

## Hydration of some large and highly charged metal ions

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EXAFS studies of metal ions with hydration numbers higher than six in aqueous solution, often show asymmetric distribution of the metal-oxygen bond distances. The hydration number can be determined from a correlation with the bond distance. The mean Ca-O distance 2.46(1) Å shows the calcium(II) ion to be eight-hydrated in a wide asymmetric distribution. Theoretically calculated EXAFS oscillations for individual snapshots from an MD simulation show large variations. The scandium(III) ion is surrounded by two groups of about eight water molecules, with the mean Sc-O distance 2.185(6) Å. The yttrium(III) ion coordinates eight waters in an asymmetric distribution at 2.368(5) Å, and the lanthanum(III) ion 6 + 3 water molecules at 2.52(2) and 2.65(3) Å, respectively. For the uranium(IV) and thorium(IV) ions, the M-O distances 2.42(1) and 2.45(1) Å, respectively, indicate hydration numbers close to 10.

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### 1. Introduction

The hydrated metal ion is the simplest species, which gives information on the coordination properties of the metal ion. The hydration structure of the metal ion is directly related to the chemical properties, e.g. redox processes, ligand exchange, reaction kinetics, hydrolysis, etc.. Even though water is the most important and studied solvent there is still much to learn about its behavior as a coordinating ligand. Highly charged metal ions polarize the water molecules in the first sphere and significantly strengthen the hydrogen bonding to the second hydration sphere, Richens (1997).

Structural information about metal ion hydration in aqueous solution has to be obtained by several methods, and evaluated properly in order to obtain as complete a picture as possible. For structure studies the principal methods mostly used are large angle X-ray scattering (LAXS), and in some cases also neutron scattering and EXAFS, giving time and space averages of the metal-water interactions. The recent development of the XAFS data treatment has significantly increased its usefulness and EXAFS now is a valuable complement to the previously established techniques. The EXAFS oscillations normally cover a larger range of the scattering variable than in LAXS because of the backscattering of the ejected photoelectron. This increases the resolution and makes it possible to evaluate configurational disorder and asymmetry in the distribution of the metal-oxygen distances in the first coordination sphere. On the other hand, the contributions from long-range interactions, such as M...O<sub>II</sub> to the second shell, are weak in EXAFS and overlapped

by multiple scattering within the first shell. Such interactions are better represented in the LAXS data for which metal - oxygen interactions to the second shell are easily evaluated, Lindqvist-Reis *et al.* (1998). The element specificity of the XAS can provide better sensitivity allowing dilute solutions to be studied since only the local structure around the absorber is probed. For Ga<sup>3+</sup>, In<sup>3+</sup> and Cr<sup>3+</sup> ions in aqueous solution K-edge transmission spectra of useful quality were obtained for concentrations down to 0.005 mol dm<sup>-3</sup>, Lindqvist-Reis *et al.* (1998). The LAXS method is restricted to concentrated solutions of the hydrated metal ion, because of the overlap with other interactions not involving the metal ion.

Both the XAFS and LAXS methods can give the interatomic distances of the dominating interactions with high accuracy, in particular the first-shell metal-oxygen bond distances. The accuracy in the direct determination of the coordination number is fairly low, however. Therefore, the strong correlation between the effective ionic radius and the coordination number is a better way to obtain reliable hydration numbers from the experimentally determined metal - oxygen distance, Lindqvist-Reis *et al.* (2000), since the ionic radii of metal ions in general increase significantly with increasing coordination number, Shannon (1976).

Another useful way of confirming hydration numbers and also to obtain qualitative information of the coordination geometry, is to compare XAFS spectra, both in the XANES and EXAFS regions, for solid hydrates with known structures with the solution spectra. Similarities in the edge structure, the multiple scattering within the first coordination sphere, and the shape of the EXAFS function can give useful indications of the coordination figure. Moreover, a closely related crystalline solvate can make it possible to obtain a reliable and transferable value for the amplitude reduction factor, S<sub>0</sub><sup>2</sup>, under the experimental condition used. In favorable cases, this may allow the accuracy in the determination of the coordination number to be better than ±0.5 units, Lindqvist-Reis *et al.* (2000). Attempts to determine coordination numbers without using well-defined calibration compounds may give very large errors, sometimes of the order of ± 25%, since the coordination number is directly proportional to the amplitude reduction factor, and also strongly correlated to the Debye-Waller factor. Quantitative evaluations require knowledge of the atomic positions in the complex in order to define the scattering paths for multiple scattering, and also for the electronic transitions in the near edge structure (XANES) of the absorption spectrum, which are sensitive to the coordination geometry.

