ba–O bond distances of 2.777 Å, in square antiprismatic configuration, and 2.832 Å, respectively (Supplementary Table S2e). Solid state structures containing dimeric hydrated barium ions have been reported with the compositions [(H₂O)₇Ba(H₂O)₂Ba(H₂O)₇]²⁺, [(H₂O)₅Ba(H₂O)₄Ba(H₂O)₅]²⁺, and [(H₂O)₆Ba(H₂O)₄Ba(H₂O)₆]²⁺, where barium is nine-, nine- and ten-coordinated, respectively (Supplementary Table S2e).

A limited number of studies have been reported on the hydrated barium ion in aqueous solution. No study in aqueous solution has detected any hydrated dimeric barium ions. These studies report a mean Ba–O bond distance close to 2.82 Å and a coordination number of eight or nine [58,69,74–76]. The hydrated barium ion has a second hydration sphere, Ba(–O–H)···O, at ca. 4.90 Å [58].

3.2.6. Radium

A theoretical simulation of the hydrated radium(II) ion in aqueous solution proposes that it is ten-coordinated with a mean Ra–O bond distance of 2.93 Å [74].

3.3. Transition Metal Ions

3.3.1. Group 3 Elements

Scandium

The hydrated scandium ion displays different coordination numbers in solid compounds, [Sc(H₂O)₆]³⁺, [Sc(H₂O)₇]³⁺, and [Sc(H₂O)₈]³⁺, with mean Sc–O bond distances of 2.09, 2.16, and 2.24 Å, respectively (Supplementary Table S3a). The [Sc(H₂O)₆]²⁺ complex

has a regular octahedral configuration, while the $[\text{Sc}(\text{H}_2\text{O})_7]^{2+}$ complex has lower symmetry with the coordination best described as a monocapped octahedron [77] or a pentagonal bipyramid [78]. The $[\text{Sc}(\text{H}_2\text{O})_8]^{3+}$ ion has an unusual structure with a dicapped trigonal prismatic configuration, with one of the capping positions empty [79–81]. The compound $[\text{Sc}(\text{H}_2\text{O})_{8.0}](\text{CF}_3\text{SO}_3)_3$ displays a phase transition from high to low symmetry between 150 and 100 K, where in the low-temperature phase, the two capping water molecules have different Sc–O bond distances [79], while in the high-temperature phase, the capping waters have the same Sc–O bond distance with an occupancy factor of 2/3. The hydrated scandium(III) ion is out of the center of gravity of the trigonal prism in the low-temperature phase and shifted towards the most strongly bound capping water molecule [81].

EXAFS studies have shown that the structure of the hydrated $[\text{Sc}(\text{H}_2\text{O})_8]^{3+}$ ion has the same structure in aqueous solution as the low-temperature phase of in the solid state, with Sc–O_{prism}, Sc–O_{cap1}, and Sc–O_{cap2} bond distances of 2.17, 2.32, and ca. 2.5 Å, respectively [81]. It is an interesting fact that the hydrated scandium(III) ion has a water deficit in one of the capping positions also in aqueous solution. The hydrated scandium(III) ion is easily hydrolyzed to the $[(\text{H}_2\text{O})_5\text{Sc}(\text{OH})_2\text{Sc}(\text{H}_2\text{O})_5]^{4+}$ complex in aqueous solution [80]. The hydrated scandium(III) ion has a well-defined second hydration sphere, Sc(–O–H)···O, around the water molecules in the prism at 4.28 Å [81].

Yttrium

In the solid state, the hydrated yttrium(III) ion in both eight- and nine-coordination are reported, $[\text{Y}(\text{H}_2\text{O})_8]^{3+}$ and $[\text{Y}(\text{H}_2\text{O})_9]^{3+}$, in square antiprismatic and tricapped trigonal prismatic configuration, respectively (Supplementary Table S3b). A majority of the reported structures of the hydrated yttrium(III) ions are eight-coordinated with a mean Y–O bond distance of 2.353 Å (Supplementary Table S3b), and structures with tricapped trigonal prismatic coordination have mean Y–O bond distances of 2.364 and 2.481 Å to the oxygen in the prism and the capping positions, respectively (Supplementary Table S3b).

The hydrated yttrium(III) ion is reported to be eight-coordinated in a square antiprismatic fashion with a mean Y–O bond distance of 2.367(5) Å [82]. A second hydration sphere with ca. 16 water molecules at a Y(–O–H)···O distance was determined to be 4.40(4) Å [82]. It is an interesting observation that scandium(III) and yttrium(III) ions have the same coordination number in aqueous solution, eight, but they have different coordination geometries as described above. The reason for this difference has not been clarified.

3.3.2. Lanthanoids

The chemistry of the lanthanoids is dominated by the oxidation state +III. However, samarium, europium, thulium, and ytterbium have well-defined chemistry in the oxidation state +II and cerium in +IV. The lanthanoid(II) ions samarium(II), thulium(II), and ytterbium(II) are all very strong reducing agents, reducing water to hydrogen gas. The only lanthanoid(II) ion stable in aqueous solution is europium(II) [83]. An EXAFS study has revealed that the hydrated europium(II) ion is seven-coordinated in aqueous solution, with a mean Eu–O bond distance of 2.584 Å [66]. The lanthanoid(II) ions and complexes are strong reducing agents of large importance in organic chemistry, and their chemistry is mainly described in non-aqueous solvents [84]. Cerium(IV) is a very strong oxidation agent, frequently used in organic chemistry [85]. The aqueous chemistry of cerium(IV) is claimed to be similar to that of actinoid(IV) ions [86]. A combined EXAFS and simulation study in perchloric acidic aqueous solution shows that hydrated cerium(IV) is hydrolyzed to a hydrated dimer with an oxygen bridge, $[(\text{H}_2\text{O})_7\text{Ce–O–Ce}(\text{OH}_2)_7]^{6+}$, with mean Ce–O_O and Ce–O_{aq} bond distances of 2.08 and 2.43 Å, respectively [87].

The solids containing hydrated lanthanoid(III) ions are eight- or nine-coordinated (Supplementary Table S4). The eight-coordinated ions, $\text{Ln}(\text{H}_2\text{O})_8]^{3+}$, have square antiprismatic configuration, and the nine-coordinated ions, $\text{Ln}(\text{H}_2\text{O})_9]^{3+}$, have either regular tricapped trigonal prismatic configuration or distorted nine-coordination without any well-defined coordination figure (Supplementary Table S4a–n). The ionic radii of the

lanthanoid(III) ions decrease along the lanthanoid series due to the lanthanoid contraction. This is caused by the poor shielding of the nuclear charge by the 4f electrons, and thereby, the electrons in the electron shell outside the fourth shell are drawn towards the nucleus, resulting in a decreasing atomic/ionic radius along the lanthanoid series. There is a clear trend in the number of reported structures with eight- and nine-coordination in the solid state along the lanthanoid series. Nine-coordination dominates for the lighter lanthanoids and eight-coordination for the heavier ones (Supplementary Table S4). The heaviest lanthanoid(III) ions, Ho–Lu, with tricapped trigonal prismatic configuration have an increasing water deficit with an increasing atomic number in the capping positions, $[\text{Ho}(\text{H}_2\text{O})_{8.91}](\text{CF}_3\text{SO}_3)_3$, $[\text{Er}(\text{H}_2\text{O})_{8.96}](\text{CF}_3\text{SO}_3)_3$, $[\text{Tm}(\text{H}_2\text{O})_{8.8}](\text{CF}_3\text{SO}_3)_3$, $[\text{Yb}(\text{H}_2\text{O})_{8.7}](\text{CF}_3\text{SO}_3)_3$, and $[\text{Lu}(\text{H}_2\text{O})_{8.2}](\text{CF}_3\text{SO}_3)_3$ [79,88]. The ionic radii of the lanthanoid(III) ions in six-, seven-, eight- and nine-coordination have been estimated from crystal structures of homoleptic lanthanoid(III) complexes with neutral oxygen donors and studies in solution using oxygen donor solvents with different space demands at coordination [89]. The derived ionic radii of the lanthanoid(III) ions form a linear relationship with the atomic number for each coordination number. The structure and mean bond distances can be estimated with high accuracy, including the radioactive element promethium [89]. However, the mean Ln–O bond distance for nine-coordinated hydrates deviates from the straight-line relationship due to the increasing water deficit starting at holmium, and thereby a coordination number less than nine.

The structure of the hydrated lanthanoid(III) ions in aqueous solution was heavily debated in the mid-1960s. The origin of this debate was the proposed presence of a “gadolinium break”. The structure of the lanthanoid(III) ions in aqueous solution was assumed to change from nine- to eight-coordination at or close to gadolinium. This was based on observed discontinuities in a number of physico-chemical properties along the lanthanoid series, including partial molar volume [90], heat capacity [91], molar entropy [91], and viscosity [92], assumed to be related to the half-filled 4f shell of gadolinium(III) [93,94]. The partial molar volumes were expected to decrease continuously if the hydrated lanthanoid (III) ions had the same coordination geometry throughout the series, considering the lanthanoid contraction. The experimentally determined physico-chemical parameters showed in fact a discontinuity with an increase in the partial molar volumes from samarium to gadolinium. This was rationalized with an expected decrease in the hydration number of the heavier lanthanoid(III) ions [90]. The water exchange rate of the hydrated lanthanoid(III) ions decreases with the increasing atomic number and decreasing size of the lanthanoid (III) ions, as expected if the coordination geometry is maintained along the lanthanoid series. This is the expected behavior due to the lanthanoid contraction. However, the activation volumes at water exchange events are almost constant with a maximum at samarium/europium [95–98]. The complex formation rates for the lanthanoid(III) ions with sulfate and acetate ions show a maximum at samarium [99,100]. Liquid–liquid extraction experiments indicated more complex relationships between the structure and the physico-chemical parameters of the hydrated lanthanoid(III) ions in aqueous solution, proposing that the lanthanoid series can be divided into two octads with gadolinium common to both, or into four tetrads intersecting at neodymium/promethium, gadolinium, and holmium/erbium [101]. The tetrad effect is discerned, e.g., in the stability constants of the EDTA complexes in aqueous solution [102–104].

