**Species fine structure of transition metal Cu(II) in aqueous
chloride-bearing solutions: Insights from X-ray absorption
spectroscopy and *ab initio* XANES calculations**

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Abstract

Knowledge of the structure and speciation of aqueous Cu(II)-chloride complexes is important for understanding Cu(II) behavior in the deep removal technology of Cu impurity from nickel electrolysis anolytes containing chloride. In this paper, X-ray absorption spectroscopic measurements are reported for dissolved copper in lithium chloride (up to $\sim 16 \text{ mol}\cdot\text{kg}^{-1}$) solutions at room temperature. The speciation and structure of corresponding solutions has been probed by performing a combined *ab initio* XANES theoretical and experimental analysis. The EXAFS spectrum was analyzed as well within this approach. Our XAS data and *ab initio* XANES calculations favored the five-coordinated $[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$ with square pyramidal configuration over the four-(square planar and tetrahedron, $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$) and six-coordinated (octahedron, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$) structure in dilute Cl^- solution ($\sim 0.55 \text{ mol}\cdot\text{kg}^{-1}$). This is also supported by the EXAFS refinement with the $[\text{CuO}_5]$ model having the lowest statistical error. In the highest Cl^- concentration solution, the results of both methods show that tetrahedral $[\text{CuCl}_4]^{2-}$ complexes are predominant. Upon manually adjusting its geometric parameter to the distortion degree α of $\sim 18^\circ$ and average Cu-Cl bond distance of $2.25 \text{ \AA}$ of a squashed tetrahedral model, not only does the calculated XANES spectrum well reproduce the experimental spectrum, but also the statistical error in the EXAFS refinements is lowest.

Keywords: XAS; XANES; EXAFS; CuCl_2 ; speciation; high Cl-bearing solution

1. Introduction

Deep removal of Cu impurity from nickel electrolysis anolytes in the chloride type hydrometallurgy is still in suspension. It is found that when the Cl^- ion concentration is more than $70 \text{ g}\cdot\text{L}^{-1}$ in the anolytes, the removal of Cu becomes very difficult due to the Cu(II) and Cl^- in the nickel anolytes forming Cu(II)-chloride complexes, which reduces the effectiveness of removal of the Cu impurity using an extraction or precipitation method (e.g., nickel thiosulfate precipitation method) [1]. Therefore, for developing a new extractant or chelator to efficiently separate these metal ions, understanding the Cu(II) behavior in Cl-bearing solution is important [2].

It has long been realized that understanding the complexation of Cu(II) by Cl ligands is important to various geochemical [3, 4] and environmental situations [5] and to hydrometallurgical extraction processing [6]. In general, Cu(II) is thought to form four consecutive chloride-complexes, $[\text{CuCl}]^+$, $[\text{CuCl}_2]^0$, $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$, in aqueous solution with increasing Cl^- concentration, as shown in Fig. 1. These complexes have been investigated mostly by UV-Vis spectrometry due to their different electronic absorption bands. Unfortunately, the bands are strongly overlapping so that it is difficult to refine experimentally the characteristic spectra of the individual complexes, although a few authors have obtained them by analyzing spectral data with the assumption that the total spectra of the system is only the sum of the characteristic spectra of the individual complexes [3, 8, 9]. The experimentally refined characteristic peak of $[\text{CuCl}]^+$ and $[\text{CuCl}_2]^0$ complexes at 250 nm and 275 nm, respectively, have been confirmed by recent density function theory (DFT) calculations [10, 11]. However, the higher-order complexes, $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$, are extremely weak and only form at very high chloride concentrations or in very low water activity solution, where media have a very high ionic strength [5]. On one hand,

