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The Structure of the Hydrated Gallium(III), Indium(III), and Chromium(III) Ions in Aqueous Solution. A Large Angle X-ray Scattering and EXAFS Study

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The structure of the hydrated gallium(III), indium(III), and chromium(III) ions has been determined in aqueous perchlorate and nitrate solutions by means of the large-angle X-ray scattering (LAXS) and extended X-ray absorption fine structure (EXAFS) techniques. The EXAFS studies have been performed over a wide concentration range, 0.005−1.0 mol·dm^{-3} (2.6 mol·dm^{-3} for chromium(III)), while the LAXS studies are restricted to concentrated solutions, ca. 1.5 mol·dm^{-3}. All three metal ions were found to coordinate six water molecules, each of which are hydrogen bonded to two water molecules in a second hydration sphere. The metal−oxygen bond distance in the first hydration sphere of the gallium(III), indium(III), and chromium(III) ions was determined by LAXS and EXAFS methods to be 1.959(6), 2.131(7), and 1.966(8) Å. The LAXS data gave mean second sphere M···O distances of 4.05(1), 4.13(1), and 4.08(2) Å for the gallium(III), indium(III), and chromium(III) ions, respectively. The perchlorate ion was found to be hydrogen bonded to 4.5(7) water molecules with the O···O distance 3.05(2) Å and Cl···O 3.68(3) Å. Analyses of the Ga, In, and Cr K-edge EXAFS data of the aqueous perchlorate and nitrate solutions showed no influence on the first shell M−O distance by a change of concentration or anion. The minor contribution from the second sphere M···O distance is obscured by multiple scattering within the tightly bonded first shell. EXAFS data for the alum salts $CsM(SO_4)_2\cdot 12H_2O$, M = Ga or In, showed the M−O bond length of the hexahydrated gallium(III) and indium(III) ions to be 1.957(2) and 2.122(2) Å, respectively.

Introduction

The hexahydrated gallium(III), indium(III), and chromium(III) ions are well characterized in the crystal structures of the alum salts $CsM(SO_4)_2\cdot 12H_2O$, where these trivalent metal ions coordinate six water molecules octahedrally with M−O distances of 1.944(3), 2.112(4), and 1.959(3) Å, respectively.[1] The corresponding distances in the isostructural indium(III) and chromium(III) selenate alum salts, $CsM(SeO_4)_2\cdot 12H_2O$, are not significantly different with In−O 2.134(6) Å and Cr−O 1.964(3) Å.[1,2]

To our knowledge no previous structural investigation has been performed using X-ray techniques on the hydrated gallium(III) ion in aqueous solution, and only a preliminary account has been given of the present EXAFS data.[3] For the hexahydrated indium(III) ion In−O bond distances of 2.15(3) and 2.17 Å have been reported from previous LAXS studies of aqueous indium perchlorate and nitrate solutions.[4−6] The structure of the hydrated chromium(III) ion in aqueous solution has been studied by large-angle X-ray and neutron scattering[4,5,7] and by EXAFS techniques,[5,8] with Cr−O bond distances reported between 1.97 and 2.03 Å.[7,9−16]

The LAXS method gives radial distribution functions where well-defined atom-pair interactions can be discerned at fairly long distances, but the superposed solvent−solvent and anion−solvent contributions often obscure the long-range metal ion−solvent interactions. Careful modeling of the composite long-range peaks is therefore necessary in order to extract reliable results on second shell interactions. A summary of results derived from such studies on chromium(III) solutions reports

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Cr$\cdots$O$_{II}$ distances between 4.0 and 4.2 Å.[5] A LAXS difference method,[4] based on the nearly isostructural surrounding of the hydrated rhodium(III) and chromium(III) ions in aqueous solution, was used to eliminate the solvent−solvent and anion contributions. This allowed the number of oxygen atoms to be estimated as 13 ± 1 in a distinct second hydration sphere around the rhodium(III) ion centered at a Rh$\cdots$O$_{II}$ distance of 4.02 Å.[17]

Neutron diffraction allows isotopic substitution methods to be used for such eliminations by first- and second-order differences, when nuclides with favorable scattering properties are available, but it is an experimentally demanding technique.[18] Such an experiment has been performed on concentrated (2.2 mol·dm^{-3}) isotopically different chromium(III) perchlorate solutions. The first-order difference revealed a distinct second hydration sphere with a mean Cr$\cdots$O$_{II}$ distance of 4.0 Å.[7] A second-order difference allowed even a Cr$\cdots$H pair distribution function to be extracted. By integrating from 3.6 to 5.5 Å over the second shell Cr$\cdots$H$_{II}$ peak, which is centered at 4.5 Å, the number of water molecules in this range was estimated to be 15.5(1.0).

NMR studies showed that the chromium(III) and gallium(III) ions are hydrated by six water molecules in aqueous solution regardless of the anion present.[5,19] Also the indium(III) ion, which only could be studied in water−acetone mixtures at low temperature, was found to coordinate six water molecules.[20] The gallium(III), indium(III), and chromium(III) ions show very different rates for the exchange of the coordinated first shell water molecules in aqueous solution, fairly rapid for indium with the rate constant $k_1 = 4 \times 10^4$ s^{-1}, somewhat slower for gallium, 400 s^{-1}, and extremely slow for chromium(III), 2.4×10^{-6} s^{-1}.[21] Tracer diffusion measurements have shown that the water molecules of the first hydration shell around the hydrated gallium(III) and chromium(III) ions move through the solution with the cation as a kinetic entity.[22] The results from incoherent quasi-elastic neutron scattering which are sensitive to the proton mobility showed a dynamic hydration number of 6 for the chromium(III) ion.[23] Water molecules in the second hydration shell were found to have a much shorter overall lifetime with diffusion coefficients intermediate to those of the ion and the bulk water.[22] Merbach et al. found with the use of high-field ^{17}O NMR methods a lifetime of 128 ps for a water molecule in the second hydration sphere around Cr^{3+}, and with a molecular dynamics (MD) simulation 144 ps.[24] A lifetime of 30 ps was obtained for dilute chromium(III) chloride solutions by means of an MD simulation using the hydrated ion approach with translational self-diffusion coefficients.[25]

The overview above verifies the existence of a well-defined first hydration shell around the gallium(III), indium(III), and chromium(III) ions in aqueous solution consisting of six water molecules. Detailed experimental information on the structure of the second hydration shell is more limited. However, the existence of strong hydrogen bonds to a second hydration sphere around the hexahydrated chromium(III), rhodium(III), and aluminum(III) ions in aqueous solution has been demonstrated by a double difference infrared spectroscopic method,[26] and is consistent with the results from the MD studies.[24,25] In the present work, which is part of a study of the structure and hydrogen bonding around trivalent ions in aqueous solution, we report the structure of the hydrated gallium(III), indium(III), and chromium(III) ions in aqueous solution. Results from the large-angle X-ray scattering and EXAFS techniques have been combined in order to give a more reliable picture of the structures of both the first and second hydration spheres.