EXAFS studies have shown that structures of the hydrated lanthanoid(III) ions in the solid trifluoromethanesulfonate salts and in aqueous solution are identical to a tricapped trigonal prismatic configuration of water molecules [88]. The capping positions are fully occupied with water molecules in the first three tetrads (lanthanum–holmium). The mean M–O bond distance in the capping position decreases continuously from 2.53 Å for lanthanum to 2.38 Å for dysprosium, while the capping positions decrease less, from 2.60 Å (lanthanum) to 2.50 Å (dysprosium). This means that the difference in the M–O bond distance between the prismatic and capping positions increases along the first three tetrads [85]. In the last tetrad (holmium–lutetium), the occupancy factor in the capping

positions decreases from ca. 2.9 for holmium to ca. 2.2 for lutetium in both the solid state and aqueous solution [88]. Crystallographic studies showed a phase transition for $[\text{Lu}(\text{H}_2\text{O})_{8,2}](\text{CF}_3\text{SO}_3)_3$ at 130 K from the hexagonal space group $P6_3/m$ (no. 176) at high temperatures to the rhombohedral (trigonal) space group $R-3$ (No. 148) at temperatures below 130 K [88]. The low-temperature phase showed that one of the capping water molecules has a significantly shorter Lu–O bond distance, 2.40 Å, than the remaining ones, 2.56 Å, both with a mean occupancy factor of 0.6 [88], and that the lutetium(III) ion has left the center of gravity towards to the most strongly bound capping water molecule. EXAFS results showed that the structure of the hydrated lutetium(III) ion aqueous solution is in principle identical to the low-temperature phase of $[\text{Lu}(\text{H}_2\text{O})_{8,2}](\text{CF}_3\text{SO}_3)_3$ [85] and that the other lanthanoid(III) ions in the fourth tetrad show a similar bonding pattern to the capping water molecules. It can be assumed that the position of the lanthanoid(III) ions in the prism and the lanthanoid(III) ions in the fourth tetrad switch position with the same rate as the water exchange rate, $k \approx 10^8 \text{ s}^{-1}$ (Table 5 in ref. [8]).

3.3.3. Actinoids

Actinoid(III) and Actinoid(IV) Ions

The ionic radii of the actinoid(III) ions are slightly larger, ca. 0.09 Å, than the corresponding lanthanoid(III) ions [105]. Their ionic radii decrease along the actinoid series for the same reason as for the lanthanoid series but for the 5f electrons. Structure determinations of the solid $[\text{An}(\text{H}_2\text{O})_9](\text{CF}_3\text{SO}_3)_3$ salts, An=U, Np, Pu, Am, Cm, and Cf [106–109], showed that they are isostructural with the $[\text{Ln}(\text{H}_2\text{O})_9](\text{CF}_3\text{SO}_3)_3$ salts (Supplementary Tables S4a–n and S5a–e).

A limited number of studies on aqueous solutions on hydrated uranium(III), neptunium(III), plutonium(III), curium(III), berkelium(III), and californium(III) report mean An–O bond distances similar to those in the solid trifluoromethanesulfonate salts [108–115]. It can be assumed that all hydrated actinoid(III) ions have full nine-coordination in the tricapped trigonal prismatic configuration as the lawrencium(III) ion has approximately the same ionic radius as the dysprosium(III) ion [105]. This strongly indicates that the actinoid(III) ions of uranium–lawrencium are nine-coordinated in the tricapped trigonal prismatic configuration with the capping positions fully occupied. The hydrated actinium(III) ion has been reported to be 11-coordinated in aqueous solution, with a mean Ac–O bond distance of 2.63 Å [116]. The chemistry of actinium has been reviewed recently [117].

Only one crystal structure reports a hydrated thorium(IV) ion, $[\text{Th}(\text{H}_2\text{O})_{10}]\text{Br}_4$ [118], where thorium(IV) is ten-coordinated with a mean Th–O bond distance of 2.498 Å. Other thorium(IV) compounds with many water molecules bound to thorium(IV) include the nine-coordinated compounds $\text{H}_5\text{O}_2[\text{Th}(\text{H}_2\text{O})_6(\text{OSO}_2\text{CF}_3)_3][\text{Th}(\text{H}_2\text{O})_3(\text{OSO}_2\text{CF}_3)_6]$ [119] and $[(\text{H}_2\text{O})_7\text{Th}(\text{OH})_2\text{Th}(\text{H}_2\text{O})_7](\text{C}_2\text{N}_8)_2\text{C}_2\text{HN}_8 \cdot 10\text{H}_2\text{O}$ [120], and the ten-coordinated $[\text{Th}(\text{H}_2\text{O})_8(\text{ClO}_4)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ [119] and $[\text{Th}(\text{H}_2\text{O})_8(\text{NO}_3)](\text{ReO}_4)_3 \cdot \text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12} \cdot 3\text{H}_2\text{O}$ [121], with mean Th–O bond distances of 2.451, 2.478, 2.499, and 2.501 Å, respectively. The mean Th–O bond distance of the hydrated thorium(IV) ion in acidic aqueous solution has been determined to be 2.45 Å by EXAFS, indicating that it is nine-coordinated, most likely in a tricapped trigonal prismatic fashion [119,122]. A second hydration sphere, Th–(O–H)···O, around the water molecules in the prism was observed at 4.55 Å, and traces of a third hydration sphere at 6.85 Å [119]. The ionic radii of the actinoid(IV) ions are ca. 0.09 Å smaller than for corresponding lanthanoid(III) ions (Table 1 in ref. [105]).

For the EXAFS studies of the hydrated actinoid(IV) ions in aqueous solution, only mean M–O bond distances are reported. This is due to the low concentrations possible to obtain for these highly radioactive elements. It can be assumed that the hydrated actinoid(IV) ions in aqueous solution are nine-coordinated in a tricapped trigonal prismatic fashion as in the solid state [110–112,123–125].

Oxoactinoid(V) and Dioxoactinoid(VI)/Actinyl(V) and Actinyl(VI)

No solid state structures containing hydrated oxoactinoid(V) ions have been reported. The structure of the dioxouranium(VI) ion has been reported in several studies (Supplementary Table S5b) with the composition $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ and mean U=O and U–O_{aq} bond distances of 1.760 and 2.422 Å, respectively, where the oxo ligands form a linear unit with the five water molecules forming a pentagon perpendicular to the oxo ligands. The hydrated dioxoneptunium(VI) and dioxoplutonium(VI) ions have the same structure as the hydrated dioxouranium(VI) ion with Np=O and Np–O_{aq} bond distances of 1.744 and 2.416 Å, and Pu=O and Pu–O_{aq} bond distances of 1.732 and 2.409 Å, respectively (Supplementary Table S5c,d).

The structure of the oxouranium(VI) ion in the solid state is maintained in aqueous solution with U=O and U–O_{aq} bond distances of 1.76 and 2.41 Å, respectively [111,113–115,122], in pentagonal bipyramidal fashion. The structures of the hydrated oxoneptunium(V), dioxoneptunium(VI), oxoplutonium(V), and dioxoplutonium(VI) complexes in aqueous solution have been determined by EXAFS. The Np=O and Np–O_{aq} bond distances in $[\text{NpO}_2(\text{H}_2\text{O})_5]^+$ and $[\text{NpO}_2(\text{H}_2\text{O})_5]^{2+}$ have been determined to 1.82 and 2.46, and 1.74 and 2.37 Å, respectively, forming pentagonal bipyramids [111,126]. The Pu=O and Pu–O_{aq} bond distances in $[\text{PuO}_2(\text{H}_2\text{O})_{<5}]^+$ and $[\text{PuO}_2(\text{H}_2\text{O})_5]^{2+}$ have both been determined to 1.74 and 2.4 Å, forming (tetra)pentagonal bipyramids [115].

3.3.4. Group 4 Elements

Titanium(III)

The hydrated titanium(III) ion (d^1 electron configuration) is six-coordinated in octahedral fashion with a mean Ti–O bond distance of 2.02 Å in three reported structures (Supplementary Table S6a). Two other six-coordinated titanium(III) complexes support this mean Ti–O bond distance (Supplementary Table S6a).

The mean Ti–O bond distance in the only reported structure of the hydrated titanium(III) ion in aqueous solution is significantly longer, 2.12 Å [127], compared to that observed in the $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ complex in the solid state, 2.02 Å. An ESR and electron-spin echo study has indicated that the hydrated titanium(III) ion has a slightly compressed octahedral structure in aqueous solution [128]. The structure of the hydrated titanium(III) ion in aqueous solution can be regarded to have an octahedral configuration, possibly slightly compressed, with a mean Ti–O bond distance close to 2.02 Å.

Titanium(IV)/Titanyl(IV)

The oxotitanium(IV) ion (d^0), or titanyl(IV) ion, $[\text{Ti}=\text{O}]^{2+}$, cannot be prepared in sufficiently high concentrations in aqueous solution for structural characterization due to the formation of the insoluble titanium oxide, TiO_2 . However, the oxotitanium(IV) ion can be stabilized, and thereby it becomes more soluble by complexation with, e.g., sulfate ligands [129]. Furthermore, the oxotitanium(IV) ion is stable and more soluble in strongly solvating solvents such as dimethylsulfoxide. The mean Ti=O, Ti–O_{eq}, and Ti–O_{ax} bond distances in the dimethylsulfoxide-solvated oxotitanium(IV) ion, $[\text{TiO}(\text{OS}(\text{CH}_3)_2)_5]^{2+}$, have been determined in the solid state to 1.645, 2.035, and 2.22 Å, respectively [129–131], and in dimethylsulfoxide solution, almost identical Ti–O bond distances have been obtained [129]. The structure of the bis(hydrogensulfonato)oxotitanium(IV) complex in aqueous solution has Ti=O, Ti–O_{eq}, and Ti–O_{ax} bond distances of 1.646, 2.034, and 2.22 Å, respectively [129]. Based on these results it can be assumed that the structure of the hydrated titanyl(IV) ion in aqueous solution has a structure and bond distances close to those in these complexes.

Zirconium(IV) and Hafnium(IV)

The hydrated zirconium(IV) and hafnium(IV) ions (d^0) do hydrolyze very easily to hydrated octahydroxidotetrazirconium(IV) and -hafnium(IV) ions in aqueous solution. It is, therefore, necessary to perform the structure determination of the hydrated zirconium(IV) and hafnium(IV) ions in strongly acidic solution [132]. The mean Zr–O and Hf–O bond

distances in the hydrated zirconium(IV) and hafnium(IV) ions have been determined to be 2.19 and 2.16 Å in perchloric acidic aqueous solution [132].

Based on the structures of the hydrated octahydroxidotetrazirconium(IV) and -hafnium(IV) ions in the solid state (Supplementary Table S6b) and in aqueous solution, with mean Zr–O_{OH} and ZrO_{aq} bond distances of 2.15 and 2.27 Å, and mean Hf–O_{OH} and Hf–O_{aq} bond distances of 2.11 and 2.23 Å, respectively [132], the coordination geometry around the hydrated zirconium(IV) and hafnium(IV) ions is assumed to be the same in the hydrolyzed complexes, square antiprismatic [132].

