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## The hydration structure of $\text{Cr}^{3+}$ in a concentrated aqueous solution

R D Broadbent†, G W Neilson† and M Sandström‡

† H H Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

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

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**Abstract.** Neutron diffraction experiments were carried out on aqueous solutions of 2.2M chromium (III) perchlorate in water, heavy water and a 'null' mixture of water and heavy water. The isotopic difference methods of neutron diffraction were applied to the scattering data, and the results were used to obtain structural information concerning the  $\text{Cr}^{3+}$  hydration. The first hydration shell of  $\text{Cr}^{3+}$  contains six water molecules with oxygen and hydrogen atoms situated at 1.98 (2) and 2.60 (3) Å, respectively, consistent with a trigonal pyramidal coordination mode for the water molecules. With a coordinated water molecule geometry appropriate to the crystal structures a mean tilt angle of  $34 \pm 6^\circ$  is calculated. A second-order difference was calculated from the results of the water and heavy water solutions, and  $g_{\text{CrH}}(r)$  was determined. The result for the 'null mixture', which is predominantly  $g_{\text{CrO}}(r)$  is compared with the appropriate combination of the results for the water and heavy water solutions, and in this way it is demonstrated that the  $\text{Cr}^{3+}$  ion does not show preferential hydration in perchlorate solutions. There is also clear evidence for orientational correlations in the second hydration sphere with broad peaks centred at 4 and 4.5 Å which are assigned to Cr–O and Cr–D correlations respectively.

### 1. Introduction

This paper contains the results of a neutron diffraction study of aqueous solutions of 2.2M  $\text{Cr}(\text{ClO}_4)_3$ . There are three aspects to this study:

- (i) a determination of the ionic hydration at the atomic level;
- (ii) a determination of  $g_{\text{CrH}}(r)$ ; and
- (iii) a test of theoretical calculations by Newton and Friedman (1985) of H/D fractionation in aqueous solution.

It is well established that the chromium (III) ion in aqueous solutions coordinates six water molecules in the first hydration sphere (Hunt and Plane 1954, Magini *et al* 1988). Results based on isotopic dilution show that the residence time of the oxygen atoms in the first hydration shell is very long (approximately  $1 \times 10^6$  s from rate constants for concentrated  $\text{Cr}(\text{ClO}_4)_3$  solutions (Easteal *et al* 1988). The lifetime of the first-shell water hydrogen atoms is much shorter, less than  $10^{-5}$  s at 25°C from proton NMR measurements (Swift and Stephenson 1966, Hertz 1973).

Strong hydrogen bonding between the first- and second-shell water molecules has been demonstrated by an infrared spectroscopic double difference method applied to  $0.2 \text{ mol dm}^{-3} \text{ Cr}(\text{ClO}_4)_3$  solutions (Bergström *et al* 1991), and a well defined second hydration shell with approximately 13 water oxygen atoms at about  $4 \text{ \AA}$  is found from a large-angle x-ray diffraction study which employed isostructural substitution on  $1 \text{ mol dm}^{-3} \text{ Cr}(\text{ClO}_4)_3$  and  $\text{Rh}(\text{ClO}_4)_3$  solutions (Read and Sandström 1991 unpublished). Transport properties of aqueous  $\text{Cr}(\text{ClO}_4)_3$  solutions show decreased mobility for second-shell water molecules (Easteal *et al* 1989), although in a quasielastic neutron scattering (QNS) study by Salmon *et al* (1989) only the first-shell water hydrogen atoms showed slow exchange ( $< 5 \times 10^{-9} \text{ s}$ ) on the experimental time scale.

It is therefore of interest to investigate the details of the local coordination of the Cr(III) cation and compare it with other ions in the transition metal series. To do this a first-order isotopic difference experiment based on neutron diffraction (NDIS) (see, for example, Enderby and Neilson (1979)) was applied to the chromium ions in chromium (III) perchlorate in heavy water. This enabled us to derive the  $\text{Cr}^{3+}$  hydration structure in terms of a linear sum over its pair distribution functions  $g_{\text{Cr}\alpha}(r)$ .

The second part of our investigations concerned experiments carried out on  $\text{Cr}(\text{ClO}_4)_3$  solutions in water ( $\text{H}_2\text{O}$ ). From the subsequent combination of results with those obtained from the heavy water solution the pair radial distribution function  $g_{\text{CrH}}(r)$  was derived. The method is similar to that applied to 2M aqueous solutions of  $\text{NiCl}_2$ , for which  $g_{\text{NiH}}(r)$  was determined (Powell *et al* 1989). The determination of  $g_{\text{CrH}}(r)$  allowed definitive comments to be made about the orientational correlations of water molecules in the second shell of  $\text{Cr}^{3+}$ .

