The solute and aquaion structure in a concentrated aqueous solution of copper(II) chloride

S Ansell, R H Tromp and G W Neilson

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

Abstract. Neutron diffraction experiments were carried out on isotopically labelled copper chloride ($CuCl_2$) salt in a 4 molal aqueous solution. The first- and second-order isotopic difference methods were used to obtain structural information on the hydration structure of the Cu^{2+} and Cl^- ions and to calculate the pair distribution functions $g_{CuCl}(r)$ and $g_{ClCl}(r)$. The results confirm the highly distorted nearest-neighbour coordination of Cu^{2+}, and give direct evidence that Cu–Cl contacts exist over a range $2.3 \leqslant r$ (Å) $\leqslant 3.5$. Analysis of $g_{ClCl}(r)$ gives consistent information with that of $g_{CuCl}(r)$ and shows that direct contacts also exist between Cl^- ions, over the range $2.8 \leqslant r$ (Å) $\leqslant 4.2$.

1. Introduction

The cupric ion, Cu^{2+}, exhibits a rich diversity of coordination in the liquid and solid states [1]. In contrast to what is found for other transition metal ions, significant distortions are evident in its local environment: x-ray crystallographic studies of the solid hydrate [2] $CuCl_2 \cdot 2H_2O$ show that the Cu^{2+} has a $4 + 2$ coordination of two oxygens at 1.96 Å, two chloride ions at 2.29 Å at equatorial sites and a further two chloride ions in axial positions; neutron diffraction studies based on isotopic substitution (NDIS) of aqueous solutions of three copper salts indicate that this structural distortion persists in the liquid [3, 4]. The origin of this structural behaviour rests, at least in part, with the Jahn–Teller effect [3, 5]. When a transition metal ion, such as Cu^{2+}, is placed in a regular octahedral environment, the symmetrical nuclear configuration will distort in order to remove a degeneracy in the electronic state of the ion. The distortion can result in a *static* deformation of the coordinates and hence a change in mean distances or it can be *dynamic* when the configuration resonates between several limiting structures each having non-degenerate electronic states. In this case a time averaging of the distances corresponding to the limiting structures will occur. Although this effect is present in many transition metal cations in the condensed state, it is demonstrably strong for Cu^{2+}.

Of particular interest to the work reported here is the influence of the Cl^- ion on the Cu^{2+} environment. Whereas it was found by NDIS that for the nitrate and perchlorate cations the $4 + 2$ configuration around Cu^{2+} could be completely identified with water molecules, results for a cupric chloride solution suggests the Cu^{2+} coordination is less well resolved. The evidence for this lies in the observation of appreciably less than four water molecules in the equatorial plane around Cu^{2+}, a result, which implies that Cl^- ions must occupy these sites as is the case in the solid. In order to confirm this proposition an NDIS study based on the *second-order difference* method was undertaken on a 4.3 molal $CuCl_2$ heavy-water

solution. The method [6] enabled a direct determination of solute structure to be made in terms of the pair radial distribution functions $g_{CuCl}(r)$ and $g_{ClCl}(r)$. (For reasons associated with the relatively small differences in the coherent scattering properties of the isotopes of copper it is not yet feasible to determine $g_{CuCu}(r)$ in aqueous solutions.) As we show below the results provide unambiguous evidence for direct contacts between Cu^{2+} and Cl^- ions, and present a self-consistent explanation of the local environment of both Cu^{2+} and Cl^- ions. Additionally, the results provide a structural explanation for the colour change from green to blue in aqueous copper chloride solutions when the ionic concentration is reduced from around 4 molal to 1 molal.

2. Experimental details

2.1. Neutron diffraction experiments

Five isotopically enriched samples of 4.3 molal copper chloride ($CuCl_2$) in heavy water were prepared by standard methods. Isotopic composition of each was determined by mass spectroscopy, light-water contamination was monitored by infra-red spectroscopy and ionic concentrations were obtained by electrical conductivity measurements (table 1).

Table 1. Mean coherent scattering lengths of copper and chloride atoms in 4 molal copper(II) chloride in heavy water.

Structure factor	$\bar{b}_{Cu}$† (b)	$\bar{b}_{Cl}$‡ (b)
$^{63}_{37}F$	6.59	3.51
$^{63}_{35}F$	6.47	11.4
$^{65}_{37}F$	9.88	3.51
$^{MIX}_{NAT}F$	9.23	9.58
$^{63}_{NAT}F$	6.43	9.58

† Calculated from relative isotopic fractions of ^{63}Cu and ^{65}Cu.
‡ Calculated from relative isotopic fractions of ^{35}Cl and ^{37}Cl.

Neutron diffraction experiments were carried out on the SANDALS diffractometer sited on the ISIS pulsed neutron source at Rutherford Appleton Laboratory, Chilton, Didcot. The samples were contained between 1.1 m thick titanium/zirconium ($Ti_{0.67}Zr_{0.33}$) 'null' plates with cell dimensions 35 mm × 45 mm × 1 mm. Time-of-flight spectra were recorded in the SANDALS detectors over a period of 14 h for each sample. Each data set covered a range in Q of $0.4 \leqslant A$ (Å^{-1}) $\leqslant 45$, where $\hbar Q$ is the momentum transfer in the scattering process. In the actual analysis, the data above 30 Å^{-1} were not used because of the poor signal–noise ratio over the range 30 Å^{-1} to 45 Å^{-1}.