3.3.5. Group 5 Elements

Vanadium(II) and Vanadium(III)

The hydrated vanadium(II) (d³) and vanadium(III) (d²) ions have a regular octahedral configuration with mean V–O bond distances of 2.13 and 1.99 Å, respectively, in the solid state (Supplementary Table S7a). An EXAFS study of the hydrated vanadium(III) ion in aqueous solution confirmed this structure also in aqueous solution with the same mean V–O bond distance, 1.99 Å [133]. An EXAFS study of the hydrated vanadium(II) and vanadium(III) ions reported mean V–O bond distances ca. 0.05 Å longer than those determined in the solid state [127]. The most likely V–O bond distances in the hydrated vanadium(II) and vanadium(III) ions in aqueous solution are most likely identical to those obtained in the solid state, 2.13 and 1.99 Å, respectively, with an octahedral configuration.

Oxovanadium(IV) and Dioxovanadium(V)/Vanadyl(IV) and Vanadyl(V)

The structure of the hydrated oxovanadium(IV) or vanadyl(IV) ion, [VO(H₂O)₅]²⁺, (d¹) in the solid state is six-coordinated with a strongly bound oxo group and five water molecules, where the water is opposite to the oxo group, O_{ax}, which is significantly weaker bound than those in the equatorial positions, O_{eq} (Supplementary Table S7a). The mean V=O, V–O_{eq}, and V–O_{ax} bond distances are 1.58, 2.03, and 2.19 Å, respectively. This structure is retained in aqueous solution with mean V=O, V–O_{eq}, and V–O_{ax} bond distances of 1.60, 2.02, and 2.20 Å [134], and 1.70 and 2.01 Å [127], respectively. The vanadyl(IV) ion has a structural configuration similar to the titanyl(IV) ion. The V=O double bond is slightly shorter than the Ti=O one, while the V–O and Ti–O bond distances to the water molecules are almost identical, *vide ultra*. A well-defined second hydration sphere around the equatorially bound water molecules, V–(O–H)···O, is observed at 4.06 Å [134]. The structure of the hydrated *cis*-dioxovanadium(V) ion, [VO₂(H₂O)₄]⁺ (d⁰), is so far only reported in acidic aqueous solution. The V=O, V–O_{cis}, and V–O_{trans} bond distances are determined to be 1.62, 1.99, and 2.22 Å, respectively [134]. A second hydration sphere, V–(O–H)···O, is observed at 4.16 and 4.27 Å to the water molecules in the *cis* and *trans* positions versus V=O, respectively [134].

3.3.6. Group 6 Elements

Chromium(II)

The structure of the hydrated chromium(II) ion (d⁴) has been reported in three solid-state structures (Supplementary Table S8). The chromium(II) ion is expected to display a Jahn–Teller distorted octahedral configuration due to its high spin d⁴ electron configuration with its doubly degenerate ground states. Two of the reported structures display the expected Jahn–Teller distortion, while the third structure does not (Supplementary Table S8). The reason is most likely that the direction of the elongated axial Cr–O bond is randomly distributed, causing a mean structure with higher symmetry and a mean bond distance of all Cr–O, as discussed for the nine-coordinated lanthanoid(III) ion, *vide ultra*, and the hydrated copper(II) ion, *vide infra*. The mean Cr–O_{eq} and Cr–O_{ax} bond distances of the reported solid-state structures with Jahn–Teller distortion are 2.08 and 2.33 Å for the water molecules in the equatorial and axial positions, respectively (Supplementary Table S8).

The mean equatorial bond distance, Cr–O_{eq}, has been determined to be 2.08 Å in aqueous solution by EXAFS [133], which is in full agreement with the observation in the

solid state. However, the mean axial bond distance was not detected. Whether the Jahn–Teller-distorted octahedral configuration is centrosymmetric or not will be discussed in the section of copper(II), *vide infra*. It can be assumed that the hydrated chromium(II) ion in aqueous solution has an octahedral Jahn–Teller configuration with Cr–O_{eq} and Cr–O_{ax} bond distances of 2.08 and ca. 2.3 Å, respectively.

Chromium(III)

The hydrated chromium(III) ion (d^3) has a well-characterized regular octahedral configuration with a mean Cr–O bond distance of 1.965 Å in the solid state (Supplementary Table S8). Numerous old studies of the hydrated chromium(III) ion in aqueous solution have been reported with a mean Cr–O bond distance of 1.99 Å [28,29]. A more recent study reports a mean Cr–O bond distance of 1.965 Å and a well-defined second hydration sphere, Cr–(O–H)···O, of ca. 12 water molecules at 4.08 Å [135]. Chromium(III) hydrolyzes easily to cationic polymeric complexes in aqueous solution in the pH range of 2–6 with $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$ and $[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$ as dominating species, depending on the total chromium(III) concentration [136]. The hydrated chromium(III) ion, $[\text{Cr}(\text{H}_2\text{O})_6(\text{H}_2\text{O})_{12}]^{3+}$, has a regular octahedral configuration with a mean Cr–O bond distance of 1.97 Å, and a well-defined second hydration sphere at 4.08 Å.

Molybdenum(II) and Molybdenum(III)

No structure of the hydrated molybdenum(II) ion (d^4) has been reported in the solid state. However, the molybdenum(II) ion is present as a dimer in aqueous solution with a strong quadruple Mo–Mo bond. Each molybdenum binds four molecules at 2.14 Å in the hydrated $[\text{Mo–Mo}]^{4+}$ ion, and the Mo–Mo bond distance is 2.12 Å [137].

The structure of the hydrated molybdenum(III) ion (d^3) has been reported in one crystal structure, $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$, with a Mo–O bond distance of 2.089 Å in a regular octahedral configuration [138]. The structure of the molybdenum(III) ion in aqueous solution is reported to be a hydrolyzed dimeric complex with double hydroxo bridges [137], but this interpretation seems questionable.

3.3.7. Group 7 Elements

Manganese(II)

The structure of the hydrated manganese(II) ion (d^5) has been reported in more than 160 crystal structure determinations to date (Supplementary Table S9). The manganese(II) ion binds six water molecules in a regular octahedron with a mean Mn–O bond distance of 2.174 Å. The same structure is present in aqueous solution with a mean Mn–O bond distance of 2.17 Å. [28,29,139,140] and a well-defined second hydration sphere, Mn–(O–H)···O, of ca. 12 water molecules at 4.25 Å [141].

Manganese(III)

The manganese(III) ion with a d^4 electron configuration is expected to be Jahn–Teller distorted similarly to the chromium(II) ion discussed above. The two reported crystal structures containing a hydrated manganese(III) ion report a regular octahedral configuration with mean Mn–O bond distances of 1.91 and 1.99 Å, respectively [27,142]. By comparing with other manganese(III) complexes with oxygen donor ligands in the solid state [143,144], the most reasonable structure of the hydrated manganese(III) ion is an octahedral Jahn–Teller-distorted complex with Mn–O_{eq} and Mn–O_{ax} bond distances of ca. 1.91 and 2.2 Å, respectively. However, this postulation needs to be proven by experimental data and/or theoretical simulations.

3.3.8. Group 8 Elements

Iron(II)

The hydrated iron(II) ion (d^6) is well characterized in the solid state, binding six water molecules in a regular octahedral fashion with a mean Fe–O bond distance of 2.120 Å

(90 reported structures) (Supplementary Table S10a). The same structure is observed in aqueous solution [28,29,145,146]. The hydrated iron(II) ion in aqueous solution has a regular octahedral configuration with a mean Fe–O bond distance of 2.12 Å. The hydrated iron(II) ion is expected to have a well-defined second hydration sphere, Fe–(O–H)···O, of ca. 12 water molecules, but no accurate data have been reported.

Iron(III)

The hydrated iron(III) ion (d^5) is well characterized in a number of crystal structures, having a regular octahedral structure with a mean Fe–O bond distance of 1.995 Å (20 reported structures) (Supplementary Table S10a). The same structure is observed in aqueous solution [28,29,145]. The hydrated iron(III) ion in aqueous solution has a regular octahedral configuration with a mean Fe–O bond distance of 1.995 Å. The hydrated iron(III) ion is expected to have a well-defined second hydration sphere, Fe–(O–H)···O, of ca. 12 water molecules, but no accurate data have been reported.

Ruthenium(II) and Ruthenium(III)

The mean Ru–O bond distances in the octahedral hydrated ruthenium(II) and ruthenium(III) ions (d^6 and d^5 , respectively) have been reported at 2.11 and 2.02 Å, respectively (Supplementary Table S10b). No experimental studies have been reported on the hydrated ruthenium(II) and ruthenium(III) ions in aqueous solution. It can be expected that the hydrated ruthenium(II) and ruthenium(III) ions retain the same structures in aqueous solution as in the solid state.

3.3.9. Group 9 Elements

Cobalt(II)

The hydrated cobalt(II) ion (d^7) binds six water molecules in a regular octahedral configuration with a mean Co–O bond distance of 2.087 Å in more than 430 reported solid-state structures (Supplementary Table S11a). A single study also reports a compound with a dimeric cobalt(II) hydrate, $[\text{Co}_2(\text{H}_2\text{O})_{10}]^{4+}$, where two water molecules bridge the cobalt ions, which are six-coordinated in octahedral fashion. The mean Co–O bond distance to the terminal water molecules is significantly shorter, ca. 2.03 Å, than the mean Co–O bond distance to the bridging water molecules, 2.17 Å (Supplementary Table S12a). No dimeric hydrated cobalt(II) ions have been reported in aqueous solution. The structure of the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion observed in the solid state is retained in aqueous solution [28,29,147–150]. The hydrated cobalt(II) ion in aqueous solution has a regular octahedral configuration, with a mean Co–O bond distance of 2.09 Å in a regular octahedral fashion and a well-defined second hydration sphere, Co–(O–H)···O, of ca. 12 water molecules at ca. 4.20 Å [151].

Cobalt(III)

The hydrated cobalt(III) ion (d^6) is a strong oxidant and is reduced in water to cobalt(II) under the release of oxygen. The only crystal structures containing a hexaaquacobalt(III) ion report a Co–O bond distance of 1.87 Å [27] (Supplementary Table S11a). No structure determination of the hydrated cobalt(III) ion in aqueous solution has been reported.

Rhodium(III)

The hydrated rhodium(III) ion is hexahydrated in the solid state forming a regular octahedron with a mean Rh–O bond distance of 2.01 Å (Supplementary Table S11b). This structure is retained in aqueous solution with a mean Rh–O bond distance of 2.03 Å and a well-defined second hydration sphere at 4.02 Å [152–154].

Iridium(III)

A single structure determination in the solid state of a compound containing an octahedral hydrated iridium(III) ion, $[\text{Ir}(\text{H}_2\text{O})_6]^{3+}$, has been reported. The mean Ir–O bond

distance is 2.04 Å (Supplementary Table S11b). It can be assumed that this structure is retained in aqueous solution even though no experimental studies are reported.