A third experiment, based on the first-order difference method applied to  $\text{Cr}^{3+}$  in a 'null' water/heavy water mixture was carried out to establish the validity of the calculations by Newton and Friedman (1986) on H/D fractionation around triply charged cations such as  $\text{Cr}^{3+}$  in aqueous electrolyte solution.

## 2. Experimental details and data analysis

Three sets of aqueous solutions of  $2.2\text{M Cr}(\text{ClO}_4)_3$  each with two different isotopic enrichments of chromium ( $^{52}\text{Cr}$  and  $^{53}\text{Cr}$ ) were prepared by dissolution of the metal in hot perchloric acid, reduction to chromium(III) with hydrogen peroxide, precipitation as chromium (III) hydroxide and dissolution in perchloric acid. After crystallization the hydrated  $\text{Cr}(\text{ClO}_4)_3$  salt was dissolved in water/heavy water, and by evaporation and subsequent additions of the particular solvent mixture the desired H/D ratio was obtained (table 1). The resulting deep blue solutions were tested for pH, density and, in the case of the heavy water solution, level of  $\text{H}_2\text{O}$  impurity by infrared spectrometry. For the 64/36 water/heavy water mixture, NMR was used to determine the  $\text{H}_2\text{O}$  content.

The samples were sealed under an inert nitrogen atmosphere and transported to ILL, Grenoble, where they were transferred into Ti/Zr 'null' alloy containers and sealed. The filled containers were positioned inside the bell jar of the D4B diffractometer which operated at a wavelength  $\lambda = 0.704 \text{ \AA}$ . Diffraction patterns were gathered sequentially on all six samples, their backgrounds, empty containers and on vanadium standards.

The data were analysed following the procedures outlined by Powell *et al* (1989), and included additional corrections for small ( $< 1\%$ ) imbalances in the water content

Table 1. Properties of samples.

Label	Electrolyte	Concentration (Molarity)	Density (g cm <sup>-3</sup> )	Scattering lengths ( $\times 10^{-12}$ cm)	Ratio of $\text{H}_2\text{O}/\text{D}_2\text{O}$
I	$^n\text{Cr}(\text{ClO}_4)_3$	2.002	1.547	0.3635	0.0050
	$^{53}\text{Cr}(\text{ClO}_4)_3$	1.999	1.530	-0.393	0.0049
II	$^n\text{Cr}(\text{ClO}_4)_3$	2.224	1.452	0.3635	9999/1
	$^{53}\text{Cr}(\text{ClO}_4)_3$	2.224	1.451	-0.393	9999/1
III	$^n\text{Cr}(\text{ClO}_4)_3$	2.144	1.419	0.3635	64/36
	$^{53}\text{Cr}(\text{ClO}_4)_3$	2.144	1.420	-0.393	64/36

within each set of solutions. As usual in these experiments, the data were normalized to give the six structure factors,  $F(k)$ , in units of barn str<sup>-1</sup>.

### 3. Results

The final  $F(k)$  for the six solutions were used to calculate for each isotopically coupled sample pair, a set of three difference functions  $\Delta_{\text{Cr}}(k)$  (figures 1 and 2). From these figures, it is clear that the statistical accuracy of the data for the solutions which contain significant amounts of  $\text{H}_2\text{O}$  are much poorer than those of the almost pure  $\text{D}_2\text{O}$  solution. This is a consequence of the much greater (about a factor of 8) incoherent scattering of hydrogenous material. The Fourier transformations of the  $\Delta_{\text{Cr}}(k)$  are the total radial distribution functions of the  $\text{Cr}^{3+}$  ions in each set of solutions, and can be written as

$$G_{\text{Cr}}(r) = Ag_{\text{CrO}}(r) + Bg_{\text{CrH}}(r) + Cg_{\text{CrD}}(r) + Dg_{\text{CrCl}}(r) + Eg_{\text{CrCr}} + F \quad (1)$$

where

$$\begin{aligned} A &= 2c_{\text{Cr}}c_{\text{O}}b_{\text{O}}\Delta b_{\text{Cr}} & B &= 2c_{\text{Cr}}c_{\text{H}}b_{\text{H}}\Delta b_{\text{Cr}} & C &= 2c_{\text{Cr}}c_{\text{D}}b_{\text{D}}\Delta b_{\text{Cr}} \\ D &= 2c_{\text{Cr}}c_{\text{Cl}}b_{\text{Cl}}\Delta b_{\text{Cr}} & E &= c_{\text{Cr}}^2\Delta b_{\text{Cr}}^2 \end{aligned}$$

and

$$\begin{aligned} F &= -(A + B + C + D + E) \\ \Delta b_{\text{Cr}} &= ({}^{\text{Nat}}b_{\text{Cr}} - {}^{53}b_{\text{Cr}}) & \Delta b_{\text{Cr}}^2 &= ({}^{\text{Nat}}b_{\text{Cr}}^2 - {}^{53}b_{\text{Cr}}^2). \end{aligned}$$

$c_{\alpha}$  is the atomic concentration of atom  $\alpha$  whose coherent neutron scattering length is  $b_{\alpha}$ .

