

# Second-Sphere Hydration of Rhodium(III) and Chromium(III) in Aqueous Solution. A Large-Angle X-Ray Scattering and EXAFS Study

Michael C. Read and Magnus Sandström\*

Department of Inorganic Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

Read, M. C. and Sandström, M., 1992. Second-Sphere Hydration of Rhodium(III) and Chromium(III) in Aqueous Solution. A Large-Angle X-Ray Scattering and EXAFS Study. – *Acta Chem. Scand.* 46: 1177–1182.

The hydration structure around Rh(III) and Cr(III) ions in 1 M aqueous perchlorate solution has been studied by X-ray scattering measurements. Isostructural substitution was used to eliminate all contributions from atom-pair distances not involving the metal ions, leading to a radial distribution function dominated by the hydration of rhodium(III). The first hydration sphere contains six water molecules with the Rh–O distance  $2.03 \pm 0.02$  Å, and the well defined second hydration sphere holds  $13 \pm 1$  water molecules at a mean Rh–O distance of  $4.02 \pm 0.02$  Å. A hydrogen bond length between the first- and second-sphere water molecules of  $2.63 \pm 0.09$  Å was calculated using reasonable assumptions about the geometry of the coordinated water molecules in rhodium(III) and chromium(III) solutions. From EXAFS studies of  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ , as a solid and in aqueous solution, no significant structural differences in the first hydration sphere of the  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  ion were found. No evidence for the existence of the well established second hydration sphere was found in our EXAFS data.

It has been shown by numerous experimental techniques that a first hydration sphere, containing six water molecules with extremely long residence times, exists around the Rh(III) and Cr(III) ions in aqueous solution.<sup>1</sup> Only recently, however, have quantitative data appeared describing the ordering of water molecules in a second hydration sphere around these strongly polarising cations in aqueous solution.<sup>2,3</sup>

Clear evidence for a second shell accommodating  $15.5 \pm 1$  water molecules (based on the number of hydrogen atoms) was found using first and second order isotopic differences in neutron diffraction studies of concentrated ( $\sim 2$  M) Cr(III) perchlorate solutions, although the high perchlorate concentration gives rise to a significant intrusion of  $\text{ClO}_4^-$  ions in the second shell.<sup>2</sup>

A double-difference infrared spectroscopic method showed that the small trivalent ions Al(III), Cr(III) and Rh(III) not only increase the hydrogen-bond strength of the first-sphere water molecules, but also significantly enhance the hydrogen bonds of those in the second sphere, as compared to bulk water.<sup>3</sup> No significant difference was found in the hydrogen-bond structure for the 0.2 M Cr(III) and Rh(III) perchlorate solutions studied. However, the indirect derivation of the number of affected water molecules only allowed a determination of a lower limit, 8.4, of the number of second-sphere water molecules around these ions.<sup>3</sup> Despite the pronounced hydrogen-bond structure

around these trivalent ions, it was found by a quasi-elastic neutron scattering study on a 1.8 M  $\text{Cr}(\text{ClO}_4)_3$  solution that the second-shell protons are in fast exchange ( $\tau_H \leq 10^{-10}$  s) with the bulk water.<sup>4</sup>

More quantitative information on the structure of an unperturbed second hydration sphere, in solutions of sufficiently low concentration to avoid outer-sphere anion effects, is therefore desirable to substantiate the interpretations from previous studies. Large-angle X-ray scattering (LAXS) methods are capable of giving radial distribution functions (RDFs) containing information on well defined atom-pair interactions at fairly long distances, but the superposed solvent-solvent and anion-solvent contributions often obscure the long-range cation-solvent interactions. In earlier LAXS studies of aqueous solutions of Rh(III) and Cr(III), the data have been interpreted by fitting a multiparameter model approximately describing the sum over the structure functions of the hexahydrated cation, the hydrated anion and bulk water, giving the first-shell metal-oxygen distances  $r(\text{Cr}-\text{O}_i) \approx 1.98\text{--}2.00$  Å and  $r(\text{Rh}-\text{O}_i) \approx 2.04$  Å.<sup>5-7</sup> In order to obtain reliable results on the second shell, isostructural substitution allowing direct elimination of the interactions not involving the metal atoms is necessary. Several similarities in the chemistry of these two ions favour the hypothesis that they are isostructural, and thus candidates for a LAXS study using isostructural substitution: (1) kinetic behaviour, (2) hydrogen-bond structure, and (3) metal-oxygen bond length and strength, reflected e.g. in the ability of the Rh(III) and Cr(III) ions to replace

\* To whom correspondence should be addressed.

each other in dimeric hydrolysis complexes without distinguishable changes in the octahedral oxygen coordination,<sup>8</sup> and in the symmetric stretching frequencies of the ions in solution ( $\nu_{M-O} = 529$  and  $522 \text{ cm}^{-1}$  for  $M = \text{Rh}$  and  $\text{Cr}$ , respectively).<sup>9</sup> Previously, isostructural substitution has been used to isolate contributions involving the metal ion for the trivalent lanthanides using yttrium as the substituent.<sup>10</sup> The present investigation has been conducted in a similar manner using chromium as the substituent, thus allowing direct determination of the rhodium–oxygen distances in the first and second hydration spheres ( $\text{Rh}-\text{O}_I$ ,  $\text{Rh}-\text{O}_{II}$ ), and the corresponding hydration numbers,  $n(\text{O}_I)$  and  $n(\text{O}_{II})$ .