use of high ionic strength media creates serious difficulties in the evaluation of activity coefficients. For example, the UV-Vis spectroscopic experiments of copper(I) chloride complexes [12] used LiCl as a background electrolyte in concentrations up to $\sim 10 \text{ mol}\cdot\text{kg}^{-1}$ and the results of this study are also potentially associated with systematic errors caused by inadequacies of the activity model (i.e., b-dot equation) employed, as indicated in the literature [13]. On the other hand, deviations from the Beer-Lambert law at high salinity are expected due to the influence of the dielectric constant (or refractive index) of the medium on the absorption of light by a particular complex [14] and because changes in the electronic structure of the complex can be induced by changes in the structure of the solvent and in the outer coordination shells of the complex (i.e., variations in ion association). These effects result in a deviation of the characteristic peak of an individual complex as a function of solution composition, and are difficult to estimate quantitatively. For example, there is an almost 20 nm deviation for the peak of $[\text{CuCl}_4]^{2-}$ refined from experimental spectra in different background electrolyte solutions (LiCl, MgCl_2 and CaCl_2) [15], indicating that characteristic spectra of individual complexes are affected by the ionic strength as well as background electrolyte. Furthermore, we also noted that characteristic peaks of $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$ are very close, with a strong peak at $\sim 270 \text{ nm}$ and a weak peak at $\sim 380 \text{ nm}$. Unfortunately, a subtle difference in these peaks is induced by either the new complex $[\text{CuCl}_4]^{2-}$ or by only a change in the degree of distortion of the $[\text{CuCl}_3(\text{H}_2\text{O})]^-$ complex due to solvent effect, as observed in the Cu(I)-bearing of high Cl^- concentration solution by Brugger et al. [16]. On the basis of their *ab initio* X-ray absorption near edge structure (XANES) studies, these authors have noted that the subtle change in XANES reflects the geometric distortions of $[\text{CuCl}_3]^{2-}$, however, the similar subtle change in UV-Vis spectra of Cu(I) solutions was erroneously

interpreted by Liu et al. [12] as a new species, $[\text{CuCl}_4]^{3-}$. Yi et al. [17] reported that the absorption bands of $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$ complexes are located at ~284 nm and 384 nm by DFT calculation with a PCM solvent model. One should keep in mind that PCM models the solvent as a polarizable continuum, which can lead to inaccurate predictions compared to models that explicitly account for complex-solvent interactions [18]. It therefore failed to distinguish the extremely weak complexes, $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$, that only formed in very low solvent activity solution (usually very high salinity).

X-ray absorption spectroscopy (XAS) has been widely used to investigate the coordination environment of metal ions in many fields [19, 20]. XAS is based on a principle of a final state interference effect arising from the scattering of the outgoing photoelectron from the neighboring atom, and is sensitive to ligand type, bond distance and the degree of geometric distortion induced by solvent. In contrast to UV-Vis spectra, XAS spectra can be routinely and accurately modeled from first principles. In the present study, we first qualitatively describe the XAS spectral behavior of Cu(II)-containing solutions with increasing Cl^- concentration. In addition, the properties of the Cu(II) complexes in the lowest and highest Cl^- concentration solutions are further investigated by *ab initio* XANES simulations combined with extended X-ray absorption fine structure (EXAFS) analysis, which provides additional information to identify the Cu(II)-Cl complexes in different Cl^- concentration solutions from molecular level insight.

2. Materials and methods

2.1. Experimental samples and XAS measurements

All solutions were prepared gravimetrically using Millipore doubly deionized water. All chemicals were of analytical grade or better and were used without further

purification. The LiCl stock solution was prepared by dissolving LiCl·H₂O_(s) in doubly deionized water. The concentration of this stock solution was determined by the Ag chloride gravimetric method [21]. A series of intermediate concentration LiCl solutions were obtained by gravimetrically mixing the LiCl stock solution and doubly deionized water. Finally, CuCl₂·2H₂O_(s) was dissolved in the LiCl solutions to obtain the different Cl⁻ concentration containing Cu(II) sample solutions. To suppress the hydrolysis of Cu(II), ~0.001 mol·kg⁻¹ hydrochloric acid was added to the sample solutions. The compositions of the sample solutions were listed in Table 1.

Copper K-edge XAS spectra were measured at the 20-BM-B bending magnet beamline (XOR/PNC sector) of the Advanced Photon Source (APS) in Chicago, USA. The APS is a 7 GeV ring and operates in top-up mode with a current of 102 mA. This beamline has a Si(111) monochromator with an energy resolution ($\Delta E/E$) of 1.4×10^{-4} (at 10 keV) [22]. Spectral data on sample solutions were acquired in transmission mode at room temperature. The details of beamline and measurement procedure are described in the literature [23].