Table 1. LAXS Solutions: Composition (mol·dm^{-3}), Density ρ, Stoichiometric Volume per Metal Atom *V*, and Linear Absorption Coefficient μ(Mo Kα)

solution	[M^{3+}]	[ClO$_4^-$]	H$_2$O	ρ/g·cm^{-3}	*V*/Å^3	μ/cm^{-1}
Ga(III)	1.44	4.86	46.1	1.415	1153	8.96
In(III)	1.46	4.75	47.9	1.503	1137	8.16
Cr(III)	1.52	4.57	47.2	1.381	1090	5.44

Experimental Section

Chemicals and Sample Preparation. Gallium(III) oxide (Waco) and indium(III) oxide (Waco) were refluxed in 50% perchloric acid (Merck) until dissolution. The solutions were filtered and crystallized in a desiccator to obtain the hydrated perchlorate salts, which were recrystallized twice from dilute perchloric acid and used for preparing the investigated solutions, see Table 1. Hexaaquachromium(III) perchlorate (G. F. Smith), hexaaquachromium(III) nitrate (Merck), and hexaaquagallium(III) nitrate (Aldrich) were recrystallized from the respective dilute acids. The alum salts CsGa(SO$_4$)$_2$·12H$_2$O and CsIn(SO$_4$)$_2$·12H$_2$O were prepared as described elsewhere.[27]

The solutions for the LAXS and EXAFS studies were prepared by dissolving the salt in dilute perchloric or nitric acid, respectively. The metal concentration was determined by EDTA titrations.[28] The densities of the solutions studied by LAXS were measured with an Anton Paar DMA35 densitometer, and the compositions are given in Table 1.

LAXS Measurements. The large-angle X-ray scattering measurements were performed by means of a $\theta-\theta$ diffractometer using semi-focusing Bragg−Brentano geometry and Mo Kα radiation, $\lambda = 0.7107$ Å, as described previously.[29] Intensity data were collected for 400 discrete values between 2 and 140° in the scattering angle 2θ, corresponding to a range of 0.3−16.5 Å^{-1} of the scattering variable $s = (4\pi \sin \theta)/\lambda$. At least 100 000 counts were accumulated for each θ value and the angular range was scanned twice. The data analysis procedure, which was performed with the KURVLR program,[30] is described elsewhere.[31] The structure-sensitive part of the experimental scattered intensities, $i(s)$, obtained by subtracting the calculated structure-independent part, was converted to a modified radial distribution function (RDF) by a Fourier transformation:[30]

$$D(r) - 4\pi r^2 \rho_o = (2r/\pi) \int_{s_{\min}}^{s_{\max}} s \cdot i(s)\, M(s) \sin(sr)\, ds \qquad (1)$$

$M(s)$ is a modification function, and ρ_o is the average bulk electronic density.[30] The experimental intensities, $i(s)$, were corrected for low-

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frequency features by removing the spurious peaks below 1 Å in the $D(r)$ function by a Fourier back-transformation procedure.[32]

Calculated intensities for well-defined short-range atom-pair interaction between the atoms p and q in the assumed model were obtained from the expression

$$i_{\text{calc}}(s) = \sum n_{\text{pq}} f_{\text{p}} f_{\text{q}} \sin(sd_{\text{pq}})/(sd_{\text{pq}}) \exp(-{}^{1}/_{2} l^{2}_{\text{pq}} s^{2}) \qquad (2)$$

The parameters are d_{pq}, the average distance within each atom-pair; l_{pq}, the variation in the distance as described by the Debye−Waller factor, $\exp(-{}^{1}/_{2} l^{2}_{\text{pq}} s^{2})$; and n_{pq}, the frequency factor or coordination number. The scattering factors f are corrected for dispersion effects.[30,31]

Least-squares refinements of some model parameters for the atom-pair contributions were performed by means of the STEPLR program.[33] The refinements were carried out in different s ranges to assess the influence of systematic deviations from the model functions, in particular to test the lower s limit above which the diffuse long-range interatomic interactions can be neglected. The final model calculations were made in the s range 5.0−16.0 Å^{-1} by minimizing the function

$$U(s) = \sum [si(s)_{\text{exp}} - si(s)_{\text{calc}}]^2 \qquad (3)$$

EXAFS Measurements. The X-ray absorption spectra at the K-edge of gallium, 10 367 eV, and indium, 27 940 eV, were measured in transmission mode at the Synchrotron Radiation Source (SRS) (Daresbury Laboratory, U.K.), which operates at 2.5 GeV with a maximum stored current of 250 mA. The indium samples were measured in transmission mode at the 9.2 wiggler beam line using a Si[220] channel cut monochromator and gas-filled ion chambers as detectors. Energy calibration was carried out using a cadmium foil. The gallium samples were measured at beam line 8.1 using a Si[220] double crystal monochromator detuned to 50% of maximum intensity to minimize higher order harmonics. Energy calibration was carried out with a zinc foil. The 1.0 mol·dm^{-3} solution was measured in transmission mode using ion chambers as detectors, while the other solutions were measured in fluorescence mode using a 13 element solid-state detector (Canberra). Experimental details for the measurements of the chromium(III) solutions are given in ref 8. The aqueous solutions were contained in specially designed liquid EXAFS cells suitable for highly corrosive solutions in a wide range of path lengths, 1−140 mm.[34]

Similar measurements at the Ga and In K-edges were made at the wiggler beam line 4-1 at the Stanford Synchrotron Radiation Laboratory (SSRL) of acidic aqueous solutions of gallium and indium perchlorate and of the alum salts $CsM(SO_4)_2·12H_2O$, M = Ga and In. SSRL operates at 3.0 GeV and a maximum current of 100 mA. The EXAFS station was equipped with a Si[220] double crystal monochromator. Internal energy calibration was made with gallium and indium foils, and higher order harmonics were reduced by detuning to 50% of maximum intensity at the end of the scans. Details of sample preparation and measurements are given elsewhere.[35] The treatment of the EXAFS data has been carried out by means of the EXAFSPAK program package,[36] using standard procedures for pre-edge subtraction and spline removal. The EXAFS functions have been curve-fitted by ab initio calculated EXAFS phase and amplitude parameters from FEFF7.[37] The most concentrated solutions and the gallium alum salt, recorded at SRS and SSRL, respectively, have been used as model compounds for calculating the ΔE_{o} and S_{o}^2 values with a fixed coordination number. For the indium alum salt the abnormally high S_{o}^2 value (1.9) is probably due to a rather large amount of fluorescence from the sample.[38] This is visible as an oscillation on top of the primary intensity in the monitor before the sample and also adds to the much weaker signal in the ion chamber after the sample.