2.2. Data analysis and results

The scattered data for each of the detectors were 'binned' and combined according to Q-value to produce an $I(Q)$ for each sample. Recall that in the scattering process, Q is related to the scattering angle 2θ by the equation $Q = (4\pi/\lambda)\sin\theta$, where λ is the wavelength of the incident neutron. $I(Q)$ was divided by the monitor spectrum and normalized to units of barns per steradian by reference to a vanadium slab of approximately the same

dimensions as the sample container. This normalized function was corrected by standard methods for multiple scattering, absorption, background and container scattering [4]. The resulting function, $F'(Q)$ can be expressed as

$$F'(Q) = F_0(Q) + \delta(Q) \tag{1a}$$

where

$$F_0(Q) = \sum_{\alpha, \beta = \text{Cu, Cl, D, O}} \sum \bar{b}_\alpha \bar{b}_\beta c_\alpha c_\beta [S_{\alpha\beta}(Q) - 1] \tag{1b}$$

and $\delta(Q)$ is the inelastic correction to the data. The values of b_α (the mean coherent scattering length) and c_α (the atomic concentration) for the elements α are given in table 1. A low-order ($\leqslant 6$) polynomial was used to calculate $\delta(Q)$ and remove it from $F'(Q)$. At the low angles (up to $21°$) $\delta(Q)$ is small.

At this point we introduce the notation $^M_X F_0$ [6] to identify the isotopic state of the sample in terms of its cation (M) and anions (X). The five $F_0(Q)$ are shown in figure 1, and cursory inspection confirms their similarity which implies that each function is dominated by correlations between water molecules.
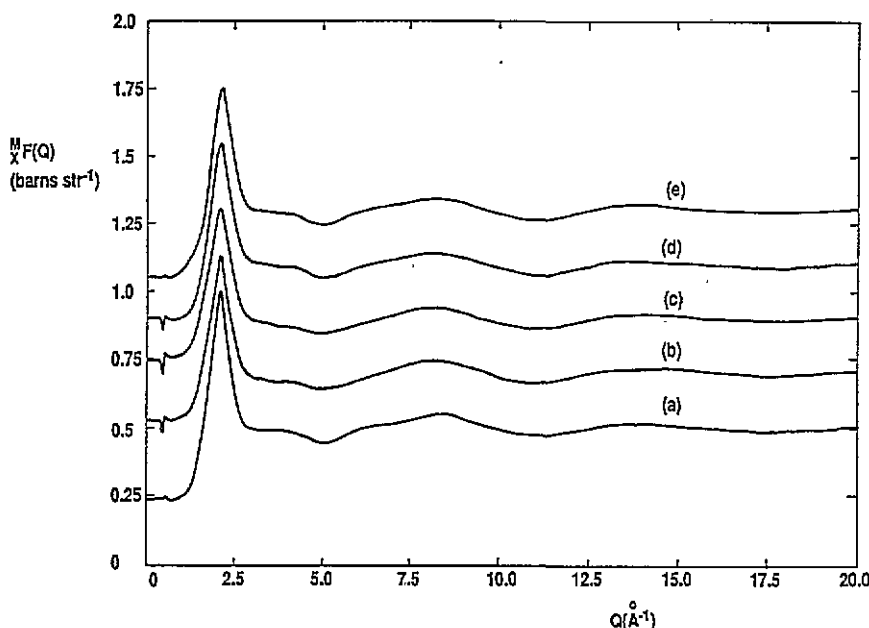

Figure 1. The structure factors, $^M_X F_0(Q)$, for the five isotopically labelled 4 molal $CuCl_2$ heavy-water solutions: (a) $^{MX}_N F_0(Q)$, (b) $^{63}_N F_0(Q) + 0.25$, (c) $^{65}_{37} F_0(Q) + 0.5$, (d) $^{63}_{37} F_0(Q) + 0.75$, (e) $^{63}_{35} F_0(Q) + 1.0$ (MX $\equiv$ mixture of ^{63}Cu and ^{65}Cu, and N = natural abundance of Cl).

The first-order difference NDIS method was used to obtain information on the coordination around the anions and cations. For the case of Cu^{2+}, a direct subtraction of $^{63}_{37} F_0(Q)$ from $^{65}_{37} F_0(Q)$ gave the difference function $\Delta_{Cu}(Q)$ (figure 2(a)):

$$\Delta_{Cu}(Q) = ^{65}_{37} F_0 - ^{63}_{37} F_0 = A S_{CuO}(Q) + B S_{CuD}(Q) + C S_{CuCl}(Q) + D S_{CuCu}(Q) + E \tag{2}$$

where $A = 2b_{Cu}b_{0Cu}C_0$, $B = 2b_{Cu}b_D C_{Cu}C_D$, $C = 2b_{Cu}b_{Cl}C_{Cu}C_{Cl}$, $D = c_{Cu}^2(\bar{b}_{65}^2 - \bar{b}_{63}^2)$ and $E = -(A + B + C + D)$. Fourier transformation of $\Delta_{Cu}(Q)$ gave the total Cu^{2+} radial distribution function (figure 2(b)):

$$G_{Cu}(r) = 0.002\,906g_{CuO} + 0.006\,632g_{CuD} + 0.000\,316g_{CuCl}$$

$$+ 0.000\,33g_{CuCu} - 0.0102 \tag{3}$$

where we have used

$$\left(g_{Cu\alpha}(r) - 1\right) = \frac{1}{2\pi\rho r^2} \int \left(S_{Cu\alpha}(Q) - 1\right) Q \sin(Qr)\,dQ. \tag{4}$$