## Experimental

**Solution preparation.** The dry acid-free compound  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  was synthesized as described previously.<sup>11</sup>  $\text{Cr}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  (GFS Chemicals) was used as supplied. Equimolar solutions containing 1.04 M  $\text{Rh}(\text{III})$  ( $\rho = 1.315$ ) and  $\text{Cr}(\text{III})$  ( $\rho = 1.261 \text{ g cm}^{-3}$ ), were prepared by dissolving the perchlorate salts in distilled water. An aqueous 1.52 M  $\text{Cr}(\text{III})$  perchlorate solution ( $\rho = 1.381 \text{ g cm}^{-3}$ ) was also investigated by LAXS methods. ICP atomic emission spectroscopy (ARL 3520) was used for the metal ion analyses; the solutions were checked for excess acidity by cation exchange (Dowex 50W–X8,  $\text{H}^+$  form) and titration of the eluted acid with standard  $\text{NaOH}$  solution. Densities were measured with an Anton Paar DMA 35 densitometer.

**Solution characterization.** From the available  $\text{p}K_a$  values<sup>12</sup> the fractions of the first deprotonated species  $[\text{M}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  could be estimated as 0.7 and 2.0 % of the total metal ion concentration for chromium(III) and rhodium(III), respectively, and were neglected in the data analysis. UV–VIS spectra<sup>12b</sup> and  $^{103}\text{Rh}$  NMR spectra were recorded on the freshly prepared aqueous rhodium(III) solution, and also after the LAXS experiment in which the solution was held at ambient temperature for 2 weeks. No changes were observed in the UV–VIS spectra, and in both cases a single NMR signal, characteristic of the  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  ion, was observed at 9919 ppm (298 K).<sup>11</sup> During the LAXS experiment there was no evidence for the slow formation of hydroxo-bridged oligomers previously studied by  $^{103}\text{Rh}$  NMR.<sup>13</sup>

**LAXS measurements.** X-Ray ( $\text{Mo } K\alpha$ ,  $\lambda = 0.7107 \text{ \AA}$ ) scattering measurements were conducted on a Rigaku  $\theta$ – $\theta$  diffractometer at ambient temperature,  $24 \pm 1^\circ\text{C}$ . The radiation scattered from the free surface of the solutions, contained in a sealed Teflon cell with a semicircular polyethylene-coated aluminium-foil window, was recorded at  $\theta$  values incremented in steps of  $0.1^\circ$  for  $1.5 < \theta < 22^\circ$  and steps of  $0.25^\circ$  for  $22 < \theta < 70^\circ$ . Exit slits corresponding to 1/6, 1/2 and  $1^\circ$  divergence of the primary X-ray beam were used to cover the whole  $\theta$ -range. A focusing single-crystal LiF monochromator was used to reduce Compton scatter-

ing reaching the scintillation counter. At least  $2 \times 10^5$  counts were collected at each  $\theta$  value, corresponding to a statistical error of less than 0.3 %. After corrections for the angle-dependent absorption effects ( $\mu = 4.99$  and  $4.05 \text{ cm}^{-1}$  for the  $\text{Rh}$  and  $\text{Cr}$  solutions, respectively), the raw intensity data for each solution were scaled to a common exit slit width.

**X-Ray data treatment.** A modified PC version of the KURVLR program<sup>14</sup> was used for the data treatment. After correction for polarisation in the sample and monochromator,<sup>5</sup> the data were normalized by comparing the high-angle region of the intensity curve,  $I(s)$ , to the sum of the theoretical structure-independent coherent scattering,  $\sum_V n_p \{f_p^2(s) + (\Delta f_p'')^2\}$ , and the fraction of Compton scattering not removed by the monochromator,  $\text{del}(s)I_{\text{incoh}}(s)$ , where  $n_p$  denotes the number of atoms of type  $p$  in a stoichiometric unit of volume,  $V$ , chosen to include one metal ion. Hence, the structure-dependent reduced intensity,  $i(s)$ , was found from eqn. (1), where  $s = (4\pi \sin \theta)/\lambda$  is the scattering variable ( $k$  in EXAFS),  $K$  is the

$$i(s) = KI(s) - \sum_V n_p [f_p^2(s) + (\Delta f_p'')^2] - \text{del}(s)I_{\text{incoh}}(s) \quad (1)$$

normalization factor,  $f_p(s)$  is the coherent scattering factor for the neutral atom  $p$  corrected for the real part of the anomalous dispersion, and  $\Delta f_p''$  is the imaginary term of the anomalous dispersion correction.<sup>15</sup>