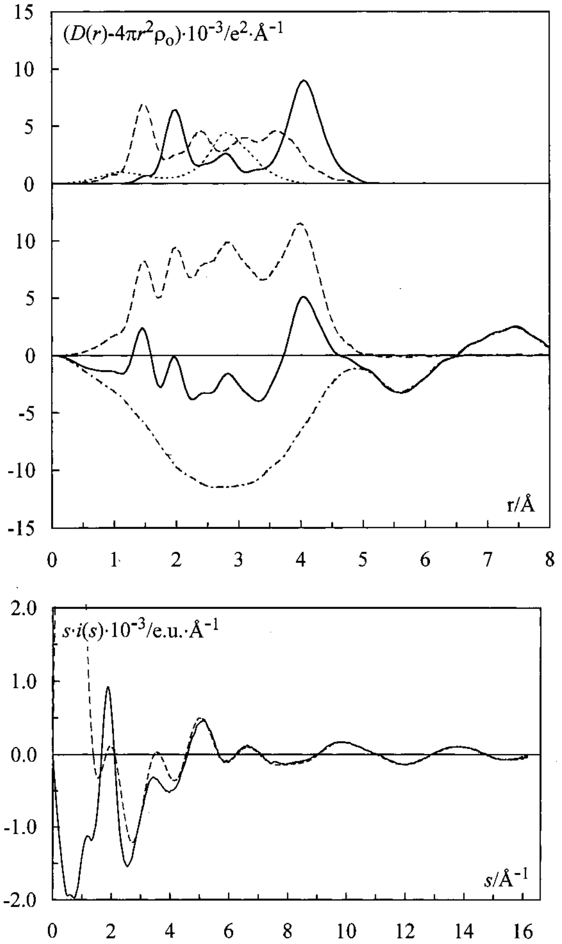

Figure 1. LAXS for 1.44 mol·dm^{-3} gallium(III) perchlorate in acidified aqueous solution. (Top) Separate model contributions with parameters from Table 2. The solid line represents the contributions from the first (Ga−O$_{\text{I}}$) and second (Ga···O$_{\text{II}}$) hydration spheres, the dashed line from the hydrated perchlorate ion, and the dotted line from the bulk water. (Middle) Radial distribution functions, $D(r) - 4\pi r^2\rho_{\text{o}}$, and the sum of the calculated peak shapes. Solid line, experimental; dashes, model; dots, difference experimental − model function. (Bottom) Structure-dependent LAXS intensity functions multiplied by the scattering variable: $s\cdot i(s)$ versus s. Solid line, experimental data; dashes, model function.

Results

LAXS Data. The experimental structure functions $s\cdot i(s)$ and the corresponding radial distribution function, RDF, in the form $D(r) - 4\pi r^2\rho_{\text{o}}$, for the aqueous gallium(III), indium(III), and chromium(III) perchlorate solutions are shown in Figures 1, 2, and 3, respectively. The most noticeable features in the three RDFs are the peak at 1.4 Å, which corresponds to the Cl−O bond distance within the perchlorate ion, and two prominent peaks at about 2.0 and 4.1 Å. The 2 Å peak represents the M−O$_{\text{I}}$ bond distance of the first hydration shell as is evident from the M−O distances of the alum salts.[1] The main contribution to

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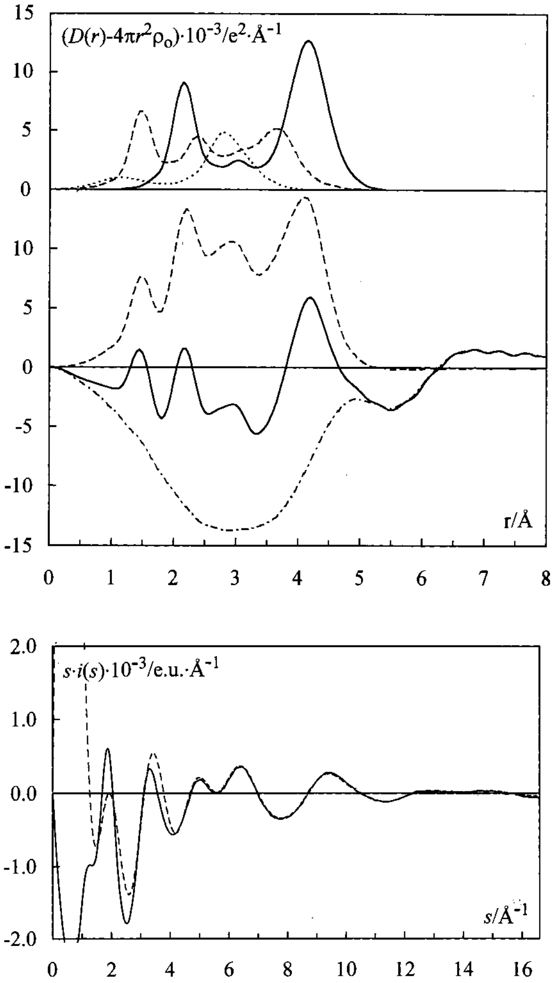

Figure 2. LAXS for 1.46 mol·dm^{-3} indium(III) perchlorate in acidified aqueous solution. (Top) Separate model contributions with parameters from Table 2. Solid line, first (In$-$O$_I$) and second (In···O$_{II}$) hydration spheres; dashes, hydrated perchlorate ion; dots, bulk water. (Middle) Radial distribution functions, $D(r) - 4\pi r^2\rho_o$, and the sum of the calculated peak shapes. Solid line, experimental; dashes, model; dots, difference experimental − model function. (Bottom) Structure-dependent LAXS intensity functions multiplied by the scattering variable: $s\cdot i(s)$ versus s. Solid line, experimental data; dashes, model function.