ρ is the total number density of the 4.3 molal $CuCl_2 \cdot D_2O$ sample and has a value of $0.0860\,Å^{-3}$.

By the same procedure the total Cl^- radial distribution was calculated from Fourier transformation of $\Delta_\alpha(Q)$ (figure 3(a)) which was obtained from the difference between $^{63}_{35}F(Q)$ and $^{63}_{37}F(Q)$:

$$G_{Cl}(r) = 0.013\,512g_{ClO}(r) + 0.031\,069g_{ClD}(r)$$

$$+ 0.001\,193g_{ClCu}(r)0.002\,89g_{ClCl}(r) - 0.048\,29. \tag{5}$$

Both $G_{Cu}(r)$ and $G_{Cl}(r)$ (figures 2(b) and 3(b)) can be analysed directly, by the assignment of prominent features to particular correlations. Moreover, integration over the range ($r_1 \leqslant r \leqslant r_2$ say) of the feature can be used to calculate a coordination number $\bar{n}_{Cu}^\alpha$ based on the equation

$$\bar{n}_{Cu}^\alpha = \frac{4\pi\rho c_\alpha}{A_\alpha} \int_{r_1}^{r_2} r^2 g_{Cu\alpha}(r)\,dr \tag{6}$$

where A_α takes the corresponding value A, B, C or D of (2).

During the calculations of $G_{Cu}(r)$ and $G_{Cl}(r)$ self-consistency checks were made on the data by the use of a maximum-entropy procedure [7] which constrained $g(r)$ to be equal to zero for $r \leqslant 1$ Å and to unity above $r = 20$ Å. We defer until the next section a detailed discussion of these two functions and now proceed to outline the derivation of the solute structure in terms of $g_{ClCl}(r)$ and $g_{CuCl}(r)$ which were obtained from the second-order difference NDIS method.

As has been previously demonstrated [6] the cross term, $S_{MX}(Q)$, is uniquely determined from four $F(k)$ associated with double substitution of the solute ions. In particular $S_{CuCl}(Q)$ (figure 4(a)) was calculated from a linear combination of the four $F(Q)$ identified in the following equation:

$$S_{CuCl}(Q) = \frac{1}{2c_{Cu}c_{Cl}(^{NAT}b - {}^{37}b)}\left[\frac{(^{63}_{37}F_0 - {}^{65}_{37}F_0)}{b_{63} - b_{65}} - \frac{(^{63}_{NAT}F_0 - {}^{MX}_{NAT}F_0)}{b_{63} - b_{MX}}\right]$$

$$= 2211\left(^{63}_{37}F_0 - {}^{65}_{37}F_0\right) - 2597\left(^{63}_{NAT}F_0 - {}^{MX}_{NAT}F_0\right). \tag{7}$$

Fourier transformation of this function gave $g_{CuCl}(r)$ (figure 4(b)).