3.3.10. Group 10 Elements

Nickel

The hydrated nickel(II) ion (d^8) binds six water molecules in a regular octahedral configuration in the solid state as reported in 376 crystal structures with a mean Ni–O bond distance of 2.055 Å (Supplementary Table S12a). Two studies report compounds with a dimeric nickel hydrate, $[\text{Ni}_2(\text{H}_2\text{O})_{10}]^{4+}$, where two water molecules bridge the nickel ions, which are six-coordinated in an octahedral fashion. The Ni–O bond distance to the terminal water molecules is significantly longer, ca. 2.06 Å, than the Ni–O bond distance to the bridging water molecules, 1.93 Å (Supplementary Table S12a). The structure of the hydrated nickel(II) ion in aqueous solution has been reported in numerous studies [28,29,155], with a mean Ni–O bond distance of 2.055 Å in a regular octahedral fashion and a well-defined second hydration sphere, $\text{Ni}-(\text{O}-\text{H})\cdots\text{O}$, of ca. 12 water molecules at ca. 4.10 Å [151].

Palladium(II) and Platinum(II)

The hydrated palladium(II) and platinum(II) ions (d^8) in the solid state are four-coordinated in square-planar fashion with mean Pd–O and Pt–O bond distances of 2.03 and 2.01 Å, respectively (Supplementary Table S12b).

Several research groups reported independently of each other that, in addition to the four strongly bound water molecules, one or two water molecules are very weakly bound in the axial positions at ca. 2.75 Å, completing tetragonally elongated square-pyramidal or octahedral configurations in aqueous solution [156–160] from EXAFS and theoretical simulation studies, or a combination of them. The hydrated palladium(II) and platinum(II) ions are five- or six-coordinated in aqueous solution with mean Pd–O and Pt–O bond distances of 2.02 and 2.02 Å, respectively, and with one or two water molecules very loosely bound at 2.7–2.8 Å.

3.3.11. Group 11 Elements

Copper(I)

The hydrated copper(I) ion (d^{10}) disproportionate metallic copper and copper(II) ions in aqueous solution of $2\text{Cu}^+ \rightleftharpoons \text{Cu}(\text{s}) + \text{Cu}^{2+}$, $K_D = [\text{Cu}^{2+}][\text{Cu}^+]^{-2}$, in water, $K_D \approx 10^6 \text{ M}^{-1}$ [161]. This means that copper(I) ion can only be the dominating copper species in sub-micromolar aqueous solution, and accurate structure determinations can hardly be performed. In order to estimate the structure of the hydrated copper(I) ion in aqueous solution, a free energy correlation was applied. The K_D values of copper(I) in some solvents, and the difference in the mean Cu–O bond distances in the solvated copper(I) and copper(II) ions in the respective solvent, assuming the copper(I) and copper(II) ions have the same configuration independent of the solvent, were used in the free energy relationship correlation [161]. The hydrated copper(I) ion was estimated from this correlation to bind four water molecules in a tetrahedral fashion with a Cu–O bond distance of ca. 2.14 Å [161].

Copper(II)

Hydrated copper(II) ions with the compositions $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$, $[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$, and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ have been reported in the solid state (Supplementary Table S13a). The $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ complex is square-planar with a mean Cu–O bond distance of 1.93 Å. The $[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$ complex has either square-pyramidal (the most common configuration) mean Cu–O bond distances of 1.956 and 2.24 Å in the equatorial and axial positions, respectively, or a trigonal bipyramidal configuration with a mean Cu–O bond distance of 1.96 Å to the strongly bound water molecules in the triangle and ca. 2.24 Å to the weakly bound water molecules in the axial positions (Supplementary Table S13a). The structure of the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex in the solid state displays a variety of configurations: the expected Jahn–Teller-distorted octahedral configuration in both centrosymmetric complexes, in

which the axial Cu–O_{ax} bond distances are identical, non-centrosymmetric ones, in which the axial Cu–O bond distances are different, regular octahedrons, and irregular octahedrons with pair-wise significantly different Cu–O bond distances (Supplementary Table S13a). The Jahn–Teller-distorted [Cu(H₂O)₆]²⁺ complexes have mean Cu–O_{eq} and Cu–O_{ax} bond distances of 1.98 and 2.33 Å, independent of centrosymmetry or not (Supplementary Table S13a). The regular octahedral [Cu(H₂O)₆]²⁺ complexes have a mean Cu–O bond distance of 2.08 Å (Supplementary Table S13a). The presence of regular [Cu(H₂O)₆]²⁺ complexes is unexpected. An EXAFS study of a series of regular octahedral copper(II) complexes was carried out, where the lattice-independent EXAFS method proved that these complexes in fact are Jahn–Teller-distorted, with the expected splitting in short equatorial and long axial Cu–ligand bonds [162]. The reason for the observed regular octahedral structure of the Jahn–Teller-distorted [Cu(H₂O)₆]²⁺ complex is that the direction of the Cu–O_{ax} bonds are randomly distributed in the structure, causing the mean structure to have higher symmetry than the individual complexes, and thereby an incorrect description the complex. In a recent study, it was shown that solid compounds crystallizing in a non-centrosymmetric space group or with the copper ion in the [Cu(H₂O)₆]²⁺ complex not in the center of symmetry all have significantly different Cu–O_{ax} bond distances. This is also the case in all compounds with [Cu(H₂O)₅(O–ligand)] complexes with an octahedral configuration, which cannot be centrosymmetric [163]. This strongly indicates that the [Cu(H₂O)₆]²⁺ ion is non-centrosymmetric and that the axial Cu–O_{ax} bonds are different.

The structure of the hydrated copper(II) ion in aqueous solution has been the theme of scientific discussion for more than 20 years. This discussion concerns whether the hydrated copper(II) ion is five- or six-coordinated, and if it is six-coordinated, whether the Jahn–Teller-distorted complex is centrosymmetric or not, *vide ultra*. Linear electric field EPR studies gave the first indications that the hydrated copper(II) ion in aqueous solution is non-centrosymmetric [164,165]. The paper initiating the scientific debate was a combined neutron and molecular dynamics study, which proposed that the hydrated copper(II) ion is five-coordinated in aqueous solution [166]. This study was followed by a large number of publications, mainly using EXAFS and XANES spectroscopy and DFT and QMCF/MD simulations to study the coordination chemistry of the hydrated copper(II) ion in aqueous solution [163,167–180]. This scientific discussion continues as no full consensus on the structure of the hydrated copper(II) ion in aqueous solution has been reached. However, it seems most likely that it has a non-centrosymmetric Jahn–Teller-distorted octahedral structure with mean Cu–O_{eq}, Cu–O_{ax1}, and Cu–O_{ax2} bond distances of ca. 1.96, 2.15, and 2.32 Å, respectively, according to the most recent studies [163,180].

Silver

The structure of the hydrated silver(I) ion (d¹⁰) in the solid state is two-coordinated in a linear fashion with a mean Ag–O bond distance of 2.13 Å, and one structure where silver is three-coordinated in a triangular fashion, but the reported Ag–O bond distance is unexpectedly long (Supplementary Table S13b).

The structure of the hydrated silver(I) ion in aqueous solution has been debated for many years as different coordination numbers and Ag–O bond distances have been proposed, with a Ag–O bond distance of ca. 2.4 Å in a tetrahedral configuration as the first one [28,29]. A combined LAXS and EXAFS proposed a linearly distorted four-coordination with two Ag–O bonds at 2.32 Å and two very weakly bound at ca. 2.5 Å [181]. A recent combined EXAFS, LAXS, and simulation study proposed a similar structure but without the two weakly bound water molecules. A mean Ag–O bond distance of 2.34 Å and a diffuse hydration shell at a longer distance, and a second hydration sphere, Ag–(O–H)···O, at 4.65 Å was proposed [182]. It is interesting to note that this diffuse hydration shell caused a lengthening of the linearly bound water molecules with ca. 0.2 Å, independent of the distance to the weakly bound water molecules.

Gold

Only one structure in the solid state has reported a hydrated gold(III) ion [183]. Gold(III) binds four water molecules in a square-planar fashion with a mean Au–O bond distance of 2.155 Å (Supplementary Table S13c). It is expected that this structure is retained in aqueous solution.

3.3.12. Group 12 Elements

Zinc

Hydrated zinc(II) ions (d^{10}) with the compositions $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$, $[\text{Zn}(\text{H}_2\text{O})_5]^{2+}$, and $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ have been reported in the solid state (Supplementary Table S14a). The $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$ complex is tetrahedral, with a mean Zn–O bond distance of 2.03 Å. The $[\text{Zn}(\text{H}_2\text{O})_5]^{2+}$ complex has a trigonal bipyramidal configuration with a mean Zn–O bond distance of 2.02 Å, and the $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ complex has a regular octahedral configuration with a mean Zn–O bond distance of 2.088 Å (Supplementary Table S14a). The Zn–O bond distances in the two reported $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$ complexes are longer than the $[\text{Zn}(\text{H}_2\text{O})_5]^{2+}$ complexes and significantly longer than tetrahedral zinc(II) complexes with oxygen donor ligands, ca. 1.95 Å [143,144]. The hydrated zinc(II) ion in aqueous solution binds six water molecules at a mean Zn–O bond distance of 2.09 Å in a regular octahedral fashion [28,29]. The hydrated zinc(II) ion has a second hydration sphere, Zn–(O–H)···O, of ca. 12 water molecules at ca. 4.2 Å [28,29].

Cadmium

The hydrated cadmium(II) ion (d^{10}) binds six water molecules with a mean Cd–O bond distance of 2.266 Å in a regular octahedral fashion in the solid state (Supplementary Table S14b). A single study reports a hydrated cadmium(II) ion with the composition $[\text{Cd}(\text{H}_2\text{O})_4]^{2+}$, but the reported Cd–O bond distance is far too long to be considered correct (Supplementary Table S14b). A single study also reports a compound with a dimeric cadmium(II) hydrate, $[\text{Cd}_2(\text{H}_2\text{O})_{10}]^{4+}$, where two water molecules bridge the cadmium ions which are six-coordinated in an octahedral fashion. The terminal Cd–O bonds are significantly shorter than the bridging ones (Supplementary Table S14b).

The structure of the hydrated cadmium(II) ion in aqueous solution has been determined in several early studies with a mean Cd–O bond distance of ca. 2.29 Å [28,29]. A combined LAXS and ab initio MD simulation study of the hydrated cadmium ion in aqueous solution showed unusually broad bond distance distribution. The mean Cd–O bond distance in the hydrated cadmium ion in aqueous solution was reported to be 2.27 Å, with a possibility of an equilibrium between six- and seven-coordination [184]. The hydrated cadmium(II) ion has a second hydration sphere, Cd–(O–H)···O, of ca. 12 water molecules at ca. 4.28 Å [184].