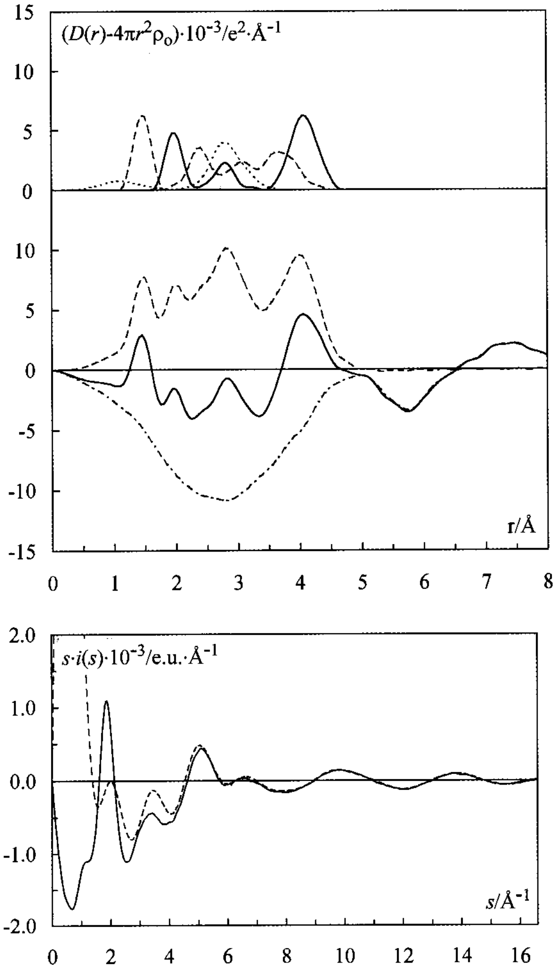

Figure 3. LAXS for 1.52 mol·dm^{-3} chromium(III) perchlorate in aqueous solution. (Top) Separate model contributions with parameters from Table 2. Solid line, first (Cr$-$O$_I$) and second (Cr···O$_{II}$) hydration spheres; dashes, hydrated perchlorate ion; dots, bulk water. (Middle) Radial distribution functions, $D(r) - 4\pi r^2\rho_o$, and the sum of the calculated peak shapes. Solid line, experimental; dashes, model; dots, difference experimental − model function. (Bottom) Structure-dependent LAXS intensity functions multiplied by the scattering variable: $s\cdot i(s)$ versus s. Solid line, experimental data; dashes, model function.

the large composite peak at 4.1 Å comes from the M···O$_{II}$ distances of the second hydration sphere around the metal ions, and a minor contribution from first-sphere trans $\underline{O}_I-(M)-\underline{O}_I$ distances. An asymmetry on the left-hand side of this peak is consistent with the existence of Cl···O distances from water molecules hydrogen bonded to the perchlorate ions, i.e., $O_3\underline{Cl}-O\cdots(H)-\underline{O}H$ distances.[39,40] The peak at 2.9 Å is mainly due to the hydrogen bonded $\underline{O}\cdots(H)-\underline{O}$ distances of bulk water.[41]

With the assumption of a regular octahedral coordination geometry for the $M(OH_2)_6^{3+}$ ions, a regular tetrahedral geometry for the ClO_4^- anion, and a tetrahedral surrounding of oxygen atoms around each bulk water molecule,[41] the short-range solution structure was modeled in terms of atomic pair interactions by means of eq 2. The structural parameters obtained from the LAXS studies of the aqueous gallium(III), indium(III), and chromium(III) perchlorate solutions are summarized in Table 2. Least-squares refinements of the M$-$O$_I$ distances (M = Ga, In, and Cr) of the first hydration shell resulted in the bond lengths 1.964(8), 2.136(6), and 1.964(9) Å, respectively. The M···O$_{II}$ distances for the second hydration sphere were found to be 4.05(1), 4.13(1), and 4.08(2) Å, respectively, with the estimated error limits (3σ) within brackets. The calculated intensity contributions, $i_{calc}(s)$, from eq 2 were Fourier transformed by means of eq 1 to give a Gaussian peak shape for each type of atom-pair interaction. The model function, consisting of the sum of the peak shapes, was subtracted from the experimental RDF function (see Figures 1−3). In all cases this resulted in a smooth difference function, which shows that all distinct interactions have been accounted for up to about 4.5 Å.

Within polynuclear complexes such as $In_4(OH)_6^{6+}$, in which each InO$_6$ octahedron shares three corners with its neighbors, In$-$O and In$-$In distances were reported as 2.17 and 3.9 Å, respectively.[6] In$-$In distances could not be detected for the acidic solutions used in this study, showing that no significant hydrolysis was present. The chromium(III) solution studied by LAXS was not acidified and thus a small amount of hydrolysis complexes has been formed. However, the data analysis shows

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Table 2. LAXS Parameters for the Atom-Pair Model Functions (Eq 2): Distance (*d*/Å), Distance Displacement Parameter (*l*/Å), and Number of Distances (*n*), for the Aqueous Perchlorate Solutions of Gallium(III), Indium(III), and Chromium(III); For Parameters Varied in the Least-Squares Refinements the Estimated Standard Deviations (3σ) Are Given within Brackets

	1.44 M $Ga(ClO_4)_3$			1.46 M $In(ClO_4)_3$			1.52 M$Cr(ClO_4)_3$		
atom-pair	*d*/Å	*l*/Å	*n*	*d*/Å	*l*/Å	*n*	*d*/Å	*l*/Å	*n*
$M-O_I$	1.964(8)	0.045(5)	6.0(1)	2.136(6)	0.087(4)	6.0(1)	1.964(9)	0.052(4)	6.0(1)
$M-O_{II}$	4.05(1)	0.185(3)	12(1)	4.13(1)	0.225(9)	12.1(9)	4.08(2)	0.17(2)	12(1)
$Cl-O$	1.456(3)	0.070(3)	4.0(1)	1.451(3)	0.064(3)	4.0(1)	1.453(3)	0.064(2)	4.0(1)
$(Cl)-\underline{O}\cdots\underline{O}$	3.06(2)	0.11(2)	4.5	3.06	0.10	4.5	3.04(2)	0.11(2)	4
$\underline{Cl}-(O)\cdots\underline{O}$	3.66(2)	0.25(3)	4.5(7)	3.67(2)	0.20(2)	4.5(7)	3.69(3)	0.25(3)	4
$\underline{O}-(H)\cdots\underline{O}^a$	2.90(1)	0.18(2)	4	2.89	0.19	4	2.89(2)	0.19(1)	4
$\underline{O}_I-(H)\cdots\underline{O}_{II}{}^b$	2.73(2)	0.12(2)	2	2.71(2)	0.07(2)	2	2.73(2)	0.11(1)	2

[a] Distance between the hydrogen-bonded oxygen atoms (assuming four neighbors of each) within the aqueous bulk. [b] Distance between the hydrogen-bonded oxygen atoms in the first and second hydration sphere with two O_{II} for each $\underline{O}_I$.