### 2. Results

The experimentally determined effective "radius" of the oxygen atom in the coordinated water molecule in a number of crystal structures of trivalent metal ions in alum salts is 1.34 Å, Beattie *et al.* (1981). We have found that this value, in combination with the effective metal ion radii given by Shannon (1976), gives good agreement with the M-O distances for known hydration numbers of almost all trivalent hydrated ions, cf. Table 1. However, for ions with lower charge density, a somewhat larger radius should be used for the coordinated water molecule, and probably a slightly smaller effective value for tetravalent metal ions.

Recently, the metal-oxygen bond distance in the first hydration sphere of the hexahydrated Ga<sup>3+</sup>, In<sup>3+</sup> and Cr<sup>3+</sup> ions in aqueous solution was determined by LAXS and EXAFS methods to 1.959(6), 2.131(7) and 1.966(8) Å, respectively. LAXS results showed mean second sphere M...O<sub>II</sub> distances of 4.05(1), 4.13(1) and 4.08(2) Å for the three ions, respectively, Lindqvist-Reis *et al.* (1998). The Fourier transforms of the EXAFS data for the

gallium(III) and chromium(III) solutions showed weak features at about 4 Å. Theoretical evaluation of the relative EXAFS

**Table 1.** Summary of the EXAFS studies of hydrated metal ions in aqueous solution. The table compares the mean M-O<sub>1</sub> distance with the sum of Shannon's effective ionic radii for the metal ion with the given coordination number of the aqua ion and the estimated radius of the water ligand, 1.34 Å, Beattie *et al.* (1981), and gives the Debye-Waller parameter,  $\sigma^2$  and the 3<sup>rd</sup> cumulant C<sub>3</sub>. The standard deviation given of the M-O<sub>1</sub> distance includes estimated systematic effects.

Aqua ion	Sum of ionic radii / Å	M-O <sub>1</sub> / Å	$\sigma^2$ / Å <sup>2</sup>	C <sub>3</sub> / Å <sup>3</sup>	Ref. No.
[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	1.96	1.966(8)	0.004(1)	-	a
[Ga(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	1.96	1.959(6)	0.005(1)	-	a
[In(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	2.14	2.131(7)	0.004(1)	-	a
[Tl(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	2.22	2.21(2)	0.006	-	b
[Sc(H <sub>2</sub> O) <sub>8</sub> ] <sup>3+</sup>	2.21	2.19(1)	0.006(1)	0.0004(1)	c
[Y(H <sub>2</sub> O) <sub>8</sub> ] <sup>3+</sup>	2.36	2.368(5)	0.0051(2)	0.00015(4)	d
[La(H <sub>2</sub> O) <sub>9</sub> ] <sup>3+</sup>	2.55	6x2.52(2) 3x2.65(3)	0.003(1) 0.005(2)	-	e
[Ca(H <sub>2</sub> O) <sub>8</sub> ] <sup>2+</sup>	2.46	2.46(2)	0.010(2)	0.0012(3)	f
[U(H <sub>2</sub> O) <sub>10</sub> ] <sup>4+</sup>	2.39 <sup>h</sup> (n=9)	2.42(1)	0.009(1)	0.0004(2)	g
[Th(H <sub>2</sub> O) <sub>10</sub> ] <sup>4+</sup>	2.43 <sup>h</sup> - 2.47 <sup>i</sup>	2.45(1)	0.007(1)	0.0006	g

<sup>a</sup>Lindqvist-Reis *et al.* (1998), <sup>b</sup>Blixt *et al.* (1995), <sup>c</sup>Lindqvist-Reis *et al.* (2000b), <sup>d</sup>Lindqvist-Reis *et al.* (2000a), <sup>e</sup>Näslund *et al.* (2000), <sup>f</sup>Jalilvand *et al.* (2000), <sup>g</sup>Moll *et al.* (1999), <sup>h</sup>Metal ion radius for coordination number 9, <sup>i</sup>for coordination number 10, Shannon (1976).