Mercury(I)

The mercury(I) ion (d^9) is dimeric and binds two water molecules in a linear fashion, $[\text{H}_2\text{O–Hg–Hg–OH}_2]^{2+}$, with mean Hg–O and Hg–Hg bond distances of 2.14 and 2.50 Å in the solid state (Supplementary Table S14c). A larger coordination number around each mercury, with three water molecules binding to each mercury, is observed in aqueous solution with mean Hg–O and Hg–Hg bond distances of 2.26 and 2.525 Å, respectively [185]. This completes a distorted tetrahedral configuration around each mercury in aqueous solution. The hydrated mercury(I) ion has a second hydration sphere, Hg–(O–H)···O, of ca. six water molecules around each $\text{Hg}(\text{H}_2\text{O})_3$ unit at ca. 4.52 Å [185]. A QMCF MD simulation study supports the experimentally obtained results [186].

Mercury(II)

The only crystal structure containing a fully hydrated mercury(II) ion is $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ (Supplementary Table S14c). The $[\text{Hg}(\text{H}_2\text{O})_6]^{2+}$ ion is reported to have a regular octahedral configuration with a Hg–O bond distance of 2.342 Å. However, an EXAFS study of this

compound showed that it has the same wide and asymmetric bond distribution as the hydrated mercury(II) ion in aqueous solution [187], *vide infra*.

EXAFS studies on the hydrated mercury(II) ion (d^{10}) in aqueous solution have reported two different coordination numbers, six [187] and seven [188], both in wide and highly asymmetric bond distance distributions, with mean Hg–O bond distances of 2.33 and 2.32 Å, respectively [187,188]. The mean Hg–O bond distance reported for the proposed seven-coordinated mercury(II) hydrate, 2.32 Å [188], should be significantly longer than the mean Hg–O bond distance observed in octahedral complexes [26]. A crystal structure of a compound containing a dimethylsulfoxide (dmsol)-solvated mercury(II) ion, $[\text{Hg}(\text{OS}(\text{CH}_3)_2)_6](\text{ClO}_4)_2$, crystallizes in a low-symmetry group ($P-1$). It shows that four of the dmsol molecules has significantly shorter Hg–O bond distance than the remaining two, 2.319 and 2.376 Å, respectively [189]. The EXAFS data of six-coordinated homoleptic mercury(II) complexes in both solid state and solution all show a significant asymmetric bond distance distribution, strongly indicating a splitting of the Hg–O bond distances in the same way as in the solid $[\text{Hg}(\text{OS}(\text{CH}_3)_2)_6](\text{ClO}_4)_2$ [187]. This indicates that all six-coordinated mercury(II) complexes have this bond distance distribution, but it is only observed in solid compounds crystallizing in low-symmetry space groups as discussed for hydrated copper(II), lanthanoid(III), and scandium ions, *vide ultra*. This bond distance distribution can be described as a so-called pseudo-Jahn–Teller effect [190]. The pseudo-Jahn–Teller effect is a destabilization of six-coordinated metal complexes, including mercury(II), with small monodentate ligands [190–192]. This asymmetric coordination figure is caused by a contribution of the mercury(II) $5d_{z^2}$ atomic orbital to the bonding molecular orbitals by vibronic coupling. The significant asymmetry of the Hg–O bond distance distribution in the hydrated mercury(II) ion in both aqueous solution and solid $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ strongly supports that the hydrated mercury(II) has a pseudo-Jahn–Teller-distorted octahedral configuration [187]. The LAXS study showed a second hydration sphere, $\text{Hg}-(\text{O}-\text{H})\cdots\text{O}$, of ca. 12 water molecules at ca. 4.20 Å [187].

3.4. Group 13 Elements

Aluminum, Gallium, Indium, and Thallium(III)

The hydrated trivalent aluminum, gallium, indium, and thallium(III) ions, $[\text{M}(\text{H}_2\text{O})_6]^{3+}$, all have a well-defined regular octahedral configuration in the solid state, with mean M–O bond distances of 1.88, 1.95, 2.12, and 2.17 Å, respectively (Supplementary Table S15); the Tl–O bond distance is shorter than expected in comparison to the observations in aqueous solution, *vide infra*. The structure of the hydrated aluminum, gallium, indium, and thallium(III) ions retain their structures observed in the solid state in aqueous solution with mean M–O bond distances of 1.89, 1.96, 2.14, and 2.23 Å, respectively [28,29,135,193,194]. Second hydration spheres, $\text{M}-(\text{O}-\text{H})\cdots\text{O}$, with ca. 12 molecules have been detected at 4.05, 4.13, and 4.2 Å for gallium, indium, and thallium(III), respectively [135,193].

3.5. $d^{10}s^2$ Metal Ions in Groups 13, 14, and 15

The coordination chemistry of metal ions with a $d^{10}s^2$ electron configuration, thallium(I), tin(II), lead(II), and bismuth(III), is dependent on the hybridization of these orbitals.

The $d^{10}s^2$ metal ions have an inert electron pair, which occupies a hybrid orbital formed by mixing the ns and np orbitals on the metal ion, according to the valence bond theory. It may be stereo-chemically active when mixing the ns and np orbitals, and a gap is formed in the coordination sphere, or it could be a pure s^2 electron pair and thereby stereo-chemically inactive, where all positions in the coordination geometry are occupied [195]. A lone electron pair acts as an additional ligand, which normally occupies more space than an ordinary ligand [196,197]. However, by applying the molecular orbital theory to the classical concept of ns/np orbital hybridization in $d^{10}s^2$ metal ions, it is regarded as incorrect. The stereo-chemical activity of the outer s^2 electron pair is instead a result of anti-bonding metal ion-donor atom interactions [198]. This results in two general geometries, a *holo-directed* one that is stereo-chemically inactive *without* a gap for the anti-bonding orbital,

and a *hemi-directed* one being stereo-chemically active *with* a gap for the anti-bonding orbital [195].

The bonding character in the metal ion complex has a large impact on the electron density of the antibonding orbital and thereby on the size of the created void [199]. For ligands forming mainly electrostatic interactions, such as oxygen-donor ligands, the antibonding M(ns)–ligand(*np*) orbital couples with the M(ns) orbital [199–201].

3.5.1. Thallium(I)

No solid compounds have been reported to contain a fully hydrated thallium(I) ion. Due to the weak hydration, only an indication of two bond distances, 2.73 and 3.18 Å, with a broad bond distance distribution, could be detected in a combined LAXS and EXAFS study [202]. It was not possible from this study to reveal any coordination geometry around thallium(I). As the thallium(I) ion has a $d^{10}s^2$ electron configuration, it can be assumed that it has a large gap in the coordination sphere with a *hemi-directed* configuration.

3.5.2. Tin(II)

The structure of the hydrated tin(II) ion has only been reported in two studies of solid $[\text{Sn}(\text{H}_2\text{O})_3](\text{ClO}_4)_2$ (Supplementary Table S16a). The $[\text{Sn}(\text{H}_2\text{O})_3]^{2+}$ ion has a mean Sn–O bond distance of 2.20 Å, and a huge gap in the coordination sphere with all O–Sn–O bond angles ca. 77°. This means that less than one-quarter of the coordination sphere is occupied by binding water molecules and thereby has a huge impact on the electrons in the anti-bonding orbitals.

Early studies reported the hydrated tin(II) ion in aqueous solution to have coordination numbers close to six and two different Sn–O bond distances [28,29], but this interpretation has not been supported by other studies. A recent combined EXAFS and XANES study reported an identical structure of the hydrated tin(II) ion in aqueous solution as in the solid state [203].

3.5.3. Lead(II)

The structure of the hydrated lead(II) ion is reported in four studies, where three contain a three-coordinate complex, $[\text{Pb}(\text{H}_2\text{O})_3]^{2+}$, and the remaining one contains a four-coordinate $[\text{Pb}(\text{H}_2\text{O})_4]^{2+}$ complex (Supplementary Table S16b). These structures are strongly affected by anti-bonding orbitals displaying all O–Pb–O bond angles close to 77° in the $[\text{Pb}(\text{H}_2\text{O})_3]^{2+}$ complex, and in the $[\text{Pb}(\text{H}_2\text{O})_4]^{2+}$ complex, the nearby O–Pb–O angles are close to 77°, and the diagonal angles are ca. 105° (Supplementary Table S16b). The mean Pb–O bond distances in the $[\text{Pb}(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Pb}(\text{H}_2\text{O})_4]^{2+}$ complexes are 2.44 and 2.40 Å, respectively.

An early NMR study reported the hydration number of lead(II) to be six in aqueous solution [204]. A number of computer simulation studies on the structure of the hydrated lead(II) ion have been reported, but they all have difficulties describing the coordination chemistry and structural effects of anti-bonding orbitals. The mean Pb–O bond distance has been reported to be 2.50 Å in an EXAFS study [205]. A combined LAXS and EXAFS study of the hydrated lead(II) reported a mean Pb–O bond distance of 2.54 Å in a very broad bond distance distribution. A second hydration sphere, $\text{Pb}-(\text{O}-\text{H})\cdots\text{O}$, of ca. 12 water molecules at 4.42 Å was detected [206]. The EXAFS and LAXS studies of the hydrated lead(II) ion have shown a very broad bond distance distribution of around 2.5 Å, and that the number of water molecules cannot be determined accurately but should be in the range of 5–7.

3.5.4. Bismuth(III)

The only reported structure containing a hydrated bismuth(III) ion in the solid state, $[\text{Bi}(\text{H}_2\text{O})_9](\text{CF}_3\text{SO}_3)_3$, is nine-coordinated in a tricapped trigonal prismatic configuration with mean Bi–O bond distances of 2.44 (prism) and 2.58 Å (capping positions) (Supplementary Table S16c). The structure of the hydrated bismuth(III) ion in aqueous

solution was proven to have a significantly different structure, being eight-coordinated in a square antiprismatic configuration. The mean Bi–O bond distance was reported to be 2.41 Å, and a second hydration sphere, Bi–(O–H) ··· O, of ca. 16 water molecules at 4.48 Å, was observed [207].

4. Summary

Table 1 summarizes the observed hydrate complexes in the solid state and aqueous solution reported so far and predicted coordination numbers of metal ions from structural relationships of the nine-coordinated lanthanoid(III) and actinoid(III) ions based on other physico-chemical or structural relationships. Table 2 summarizes the mean M–O bond distances in hydrated metal ions in the solid state and aqueous solution. It has not for any metal ion been proven that the coordination number or structure in aqueous solution is concentration-dependent as long as any complex formation with, e.g., counter ions or hydrolysis does not take place. Many metal ions have several coordination numbers, configurations, and formations of dimeric and polymeric hydrate complexes with bridging water molecules in the solid state, but in aqueous solution, one coordination number with a specific configuration strongly dominates (Table 1).