The difference between the low-Q ($< 0.6\,Å^{-1}$) part of the data in figure 4(a) and the back transform is expected; the error on the data points is large because fewer long-wavelength neutrons are produced per pulse and during the course of our experiments
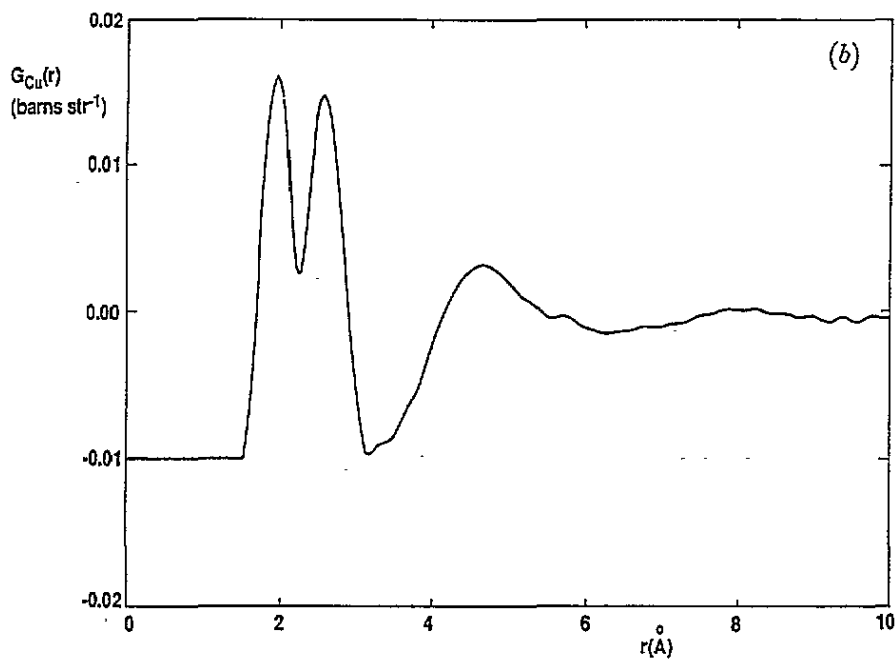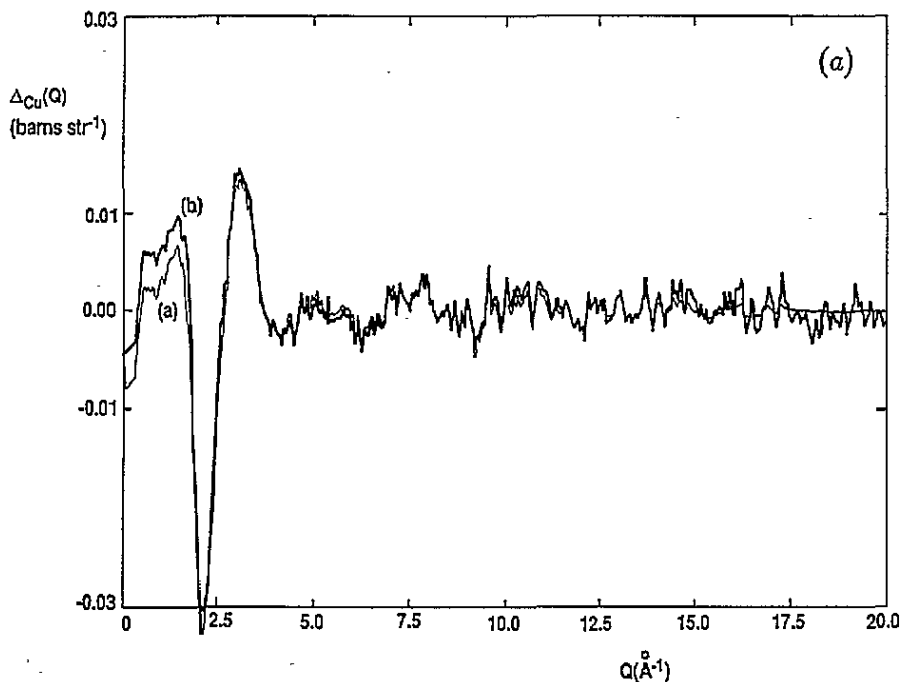
Figure 2. (a) The Cu^{2+} first-order difference function, $\Delta_{Cu}(Q)$, for 4 molal $CuCl_2$ in heavy water. $\Delta_{Cu}(Q)$ was derived from the difference between $^{65}_{37}F_0(Q)$ and $^{63}_{37}F_0(Q)$. The heavy curve (b) is the result prior to Fourier transformation, and the lightly drawn curve (a) is the back (Fourier) transformation of figure 2(b). (b) The total Cu^{2+} pair distribution function $G_{Cu}(r)$, in 4 molal copper chloride in heavy water. The function was set equal to $G_{Cu}(0) = 0.010$ for $r < 1.6$ Å.

SANDALS had no detectors below 10°. Additionally, the exact nature of the low-Q data is relatively unimportant in the Fourier transformation to $g(r)$ (see (4)). A linear combination of all five 5-functions $^M_X F_0$ were used to give a good approximation to $S_{ClCl}(Q)$ (figure 5(a)):

$$S'_{ClCl}(Q) = S_{ClCl}(Q) - 0.01 S_{CuCu}(Q) = 5190\,^{63}_{35}F_0 + 1270\,^{63}_{37}F_0$$
$$- 6333\,^{63}_{NAT}F_0 - 110\,^{65}_{37}F_0 - 17\,^{MX}_{NAT}F_0. \qquad (8)$$

Because of the conditioning of the equations for $F_0(Q)$, calculation of $S_{CuCu}(Q)$ is found to be impracticable.

Fourier transformation of the two functions (equations (7) and (8)) gives the corresponding $g_{ij}(r)$. However, because the experimental constraints are severe, care must be taken when interpreting these functions. To distinguish between structure and noise, the maximum-entropy method described in detail by Soper [7] was used. The method is designed to yield a $g(r)$ which on Fourier transformation to $S^{fit}(Q)$ is as smooth and consistent as possible with the experimental $S^{expt}(Q)$ data. The programme forces $g(r)$ to become equal to unity for $r \geqslant r_{max}$ and to zero for $r \leqslant r_{min}$. For the case here $r_{max} = 30$ Å and $r_{min} = 0.7$ Å. An additional constraint was introduced which required $S^{fit}(Q)$ to differ from $S^{expt}(Q)$ by less than the Gaussian error function of the data. Practically, this means that 67% of the data points of $S^{fit}(Q)$ are within one standard deviation of the data points of $S^{expt}(Q)$, and 95% are within two standard deviations. As with all smoothing procedures, the results which are presented constitute the minimum structure required to generate the experimental results. The resulting functions displayed in figures 4(b) and 5(b) are those which we found to be most consistent with the Q-space information.