Fourier transformation [eqn. (2)] of the  $i(s)$  curves for both solutions gave the modified radial distribution functions,  $D^{\text{Cr}}(r)$  and  $D^{\text{Rh}}(r)$  for  $\text{Cr}(\text{III})$  and  $\text{Rh}(\text{III})$ , respec-

$$D(r) = 4\pi r^2 \rho_0 + 2r\pi^{-1} \int_0^{s_{\text{max}}} si(s)M(s)\sin(rs)ds \quad (2)$$

tively. The modification function  $M(s)$  was chosen to be  $\{f_M^2(0) + (\Delta f_M'')^2\} \{f_M^2(s) + (\Delta f_M'')^2\}^{-1} \exp(-0.01s^2)$ , with  $M = \text{Rh}$  or  $\text{Cr}$ , in order to sharpen the peaks and reduce termination errors, and  $\rho_0 = \{\sum n_p f_p(0)\}^2/V$  is the electronic number density.

The method of data treatment described previously for LAXS isostructural substitution was followed.<sup>10</sup> In a single LAXS experiment, the structure-sensitive reduced intensity,  $i(s)$ , can be written as the sum over the different partial structure functions each weighted by the product of the scattering factors,  $f_p$  and  $f_q$ , for the two atomic species involved in the interaction [eqn. (3)].

$$i(s) = \sum_p \sum_q^{p \neq q} n_p n_q f_p(s) f_q(s) [S_{pq}(s) - 1] \quad (3)$$

For a liquid containing  $p$  atomic species there are  $p(p+1)/2$  different partial structure functions,  $S_{pq}$ . Thus, in an

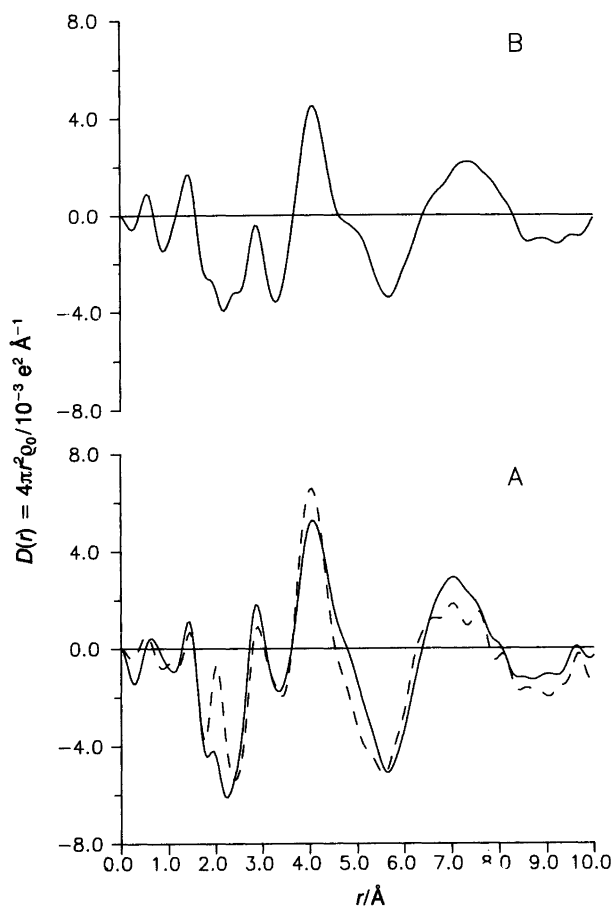


Fig. 1. Radial distribution functions,  $D(r) - 4\pi r^2 \rho_0$ , from LAXS studies on aqueous perchlorate solutions of (A) 1.04 M Cr(III) (solid line) and 1.04 M Rh(III) (dashed line); (B) 1.52 M Cr(III).

aqueous solution of a metal perchlorate,  $M(\text{ClO}_4)_n$ , the four atomic species M, Cl, O and H give rise to ten partial structure functions;  $S_{\text{MCl}}$ ,  $S_{\text{MO}}$ ,  $S_{\text{MH}}$ ,  $S_{\text{MM}}$ ,  $S_{\text{Cl}}$ ,  $S_{\text{ClO}}$ ,  $S_{\text{ClH}}$ ,  $S_{\text{OH}}$ ,  $S_{\text{OO}}$  and  $S_{\text{HH}}$ . However, in hydration studies concerning metal ions only the four structure functions involving the metal,  $S_{\text{MX}}$ , are of interest. For two metal ions M and M', which give isostructural solutions in equimolar concentrations, all partial structure functions not involving the metal ions are identical and are eliminated in eqn. (4), where  $\Delta f_{\text{M}} = f_{\text{M}}(s) - f_{\text{M}'}(s)$ .

$$\begin{aligned} \Delta i(s) &= i_{\text{M}}(s) - i_{\text{M}'}(s) = 2 n_{\text{M}} n_{\text{Cl}} \Delta f_{\text{M}}(s) f_{\text{Cl}}(s) [S_{\text{MCl}}(s) - 1] \\ &+ 2 n_{\text{M}} n_{\text{O}} \Delta f_{\text{M}}(s) f_{\text{O}}(s) [S_{\text{MO}}(s) - 1] \\ &+ 2 n_{\text{M}} n_{\text{H}} \Delta f_{\text{M}}(s) [S_{\text{MH}}(s) - 1] \\ &+ n_{\text{M}}^2 [f_{\text{M}}^2(s) - f_{\text{M}'}^2(s)] [S_{\text{MM}}(s) - 1] \end{aligned} \quad (4)$$