The monovalent metal ions, with the exception of the lithium and silver(I) ions, have one well-defined first hydration shell, but the water molecules outside it are not spectroscopically distinguishable from the aqueous bulk [9,10]. Di- and trivalent metal ions have a well-defined second hydration there on average; one water molecule in the first hydration sphere hydrogen binds two water molecules in the second hydration sphere, as can be shown by double difference infrared spectroscopy [9] and the LAXS and LANS methods [28,29]. Four-valent and small trivalent metal ions may have at least traces of a third hydration as, e.g., shown in the hydrated thorium(IV) ion [118].

Table 1. Summary of metal ion aqua complexes reported in the solid state and aqueous solution. Complexes in italics highlight the complexes present in aqueous solution not observed in the solid state, and underlined complexes are either extrapolated from the structures of metal ion solvates of non-aqueous solvents, from physico-chemical relationships.

Metal Ion	Solid State	Aqueous Solution
Lithium(I)	$[\text{Li}(\text{H}_2\text{O})_4]^+$, $\text{Li}(\text{H}_2\text{O})_5^+$, $[\text{Li}(\text{H}_2\text{O})_6]^+$, $[\text{Li}_2(\text{H}_2\text{O})_6]^{2+}$, $[\text{Li}_2(\text{H}_2\text{O})_7]^{2+}$, $[\text{Li}_3(\text{H}_2\text{O})_6]^{3+}$, $[\text{Li}_3(\text{H}_2\text{O})_8]^{3+}$	$[\text{Li}(\text{H}_2\text{O})_4]^+$
Sodium(I)	$[\text{Na}(\text{H}_2\text{O})_2]^+$, $[\text{Na}(\text{H}_2\text{O})_4]^+$, $[\text{Na}(\text{H}_2\text{O})_5]^+$, $[\text{Na}(\text{H}_2\text{O})_6]^+$, $[\text{Na}(\text{H}_2\text{O})_8]^+$, $[\text{Na}_2(\text{H}_2\text{O})_6]_n^{2+}$, $[\text{Na}_2(\text{H}_2\text{O})_7]_n^{2+}$, $[\text{Na}_2(\text{H}_2\text{O})_8]_n^{2+}$, $[\text{Na}_2(\text{H}_2\text{O})_8]_n^{2+}$, $[\text{Na}_2(\text{H}_2\text{O})_9]_n^{2+}$, $[\text{Na}_2(\text{H}_2\text{O})_{10}]_n^{2+}$, $[\text{Na}_2(\text{H}_2\text{O})_{13}]_n^{2+}$, $[\text{Na}_4(\text{H}_2\text{O})_{14}]_n^{4+}$, $[\text{Na}_4(\text{H}_2\text{O})_{14}]_n^{4+}$, $[\text{Na}_4(\text{H}_2\text{O})_{18}]_n^{4+}$, $[\text{Na}_5(\text{H}_2\text{O})_{14}]_n^{5+}$, $[\text{Na}_8(\text{H}_2\text{O})_{24}]_n^{8+}$	$[\text{Na}(\text{H}_2\text{O})_6]^+$
Potassium(I)	$[\text{K}(\text{H}_2\text{O})_6]^+$, $[\text{K}(\text{H}_2\text{O})_7]^+$, $[\text{K}(\text{H}_2\text{O})_8]^+$, $[\text{K}_2(\text{H}_2\text{O})_9]_n^{2+}$	$[\text{K}(\text{H}_2\text{O})_7]^+$
Rubidium(I)	$[\text{Rb}(\text{H}_2\text{O})_9]^+$	$[\text{Rb}(\text{H}_2\text{O})_8]^+$
Cesium(I)	$[\text{Cs}(\text{H}_2\text{O})_{10}]^+$	$[\text{Cs}(\text{H}_2\text{O})_8]^+$
Beryllium(II)	$[\text{Be}(\text{H}_2\text{O})_4]^{2+}$	$[\text{Be}(\text{H}_2\text{O})_4]^{2+}$
Magnesium(II)	$[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$
Calcium(II)	$[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ca}(\text{H}_2\text{O})_7]^{2+}$, $[\text{Ca}(\text{H}_2\text{O})_8]^{2+}$, $[\text{Ca}_2(\text{H}_2\text{O})_{10}]^{4+}$, $[\text{Ca}_2(\text{H}_2\text{O})_{11}]^{4+}$, $[\text{Ca}_2(\text{H}_2\text{O})_{14}]^{4+}$	$[\text{Ca}(\text{H}_2\text{O})_8]^{2+}$
Strontium(II)	$[\text{Sr}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Sr}(\text{H}_2\text{O})_8]^{2+}$, $[\text{Sr}(\text{H}_2\text{O})_9]^{2+}$, $[\text{Sr}_2(\text{H}_2\text{O})_{14}]^{4+}$	$[\text{Sr}(\text{H}_2\text{O})_8]^{2+}$
Barium(II)	$[\text{Ba}(\text{H}_2\text{O})_8]^{2+}$, $[\text{Ba}(\text{H}_2\text{O})_9]^{2+}$, $[\text{Ba}_2(\text{H}_2\text{O})_{14}]^{4+}$, $[\text{Ba}_2(\text{H}_2\text{O})_{18}]^{4+}$	$[\text{Ba}(\text{H}_2\text{O})_{8-9}]^{2+}$
Radium(II)		$[\text{Ra}(\text{H}_2\text{O})_{\approx 10}]^{2+}$
Scandium(III)	$[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Sc}(\text{H}_2\text{O})_7]^{3+}$, $[\text{Sc}(\text{H}_2\text{O})_{8.0}]^{3+}$	$[\text{Sc}(\text{H}_2\text{O})_{8.0}]^{3+}$

Table 1. Cont.

Metal Ion	Solid State	Aqueous Solution
Yttrium(III)	$[Y(H_2O)_8]^{3+}, [Y(H_2O)_9]^{3+}$	$[Y(H_2O)_8]^{3+}$
Lanthanum(III)	$[La(H_2O)_6]^{3+}, [La(H_2O)_8]^{3+}, [La(H_2O)_9]^{3+}$	$[La(H_2O)_9]^{3+}$
Cerium(III)	$[Ce(H_2O)_8]^{3+}, [Ce(H_2O)_9]^{3+}$	$[Ce(H_2O)_9]^{3+}$
Cerium(IV)		$[Ce(H_2O)_8]^{4+}$
Praseodymium(III)	$[Pr(H_2O)_8]^{3+}, [Pr(H_2O)_9]^{3+}$	$[Pr(H_2O)_9]^{3+}$
Neodymium(III)	$[Nd(H_2O)_8]^{3+}, [Nd(H_2O)_9]^{3+}$	$[Nd(H_2O)_9]^{3+}$
Prometium(III)		$[Pm(H_2O)_9]^{3+}$
Samarium(III)	$[Sm(H_2O)_8]^{3+}, [Sm(H_2O)_9]^{3+}$	$[Sm(H_2O)_9]^{3+}$
Europium(II)		$[Eu(H_2O)_7]^{2+}$
Europium(III)	$[Eu(H_2O)_8]^{3+}, [Eu(H_2O)_9]^{3+}$	$[Eu(H_2O)_9]^{3+}$
Gadolinium(III)	$[Gd(H_2O)_8]^{3+}, [Gd(H_2O)_9]^{3+}$	$[Gd(H_2O)_9]^{3+}$
Terbium(III)	$[Tb(H_2O)_8]^{3+}, [Tb(H_2O)_9]^{3+}$	$[Tb(H_2O)_9]^{3+}$
Dysprosium(III)	$[Dy(H_2O)_8]^{3+}, [Dy(H_2O)_9]^{3+}$	$[Dy(H_2O)_9]^{3+}$
Holmium(III)	$[Ho(H_2O)_8]^{3+}, [Ho(H_2O)_{8.91}]^{3+}, [Ho(H_2O)_9]^{3+}$	$[Ho(H_2O)_{8.91}]^{3+}$
Erbium(III)	$[Er(H_2O)_8]^{3+}, [Er(H_2O)_{8.95}]^{3+}, [Er(H_2O)_9]^{3+}$	$[Er(H_2O)_{8.95}]^{3+}$
Thulium(III)	$[Tm(H_2O)_8]^{3+}, [Tm(H_2O)_{8.8}]^{3+}, [Tm(H_2O)_9]^{3+}$	$[Tm(H_2O)_{8.8}]^{3+}$
Ytterbium(II)		$[Yb(H_2O)_8]^{2+}$
Ytterbium(III)	$[Yb(H_2O)_8]^{3+}, [Yb(H_2O)_{8.7}]^{3+}, [Yb(H_2O)_9]^{3+}$	$[Yb(H_2O)_{8.7}]^{3+}$
Lutetium(III)	$[Lu(H_2O)_8]^{3+}, [Lu(H_2O)_{8.2}]^{3+}, [Lu(H_2O)_9]^{3+}$	$[Lu(H_2O)_{8.2}]^{3+}$
Actinium(III)		$[Ac(H_2O)_{11}]^{3+}$
Thorium(IV)	$[Th(H_2O)_8]^{4+}, [Th(H_2O)_9]^{4+}, [Th(H_2O)_{10}]^{4+}$	$[Th(H_2O)_9]^{4+}$
Uranium(III)	$[U(H_2O)_9]^{3+}$	$[U(H_2O)_9]^{3+}$
Uranium(IV)		$[U(H_2O)_9]^{4+}$
Uranium(VI)	$[UO_2(H_2O)_5]^{2+}$	$[UO_2(H_2O)_5]^{2+}$
Neptunium(III)	$[Np(H_2O)_9]^{3+}$	$[Np(H_2O)_9]^{3+}$
Neptunium(IV)		$[Np(H_2O)_9]^{4+}$
Neptunium(V)		$[NpO_2(H_2O)_5]^+$
Neptunium(VI)	$[NpO_2(H_2O)_5]^{2+}$	$[NpO_2(H_2O)_5]^{2+}$
Plutonium(III)	$[Pu(H_2O)_9]^{3+}$	$[Pu(H_2O)_9]^{3+}$
Plutonium(IV)		$[Pu(H_2O)_9]^{4+}$
Plutonium(V)		$[PuO_2(H_2O)_5]^+$
Plutonium(VI)	$[PuO_2(H_2O)_5]^{2+}$	$[PuO_2(H_2O)_5]^{2+}$
Americium(III)	$[Am(H_2O)_9]^{3+}$	$[Am(H_2O)_9]^{3+}$
Curium(III)	$[Cm(H_2O)_9]^{3+}$	$[Am(H_2O)_9]^{3+}$
Berkelium(III)		$[Bk(H_2O)_9]^{3+}$
Californium(III)	$[Cf(H_2O)_9]^{3+}$	$[Cf(H_2O)_9]^{3+}$
Einsteinium(III)		$[Es(H_2O)_9]^{3+}$
Fermium(III)		$[Fm(H_2O)_9]^{3+}$
Mendelevium(III)		$[Md(H_2O)_9]^{3+}$

Table 1. Cont.