3. Discussion

3.1. Ion–water coordination

The most interesting observation here is the extent of agreement between the $G_x(r)$ obtained on the SANDALS instrument and those obtained on the D4B diffractometer at ILL [3]. The results confirm that the Cu^{2+} coordination is significantly distorted with about 3.3(3) nearest-neighbour water molecules whose oxygen atoms are centred at ~ 1.95 Å and a mixture of Cl^- and D atoms situated under the composite feature at ~ 2.5 Å. As was mentioned by Salmon *et al* in [3], knowledge of $g_{CuCl}(r)$ is required to determine the full character of the Cu^{2+} coordination. Nevertheless, an approximate estimate of n^{Cl}_{Cu} can be obtained by integration over the composite feature at ~ 2.5 Å. After subtracting 6.6 D atoms associated with the nearest-neighbour 3.3 water molecules it is found that ~ 3 Cl^- atoms can be accommodated over the range of this compound feature. This result is consistent with that obtained directly (see section 4.2) from analysis of $g_{CuCl}(r)$.

The corresponding function for the Cl^- coordination, $G_{Cl}(r)$, (figure 3(b)) shows that as in other chloride salts there exists a relatively strong interaction between Cl^- and surrounding water molecules. The first peak centred at 2.25 Å is attributed to direct contacts between Cl^- and deuterium atoms of the hydrated water molecules. Integration over the range $1.90 \leqslant r$ (Å) $\leqslant 2.85$ shows that there are $\sim 3.2(3)$ water molecules in the first hydration zone around the Cl^- anion, a value significantly less than the 'infinite' dilution value of six [8], and in excellent agreement with earlier NDIS studies [9]. At this point it is worth reiterating the main conclusion drawn from that work, which was that the origin of the distorted (sixfold) structure around the Cu^{2+} is a direct result of a demonstrable dynamical Jahn–Teller effect. To obtain more exact details of the Cu^{2+} coordination it is necessary to determine $g_{CuCl}(r)$.
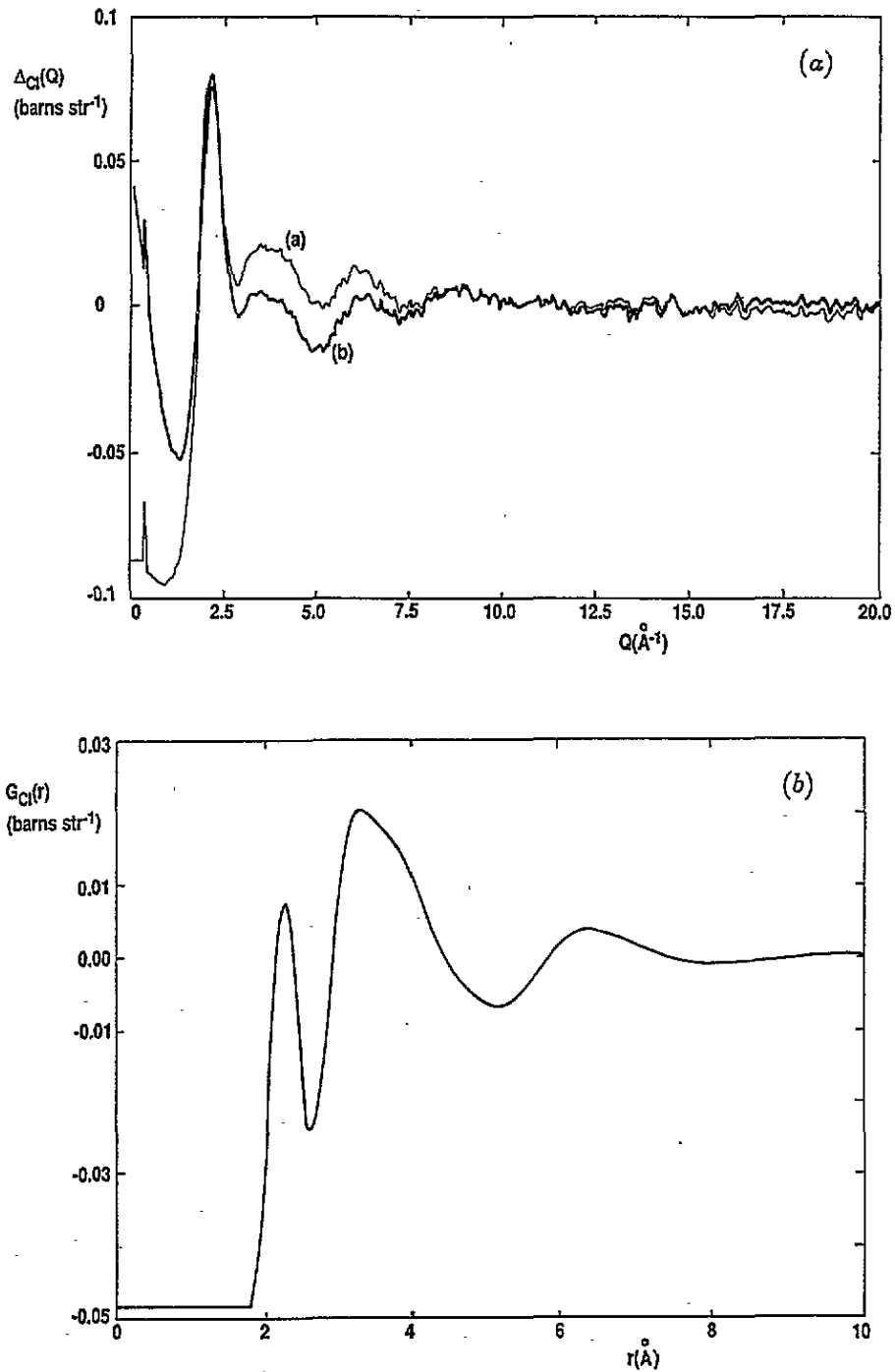
Figure 3. (a) The Cl⁻ first-order difference function, $\Delta_{Cl}(Q)$, for 4 molal CuCl$_2$ in heavy water. $\Delta_{Cl}(Q)$ was calculated from the difference between $^{63}_{35}F_0(Q)$ and $^{63}_{37}F_0(Q)$. The lightly drawn curve (a) is the result prior to Fourier transformation, and the heavy curve (b) is that after back transformation of the result in figure 3(b). (b) The total Cl⁻ pair radial distribution function $G_{Cl}(r)$ in 4 molal copper chloride in heavy water. The value of $G_{Cl}(r)$ is set to $G_{Cl}(0) = 0.048$ for $r < 2.0$ Å.