The radial distribution functions  $g_{\text{Cr}\beta}(r)$  contain the basic structural information of the solution from which properties such as nearest- and next-nearest-neighbour distances to  $\text{Cr}^{3+}$  can be determined. It is also possible to calculate coordination numbers  $n_{\text{Cr}}^{\alpha}$ , which gives the number of  $\alpha$  atoms within a certain range  $r_1 < r < r_2$ , of the  $\text{Cr}^{3+}$  from the formula:

$$n_{\text{Cr}}^{\alpha} = (4\pi\rho c_{\alpha}/A_{\alpha}) \int_{r_1}^{r_2} \{G_{\text{Cr}}(r) - F\} r^2 dr \quad (2)$$

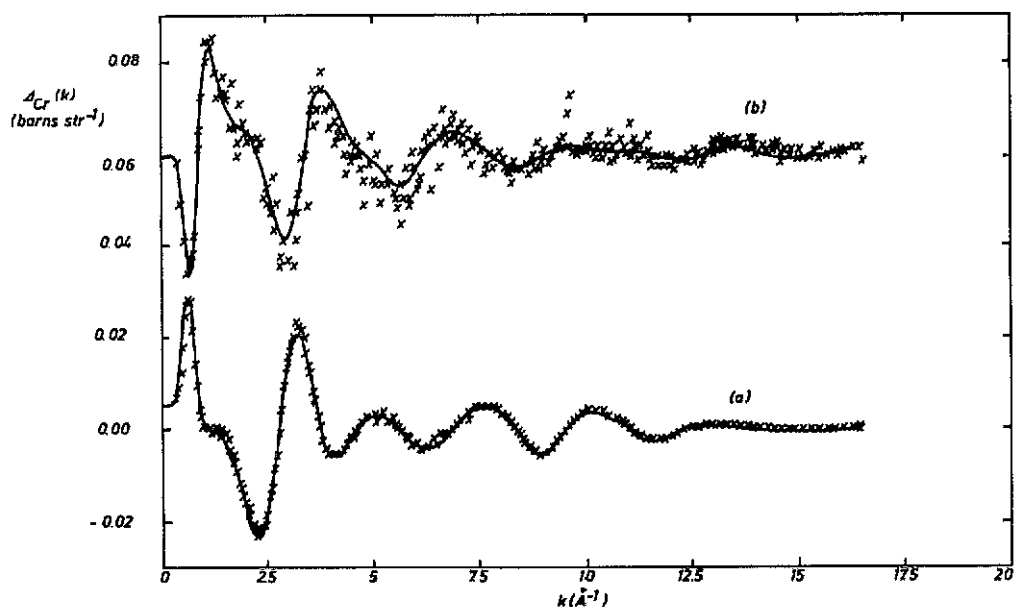


Figure 1. Total  $\text{Cr}^{3+}$  first-order difference structure functions  $\Delta_{\text{Cr}}(k)$  for (a) 2M  $\text{Cr}(\text{ClO}_4)_3$  in heavy water, and (b) 2.244M  $\text{Cr}(\text{ClO}_4)_3$  in water. ( $\Delta_{\text{Cr}}(k)$  for the latter is displaced by 0.06 barn  $\text{sr}^{-1}$ .) The full curves represent the back transform of the results shown in figure 3.

Table 2. Coefficients (in mbarn  $\text{sr}^{-1}$ ) of terms in equation (1) of text.

Label of solution	A	B	C	D	E	F
I	3.94	0.00	6.07	0.526	-0.0027	-10.52
II	3.93	-3.42	0.00	0.526	-0.0027	-1.03
III	3.93	-2.19	2.19	0.529	-0.0027	-4.47

where  $A_\alpha = A, B, C, D$  or  $E$  and  $\rho$  is the total number density of the solution and is typically approximately  $0.1 \text{ \AA}^{-3}$ .