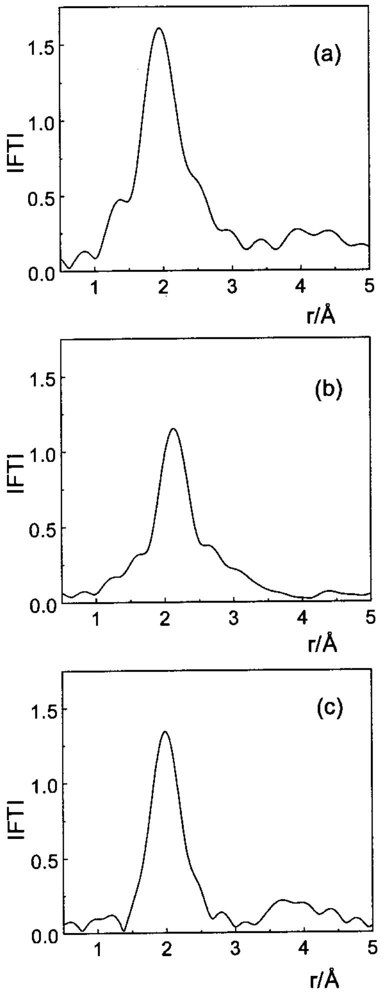

Figure 4. M−O phase corrected Fourier transforms of k^2-weighted experimental EXAFS data for 0.1 mol·dm^{-3} solutions of (a) gallium(III), (b) indium(III), and (c) chromium(III) using the data plotted in Figures 6−8; Δk ranges (Å^{-1}): 3.2−10.6 (gallium); 3.1−12 (indium); 2.8−12.5 (chromium).

that the amount of the first dimeric hydrolysis complex[42] is below the detection limit (a few percent) and will not significantly affect the results obtained.

EXAFS Data. The Fourier transforms of the k^2-weighted EXAFS functions for the aqueous gallium(III), indium(III), and chromium(III) solutions are shown in Figure 4. For the three metal ions studied the Fourier transforms display one major peak which corresponds to the metal−oxygen $M-O_I$ bond distance. In addition there are some minor features at about twice this distance, see Figure 4. A single backscattering path from the second hydration shell is expected to contribute in this region, but multiple scattering paths within the distinct first shell are of greater importance, especially as their mean square deviation parameters, σ^2, in the Debye−Waller expression generally are smaller, as discussed elsewhere.[43] The FEFF7 code,[35] employing ab initio methods to calculate phase and amplitude parameters, has been used to generate the relative contributions (albeit all with $\sigma^2 = 0$) to the EXAFS spectra from all possible scattering paths of importance within the symmetrical hexaaqua complexes surrounded by a second hydration shell, $M(H_2O)_6(H_2O)_{12}{}^{3+}$ (Table 6). The bond lengths and geometry of these complexes are based on the results from the present LAXS study (Table 2).

The EXAFS spectra of the aqueous gallium(III), indium(III), and chromium(III) nitrate solutions with concentrations ranging from 0.005 to 1.0 mol·dm^{-3} (2.6 mol·dm^{-3} for chromium(III)) and the model functions are shown in Figures 5, 6, and S2. The refined model parameters are listed in Tables 3−5, resulting in the mean $M-O_I$ bond distances 1.954(3), 2.124(3), and 1.965(4) Å, for M = Ga, In, and Cr, respectively. The final results obtained by combining the results from the LAXS and EXAFS measurements are given in Table 7.

Discussion

Metal Ion Hydration. 1. First Shell. The high quality of the EXAFS data obtained for the $CsM(SO_4)_2{\cdot}12H_2O$ alum salts recorded at SSRL and the most concentrated samples recorded at SRS allowed simultaneous least-squares refinements of ΔE_o and the $M-O_I$ distances, Tables 3−5. For the alum salts the bond lengths Ga−O 1.957(2) Å and In−O 2.121(2) Å were obtained, which can be compared to the interatomic distances from the crystal structures, 1.944(3) and 2.112(4) Å, respectively (Table 7). The reason for this difference is probably due to atomic displacements arising from thermal motion which cause the interatomic distance between the independently determined mean M and O atomic positions in a crystal structure to appear shorter, often 0.01 Å or more, than the mean M−O bond length as measured by EXAFS or LAXS methods.[31] This means that the EXAFS values of the M−O bond distances in the alum salts should represent the true bond lengths more accurately than the crystal structure values. The $M-O_I$ bond distances obtained from the different EXAFS measurements of the gallium(III), indium(III), and chromium(III) solutions are in good agreement, with no significant shifts due to concentration or anion changes (Tables 3 and 4). Moreover, the structure of the first hydration

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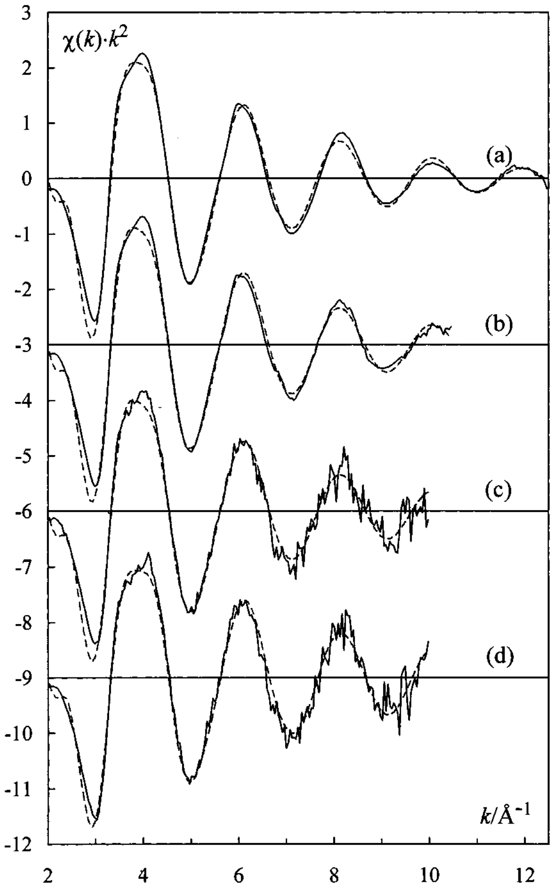

Figure 5. EXAFS data for aqueous gallium nitrate solutions (solid lines), and model functions with parameters from Table 3 for the M$-$O$_I$ distances including a minor multiple scattering contribution (dashes): (a) 1.0, (b) 0.10, (c) 0.010, and (d) 0.005 mol·dm^{-3}.

sphere for the hydrated gallium(III) and indium(III) ions are very similar in aqueous solution and in the alum salt, as is evident from their almost identical EXAFS spectra (Figure S3). The coordination number of the first sphere oxygen atoms in solution was obtained as n(M$-$O$_I$) = 6.0(2) and 6.1(3) for Ga and In, respectively, by using the S_o^2 values from the alum salt (Ga) or the most concentrated solution (Ga, In) as a reference.

The results from LAXS measurements gave M$-$O bond distances of 1.964(8), 2.136(6), and 1.964(9) Å, with small Debye$-$Waller parameters corresponding to a small variation in the distance as expected for strongly hydrated three-valent metal ions. The number of water molecules in the first coordination sphere is 6, see Table 2, which is similar to the EXAFS values for the solutions.