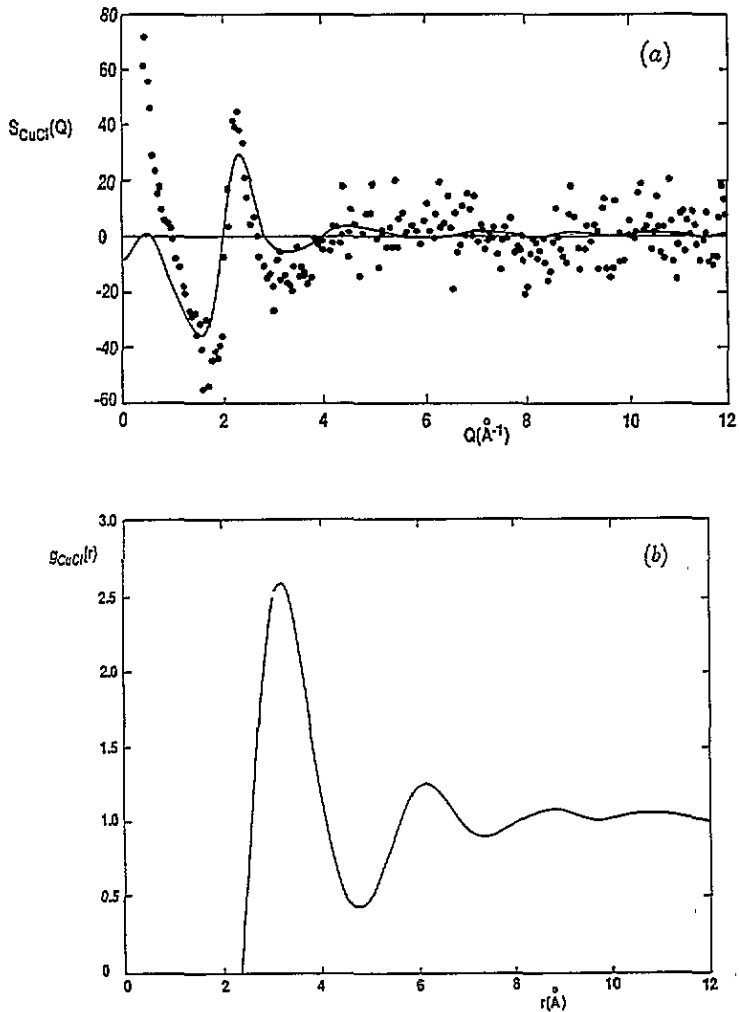**Figure 4.** (a) The partial structure factor, $S_{CuCl}(Q)$, in 4 molal copper chloride in heavy water. The dots represent the experimentally derived data, and the full curve is the result of the back transformation of the $g_{CuCl}(r)$ present in figure 4(b). (b) The pair radial distribution function $g_{CuCl}(r)$ in 4 molal copper chloride in heavy water. Details of the calculation are included in the text.

3.2. The solute structure

As explained above and in [2], the first-order difference method is unable to resolve any of the details for the solute–solute structure. It is the second-order difference isotopic substitution method which enables one to calculate $g_{CuCl}(r)$ and $g_{ClCl}(r)$ from the appropriate combination of structure factors. A knowledge of the former enables one to resolve the composite peak centred at 2.54 Å in $G_{Cu}(r)$. It is clear from $g_{CuCl}(r)$ that there is a strong correlation between Cu and Cl in the range $2.6 \leqslant r$ (Å) $\leqslant 4.4$. Integration over this range gives a coordination number of 2.5(5), and provides the first direct evidence that contacts occur between Cu^{2+} and Cl^{-}. Interestingly the fact that the number appears greater than 2 has implications for a colour change in the liquid.