Metal Ion	Solid State	Aqueous Solution
Nobelium(III)		$[No(H_2O)_9]^{3+}$
Lawrentium(III)		$[Lr(H_2O)_9]^{3+}$
Titanium(III)	$[Ti(H_2O)_6]^{3+}$	$[Ti(H_2O)_6]^{3+}$
Titanium(IV)		$[TiO(H_2O)_5]^{2+}$
Zirconium(IV)		$[Zr(H_2O)_8]^{4+}$
Hafnium(IV)		$[Hf(H_2O)_8]^{4+}$
Vanadium(II)	$[V(H_2O)_6]^{2+}$	$[V(H_2O)_6]^{2+}$
Vanadium(III)	$[V(H_2O)_6]^{3+}$	$[V(H_2O)_6]^{3+}$
Vanadium(IV)	$[VO(H_2O)_6]^{2+}$	$[VO(H_2O)_5]^{2+}$
Vanadium(V)		<i>cis</i> - $[VO_2(H_2O)_4]^+$
Chromium(II)	$[Cr(H_2O)_6]^{2+}$	$[Cr(H_2O)_6]^{2+}$
Chromium(III)	$[Cr(H_2O)_6]^{3+}$	$[Cr(H_2O)_6]^{3+}$
Molybdenum(II)		$[Mo_2(H_2O)_4]^{4+}$
Molybdenum(III)	$[Mo(H_2O)_6]^{3+}$	$[Mo(H_2O)_6]^{3+}$
Manganese(II)	$[Mn(H_2O)_6]^{2+}$	$[Mn(H_2O)_6]^{2+}$
Manganese(III)	$[Mn(H_2O)_6]^{3+}$	$[Mn(H_2O)_6]^{3+}$
Iron(II)	$[Fe(H_2O)_6]^{2+}$	$[Fe(H_2O)_6]^{2+}$
Iron(III)	$[Fe(H_2O)_6]^{3+}$	$[Fe(H_2O)_6]^{3+}$
Ruthenium(II)	$[Ru(H_2O)_6]^{2+}$	$[Ru(H_2O)_6]^{2+}$
Ruthenium(III)	$[Ru(H_2O)_6]^{3+}$	$[Ru(H_2O)_6]^{3+}$
Cobalt(II)	$[Co(H_2O)_6]^{2+}$, $[Co_2(H_2O)_{10}]^{4+}$	$[Co(H_2O)_6]^{2+}$
Cobalt(III)	$[Co(H_2O)_6]^{3+}$	$[Co(H_2O)_6]^{3+}$
Rhodium(III)	$[Rh(H_2O)_6]^{3+}$	$[Rh(H_2O)_6]^{3+}$
Iridium(III)	$[Ir(H_2O)_6]^{3+}$	$[Ir(H_2O)_6]^{3+}$
Nickel(II)	$[Ni(H_2O)_6]^{2+}$, $[Ni_2(H_2O)_{10}]^{4+}$	$[Ni(H_2O)_6]^{2+}$
Palladium(II)	$[Pd(H_2O)_4]^{2+}$	$[Pd(H_2O)_{5/6}]^{2+}$
Platinum(II)	$[Pt(H_2O)_4]^{2+}$	$[Pt(H_2O)_{5/6}]^{2+}$
Copper(I)		$[Cu(H_2O)_4]^+$
Copper(II)	$[Cu(H_2O)_4]^{2+}$, $[Cu(H_2O)_5]^{2+}$, $[Cu(H_2O)_6]^{2+}$	$[Cu(H_2O)_6]^{2+}$
Silver(I)	$[Ag(H_2O)_2]^+$, $[Ag(H_2O)_3]^+$	$[Ag(H_2O)_2]^+$
Gold(III)	$[Au(H_2O)_4]^{3+}$	$[Au(H_2O)_4]^{3+}$
Zinc(II)	$[Zn(H_2O)_4]^{2+}$, $[Zn(H_2O)_5]^{2+}$, $[Zn(H_2O)_6]^{2+}$	$[Zn(H_2O)_6]^{2+}$
Cadmium(II)	$[Cd(H_2O)_6]^{2+}$, $[Cd_2(H_2O)_{10}]^{4+}$	$[Cd(H_2O)_6]^{2+}$
Mercury(I)	$[Hg_2(H_2O)_2]^{2+}$	$[Hg_2(H_2O)_6]^{2+}$
Mercury(II)	$[Hg(H_2O)_6]^{2+}$	$[Hg(H_2O)_6]^{2+}$
Aluminum(III)	$[Al(H_2O)_6]^{3+}$	$[Al(H_2O)_6]^{3+}$
Gallium(III)	$[Ga(H_2O)_6]^{3+}$	$[Ga(H_2O)_6]^{3+}$
Indium(III)	$[In(H_2O)_6]^{3+}$	$[In(H_2O)_6]^{3+}$
Thallium(I)		$[Tl(H_2O)_n]^+$

Table 1. Cont.

Metal Ion	Solid State	Aqueous Solution
Thallium(III)	$[\text{Tl}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Tl}(\text{H}_2\text{O})_6]^{3+}$
Tin(II)	$[\text{Sn}(\text{H}_2\text{O})_3]^{2+}$	$[\text{Sn}(\text{H}_2\text{O})_3]^{2+}$
Lead(II)	$[\text{Pb}(\text{H}_2\text{O})_3]^{2+}$, $[\text{Pb}(\text{H}_2\text{O})_4]^{2+}$	$[\text{Pb}(\text{H}_2\text{O})_{5-7}]^{2+}$
Bismuth(III)	$[\text{Bi}(\text{H}_2\text{O})_9]^{3+}$	$[\text{Bi}(\text{H}_2\text{O})_8]^{3+}$

Table 2. Summary of mean M–O bond distances in hydrated metal ions in solid state and solution determined experimentally. The following abbreviations are used in this table, coordination, and configuration: two—linear, $D_{\infty h}$, three: triangular, $D_{3h}(3)$, trigonal pyramidal, C_{3v} , four—tetrahedral, T_d , and square-planar, $D_{4h}(4)$, five: square pyramidal, C_{4v} , and trigonal bipyramidal, $D_{3h}(5)$, six: octahedral O_h , and tetragonally elongated octahedral (Jahn–Teller distorted octahedral), C_{4v} , eight: square antiprism, $D_{4h}(8)$, nine: tricapped prismatic, $D_{3h}(9)$, and compounds without a well-defined coordination geometry, the coordination number is given by a figure.

Metal Ion	Solid State	Aqueous Solution
$\text{Li}(\text{H}_2\text{O})_4^+$	1.941– T_d (Table S1a)	1.95– T_d [10–16]
$\text{Na}(\text{H}_2\text{O})_6^+$	2.417– O_h (Table S1b)	2.43– O_h [10,21–25]
$\text{Na}(\text{H}_2\text{O})_5^{3+}$	2.341– D_{3h} (Table S1b)	
$\text{K}(\text{H}_2\text{O})_7^+$		2.81–7 [10,28–30,32]
$\text{Rb}(\text{H}_2\text{O})_8^+$		2.98– $D_{4h}(8)$ [33,34]
$\text{Cs}(\text{H}_2\text{O})_8^+$		3.10– $D_{4h}(8)$ [10,33,36,37]
$\text{Be}(\text{H}_2\text{O})_4^{2+}$	1.613– T_d (Table S2a)	1.62– T_d ^a
$\text{Mg}(\text{H}_2\text{O})_6^{2+}$	2.066– O_h (Table S2b)	2.07– O_h [28,29]
$\text{Ca}(\text{H}_2\text{O})_8^{2+}$	2.476– $D_{4h}(8)$ (Table S2c)	2.48– $D_{4h}(8)$ [28,29,43–52]
$\text{Ca}(\text{H}_2\text{O})_7^{3+}$	2.401– $C_{3v}(7)$ (Table S2c)	
$\text{Ca}(\text{H}_2\text{O})_6^{3+}$	2.324– O_h (Table S2c)	
$\text{Sr}(\text{H}_2\text{O})_8^{2+}$	2.613– D_{4h} (Table S2d)	2.61– $D_{4h}(8)$ [58–67]
$\text{Ba}(\text{H}_2\text{O})_8^{2+}$	2.80– D_{4h} (Table S2e)	2.81– $D_{4h}(8)$ [58,69,74–76]
$\text{Ra}(\text{H}_2\text{O})_{10}^{2+}$		2.93–10 [74]
$\text{Sc}(\text{H}_2\text{O})_8^{3+}$	2.170 + 2.459– $D_{3h}(9)$ (Table S3a)	2.17 + 2.33– $D_{3h}(9)$ [81]
$\text{Y}(\text{H}_2\text{O})_8^{3+}$	2.353– $D_{4h}(8)$ (Table S3b)	2.367– $D_{4h}(8)$ [82]
$\text{La}(\text{H}_2\text{O})_9^{3+}$	2.528 + 2.611– $D_{3h}(9)$ (Table S4a)	2.53 + 2.60– $D_{3h}(9)$ [88]
$\text{La}(\text{H}_2\text{O})_8^{3+}$	2.495– $D_{4h}(8)$ (Table S4a)	
$\text{Ce}(\text{H}_2\text{O})_9^{3+}$	2.491 + 2.597– $D_{3h}(9)$ (Table S4b)	2.49 + 2.62– $D_{3h}(9)$ [88]
$\text{Ce}(\text{H}_2\text{O})_8^{3+}$	2.485– $D_{4h}(8)$ (Table S4b)	
$\text{Pr}(\text{H}_2\text{O})_9^{3+}$	2.475 + 2.568– $D_{3h}(9)$ (Table S4c)	2.48 + 2.58– $D_{3h}(9)$ [88]
$\text{Pr}(\text{H}_2\text{O})_8^{3+}$	2.476– $D_{4h}(8)$ (Table S4c)	
$\text{Nd}(\text{H}_2\text{O})_9^{3+}$	2.458 + 2.565– $D_{3h}(9)$ (Table S4d)	2.47 + 2.60– $D_{3h}(9)$ [88]
$\text{Nd}(\text{H}_2\text{O})_8^{3+}$	2.439– $D_{4h}(8)$ (Table S4d)	
$\text{Sm}(\text{H}_2\text{O})_9^{3+}$	2.436 + 2.545– $D_{3h}(9)$ (Table S4e)	2.43 + 2.53– $D_{3h}(9)$ [88]
$\text{Sm}(\text{H}_2\text{O})_8^{3+}$	2.430– $D_{4h}(8)$ (Table S4e)	

Table 2. Cont.