One observes from table 2 that  $G_{\text{Cr}}(r)$  is dominated by  $g_{\text{CrO}}(r)$  and  $g_{\text{CrH}}(r)$  or  $g_{\text{CrD}}(r)$  or, in the case of the 'null' mixture, by  $g_{\text{CrO}}(r)$  to a good approximation. It is therefore legitimate to discuss the  $\text{Cr}^{3+}$  structure purely in terms of its hydration. Furthermore, the chromium-hydrogen distribution function  $g_{\text{CrH}}(r)$  may be separated out completely by an appropriate combination of  $\Delta_{\text{Cr}}^{\text{D}_2\text{O}}$  and  $\Delta_{\text{Cr}}^{\text{H}_2\text{O}}$ , i.e. because  $B_{\text{D}_2\text{O}} = C_{\text{H}_2\text{O}} = 0$ , equation (1) can be used for the two solutions to give

$$g_{\text{CrH}}(r) = (C_{\text{D}_2\text{O}} - B_{\text{H}_2\text{O}})^{-1} (G_{\text{Cr}}^{\text{D}_2\text{O}} - G_{\text{Cr}}^{\text{H}_2\text{O}})$$

where the sub- and super-scripts  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  refer to the solvent of the particular solution. Similarly, an appropriate combination of  $G_{\text{Cr}}^{\text{D}_2\text{O}}$  and  $G_{\text{Cr}}^{\text{H}_2\text{O}}$  can be made to produce the  $G_{\text{Cr}}$  for a 'null' mixture of water and heavy water, namely

$$G_{\text{Cr}}^{\text{null}} = (C_{\text{D}_2\text{O}} - B_{\text{H}_2\text{O}})^{-1} (C_{\text{D}_2\text{O}} G_{\text{Cr}}^{\text{H}_2\text{O}} - B_{\text{H}_2\text{O}} G_{\text{Cr}}^{\text{D}_2\text{O}}).$$

## 4. Discussion

### 4.1. The hydration structure of $\text{Cr}^{3+}$ in water and heavy water

This is illustrated by figure 3 which shows  $G_{\text{Cr}}(r)$  for both the water and heavy water solutions. These two functions show a well resolved nearest-neighbour hydration shell around the  $\text{Cr}^{3+}$  cation. The peak centred at 1.98(2) Å can be identified immediately with the  $\text{Cr}^{3+}$ -oxygen correlation and that at 2.60(2) Å is due to the  $\text{Cr}^{3+}$ -deuterium correlation, a result confirmed when these peaks are integrated to give coordination numbers of 6.0(3) and 12.0(4) for  $n_{\text{Cr}}^{\text{O}}$  and  $n_{\text{Cr}}^{\text{D}}$  respectively. The fact that  $n_{\text{Cr}}^{\text{H}} = 2n_{\text{Cr}}^{\text{O}}$  for both the  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  solutions confirms the absence of serious systematic errors.

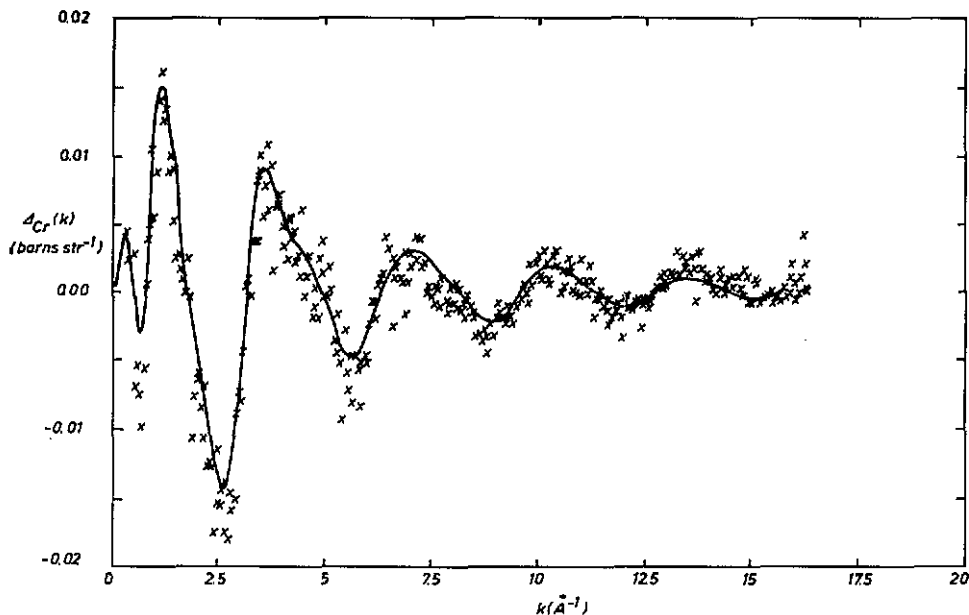


Figure 2. Total  $\text{Cr}^{3+}$  first-order difference function  $\Delta_{\text{Cr}}(k)$  for a 2.144M  $\text{Cr}(\text{ClO}_4)_3$  in a 'null' mixture of water and heavy water ( $\text{H}_2\text{O}_{0.357}/\text{D}_2\text{O}_{0.643}$ ). The full curve represents the back transform of the full curve in figure 6.