2. LAXS Second Shell. The radial distribution functions from the LAXS studies show a distinct second hydration shell with M···O$_{II}$ distances at about 4.1 Å for the three hexahydrated metal ions. The best fit of the hydrogen bonded O$_I$···O$_{II}$ distance linking the first sphere water molecules to the second shell was obtained at 2.72(2) Å. From the previous infrared spectroscopic study of rhodium(III), aluminum(III), and chromium(III) ions in aqueous solution the corresponding O$_I$···O$_{II}$ distance was estimated to 2.63(9) Å by means of a correlation with hydrogen-bonded O$-$D stretching frequencies in crystal structures.[26] In the structure of CrH(SO$_4$)$_2$·7H$_2$O the Cr$-$O$_I$ bond distance of 1.97 Å was found to correspond to a O$_I$$-$(H)···O$_{II}$ hydrogen bond distance of 2.66 Å between a water molecule and a sulfate oxygen atom.[44] Thus, the O$_I$···O$_{II}$ mean distance of 2.41 Å proposed from an MD simulation of a chromium(III) solution is unrealistically short.[24] However, a more recent MD simulation using the hydrated ion model yielded a value of 2.58 Å.[25]

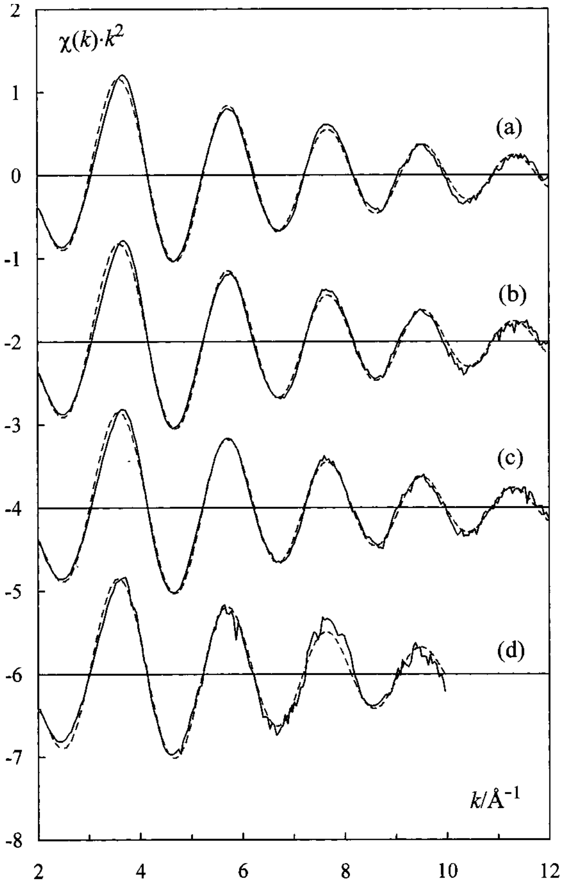

Figure 6. EXAFS data for aqueous indium nitrate solutions (solid lines), and model functions with parameters from Table 4 for the M$-$O$_I$ distances including a minor multiple scattering contribution (dashes): (a) 1.0, (b) 0.10, (c) 0.010, and (d) 0.005 mol·dm^{-3}.

Table 3. EXAFS Parameters for the First Hydration Shell of the Aqueous Solutions of Gallium(III) Nitrate and Perchlorate and of the Alum Salt CsGa(SO$_4$)$_2$·12H$_2$O; Estimated Standard Deviations (3σ) from the Least-Squares Fitting Procedure Are Given within Brackets

concn/mol·dm^{-3}	d/Å	σ^2/Å^2	n	k-range/Å^{-1}
1.0	1.954(3)	0.0058(3)	6^c	2.0$-$12.4
0.5^a	1.958(2)	0.0049(3)	6.0(2)^b	2.0$-$14.0
0.1	1.954(3)	0.0060(3)	6.0(3)^c	2.0$-$10.5
0.01	1.952(6)	0.0056(8)	5.6(6)^c	2.0$-$10.0
0.005	1.951(5)	0.0034(13)	5.3(6)^c	2.0$-$10.0
CsGa(SO$_4$)$_2$·12H$_2$O(s)	1.957(3)	0.0044(3)	6^b	2.0$-$14.0

^{a} Perchlorate solution. ^{b} S_o^2 = 1.01. ^{c} S_o^2 = 1.12.

From the M···O$_I$, M···O$_{II}$, and O$_I$···O$_{II}$ distances in Table 2, a mean tilt angle of the first sphere water molecules[18] can be estimated. Assuming the normal water molecule geometry and linear O$_I$···O$_{II}$ hydrogen bonding, tilt angles of 34°, 39°, and 31°, with an estimated error limit of about ±7°, are obtained for these concentrated Ga, In, and Cr solutions, respectively. These values are in the same range as that previously obtained for a concentrated chromium(III) solution from a neutron diffraction study, 34 ± 6°.[7]

The RDFs from the LAXS studies of the aqueous gallium(III), indium(III), and chromium(III) perchlorate solutions all

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Table 4. EXAFS Parameters for the First Hydration Shell of the Aqueous Solutions of Indium(III) Nitrate and Perchlorate and of the Alum Salt $CsIn(SO_4)_2\cdot 12H_2O$; Estimated Standard Deviations (3σ) from the Least-Squares Refinements Are Given within Brackets

concn/mol·dm^{-3}	d/Å	σ^2/Å^2	n	k-range/Å^{-1}
1.46[a]	2.123(3)	0.0043(3)	5.6(3)[b]	2.0−14.0
1.0	2.124(3)	0.0036(5)	6[b]	2.0−12.0
0.1	2.124(3)	0.0036(5)	6.1(4)[b]	2.0−12.0
0.01	2.128(3)	0.0035(4)	5.9(3)[b]	2.0−11.7
0.005	2.131(6)	0.0044(11)	6.2(7)[b]	2.0−10.0
$CsIn(SO_4)_2\cdot 12H_2O$(s)	2.121(3)	0.0049(3)	6[c]	2.0−14.0

[a] Perchlorate solution for LAXS, see Table 1. [b] $S_o^2 = 0.95$. [c] $S_o^2 = 1.9$ (contribution from fluorescence, see text).

Table 5. EXAFS Parameters for the First Hydration Shell of the Aqueous Solutions of Chromium(III) Nitrate; Estimated Standard Deviations (3σ) Are Obtained from the Least-Squares Fitting Procedure

concn/mol·dm^{-3}	d/Å	σ^2/Å^2	n	k-range/Å^{-1}
2.6	1.965(4)	0.0035(4)	6[a]	3.5−14.0
1.5	1.963(3)	0.0045(5)	6.6(6)[a]	3.5−14.0
0.1	1.968(5)	0.0041(12)	5.9(8)[a]	3.5−12.0
0.05	1.967(7)	0.0026(18)	4.6(9)[a]	3.5−11.0
0.01	1.968(6)	0.0012(15)	5.1(9)[a]	3.5−11.0
0.005	1.969(8)	0.0017(20)	5.4(2.0)[a]	3.5−9.5

[a] $S_o^2 = 0.79$.

show a minor broad peak at about 5 Å, which has not been included in the model calculations. A similar feature has previously been reported for a LAXS study of iron(III) in aqueous perchlorate solution, and was attributed to the formation of outer sphere $Fe(OH_2)_6^{3+}-ClO_4^-$ complexes giving rise to M···Cl distances in this region.[45] The interpretation is supported by the observation that this peak is much less prominent in a 1.0 mol·dm^{-3} $Cr(ClO_4)_3$ solution,[17] for which the perchlorate concentration is 1.5 mol·dm^{-3} lower than in the present solution. The stoichiometric ratio (Table 1) gives, for a statistical distribution of water molecules and perchlorate ions, an average of about 1.5 ClO_4^- ions in the second shell around the $M(OH_2)_6^{3+}$ ions in the present solutions.

