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LETTER TO THE EDITOR

The coordination of Cu(II) in a concentrated copper nitrate solution

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Abstract. The first-order difference method of neutron diffraction has been applied to a 1.00 molal (mol kg^{-1}) $\text{Cu}(\text{NO}_3)_2$ heavy water solution. The results show a nearest-neighbour distance given by $\bar{r}_{\text{CuO}} = 1.96 \pm 0.03 \text{ \AA}$, a hydration number $\bar{n}_{\text{Cu}}^{\text{h}} = 4.0 \pm 0.2$ and are consistent with a Jahn–Teller distortion of the $\text{Cu}^{2+}(\text{aq})$ complex to give a (4 + 2) coordination group.

In this Letter the results from a neutron diffraction study of a 1.00 molal (mol kg^{-1}) copper nitrate solution in heavy water are reported. In particular the first-order difference method of neutron diffraction (Soper *et al* 1977, Enderby *et al* 1987) was used to focus on the structure of the Cu(II) aqua-ion, $\text{Cu}^{2+}(\text{aq})$. Work has recently been undertaken by Salmon *et al* (1988) on heavy water solutions of CuCl_2 and $\text{Cu}(\text{ClO}_4)_2$ using the same method. The present study thus allows for a comparison between the effects of three different counter-ions on the nature of $\text{Cu}^{2+}(\text{aq})$.

Diffraction experiments were carried out on two isotopically enriched samples using the D4B diffractometer of the ILL, Grenoble, France. The solutions were prepared by a method which involved dissolution of the metal isotopes in nitric acid and subsequent removal of light water by a repeated process of evaporation followed by dilution with pure heavy water. The properties of the $^{63}\text{Cu}(\text{NO}_3)_2$ and $^{65}\text{Cu}(\text{NO}_3)_2$ solutions thus prepared are summarised in table 1; the other experimental details are as described by Salmon *et al* (1988).

The Cu(II) difference function $\Delta_{\text{Cu}}(k)$, where k is the scattering vector, was obtained by subtracting the corrected sample diffraction patterns and shifting the result by 0.0058 b sr^{-1} to account for the different self-scattering cross sections of the two solutions. $\Delta_{\text{Cu}}(k)$ is given in figure 1 and shows that there is a significant contrast between the total diffraction patterns of the two solutions.

The real-space function $\Delta G_{\text{Cu}}(r)$, which was used to interpret the local coordination environment of the Cu(II) ion, was obtained by Fourier transformation of $\Delta_{\text{Cu}}(k)$. $\Delta G_{\text{Cu}}(r)$ is, for the 1.00 molal $\text{Cu}(\text{NO}_3)_2$ solution (figure 2), given by

$$\begin{aligned} \Delta G_{\text{Cu}}(r) = & (1.11 \pm 0.06) [g_{\text{CuO}}(r) - 1] + (2.27 \pm 0.13) [g_{\text{CuD}}(r) - 1] \\ & + (0.063 \pm 0.004) [g_{\text{CuN}}(r) - 1] + (0.030 \pm 0.002) [g_{\text{CuCu}}(r) - 1] \end{aligned}$$

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Table 1. Parameters used in the analysis of the $\text{Cu}(\text{NO}_3)_2$ solution data. The cross sections were obtained from the tables of Sears (1984) except those for Cu which were taken from Koester *et al.* (1981). The isotopic compositions were measured using mass spectrometry. The light-water content is expressed as a fraction of the total water ($\text{H}_2\text{O} + \text{D}_2\text{O}$) present and was determined from infrared measurements. The solution mass densities were $1.260 \pm 0.001 \text{ g cm}^{-3}$ at 20°C .