In the present experiment, where M = Rh(III) and M' = Cr(III), Fourier transformation of  $\Delta i(s)$ , multiplied with the scaling function  $f_{\text{Rh}}(s)/[f_{\text{Rh}}(s) - f_{\text{Cr}}(s)]$ , gives a difference distribution function  $\Delta D^{\text{Rh}}(r)$  with terms involving the rhodium ion only<sup>10</sup> [eqn. (5)].

$$\begin{aligned} \Delta D^{\text{Rh}}(r) &= 4\pi r^2 \rho_0^{\text{Rh}} + 2r\pi^{-1} \int_0^{s_{\text{max}}} s \Delta i(s) M(s) \sin(rs) \cdot \\ &f_{\text{Rh}}(s) [f_{\text{Rh}}(s) - f_{\text{Cr}}(s)]^{-1} ds \end{aligned} \quad (5)$$

*Analysis of  $\Delta D^{\text{Rh}}(r)$ .* The radial distribution difference function  $\Delta D^{\text{Rh}}(r)$  was analyzed by comparison with model peaks obtained by Fourier transformation of theoretical intensities,  $i_{\text{RhO}}(s)$ , calculated for pair interactions between rhodium and oxygen atoms, using the Debye expression [eqn. (6)] in which  $\sigma$  is the root-mean-square deviation<sup>16a</sup>

$$\begin{aligned} i_{\text{RhO}}(s) &= n_{\text{Rh}} n_{\text{O}} f_{\text{Rh}}(s) f_{\text{O}}(s) \sin(r_{\text{RhO}} s) \\ &(r_{\text{RhO}} s)^{-1} \exp(-2\sigma_{\text{RhO}}^2 s^2) \end{aligned} \quad (6)$$

( $b = 2\sigma^2$  in the KURVLR program<sup>14</sup> for X-ray data) from the mean distance,  $r_{\text{RhO}}$ . Visual comparison of the resolved peaks in  $\Delta D^{\text{Rh}}(r)$  with the model peaks was used to estimate the maximum errors in the parameters,  $r_{\text{RhO}}$ ,  $\sigma_{\text{RhO}}$  and  $n_{\text{O}}$ , the number of oxygen atoms involved in each interaction with the Rh atom.

*EXAFS measurements and data treatment.* Rhodium K-edge X-ray absorption spectra were collected in transmission mode at ambient temperature on the wiggler station 9.2 at the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory under dedicated conditions (2.0 GeV and 160 mA maximum current). An Si(220) double monochromator was used at 60% of maximum intensity to give rejection of higher-order harmonics. Measurements were performed on a 1 M solution of  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  in 1 M  $\text{HClO}_4$ , contained in a cell with polyethylene windows and a 4 mm spacer, and on the solid perchlorate salt 'diluted' with BN and held between strips of Sellotape. The energy scale was calibrated by simultaneous measurement of a 10  $\mu\text{m}$  Rh foil, assigning the first inflection point of the K-edge spectrum of the Rh metal to 23 220 eV.<sup>16b</sup> All EXAFS data were treated with the XFPKG program system,<sup>17</sup> involving standard methods, of pre-edge subtraction, spline removal of background and model refinement.<sup>16b</sup>

## Results

*Radial distribution functions for Rh(III) and Cr(III).* The similarity in the modified RDFs, given as  $D(r) - 4\pi r^2 \rho_0$  [eqn. (2)] for the solutions containing 1.04 M  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , can be seen in Fig. 1A. Qualitatively, peaks due to the following pair interactions can be identified: Cl-O  $\approx 1.5$  Å in the  $\text{ClO}_4^-$  ion, Rh-O<sub>I</sub>  $\approx 2.0$  Å with O<sub>I</sub> representing first-sphere water oxygen, and O-O  $\approx 2.9$  Å, corresponding to the hydrogen bond length between bulk water molecules. The large peak at ca. 4.0 Å contains contributions from M-O<sub>II</sub> (O<sub>II</sub> represents second-sphere oxygen atoms), and *trans* O<sub>I</sub>-M-O<sub>I</sub> interactions in the hy-