The function $g_{ClCl}(r)$ appears strongly correlated with direct contacts evident between
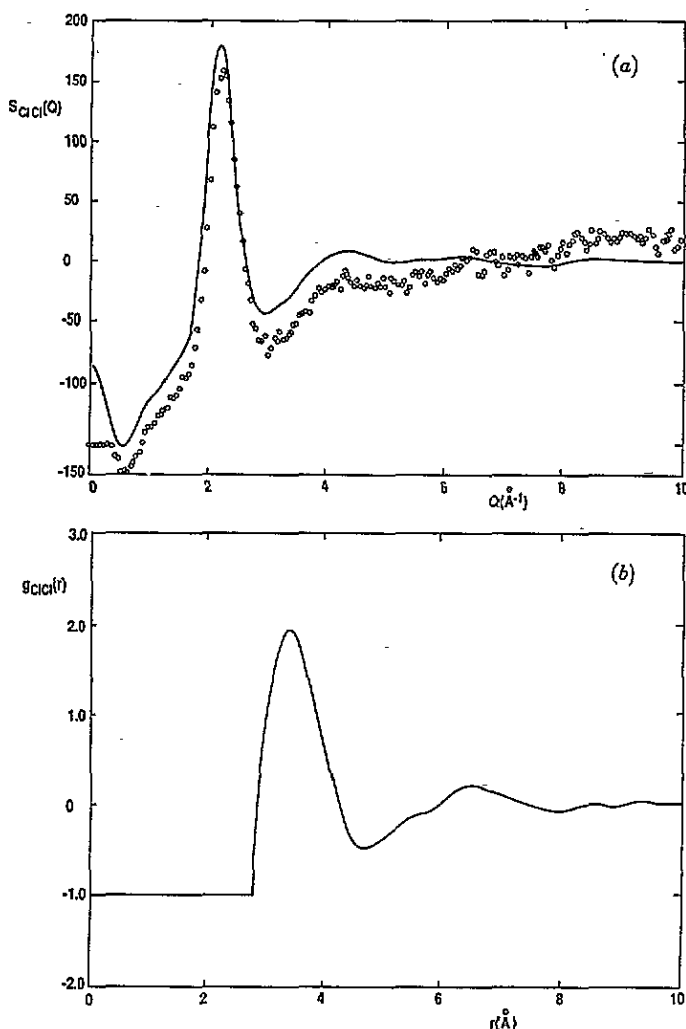
Figure 5. (a) The partial structure factor $S_{ClCl}(Q)$ in 4 molal copper chloride in heavy water. The full curve is the Fourier transformation of $g_{ClCl}(r)$ presented in figure 5(b). (b) The pair radial distribution function $g_{ClCl}(r)$ in 4 molal copper chloride in heavy water.

Cl^- in the range $2.8 \leqslant r$ (Å) $\leqslant 3.5$. Integration over this range gives a value for the coordination number $\bar{n}_{Cl}^{Cl}$ of 3, which when considered with the result for n_{Cl}^{D} from $G_{Cl}(r)$ obtained from the first-order NDIS measurements is consistent with a sixfold coordination of Cl^-. The longer range of $g_{ClCl}(r)$ is similar in shape to that found in concentrated aqueous solutions of lithium chloride and nickel chloride, albeit that there are small shifts in positions of maxima.

3.3. Further discussion

Within the general context of Cu^{2+} coordination in condensed phases, the neutron results confirm the nearest-neighbour structure to be a distorted sixfold structure, the origins of which are associated with its d^9 valence state. In contrast to the Ni^{2+} d^8 cation, which shows no direct [6] contacts (figure 6), at a similar concentration the $g_{MCl}(r)$ show *direct*

ionic contacts and a strong degree of correlation out to ~10 Å (figure 4(b)). Although a bridge-like structure is possible between the Cu^{2+} and Cl^-, it is felt in the light of a relatively low coordination number in Cu–Cl to be unlikely. It is also clear that the $g_{ClCl}(r)$ in the two systems are significantly different; whereas direct contacts exist in the case of the copper chloride solution, none are evident in the case of nickel chloride solution (figure 6). Viewed from the position of the water molecules, it would seem that the coupling to Ni^{2+} is highly favoured even in the presence of the relatively strong Cl^- anion. By contrast Cu^{2+} offers a highly anisotropic potential to water molecules which interact strongly in their equatorial planes but are relatively weak in the axial direction. This, together with the inherent dynamics of the situation, serves to explain the distortion brought about by a dynamical Jahn–Teller effect.
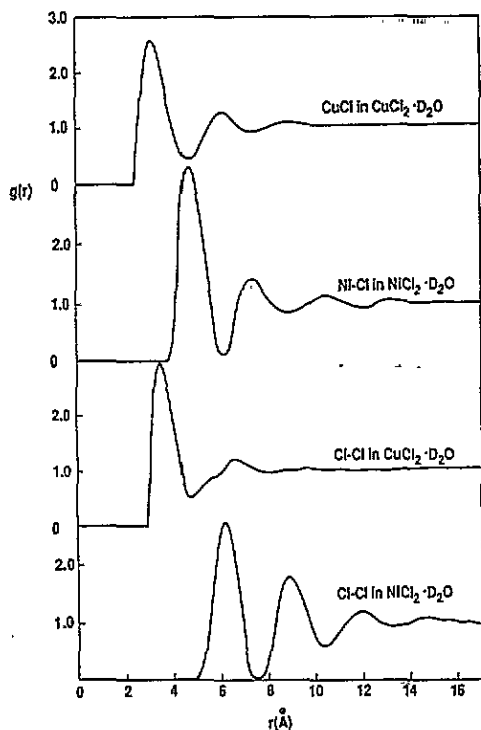