An interesting and significant aspect of these results is the relative sharpness of the peaks in the first hydration shell, and the fact that  $G_{\text{Cr}}(r) = 0.0$  for  $r = 4$  Å. This is similar to the result for  $\text{Ni}^{2+}$  where the water correlation is almost as well defined and justifies the assumption for modelling these ions as being 'dressed' by six waters of hydration.

A few crystallographic studies have been performed on hexahydrated trivalent transition metal cations, with coordinated water molecules directly bonded to water molecules in the second sphere. For example the structures of the alums,  $\text{M}(\text{I})\text{M}(\text{III})(\text{XO}_4)_2 \cdot 12\text{H}_2\text{O}$  ( $\text{X} \equiv \text{S}$  or  $\text{Se}$ ), provide information of interest for comparison with the solution results, and show a flexible stereochemistry of the water coordination about  $\text{M}(\text{III})$ . Bacon and Gardner (1958) made a neutron diffraction study of  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , which shows 12 Cr-H distances of 2.66 Å in the  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  ion (see also Beattie *et al* (1981) for x-ray results). Precise low-temperature

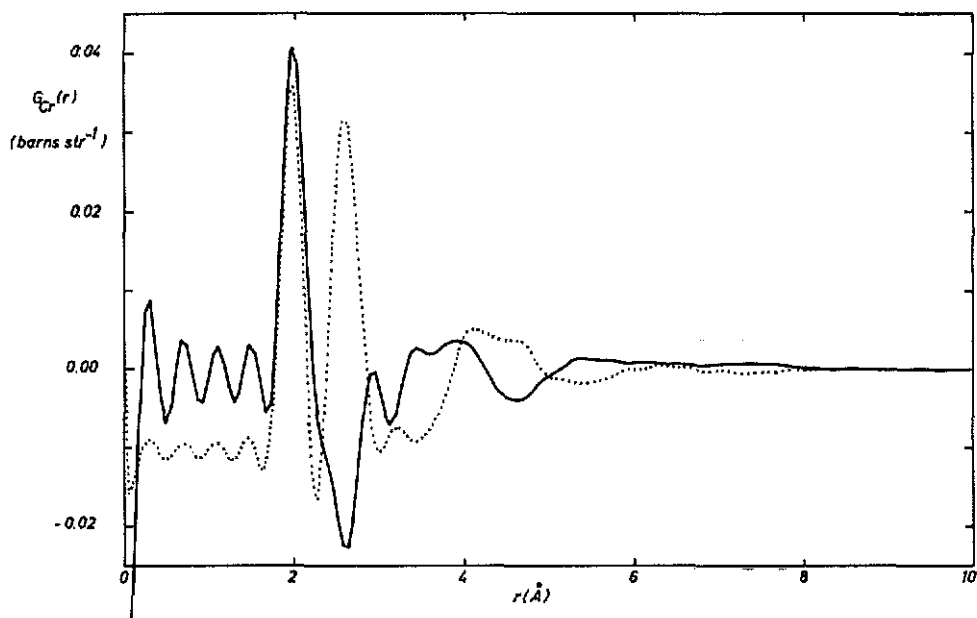


Figure 3. Total  $\text{Cr}^{3+}$  radial distribution function  $G_{\text{Cr}}(r)$  for 2M  $\text{Cr}(\text{ClO}_4)_3$  in heavy water (broken curve), and 2.224M  $\text{Cr}(\text{ClO}_4)_3$  in water (full curve).

studies have been performed more recently for the alums  $\text{CsFe}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$ ,  $\text{CsFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{CsRu}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (Best and Forsyth 1990) and for  $\text{V}^{3+}$  in  $[\text{V}(\text{H}_2\text{O})_6][\text{H}_5\text{O}_2](\text{CF}_3\text{SO}_3)_2$  (Cotton *et al* 1984). In the latter three compounds the coordination mode of the strongly bound water molecules is essentially trigonal planar, although in  $\text{CsFe}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$  the water molecules are tilted out the plane by  $18.6^\circ$ . It is clear that the potential energy surface for tilting the plane is shallow and readily influenced by the surroundings.

Table 3. Mean distances, full widths at half height ( $\Delta r_{\text{MO}}$ ) of correlations and coordination numbers for 2M  $\text{Cr}(\text{ClO}_4)_3$  aqueous solutions obtained from (a) first- and (b) second-order difference experimental results.