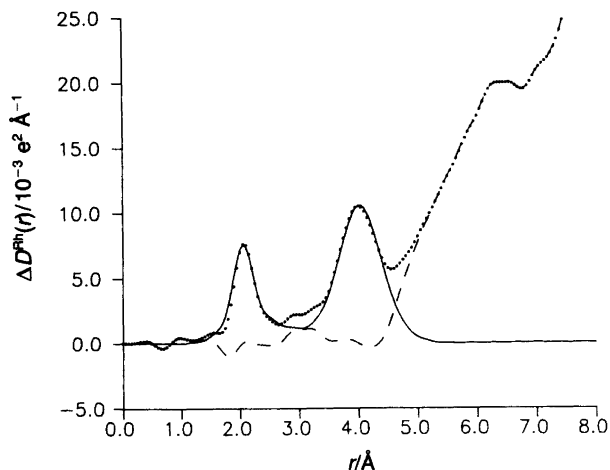


Fig. 2. Differential RDF curve,  $\Delta D^{Rh}(r)$  (dotted line). The theoretical peaks (solid curve) are calculated for  $r(\text{Rh}-\text{O}_I) = 2.03 \text{ \AA}$ ,  $n(\text{O}_I) = 6 \text{ H}_2\text{O}$ ,  $\sigma(\text{Rh}-\text{O}_I) = 0.05 \text{ \AA}$ , and  $r(\text{Rh}-\text{O}_{II}) = 4.02 \text{ \AA}$ ,  $n(\text{O}_{II}) = 13 \text{ H}_2\text{O}$ ,  $\sigma(\text{Rh}-\text{O}_{II}) = 0.28 \text{ \AA}$ . The difference is given by the dashed line.

drated cation. For comparison, the RDF function for the 1.52 M  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  solution is given in Fig. 1B. The shoulder appearing at ca. 5.0  $\text{\AA}$  in this more concentrated solution can be attributed to the entry of perchlorate ions into the outer hydration sphere,<sup>18</sup> and thus corresponds to solvent-separated  $\text{Cr} \cdots \text{ClO}_4^-$  interactions. Spurious peaks are found below 1.0  $\text{\AA}$  in the RDFs and result from systematic errors in the data correction procedures.

The large number of pair interactions contributing to the total RDFs complicates the extraction of quantitative data concerning the hydration structure of these cations, namely the mean  $\text{M}-\text{O}_I$  and  $\text{M}-\text{O}_{II}$  distances and the corresponding hydration numbers  $n(\text{O}_I)$  and  $n(\text{O}_{II})$ .

**Radial distribution difference function,  $\Delta D^{Rh}(r)$ .** By Fourier-transforming the difference in the structure-dependent scattering intensity of the 1.04 M Rh(III) and Cr(III) so-

lutions according to eqns. (4) and (5), the radial distribution difference function,  $\Delta D^{Rh}(r)$ , was obtained and is shown in Fig. 2, together with calculated model peaks. The two well defined peaks in the  $\Delta D^{Rh}(r)$  function at 2 and 4  $\text{\AA}$  can be immediately assigned to the  $\text{Rh}-\text{O}_I$  and  $\text{Rh}-\text{O}_{II}$  distances of water molecules in the first and second hydration spheres of the Rh(III) ion, respectively. There are no significant peaks at distances below 2  $\text{\AA}$ , indicating that the systematic errors normally present in a single LAXS experiment have been eliminated along with the intramolecular  $\text{ClO}_4^-$  interactions.

The distinct peak resolved at 2  $\text{\AA}$  in  $\Delta D^{Rh}(r)$  was satisfactorily fitted with a model peak having  $n(\text{O}_I) = 6 \pm 0.5$  water molecules at an  $\text{Rh}-\text{O}$  distance of  $2.03 \pm 0.02 \text{ \AA}$  and  $\sigma = 0.05 \pm 0.01 \text{ \AA}$ . Appreciable differences in the  $\text{M}-\text{O}$  bond lengths of the hydration structures of Rh(III) and Cr(III) would lead to asymmetry in the 2  $\text{\AA}$  peak and a deviating  $n(\text{O}_I)$  value. A minor theoretical peak corresponding to the 12 hydrogen atoms of the first hydration sphere was included at 2.6  $\text{\AA}$ .<sup>2</sup> The second hydration sphere gives rise to the peak at  $4.02 \pm 0.02 \text{ \AA}$ , which is partly overlapped by longer-range interactions. Assuming a Gaussian distribution of the  $\text{Rh}-\text{O}_{II}$  distances with  $\sigma = 0.28 \pm 0.05 \text{ \AA}$  a second-sphere hydration number,  $n(\text{O}_{II}) = 13 \pm 1$ , could be obtained.

**EXAFS investigation of hydrated rhodium(III).** The unfiltered Rh  $K\alpha$  EXAFS spectra for the acidic 1 M solution of  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  and for the solid  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  compound are shown in Fig. 3, with the corresponding Fourier transforms in Fig. 4. The close similarity of the aqueous solution to the solid salt data is obvious from both figures. The single dominant peak in the Fourier transforms can be attributed to the rhodium–oxygen distance in the first hydration sphere. The Fourier-filtered, back-transformed EXAFS data for the 1 M solution of  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  were used to extract phase shifts and amplitudes for the  $\text{Rh}-\text{O}$  interactions assuming  $r(\text{Rh}-\text{O}) = 2.03 \text{ \AA}$  and hexacoordi-