Molality (mol kg ⁻¹)	Solute	Isotopic composition		Mean scattering cross section per atom ^a (b atom ⁻¹)	Mean absorption cross section per atom ^b (b atom ⁻¹)	Light-water content (%)
		⁶³ Cu(%)	⁶⁵ Cu(%)			
1.00	⁶³ Cu(NO ₃) ₂	99.4	0.6	3.97	0.0208	0.28
	⁶⁵ Cu(NO ₃) ₂	0.7	99.3	4.02	0.0151	0.27

^a Calculated using a total scattering cross section for D_2O of 11.5 b at the experimental wavelength (Garber and Kinsey 1976).

^b Values are quoted for the experimental wavelength of 0.704 \AA .

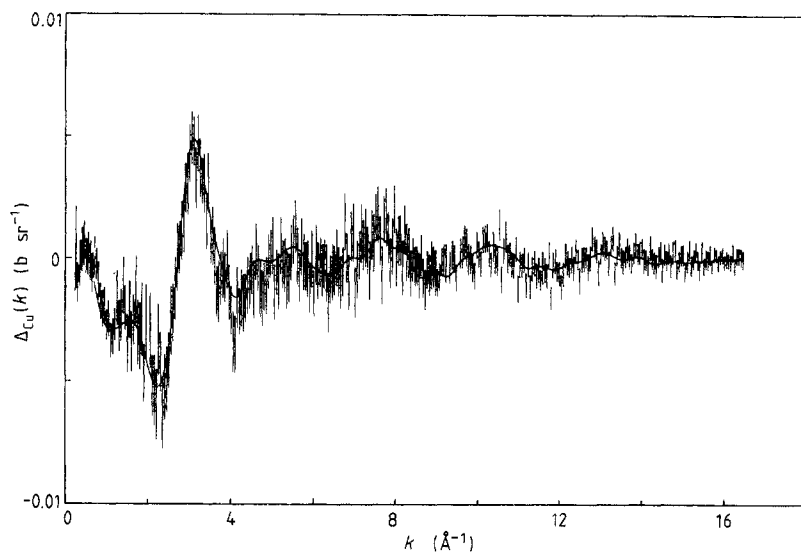


Figure 1. The first-order difference function, $\Delta_{\text{Cu}}(k)$, for a 1.00 molal solution of $\text{Cu}(\text{NO}_3)_2$ in D_2O . The points represent the experimental data and the full curve is the Fourier back-transform of the $\Delta G_{\text{Cu}}(r)$ given by the full curve in figure 2.

where the $g_{\text{Cu}\alpha}(r)$ are the partial pair distribution functions involving copper and the units of $\Delta G_{\text{Cu}}(r)$ are mb sr^{-1} . The coordination number of a specific atom α around $\text{Cu}(\text{II})$, in the range $r_1 \leq r \leq r_2$, is given by

$$\bar{n}_{\text{Cu}}^{\alpha} = 4\pi\rho c_{\alpha} \int_{r_1}^{r_2} r^2 g_{\text{Cu}\alpha}(r) \text{d}r$$

where $\rho = 0.0101 \text{ \AA}^{-3}$ is the total number density of atoms in the solution and c_{α} is the atomic fraction of species α .