Figure 6. *Comparison of the pair distribution functions $g_{MCl}(r)$ and $g_{ClCl}(r)$ in a 4.3 molal $NiCl_2$ heavy-water solution and the 4 molal $CuCl_2$ heavy-water solution.*

It is interesting to note that in aqueous cupric chloride a colour change occurs from green to blue as the ionic concentration of the solution is reduced. The commonly accepted view of this is that there is a change in the Cu^{2+} environment. Based on the above results it would seem likely that the most obvious structural consequence is a removal of Cl^- by water molecules in the equatorial environment of four water molecules of the cupric ion. The concentration range over which such a colour change occurs is between 4 molal and 1 molal; the corresponding structural changes have yet to be fully characterized over the entire range of concentration. However, in heavy-water solutions of 1 molal copper nitrate and 2 molal copper perchlorate which are both blue Cu^{2+} does indeed have almost exactly four oxygen atoms in the nearest-neighbour region. Clearly, it is of interest to examine the chloride system at lower concentrations and determine exactly how rapidly the Cu^{2+} coordinates to exactly four D_2O molecules in the equatorial plane.

Table 2. Structural properties of $[Cu^{2+}]_{aq}$ and $[Cl^-]_{aq}$ in 4 molal copper chloride in heavy water.

	r_{CuO}	$\bar{n}_{Cu}^{O}$	r_{CuD}	$\bar{n}_{Cu}^{D}$	r_{Cu}^{Cl}	$\bar{n}_{Cu}^{Cl}$
Cu^{2+}	1.96 ± 0.03	3.3 ± 0.2	2.58 ± 0.03	7.6 ± 0.5	3.1 ± 0.2	2.0 ± 0.5
Cu^{2+} [D4B]	1.96 ± 0.03	3.4 ± 0.2	2.4 ± 0.03	—	—	—

	r_{ClD}	$\bar{n}_{Cl}^{D}$	r_{ClCl}	$\bar{n}_{Cl}^{Cl}$
Cl^-	2.25 ± 0.03	3.2 ± 0.3	3.4 ± 0.4	3.0 ± 2.0
Cl^- [D4B]	2.27 ± 0.03	3.4 ± 0.3	—	—

4. Conclusions

The above study demonstrates the power of the NDIS method in resolving interatomic structure in a complex liquid. The results clearly show that the detailed environment of Cu^{2+} in a concentrated salt solution comprises both water molecules and Cl^- ions, and confirms inferences drawn from previous structural studies of aqueous copper chloride. The challenge to experimentalists is to use these results to help unravel the complete structure. One of our colleagues, Dr P de Jong, is investigating the use of the reverse Monte Carlo method in the determination of all other pair distribution functions which will provide a more detailed picture of the solution structure, including angular correlations between Cu^{2+}, Cl^- and the H-bond network. The challenge to theorists is to see whether on the basis of model potentials it is possible to generate such a complex structure in solution.

Acknowledgments

References

[1]   See, e.g.,
      Cotton F A and Wilkinson C 1980 *Advanced Inorganic Chemistry* 4th edn (New York: Wiley) ch 21-H-3
[2]   Wells A F 1984 *Structural Inorganic Chemistry* (Oxford: Clarendon)
[3]   Salmon P S, Neilson G W and Enderby J E 1988 *J. Phys. C: Solid State Phys.* **21** 1335
[4]   Salmon P S and Neilson G W 1989 *J. Phys.: Condens. Matter* **1** 5291
[5]   Beagley B, Eriksson A, Lindgren J, Persson I, Pettersson G M, Sandström M, Wahlgren U and White E W
      1989 *J. Phys.: Condens. Matter* **1** 2395
[6]   Neilson G W and Enderby J E 1983 *Proc. R. Soc.* A **390** 353
[7]   Soper A K 1989 *Inst. Phys. Conf. Proc.* **97** (Bristol: Institute of Physics Publishing) p 711
[8]   Powell D H, Neilson G W and Enderby J E 1993 *J. Phys.: Condens. Matter* **5** 5723
[9]   Enderby J E, Cummings S, Herdman J, Neilson G W, Salmon P S and Skipper N 1987 *J. Phys. Chem.* **91**
      5851