Label of solution	$r_{\text{MO}}$ (Å)	$\Delta r_{\text{MO}}$ (Å)	$n_{\text{M}}^{\text{O}}$	$r_{\text{MH}}$ (Å)	$\Delta r_{\text{MH}}$ (Å)	$n_{\text{M}}^{\text{H}}$
I(a)	1.98(2)	0.27(4)	6.0(5)	2.60(3)	0.36(4)	11.5(5)
II(a)	1.98(2)	0.27(4)	6.0(5)	2.60(3)	0.36(5)	12.0(5)
III(a) figure 6	1.98(2)	0.27(3)	6.0(5)	—	—	—
(I-II)(b) figure 5	—	—	—	2.59(3)	0.34(3)	12.0(5)

The O-H bond lengths of the coordinated water molecules are relatively long with a mean value of  $0.99 \text{ \AA}$ , and the HOH angles range from  $108^\circ$  to  $114^\circ$ , with a mean of  $110^\circ$ . From these values and the Cr-O and Cr-D distances (table 3), a mean value for the Cr(III)-D<sub>2</sub>O tilt angle (see, e.g., Friedman 1985) of  $34 \pm 6^\circ$  is calculated.

There is also clear evidence of a second hydration shell, and integration over the range  $3.5 < r < 5.5 \text{ \AA}$  shows that 17(1) water molecules can be accommodated.

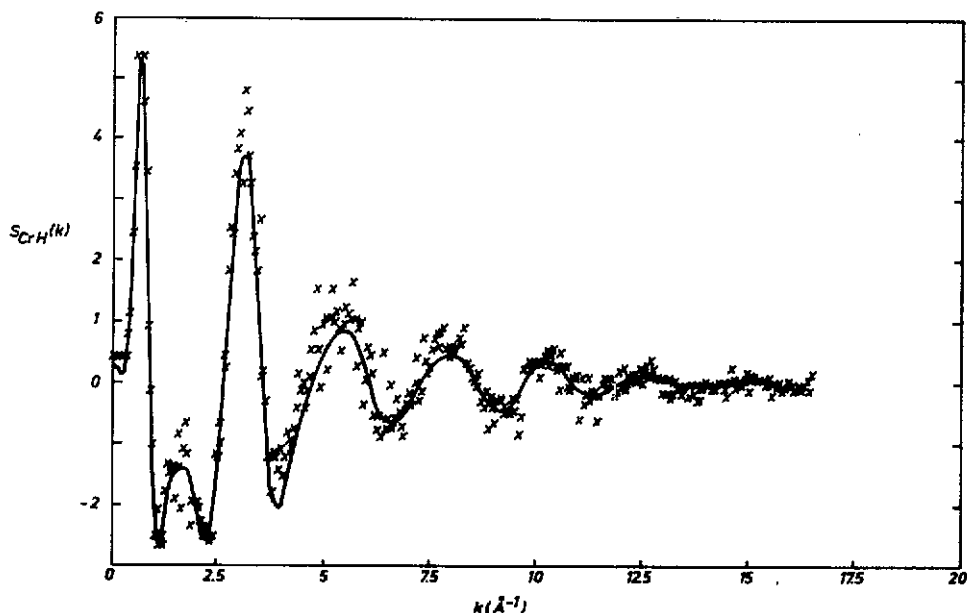


Figure 4. The partial structure factor  $S_{\text{CrH}}(k)$ , calculated from the second-order difference method applied to the data for solutions I and II. The full curve through the data represents the back transformation of the result shown in figure 5.

However, at the high concentrations investigated the number of free water molecules per  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  or  $\text{Cr}(\text{D}_2\text{O})_6^{3+}$  cation is 19, and thus the ratio of perchlorate ions to free water (not bonded to  $\text{Cr}^{3+}$ ) is approximately 1:6. Statistically, at least two perchlorate anions would then be able to enter the second shell. In fact, Anderson (1974) and also Hunt and Friedman (1983) find from NMR shifts that there appears to be no discrimination between water molecules and perchlorate ions over a wide range of sample compositions for chromium(III) perchlorate solutions. Moreover, in the alum structures discussed earlier, water molecules are found which are not bonded to the central metal ion but are coordinated to it with six H atoms at 4.5–4.6 Å and the other H and O atoms at distances of about 5 Å. Consequently, for the solutions here the inhomogeneity in the second shell and probable disruption in the hydrogen bond structure by the intrusion of perchlorate ions will cause a larger uncertainty in the number of water molecules than previously indicated.