Metal Ion	Solid State	Aqueous Solution
Eu(H ₂ O) ₈ ²⁺		2.584–D _{4h} (8) [66]
Eu(H ₂ O) ₉ ³⁺	2.414 + 2.535–D _{3h} (9) (Table S4f)	2.42 + 2.57–D _{3h} (9) [88]
Eu(H ₂ O) ₈ ³⁺	2.416–D _{4h} (8) (Table S4f)	
Gd(H ₂ O) ₉ ³⁺	2.404 + 2.542–D _{3h} (9) (Table S4g)	2.41 + 2.53–D _{3h} (9) [88]
Gd(H ₂ O) ₈ ³⁺	2.403–D _{4h} (8) (Table S4g)	
Tb(H ₂ O) ₉ ³⁺	2.388 + 2.514–D _{3h} (9) (Table S4h)	2.40 + 2.53–D _{3h} (9) [88]
Tb(H ₂ O) ₈ ³⁺	2.381–D _{4h} (8) (Table S4h)	
Dy(H ₂ O) ₉ ³⁺	2.368 + 2.519–D _{3h} (9) (Table S4i)	2.38 + 2.50–D _{3h} (9) [88]
Dy(H ₂ O) ₈ ³⁺	2.371–D _{4h} (8) (Table S4i)	
Ho(H ₂ O) ₉ ³⁺	2.375 + 2.494–D _{3h} (9) (Table S4j)	2.37 + 2.50–D _{3h} (9) [88]
Ho(H ₂ O) ₈ ³⁺	2.356–D _{4h} (8) (Table S4j)	
Er(H ₂ O) _{8,9} ³⁺	2.351 + 2.515–D _{3h} (9) (Table S4k)	2.36 + 2.48–D _{3h} (9) [88]
Er(H ₂ O) ₈ ³⁺	2.345–D _{4h} (8) (Table S4k)	
Tm(H ₂ O) _{8,9} ³⁺	2.331 + 2.513–D _{3h} (9) (Table S4l)	2.35 + 2.47–D _{3h} (9) [88]
Tm(H ₂ O) ₈ ³⁺	2.339–D _{4h} (8) (Table S4l)	
Yb(H ₂ O) _{8,7} ³⁺	2.314 + 2.501–D _{3h} (9) (Table S4m)	2.32 + 2.43–D _{3h} (9) [88]
Yb(H ₂ O) ₈ ³⁺	2.326–D _{4h} (8) (Table S4m)	
Lu(H ₂ O) _{8,2} ³⁺	2.296 + 2.506–D _{3h} (9) (Table S4n)	2.28 + 2.37–D _{3h} (9) [88]
Lu(H ₂ O) ₈ ³⁺	2.318–D _{4h} (8) (Table S4n)	
Ac(H ₂ O) ₁₁ ³⁺		2.63–11 [116]
Th(H ₂ O) ₁₀ ⁴⁺	2.498–10 2.345–D _{4h} (8) (Table S4k)	
Th(H ₂ O) ₉ ⁴⁺	2.448–9 (Table S5a)	2.45–9 [119,122]
U(H ₂ O) ₉ ³⁺	2.509 + 2.596–D _{3h} (9) (Table S5b)	2.50 + 2.58–D _{3h} (9) [110]
U(H ₂ O) ₉ ⁴⁺	2.41–9 (Table S5b)	2.42–9 [123,124]
U(H ₂ O) ₈ ⁴⁺	2.395–D _{4h} (8) (Table S5b)	
UO ₂ (H ₂ O) ₅ ²⁺	1.760 + 2.444–D _{5h} (Table S5b)	1.77 + 2.42–D _{5h} [111,122]
Np(H ₂ O) ₉ ³⁺	2.491 + 2.571–D _{3h} (Table S5c)	2.48 + 2.56–D _{3h} [111]
Np(H ₂ O) ₉ ⁴⁺		2.40–9 [110]
Np(H ₂ O) ₈ ⁴⁺	2.335–D _{4h} (8) (Table S5c)	
NpO ₂ (H ₂ O) ₅ ²⁺	1.744 + 2.416–D _{5h} (Table S5c)	1.83 + 2.48–D _{5h} [111,126]
Pu(H ₂ O) ₉ ³⁺	2.475 + 2.571–D _{3h} (Table S5d)	2.45 + 2.55–D _{3h} (9) [110–112,114,115]
Pu(H ₂ O) ₈ ⁴⁺	2.39–9 (Table S5d)	2.395–D _{4h} (8) [114,115]
PuO ₂ (H ₂ O) ₅ ⁺		1.81 + 2.47–D _{5h} [114,115]
PuO ₂ (H ₂ O) ₅ ²⁺	1.732 + 2.409–D _{3h} (Table S5d)	1.75 + 2.41–D _{5h} [114,115]
Am(H ₂ O) ₉ ³⁺	2.466 + 2.578–D _{3h} (9) (Table S5e)	2.43 + 2.54–D _{3h} (9) [108,110,113]
Cm(H ₂ O) ₉ ³⁺	2.453 + 2.555–D _{3h} (9) (Table S5e)	2.40 + 2.53–D _{3h} (9) [108,110,113]
Bk(H ₂ O) ₉ ³⁺		2.38 + 2.50–D _{3h} (9) [110]
Cf(H ₂ O) ₉ ³⁺	2.423 + 2.550–D _{3h} (9) (Table S5e)	2.37 + 2.49–D _{3h} (9) [110]

Table 2. Cont.

Metal Ion	Solid State	Aqueous Solution
Ti(H ₂ O) ₆ ³⁺	2.02–O _h (Table S6a)	2.03–O _h ^a
TiO(H ₂ O) ₅ ²⁺	1.644 + 2.034 + 2.233 ^a (Table S6a)	
Zr(H ₂ O) ₈ ⁴⁺		2.19–D _{4h} (8) [132]
Hf(H ₂ O) ₈ ⁴⁺		2.16–D _{4h} (8) [132]
V(H ₂ O) ₆ ²⁺	2.131–O _h (Table S7)	2.13–O _h ^a
V(H ₂ O) ₆ ³⁺	1.994–O _h (Table S7)	1.99–O _h [133]
VO(H ₂ O) ₅ ²⁺	1.580 + 2.026 + 2.187 (Table S7)	1.60 + 2.03 + 2.20 [134]
VO ₂ (H ₂ O) ₄ ⁺		1.62 + 1.99 + 2.22 [134]
Cr(H ₂ O) ₆ ²⁺	2.083 + 2.333–C _{4v} (Table S8)	2.08 + ~2.3–C _{4v} [133]
Cr(H ₂ O) ₆ ³⁺	1.965–O _h (Table S8)	1.97–O _h [28,29,135]
Mo(H ₂ O) ₆ ³⁺	2.089–O _h (Table S8)	2.09–O _h [138]
Mn(H ₂ O) ₆ ²⁺	2.174–O _h (Table S9)	2.17–O _h [28,29,139,140]
Mn(H ₂ O) ₆ ³⁺	2.088–O _h (Table S9)	
Fe(H ₂ O) ₆ ²⁺	2.120–O _h (Table S10a)	2.12–O _h [28,29,145,146]
Fe(H ₂ O) ₆ ³⁺	1.995–O _h (Table S10a)	2.00–O _h [28,29,145]
Ru(H ₂ O) ₆ ²⁺	2.111–O _h (Table S10b)	2.11–O _h ^a
Ru(H ₂ O) ₆ ³⁺	2.021–O _h (Table S10b)	2.03–O _h ^a
Co(H ₂ O) ₆ ²⁺	2.087–O _h (Table S11a)	2.09–O _h [28,29,147–150]
Co(H ₂ O) ₆ ³⁺	1.873–O _h (Table S11a)	
Rh(H ₂ O) ₆ ³⁺	2.014–O _h (Table S11b)	2.04–O _h [152–154]
Ir(H ₂ O) ₆ ³⁺	2.04–O _h (Table S11b)	
Ni(H ₂ O) ₆ ²⁺	2.055–O _h (Table S12a)	2.055–O _h [28,29,155]
Pd(H ₂ O) ₆ ²⁺		2.01 + 2.8–D _{4h} (6) [156–160]
Pd(H ₂ O) ₄ ²⁺	2.029–D _{4h} (4) (Table S12b)	
Pt(H ₂ O) ₆ ²⁺		2.02 + 2.8–D _{4h} (6) [156–160]
Pt(H ₂ O) ₄ ²⁺	2.012–D _{4h} (4) (Table S12b)	
Cu(H ₂ O) ₄ ⁺		2.14–T _d ^b [161]
Cu(H ₂ O) ₆ ²⁺	1.980 + 2.322–C _{4v} (6) (Table S13a)	1.96 + 2.32–D _{4h} (6) [163,167]
Cu(H ₂ O) ₆ ²⁺	1.944 + 2.248–C _{4v} (5) (Table S13a)	
Ag(H ₂ O) ₄ ⁺		2.32 + 2.54–2 + 2 [181]
Ag(H ₂ O) ₂ ⁺	2.129–D _{∞h} (Table S13b)	2.34–2 [182]
Au((H ₂ O) ₄) ₃ ⁺	2.155–D _{4h} (4) (Table S13c)	
Zn(H ₂ O) ₆ ²⁺	2.088–O _h (Table S14a)	2.09–O _h [28,29]
Zn(H ₂ O) ₅ ²⁺	2.017–D _{3h} (5) (Table S14a)	
Cd(H ₂ O) ₆ ²⁺	2.266–O _h (Table S14b)	2.27–O _h [184]
Hg ₂ (H ₂ O) ₆ ²⁺		2.26–T _d [185]
Hg ₂ (H ₂ O) ₂ ²⁺	2.14–T _d (Table S14c)	
Hg(H ₂ O) ₇ ²⁺		2.32–7 [188]
Hg(H ₂ O) ₆ ²⁺	2.342–O _h (Table S14c)	2.34–O _h [187]

Table 2. Cont.

Metal Ion	Solid State	Aqueous Solution
Al(H ₂ O) ₆ ³⁺	1.883–O _h (Table S15a)	1.89–O _h [28,29]
Ga(H ₂ O) ₆ ³⁺	1.946–O _h (Table S15b)	1.96–O _h [28,29,135]
In(H ₂ O) ₆ ³⁺	2.124–O _h (Table S15c)	2.14–O _h [135]
Ti(H ₂ O) _n ⁺		2.73 + 3.18–2 + 2 [202]
Tl(H ₂ O) ₆ ³⁺	2.23–O _h (Table S15d)	2.23–O _h [193,194]
Sn(H ₂ O) ₃ ²⁺	2.204–C _{3v} (Table S16a)	2.21–C _{3v} [203]
Pb(H ₂ O) ₆ ²⁺		2.53–6 [204,205]
Bi(H ₂ O) ₉ ³⁺	2.440 + 2.582–D _{3h} (9) (Table S16c)	
Bi(H ₂ O) ₈ ³⁺		2.41–D _{4h} (8) [207]

^a Extrapolated from solid state structures; ^b Extrapolated from physico-chemical parameters.

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