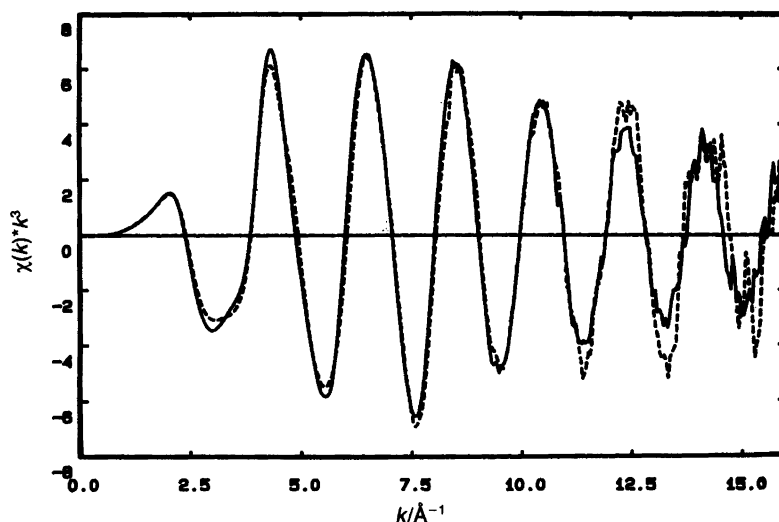


Fig. 3. EXAFS Rh  $K\alpha$  spectra, weighted by  $k^2$ , of an acidic 1 M aqueous perchlorate solution of  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  (solid line) and of solid  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  'diluted' with BN (dashed line).

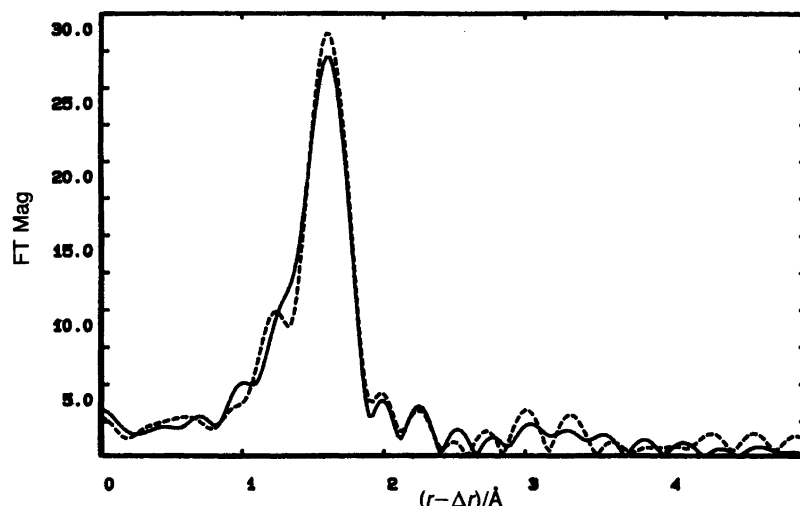


Fig. 4. Fourier transforms of the  $k^3$ -weighted EXAFS spectra shown in Fig. 3, 1 M  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  in aqueous solution (solid line) and of solid  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  (dashes). The phase shift gives a correction factor  $\Delta r = 0.42 \text{ \AA}$  to be added to the Rh–O peak distance obtained from the figure.

nation. Using the derived amplitudes and phases, the EXAFS data for the  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  salt were fitted by varying the Rh– $\text{O}_I$  bond length, coordination number and relative Debye–Waller factor ( $\Delta\sigma = \sigma_{\text{ref}} - \sigma_{\text{sample}}$ ). The refined parameters for the salt; Rh– $\text{O}_I = 2.02 \text{ \AA}$ ,  $n(\text{O}_I) = 5.8$  and  $\Delta\sigma = 0.006 \text{ \AA}$ , were not significantly different from the solution results.

## Discussion

*The hydration structure in aqueous Rh(III)/Cr(III) solutions.* A fairly large difference in the M– $\text{O}_I$  distances for the two hexahydrated metal ions has been found from single-crystal X-ray structure determinations of the isomorphous  $\text{CsM}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  alum salts, 2.016(3) and 1.959(3)  $\text{\AA}$  for M = Rh(III) and Cr(III), respectively.<sup>9,19</sup> Also, direct LAXS studies of aqueous Rh(III) and Cr(III) in solution<sup>5–7</sup> show a similar separation of the M– $\text{O}_I$  distances with  $r(\text{Rh}–\text{O}_I) \approx 2.04 \text{ \AA}$  and  $r(\text{Cr}–\text{O}_I) = 1.98–2.00 \text{ \AA}$  [1.98(2)  $\text{\AA}$  from a neutron diffraction study using isotopic substitution].<sup>2</sup> An *ab initio* SCF calculation on the isolated hexahydrated ions gave a difference of 0.033  $\text{\AA}$  (Rh– $\text{O}_I$  2.055  $\text{\AA}$  and Cr– $\text{O}_I$  2.025  $\text{\AA}$ ).<sup>20</sup> However, from the  $\Delta D^{\text{Rh}}(r)$  difference curve presented above it is evident that their hydration structures in solution are sufficiently equivalent for the following conclusions to be made: (1) an efficient elimination of interactions other than those involving the metal ion can be achieved, (2) the well formed peaks in the difference function are representative of the hexahydrated Rh(III) ion with an Rh– $\text{O}_I$  bond length of  $2.03 \pm 0.02 \text{ \AA}$ , surrounded by a strongly hydrogen-bonded second hydration sphere with an Rh– $\text{O}_{II}$  distance of  $4.02 \pm 0.02 \text{ \AA}$ . This conclusion is supported by a recent X-ray structure investigation<sup>8</sup> of the apparently centrosymmetric chromium(III)–rhodium(III) heterometallic hydrolytic dimer,  $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{-OH})_2\text{Cr}(\text{OH})_2]_2(\text{Me}_3\text{C}_6\text{H}_2\text{SO}_3)_4 \cdot 4\text{H}_2\text{O}$ , which resulted