Even though the outer sphere water molecules, which are strongly hydrogen bonded to those in the first shell, are more polarized and form stronger hydrogen bonds than water molecules of the bulk (Bergström *et al* 1991), they exchange rapidly in the second shell and the residence is short ( $< 5 \times 10^{-9}$ s) as inferred from the QNS results of Salmon *et al* (1989). However, the second-order difference results of section 4.2 indicate that there must be a significant degree of angular correlation between the second-shell water molecules and the  $\text{Cr}^{3+}$  cation.

#### 4.2. Determination of $g_{\text{CrH}}(r)$ and isotopic fractionation of hydrated water

Based on the assumption that the partial structure factors  $S_{\text{CrD}}(k)$  and  $S_{\text{CrH}}(k)$  are the same in water and heavy water, a combination of the two  $\Delta_{\text{Cr}}(k)$  for the solutions in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  yields the partial structure factor  $S_{\text{CrH}}(k)$  (see figure 4) and by



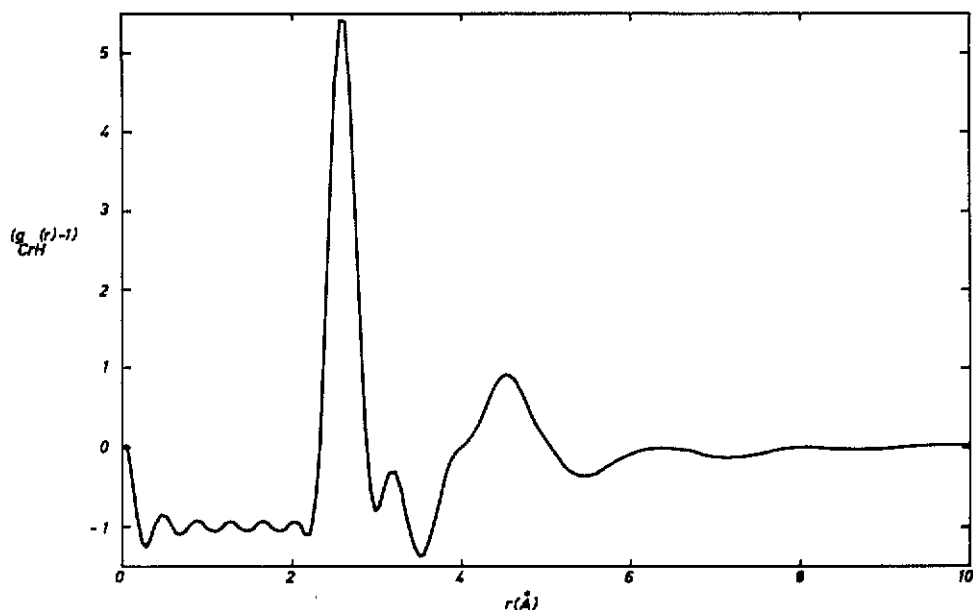


Figure 5. The pair distribution function,  $g_{\text{CrH}}(r)$ , of a 2M solution of chromium perchlorate in water, calculated from Fourier transformation of the data shown in figure 4.

Fourier transformation  $g_{\text{CrH}}(r)$ , (figure 5). The first peak is centred at  $2.59(3)$  Å, and integration between  $r_1 = 0$  Å and  $r_2 = 3.6$  Å gives according to equation (2) a coordination number of  $12.0(5)$  hydrogen atoms, corresponding to six water molecules in the first hydration shell, a result consistent with that stated in the previous section. Integration over the composite structure between  $r_1 = 3.6$  Å and  $r_2 = 5.5$  Å yields a coordination number of  $31 \pm 2$  corresponding to  $15.5 \pm 1$  water molecules in the second shell. It is also interesting to note that the second peak in  $g_{\text{CrH}}(r)$  centred at  $4.5$  Å is well enough defined to give credence to a second shell of angularly correlated water molecules whose metal-hydrogen distances compare favourably with those found in the alum crystals mentioned earlier.

When  $G_{\text{Cr}}(r)$  is obtained for the solution of a 'null'  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixture and compared with the appropriate combination of the  $G_{\text{Cr}}(r)$  in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  (figure 6) the two curves are identical over the region of the first hydration zone. The neutron scattering cross sections of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are well known (Hughes and Harvey 1985), but those for a 'null' mixture are not. In the analysis it was assumed that the cross section for the 'null' mixture was a weighted average of the cross sections for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , but given the large concentration of HOD in the 'null' mixture, this approximation could lead to significant errors in the region of the first peak in  $g_{\text{CrO}}(r)$ . The uncertainty in table 3 assumes a normalization error of 10%.