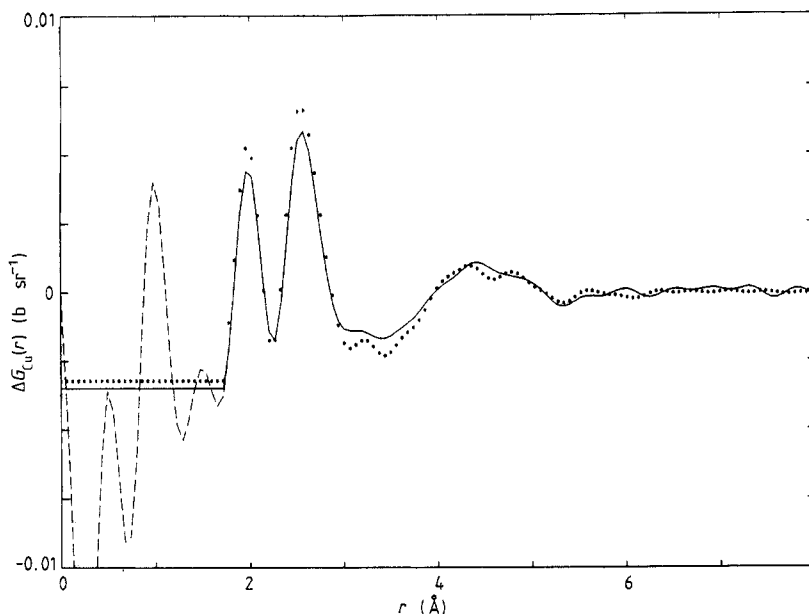


Figure 2. $\Delta G_{\text{Cu}}(r)$ for a 1.00 molal solution of $\text{Cu}(\text{NO}_3)_2$ in D_2O (full curve) and for a 2.00 molal solution of $\text{Cu}(\text{ClO}_4)_2$ in D_2O scaled by a factor of 0.5 (dotted curve). This scaling factor ensures that the contribution of $g_{\text{CuO}}(r)$ is the same for both solutions on the plotted scale. The broken curve shows the unphysical features at $r < 1.72 \text{ \AA}$ that result from Fourier transforming the $\Delta_{\text{Cu}}(k)$ given by the points in figure 1.

The results for $\Delta G_{\text{Cu}}(r)$ (figure 2) show a well defined environment for Cu(II) in the range $1.72 \text{ \AA} \leq r \leq 3.37 \text{ \AA}$ which may be considered as the region of the first coordination shell. The first peak centred at $1.96 \pm 0.03 \text{ \AA}$ is identified with $g_{\text{CuO}}(r)$ (cf Salmon *et al* 1988) and its integration over the range $1.72 \text{ \AA} \leq r \leq 2.27 \text{ \AA}$ gives a hydration number $\bar{n}_{\text{Cu}}^{\text{O}} = 4.0 \pm 0.2$. Analysis of the broad peak centred at $2.58 \pm 0.03 \text{ \AA}$ is, however, less straightforward: its integration over the range $2.27 \text{ \AA} \leq r \leq 3.07 \text{ \AA}$, for example, gives $\bar{n}_{\text{Cu}}^{\text{D}} = 10.3 \pm 0.6$ which is too large i.e. greater than twice $\bar{n}_{\text{Cu}}^{\text{O}}$.

In order to progress with the interpretation of the second peak it is useful to compare the present results with the $\Delta G_{\text{Cu}}(r)$ obtained by Salmon *et al* (1988) for a 2.00 molal $\text{Cu}(\text{ClO}_4)_2$ solution (see figure 2). The perchlorate ion is not prone to inner-sphere complexing with Cu(II) (see Nomura and Yamaguchi (1988) and references therein) whereas there is evidence for a strong interaction between Cu(II) and the NO_3^- ion at concentrations ≥ 1 molal (e.g. Licheri *et al* 1984, Rosi and Fontana 1987). The comparison shows that there is a marked similarity between the local coordination group of Cu(II) in the two solutions (also see table 2) which, together with the lower concentration of the nitrate solution, lends support to an interpretation of the second peak in $\Delta G_{\text{Cu}}(r)$ in terms of a negligible contribution from the nitrate anion. This is in contrast to the results for a 4.32 molal CuCl_2 solution (Salmon *et al* 1988) where there is evidence for significant counter-ion penetration of the Cu(II) first coordination shell. All three solutions do, however, have the same nearest-neighbour oxygen distance of $1.96 \pm 0.03 \text{ \AA}$ (see table 2).

An interpretation of the first coordination shell for Cu(II) in the nitrate solution, assuming negligible anion penetration, shows that the area under the second peak in

Table 2. The copper–water coordination in $\text{Cu}(\text{NO}_3)_2$ aqueous solution as determined using first-order difference neutron diffraction (N), x-ray diffraction (X) and EXAFS methods. The copper–water coordination in a 2.00 molal $\text{Cu}(\text{ClO}_4)_2$ aqueous solution and in a 4.32 molal CuCl_2 are given for comparison. In the x-ray diffraction and EXAFS data analysis a tetragonal distortion of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ octahedron was assumed with the equatorial coordination number of oxygen atoms fixed at 4 and the axial coordination number of oxygen atoms fixed at 2.