3. EXAFS Multiple Scattering. Fourier transforms of the k^2-weighted EXAFS data for the gallium and chromium(III) solutions show weak features up to about 4 Å (Figure 4) which originate from both multiple scattering within the first hydration shell and single scattering from the second hydration shell, see Table 6. No significant contribution is, however, apparent for the indium solution. From previous EXAFS studies on the hydrated rhodium(III) ion the 4 Å contribution can be seen to be weaker than that for chromium(III).[3,4,17]

To find a pattern in these observations the FEFF7 ab initio calculations of scattering paths were extended to a number of metal ions octahedrally surrounded by six oxygen atoms at 2.0 Å, and by 12 oxygen atoms at 4.1 Å as in a hydrogen-bonded second hydration sphere. Effective charges of 0 and +2 were used for the metal atoms in the calculation. The latter value is close to the Mulliken charges obtained from ab initio SCF calculations on hexaaqua metal ion complexes.[46] The results of the FEFF calculations show the relative contribution to the EXAFS from the single backscattering of the second hydration shell to decrease monotonically with increasing threshold energy, see Table 6 and Figure 7. Also, the multiple scattering within the first hydration shell shows an overall decrease, albeit with some irregularities (Figure 7) related to the effective charge of the metal atom. Furthermore, the relative contributions given in Table 6 are obtained with the mean square displacement parameter σ^2 equal to zero. The corresponding Debye−Waller parameters from the LAXS results in Table 2 show a rather broad distribution of the second shell $M\cdots O_{II}$ distances (l values of 0.17−0.23 Å) at about 4.1 Å. Within the tightly bonded first shell the multiple scattering paths of similar length will in general have smaller total mean square displacements than that of the single scattering from the second shell, and their contributions will thus be less damped.[43] On the other hand, different phase shifts for multiple scattering paths of equal length may imply that they counteract mutually. This is the case for the two multiple scattering paths for the O'_I-M-O_I entity including oxygen atoms in trans position, i.e., the paths $M-O_I-O'_I$ and $M-O_I-M-O'_I$.[43] The present EXAFS data showed a slight improvement in the least-squares refinements when a multiple scattering $M-O_I-O'_I$ path was included at about 4.0 Å in the model, but this minor contribution (see Figure S4) did not have any significant influence on the single scattering $M-O_I$ parameters.

Table 6. Calculated Contributions (FEFF7) from the Main Scattering Paths in the K-edge EXAFS Spectra for Octahedral $M(H_2O)_6(H_2O)_{12}^{3+}$ Complexes with the Distances $M-O_I = 2.0$ Å and $M\cdots O_{II} = 4.1$ Å in an Assumed Hydrogen-Bonded Structure of T_h Symmetry; Contributions Are Given for Each Complex Relative to the Single Scattering $M-O_I$ at 2.0 Å (100%), with the Mean Square Displacement Parameter $\sigma^2 = 0$ and the Effective Metal Atom Charges +2 and 0 (within Brackets)

element M	ss[a] 2.0 Å	ms *cis*[b] 3.4 Å	ms *trans*[c] 4.0 Å	ss[d] 4.1 Å	ms[e] 4.4 Å
Sc	100	19(19)	42(58)	34(34)	24(24)
Cr	100	19(19)	44(40)	33(33)	23(23)
Ga	100	18(17)	63(47)	29(30)	20(20)
Y	100	13(13)	57(60)	25(25)	15(15)
Rh	100	11(11)	30(35)	20(20)	10(10)
In	100	9(8)	21(20)	17(17)	8(8)
La	100	5(5)	20(21)	11(11)	4(4)

[a] Single scattering (ss) M−O paths. [b] Multiple scattering (ms) *cis*-$M-O_I-O_I$. [c] *trans*-$M-O_I-O_I$ and $M-O_I-M-O_I$. [d] $M-O_{II}$. [e] $M-O_I-O_{II}$.

For the hydrated gallium and chromium(III) ions, which both have relatively low threshold energies and well-defined hydration spheres, the observed minor features at about 4 Å (Figure 4) thus contain contributions mainly from multiple scattering within the first hydration shell but also due to single scattering from the second shell. On the other hand, for the indium(III) ion with higher threshold energy and larger displacement parameters for both hydration spheres (cf. l values in Table 2), these contributions become too weak to be observed in the Fourier transform. The hydrated rhodium(III) ion has lower oxygen and proton exchange rates for its first hydration shell than chromium(III),[19,47] however, the hydrogen bonding is of similar strength.[26] The displacement parameter for its second shell $M\cdots O_{II}$ distances should therefore be comparable to, or smaller, than that for chromium(III). Despite the overall intensity reduction due to the higher threshold energy (Table 6) a small contribution at about 4 Å is also visible for rhodium(III) in the EXAFS Fourier transform.[43,47]

The previous LAXS study, assuming isostructural rhodium and chromium solutions, resulted in a residual peak at 4.02(2) Å corresponding to the $Rh\cdots O_{II}$ distance when the $Cr\cdots O_{II}$

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Table 7. M−O Bond Distances (Å) and Symmetric Stretching Frequencies (cm^{-1}) for Hexahydrated Gallium(III), Indium(III), and Chromium(III) Ions in Aqueous Solution and in the Cesium Alum Salts

ion M	solution[a] $d(M-O_6)$	sulfate alum[b,c] $d(M-O_6)$	sulfate alum[b,d,e] $d(M-O_6)$	selenate alum[d,e,f] $d(M-O_6)$	solution[g,h] $\nu(M-O_6)$	sulfate alum[d,h] $\nu(M-O_6)$	$\Delta\nu/cm^{-1}$
Ga^{3+}	1.959(6)	1.957(2)	1.944(3)		521	537	16
In^{3+}	2.131(7)	2.121(2)	2.112(4)	2.134(6)	485	505	20
Cr^{3+}	1.966(8)		1.959(3)	1.964(3)	522	540	18

[a] The combined EXAFS and LAXS mean value from the present study. [b] $CsM(SO_4)_2 \cdot 12H_2O$. [c] This work, EXAFS data. [d] References 1 and 2. [e] Crystallographic data. [f] $CsM(SeO_4)_2 \cdot 12H_2O$. [g] Reference 46. [h] Raman data.