In contrast to the  $\text{Ni}^{2+}$  result which showed a 5% preferential deuteration, a quantitative analysis of figure 6 shows that there is no significant fractionation, and the coordination is as might be expected on averaging over the relative amounts of water and heavy water. The theoretical predictions of Newton and Friedman (1985), on the other hand, suggest a 15% preferential hydrogenation for triply charged cations. To illustrate such an effect the Cr-H correlation centred at  $2.60$  Å (see figure 5) is clearly absent in figure 6, a consequence of cancellation of the almost equal and opposite

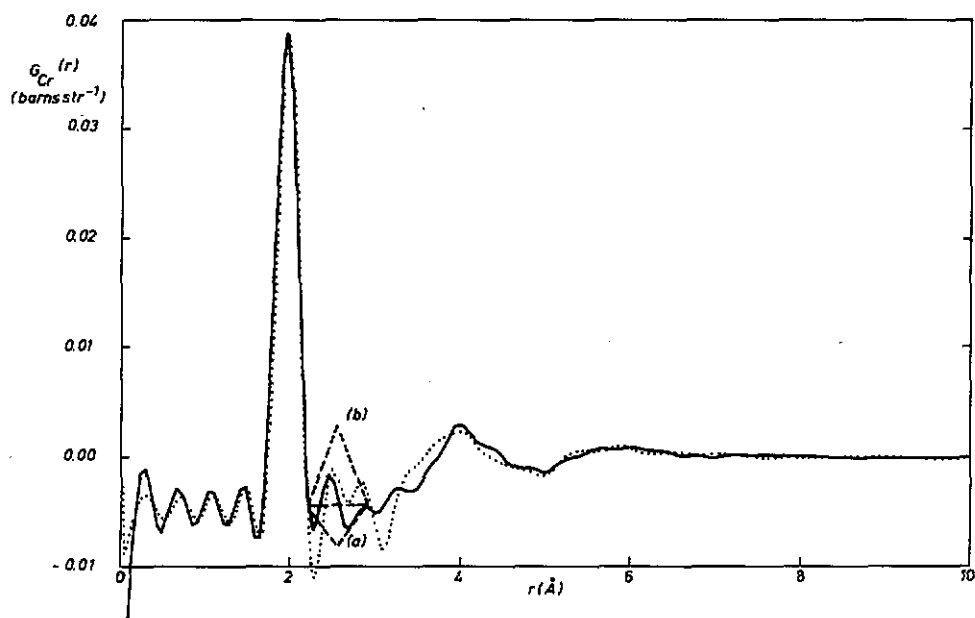


Figure 6. Comparison of experimentally determined total radial distribution function  $G_{\text{Cr}}(r)$  in 2.144M  $\text{Cr}(\text{ClO}_4)_3$  solution in 'null' water (full curve) by Fourier transformation of result shown in figure 2, and a  $G_{\text{Cr}}(r)$  (dotted curve) calculated by combining results in figure 3 according to the equation:

$$G_{\text{Cr}}(r) = G_{\text{Cr}}^{\text{H}_2\text{O}}(r) - G_{\text{Cr}}^{\text{D}_2\text{O}}(r) = 3.94g_{\text{CrO}}(r) + 0.529g_{\text{CrCl}}(r) - 0.0027g_{\text{CrCr}}(r).$$

This allows a direct comparison to be made between what might be expected regarding fractionation if one assumes no *a priori* preference between  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  with that determined experimentally. The two functions show no significant difference within error, and demonstrate no preferential hydration or deuteration in the region of interest. (To assist the reader, broken triangular curves centred at 2.60 Å and accounting for (a) 15% preferential hydration and (b) 15% preferential deuteration are also presented.)

Cr-H and Cr-D contributions to  $G_{\text{Cr}}(r)$ . It is also clear from figure 6 that there is no significant hydration or for that matter deuteration. However, the Newton/Friedman calculation is based on free energy arguments and is sensitive to temperature and input of data from spectroscopy and kinetic measurements. It will clearly be useful, therefore, to carry out further experiments under non-ambient conditions.

## 5. Conclusions

These results, based on the first- and second-order difference methods of neutron diffraction, provide a clear demonstration that  $\text{Cr}^{3+}$  possesses a well defined hydration shell of six water molecules, and a much weaker second shell of between 15 and 18 water molecules. Furthermore, they also show that there is no evidence of preferential hydration of triply charged cations as predicted by quantum mechanical calculations. To clarify this latter point, further experimentation is planned for an NDIS study of  $\text{Cr}^{3+}$  hydration as a function of counterion ( $\text{Cl}^-$  for  $\text{ClO}_4^-$ ) and temperature.

## Acknowledgments

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