in an average Rh/Cr–OH<sub>2</sub> distance of 2.03(2)  $\text{\AA}$ , in excellent agreement with our LAXS results.

By combining our results with those obtained from neutron diffraction using isotopic substitution on concentrated ( $\geq 2 \text{ M}$ ) Cr(III) solutions, further information about the hydration structure around these apparently isostructural cations may be obtained. The tilt angle between the Cr– $\text{O}_I$  axis and the bisector of the HOH angle was found to be  $34 \pm 6^\circ$  by neutron diffraction,<sup>2</sup> on the basis of a Cr– $\text{O}_I$  bond length of  $1.99 \pm 0.01 \text{ \AA}$ , and a coordinated water geometry with O–H =  $0.99 \pm 0.01 \text{ \AA}$  and an HOH angle of  $110 \pm 2^\circ$  (from suitable alum structures).<sup>19</sup> With the M– $\text{O}_{II}$  distance of  $4.02 \pm 0.02 \text{ \AA}$  and the assumption of a linear hydrogen bond between the first and second hydration spheres, a short hydrogen bond length emerges,  $\text{O}_I \cdots \text{O}_{II} = 2.63 \pm 0.09 \text{ \AA}$ . This value, obtained by geometric considerations, is in good agreement with that obtained for the trivalent cations Al(III) and Cr(III), based on an IR difference study of the  $\nu_{\text{OH}}$  stretching frequencies of water molecules in the first hydration spheres of these metal ions, namely  $\text{O}_I \cdots \text{O}_{II} \approx 2.6 \text{ \AA}$ .<sup>3</sup> This provides further evidence for the existence of a well defined strongly hydrogen-bonded second hydration sphere around these trivalent cations in aqueous solution.

From the IR study it can be concluded that all 12 hydrogen atoms of the first hydration sphere are hydrogen-bonded to water oxygen atoms in the second hydration sphere in the presence of a large excess of water, consistent with the value  $n(\text{O}_{II}) = 13 \pm 1$  obtained here. It has been proposed from NMR studies that the relative amounts of  $\text{H}_2\text{O}$  and  $\text{ClO}_4^-$  in the outer hydration sphere of Cr(III) are directly proportional to their free concentrations in the solution.<sup>1,21</sup> Assuming a statistical distribution over 12 hydrogen bond sites, it follows that 0.8 and 1.3  $\text{ClO}_4^-$  ions per metal ion would be present in the second hydration spheres of the Cr(III) ions in the 1.04 and 1.52 M solutions, respectively. This would probably not influence the numerical

value of  $n(\text{O}_{\text{II}})$  obtained here, since oxygen atoms will be hydrogen bonded to the water molecules in the first sphere regardless of whether the solvating species is  $\text{H}_2\text{O}$  or  $\text{ClO}_4^-$ . However, the hydrogen bond to a  $\text{ClO}_4^-$  oxygen atom is weaker,<sup>22</sup> and additional, somewhat longer, distances from Cr to Cl and other  $\text{ClO}_4^-$  oxygen atoms would be expected.<sup>18</sup> This is seen in the 1.52 M solution (Fig. 1B), where the pronounced shoulder at ca. 5.0 Å in the RDF can be ascribed to Cr– $\text{ClO}_4^-$  interactions.

*Hexahydrated Rh(III) ions in aqueous and solid phases.* Recently, anomalously long Rh– $\text{O}_I$  bond distances, 2.128(6) and 2.136(6) Å,<sup>23</sup> were reported from a crystal structure study on  $[\text{Rh}(\text{H}_2\text{O})_6](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ . However, it is well known that partial disorder frequently occurs in many crystal structures of a similar type, e.g.  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,<sup>24,25</sup> which may affect the derived bond distances. As expected, our EXAFS data showed no significant differences in the Rh– $\text{O}_I$  distance or coordination between the solid  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  compound and the 1 M acidic Rh(III) perchlorate solution. This is also consistent with the Rh– $\text{O}_I$  bond length of 2.016(3) Å for the  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  ion in a caesium  $\alpha$ -alum structure,<sup>19</sup> and the similar bond strength of the hydrated Rh(III) ions in the crystal structure and in solution as indicated by their Raman spectra.<sup>9</sup>