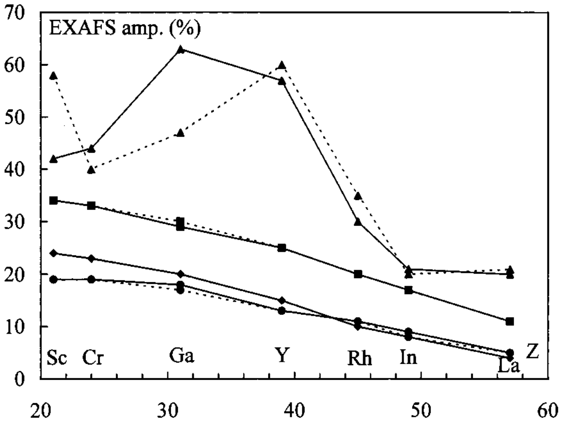

Figure 7. Relative FEFF7 amplitudes for EXAFS contributions calculated for the main scattering paths in the K-edge EXAFS spectra for $M(H_2O)_6(H_2O)_{12}^{3+}$ complexes with assumed distances $M-6O_I = 2.0$ Å and $M\cdots12O_{II} = 4.1$ Å. The contributions are given for each complex relative to the single scattering $M-O_I$ at 2.0 Å (100%) and without atomic displacements. The solid and dashed lines represent effective metal atom charges +2 and 0, respectively. The multiple (ms) and single scattering (ss) paths are: cis $M-O_I-O_I$ (circles); trans $M-O_I-O_I$ and $M-O_I-M-O_I$ (triangles); $M-O_{II}$ (squares); $M-O_I-O_{II}$ (diamonds).

contribution and the solvent background was subtracted in a difference procedure.[17] However, this difference peak became broader than the $M\cdots O_{II}$ peaks in the present study, and considering the probable displacement caused by the slightly longer $Cr\cdots O_{II}$ distance of 4.08(2) Å (Table 2), a more accurate value for the $Rh\cdots O_{II}$ distance should then be 4.05(2) Å.

Generally, the EXAFS single scattering contribution from the second hydration shell is smaller than the multiple scattering within the first hydration shell, as discussed above and elsewhere.[43] Therefore, to obtain a reliable description of the second hydration shell, complementary information is required, such as that provided by the LAXS technique. For example, the LAXS value obtained in this study for the $Cr-O_{II}$ distance, 4.08(2) Å, is slightly longer than that obtained in the previous EXAFS analysis, 3.97 ± 0.04 Å.[43] However, considering that the error limits given are probably too optimistic, in particular for EXAFS, since they mainly account for statistical variations in the data and not systematic errors, the agreement is reasonable.

Vibrational Spectroscopy on the Hydrated Metal Ions. Raman studies further support that the hydrated gallium(III), indium(III), and chromium(III) ions exist in aqueous solution as stable hexaaqua complexes. The $M-O_I$ symmetric stretching Raman frequency for aqueous gallium(III), indium(III), and chromium(III) solutions and the solid alum salts is given in Table 7. Comparisons of these values with the theoretically calculated frequencies[1,46,48,49] confirm the presence of hexahydrated metal ions in aqueous solution. The experimental value of the $\nu_1(MO_6)$ frequency is 16, 20, and 18 cm^{-1} lower than in the gallium(III), indium(III), and chromium(III) alum salts, respectively, but the shifts are due to the lower temperature of the samples studied in solid state (90 K) and also the difference in hydrogen bond strength.[1,48]

Anion Hydration. The Cl−O bond distances within the perchlorate ion, obtained in the range 1.451−1.456 Å, do not differ significantly from those found for hydrogen bonded ions in crystal structures. A neutron diffraction isotopic substitution study on a concentrated sodium perchlorate solution gave a hydration number of 4.6 ± 0.5 with a hydrogen bonded $Cl-(O)\cdots O$ distance of about 3.7 Å.[39] For the present LAXS data a hydration number of 4.5(7) gave a satisfactory fit to the RDFs with the mean $\underline{Cl}-O\cdots(H)-\underline{O}$ distance of 3.68(3) Å for the gallium(III), indium(III), and chromium(III) solutions. The hydrogen bonded $\underline{O}\cdots(H)-\underline{O}$ distance between the perchlorate oxygen atom and the water molecules was found to be 3.05(2) Å (Table 2). This is in good agreement with the value obtained from a previous double difference infrared spectroscopic study, 3.07(1) Å, from which a hydration number of 3.8(3) was reported.[40]

Conclusions

Both the EXAFS and LAXS data show the gallium(III), indium(III), and chromium(III) ions in aqueous solution to be hydrated by six water molecules in a tightly bonded first hydration sphere with the $M-O_I$ bond distance 1.959(6), 2.131(7), and 1.966(8) Å, respectively. A distinct hydrogen-bonded second coordination sphere with 12 ± 1 oxygen atoms was found from the LAXS studies at the $M\cdots O_{II}$ distance of 4.05(1), 4.13(1), and 4.08(2) Å for gallium(III), indium(III), and chromium(III), respectively. In the EXAFS spectra for gallium and chromium, features occur which are probably partly caused by the second hydration shell, but are overlapped by the more intense multiple scattering within the first hydration shell.

The perchlorate ion in these concentrated solutions is found from the LAXS results to be weakly hydrogen bonded to four water molecules with the $Cl\cdots O$ distance of 3.68(3) Å.

The $Cr-O_I$ and $In-O_I$ bond distances reported in previous EXAFS and LAXS investigations for the hydrated metal ions in aqueous solution are somewhat longer than those obtained in this study.[4−16] However, the present EXAFS results for the $Ga-O_I$ and $In-O_I$ bond lengths of the hexahydrated ions in cesium alum salts are, as expected, slightly longer than the crystal structure distances. Moreover, this study shows good agreement between LAXS and EXAFS methods for the M−O distances of the three metal ions in aqueous solution, see Table 7. The consistency of the present results supports their accuracy and absence of significant systematic errors.

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Supporting Information Available: Separate calculated intensity contributions of the LAXS models for the gallium(III), indium(III), and chromium(III) solutions (Figure S1); EXAFS data and model functions for aqueous chromium(III) nitrate solutions of different concentrations (Figure S2); comparison between the k^3-weighted EXAFS functions for the gallium and indium aqueous solutions and the corresponding alum salts $CsM(SO_4)_2 \cdot 12H_2O$ (M = Ga, In) (Figure S3); fit of the EXAFS model including separate contributions from $M-O_I$ single scattering and an $M-O_I-O_I$ multiple scattering paths for each gallium(III), indium(III), and chromium(III) solution (Figure S4) (9 pages). Ordering information is given on any current masthead page.

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