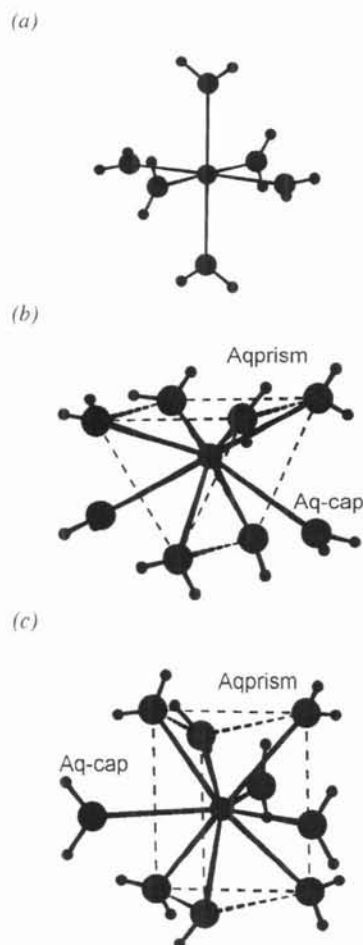
contributions, by means of the FEFF code, Rehr *et al.* (1998), showed that these features were in fact due to multiple scattering within the well-defined octahedral first hydration sphere, in particular due to the focusing effect of the 3 and 4 leg *trans*-M-O<sub>1</sub>-O<sub>1</sub> and *trans*-M-O<sub>1</sub>-M-O<sub>1</sub> pathways. For the indium(III) solution the weaker amplitude of the multiple scattering, and the higher disorder in the second shell, led to virtually no visible contribution outside the first hydration shell. This is also the situation for all the ions with higher hydration number than six in the present study. The coordination geometry is as a rule irregular with asymmetric distributions of the metal - oxygen distances, which means negligible multiple scattering and no observable second shell backscattering in the EXAFS range. The asymmetry is modeled by introducing the 3<sup>rd</sup> cumulant C<sub>3</sub>, accounting for the phase shift from an asymmetric distribution of the M-O distances, Rehr *et al.* (1998), cf. eq. 1.

$$\chi_{MO}(k) = \frac{n_O \Delta_{O_1}^2}{k \cdot d_{MO}} \left[ f_{O_1}(k) \right]_O \exp(-2k^2 \sigma^2) \exp[-2d_{MO} / \lambda(k)] \times \sin[2kd_{MO} + \phi_{MO}(k) - (1/3)C_3 k^3] \quad (1)$$

### 3. Discussion

Comparisons with solid state structures and the results in Table 1 showed that the trivalent group 13 gallium, indium and thallium ions with filled d-shells, have octahedral coordination geometry, Lindqvist-Reis *et al.* (1998). The group 3 ion scandium(III) without

d-electrons, is smaller in six-coordination than both indium(III) and thallium(III), as shown by the mean Sc-O distance 2.09 Å for [Sc(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> ions in a crystalline hexahydrate, Lindqvist-Reis *et al.* (2000c). However, in aqueous solution a higher hydration number is preferred, probably eight. The similarity with the XAFS spectra from the triflate structure [Sc(H<sub>2</sub>O)<sub>8</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, which contains [Sc(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup> ions with the oxygen atoms in a distorted bicapped trigonal prism, Lindqvist-Reis *et al.* (2000c), makes a capped trigonal prismatic coordination geometry likely also in aqueous solution. The reason for this increase in hydration number must be electronic. The mean Sc-O<sub>II</sub> distance to the water molecules in the second sphere, 4.27(1) Å, has been obtained by the LAXS method, Lindqvist-Reis *et al.* (2000b), and indicates that the tilt angle of the first sphere waters is smaller than for Ga<sup>3+</sup> and In<sup>3+</sup>, ca 35°.