Solute	Concentration (mol l ⁻¹)	\bar{r}_{CuO} (eq) (Å)	\bar{r}_{CuO} (ax) (Å)	Method	Reference
$\text{Cu}(\text{NO}_3)_2$	0.2	1.99 ± 0.02	2.29 ± 0.05	EXAFS	Beagley <i>et al</i> (1989)
	1.06	1.96 ± 0.03	—	N	Present work
	1.5	2.00 ± 0.02	2.12 ± 0.02	X	Licheri <i>et al</i> (1984)
	3.0	2.00 ± 0.02	2.22 ± 0.02	X	Licheri <i>et al</i> (1984)
$\text{Cu}(\text{ClO}_4)_2$	1.90	1.96 ± 0.03	—	N	Salmon <i>et al</i> (1988)
	4.24	1.96 ± 0.03	—	N	Salmon <i>et al</i> (1988)

$\Delta G_{\text{Cu}}(r)$ can accommodate a further $1.6 \pm 0.4 \text{D}_2\text{O}$ molecules in addition to the 8.0 ± 0.4 deuterium atoms associated with the nearest-neighbour oxygens. The position of these latter molecules cannot however be defined to better than $2.27 \text{Å} \leq r \leq 3.37 \text{Å}$ in view of the overlapping Cu–O and Cu–D correlations.

$\Delta G_{\text{Cu}}(r)$ also shows, for the range $3.4 \text{Å} \leq r \leq 5.3 \text{Å}$, a second coordination shell which may contain a contribution from the anions in addition to further water molecules. The binding time of these ligands to the Cu(II) ion will be less than that for water molecules in the first coordination shell which has been established as $\approx 10^{-10}$ s from NMR and incoherent quasi-elastic neutron scattering experiments (Salmon *et al* 1987).

The present results are also compared in table 2 with those obtained for other $\text{Cu}(\text{NO}_3)_2$ aqueous solutions by conventional x-ray diffraction and extended x-ray absorption fine structure (EXAFS) techniques. In each case the structural results were obtained by assuming a tetragonal distortion of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ octahedron to give four short equatorial (eq) and two longer axial (ax) bonds. It is found that the values of $\bar{r}_{\text{CuO}}(\text{eq})$ obtained from the x-ray work are larger than that obtained in the present study and that the $\bar{r}_{\text{CuO}}(\text{ax})$ values fall near the *minimum* of $\Delta G_{\text{Cu}}(r)$ at 2.27Å . This discrepancy may result from the problem associated with the dominant contribution to the scattering from the four equatorial neighbours in the EXAFS study (Beagley *et al* 1989) and from the need to involve particular structural models in order to interpret total x-ray diffraction patterns (Licheri *et al* 1984).

Garcia *et al* (1989), in a recent paper, have argued that it is impossible to distinguish between undistorted and tetragonally distorted $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ octahedra in aqueous solution on the basis of EXAFS data alone. However, from an analysis of x-ray absorption near-edge structure (XANES) data for aqueous CuCl_2 solutions, they identify a tetragonal distortion and estimate that the axial oxygen position is $(0.58 \pm 0.06) \text{Å}$ greater than the equatorial oxygen position. A distortion of this magnitude is in broad agreement with the measured $\Delta G_{\text{Cu}}(r)$ presented in figure 2.

In summary, our results are consistent with a $\text{Cu}^{2+}(\text{aq})$ complex that is Jahn–Teller distorted to give a (4 + 2) coordination group. No evidence is found for a distance $\bar{r}_{\text{CuO}}(\text{eq})$ that is sensitive to the counter-ion species which supports the conjecture of Licheri *et al* (1984) that the variation observed in this distance from conventional x-ray diffraction results is not significant.

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