### Concluding remarks

It has been shown that the trivalent Rh(III) and Cr(III) ions are sufficiently isostructural with respect to their hydration structure in aqueous solution to allow elimination of all atom-pair interactions not involving the metal atoms in LAXS data. The method of isostructural substitution for Rh(III) solutions with chromium as substituent was used to extract first- and second-shell hydration structure parameters, yielding Rh– $\text{O}_I$  and Rh– $\text{O}_{\text{II}}$  distances and hydration numbers,  $n(\text{O}_I)$  and  $n(\text{O}_{\text{II}})$ . The results have been combined with information from other studies, notably neutron diffraction and IR spectroscopic difference methods, to obtain a more complete picture of the hydrogen bonding geometry and structure in the vicinity of the trivalent ions. However, it is evident from the EXAFS results (Fig. 4) that the screening effect of the first hydration sphere water molecules around Rh(III) is so efficient for the back-scattering process of the Rh  $K$ -electron, that no information concerning the well established second sphere of water molecules can be obtained with this method.

In a similar way that neutron isotopic difference studies are limited by the number of elements having suitable isotopes, X-ray isostructural substitution is restricted by the number of suitable pairs of ions. However, in favourable cases, as for Cr(III) and Rh(III), data from both methods are available and can be combined to extract a detailed picture of the hydration structure around the cations in solution.

*Acknowledgements.* We acknowledge the Swedish Natural Science Research Council (NFR) for continuing financial support and a research studentship (M.C.R.), and OKs Miljöstiftelse for a supporting grant. Thanks are due to Professor Ingmar Persson for assistance with the EXAFS programs and Dr. Georg Johansson for help with the PC version of the KURVLR programs.

### References

- Hunt, J. P. and Friedman, H. P. *Progr. Inorg. Chem.* 30 (1983) 359.
- Broadbent, R. D., Neilson, G. W. and Sandström, M. *J. Phys. Condens. Mater.* 4 (1992) 639.
- Bergström, P.-Å., Lindgren, J., Read, M. C. and Sandström, M. *J. Phys. Chem.* 95 (1991) 7650.
- Salmon, P. S., Herdman, G. J., Lindgren, J., Read, M. C. and Sandström, M. *J. Phys. Condens. Mater.* 1 (1989) 3459.
- Magini, M., Licheri, G., Paschina, G., Piccaluga, G. and Pinna, G. *X-Ray Diffraction of Ions in Aqueous Solutions: Hydration and Complex Formation*, CRC Press, Boca Raton, FL 1988, Chap. 3.
- Marcus, Y. *Chem. Rev.* 88 (1988) 1475.
- Caminiti, R. and Cucca, P. *Chem. Phys. Lett.* 108 (1984) 51.
- Crimp, J., Fallon, G. D. and Spiccia, L. *J. Chem. Soc., Chem. Commun.* (1992) 197.
- (a) Best, S. P., Beattie, J. K., Armstrong, R. S. and Braithwaite, G. P. *J. Chem. Soc., Dalton Trans.* (1989) 1771; (b) Best, S. P., Beattie, J. K. and Armstrong, R. S. *Ibid.* (1984) 2611.
- Johansson, G. and Yokoyama, H. *Inorg. Chem.* 29 (1990) 2460.
- Read, M. C., Glaser, J. and Sandström, M. *J. Chem. Soc., Dalton Trans.* (1992) 233.
- (a) Stünzi, H. and Marty, W. *Inorg. Chem.* 22 (1983) 2145. (b) Buchacek, R. J. and Harris, G. M. *Inorg. Chem.* 15 (1976) 926.
- Read, M. C., Glaser, J., Sandström, M. and Toth, I. *Inorg. Chem.* (1992). *In press.*
- Johansson, G. and Sandström, M. *Chem. Scr.* 4 (1973) 195 and references therein.
- International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1968 (Vol. 3) and 1974 (Vol. 4).
- (a) Crozier, E. D., Rehr, J. J. and Ingalls, R. In: Koningsberger, D. C. and Prins, R., Eds., *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, Wiley, New York 1988, Chap. 9.2; (b) Sayers, D. E. and Bunker, B. A. *Ibid.*, Chap. 6.2.
- Scott, R. A. *Methods Enzymol.* 117 (1985) 414.
- Magini, M. and Giubileo, G. *Gazz. Chim. Ital.* 111 (1981) 449.
- Beattie, J. K., Best, S. P., Skelton, B. W. and White, A. H. *J. Chem. Soc., Dalton Trans.* (1981) 2105.
- Åkesson, R. and Sandström, M. Unpublished data.
- Anderson, C. F. L. *PhD Thesis, Diss. Abstr. Int. B* 34(a) (1974) 4264.
- Kristiansson, O. and Lindgren, J. *J. Phys. Chem.* 95 (1991) 1488.
- Fallon, G. D. and Spiccia, L. *Aust. J. Chem.* 42 (1989) 2051.
- Ghosh, M. and Ray, S. *Ind. J. Phys.* 48 (1974) 1149; *Z. Kristallogr.* 145 (1977) S146.
- Johansson, G. and Sandström, M. *Acta Chem. Scand., Ser. A* 41 (1987) 113.

Received May 18, 1992.