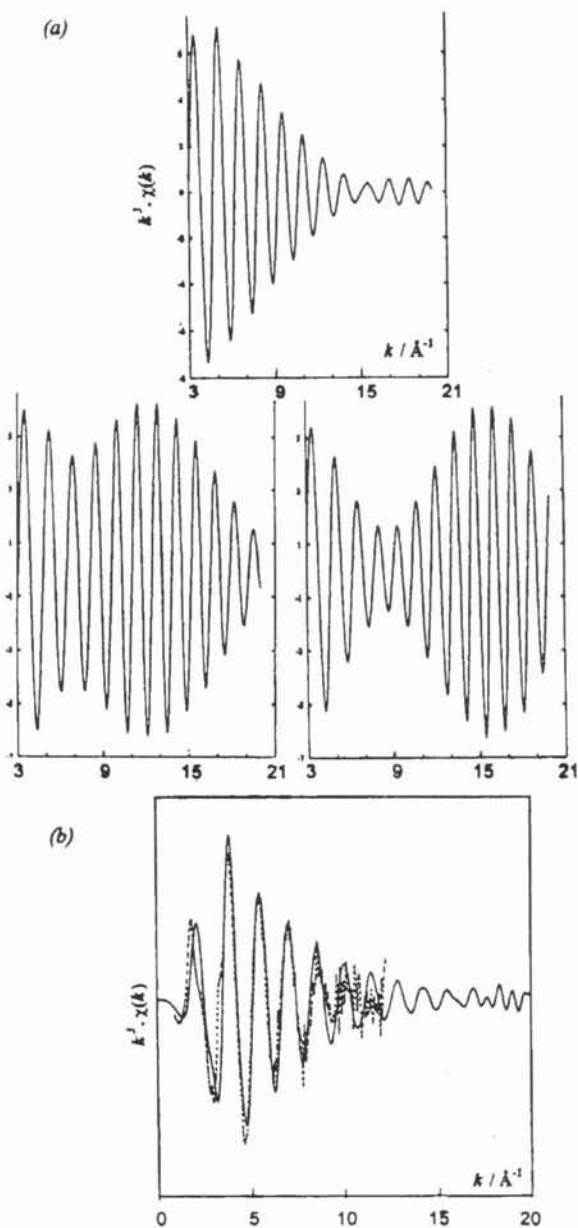


**Figure 1**

The probable coordination figures for the ions in Table 1. (a) octahedral for Cr<sup>3+</sup>, Ga<sup>3+</sup>, In<sup>3+</sup>; (b) bi-capped trigonal prism or distorted square anti-prism for Y<sup>3+</sup>, Ca<sup>2+</sup> and probably Sc<sup>3+</sup>; (c) tricapped trigonal prism for La<sup>3+</sup>, while U<sup>4+</sup> and Th<sup>4+</sup> possibly have an even higher hydration number.

The larger yttrium(III) ion of group 3 is shown by comparisons with solid state structures to have eight-coordination in aqueous solution, probably in a distorted bicapped trigonal prism or square antiprism, cf. Figure 1b. The distribution of the Y-O bond distances is slightly asymmetric around 2.368(5) Å with a width implying a contribution from configurational disorder of about 0.1 Å on top of the thermally induced variation in the Y-O bond distances, Lindqvist-Reis *et al.* (2000a).

The largest ion in group 3 is  $\text{La}^{3+}$ , which shows two groups of distances in aqueous solution, most probably with the same coordination figure as in the tricapped trigonal prism of the triflate  $[\text{La}(\text{H}_2\text{O})_9](\text{CF}_3\text{SO}_3)_3$ , Näslund *et al.* (2000), cf. Figure 1c.



**Figure 2**

Theoretically calculated Ca K-edge EXAFS oscillations from MD-simulation of  $\text{CaCl}_2(\text{aq})$  using the GROMOS potential (a) for three individual snapshots for Ca-8O, the top one with all distances similar, the two below with different distances; (b) theoretical spectrum (solid line) averaged for 2000 instantaneous configurations 7.5 fs apart, compared with experimental data for  $0.94 \text{ mol dm}^{-3} \text{Ca}(\text{ClO}_4)_2$  aqueous solution.

The EXAFS data for the biochemically important  $\text{Ca}^{2+}$  ion show a broad and asymmetric distribution of the Ca-O bond distances. In combination with LAXS results the centroid is obtained at  $2.46(1)$

Å, Jalilehvand *et al.* (2000). A hydration number of eight is probable from correlation with mean Ca-O distances from hydrated crystal structures. Molecular dynamics simulations of  $\text{CaCl}_2(\text{aq})$  using a  $\text{Ca}^{2+}\text{-OH}_2$  pair potential from the GROMOS program gave results in close agreement with those from the current EXAFS data. For the Ca-O configuration corresponding to each individual MD snapshot the theoretical EXAFS oscillation was computed by means of the FEFF code, Rehr *et al.* (1998), showing large variations, cf. Figure 2a. However, the average spectrum from 2000 snapshots was similar to the experimental spectra and gave thermal Ca-O parameters including configurational disorder, in good agreement with the experimental values, Jalilehvand *et al.* (2000).

The uranium(IV) and thorium(IV) ions, which are of similar size or slightly smaller than the calcium(II) ion, Table 1, have even higher hydration numbers, Moll *et al.* (1999). The strong ion-dipole interaction for these highly charged metal ions causes increased electrostriction of the water ligand, as compared to that of the calcium(II) ion, and a slightly smaller effective "radius" of the water ligand than  $1.34 \text{ \AA}$  may be anticipated, making the hydration number of 10 most probable. The Debye-Waller factor and the asymmetry parameter  $C_3$  are also smaller for the uranium(IV) and thorium(IV) ions, than for calcium.

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