2.2. EXAFS data analysis

The collected XAS transmission data were analyzed by the Demeter package [24]. The following procedure was used [25]: i) background subtraction and normalization of raw spectral data; ii) extraction of EXAFS oscillations (the two steps above were performed by the ATHENA module in the Demeter package); and iii) EXAFS fitting of structural parameters using the ARTEMIS module, with all calculations based on FEFF8 [26]. All EXAFS refinements were performed based on k^3 -weighted data in R-space using a Hanning window. The fitting structure parameters include the energy shift (ΔE_0), the number of ligands (water molecule, N_O ; chlorine, N_{Cl}) in the first coordination shell of Cu²⁺, the bond distance of Cu-O (R_O) and Cu-Cl

(R_{Cl}), as well as the Debye-Waller factors for the O and Cl atoms (σ_{O} and σ_{Cl}). The value of the amplitude reduction function (S_0^2) was fixed to 0.85 for all EXAFS refinements, the value recommended by the literature [27] for fitting Cu(II) species under hydrothermal conditions.

2.3. *Ab initio* XANES calculations

The computation of the XANES spectra was carried out using the FDMNES package developed by Joly et al. [28, 29], in which the final states and resulting absorption cross-sections can be calculated by either multiple scattering (MS) theory with the Muffin Tin (MT) approximation method or the Finite Difference Method (FDM). The latter has been demonstrated to more accurately reproduce spectral features within the first 20 eV of the edge region than the former, especially for the present aqueous systems with low-symmetry and/or non-dense structures [16]. Thus, the FDM method was chosen to calculate all XANES spectra of known Cu(II) speciation structures. To compare to the experimental spectra, these theoretical calculations have been further convoluted with a Lorentzian shape function to account for the core-hole lifetime broadening (1.55 eV for the copper K-edge [30]) and a Gaussian function to reproduce the resolution of experiment, 0.46 eV in this case [31].

To calculate the Cu K-edge XANES spectra of Cu(II) species in the present systems, the structural parameters were taken first from previous published literature. For $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ ($n = 4, 5$ and 6) species, we considered the different four- (square planar and tetrahedron), five- (square pyramidal), and six-fold (octahedron) coordination models with parameters from DFT [11] and MXAN code [32] optimization, while the structures of other aqueous species were mainly extracted from DFT calculations [17]. It is noted that the structural parameters from the DFT calculations, due to their inherent limitations (e.g., not considering explicit solvation

effect) [33], usually do not accurately reproduce the features of experimental XANES spectra (see section 3.2.2). Therefore, the method of manually adjusting the parameters (e.g., bond length and angle) to evaluate the origin of each feature and their dependence on structural parameters was used. All calculations were carried out on neutral atoms without hydrogen atoms.

3. Results and discussion

3.1. Qualitative description

The measured Cu K-edge XANES spectra are shown in Fig. 2 as a function of LiCl concentration (Table 1) at room temperature. Details of the spectral evolution are zoomed in the insets a, b and c. With increasing chloride ion concentration, the XANES spectra show the following systemic changes: i) an increase in the intensity of the pre-peak at ~8977 eV (inset a in Fig. 2); ii) a decrease in the intensity of the white line and shift of the white line towards lower energy (arrow C in Fig. 2); iii) growth of a shoulder at ~8986 eV on the low energy side of the white line (arrow B in the inset b of Fig. 2); iv) an increase in the intensity of the feature at ~9017 eV (arrow D in the inset c of Fig. 2); and v) a blue-shift of the absorption band in the energy range 9030 to 9080 eV (arrow E in the inset c of Fig. 2). These features are only observed for Ni(II) [25] and Co(II) [34] in Cl-bearing solutions at elevated temperature, indicating stronger competition for Cl^- ions and water molecules coordinating to Cu^{2+} . These changes reflected that increasing salinity promotes the dehydration of Cu complexes and the replacement of water by Cl ligands.

The pre-edge peak at 8977 eV has been assigned to a $1s \rightarrow 3d$ transition, which is electric dipole forbidden in a centrosymmetric environment, but a slight intensity can still be observed due to a small amount of thermal disorder or quadrupolar coupling [27]. In contrast, the transition is significantly more pronounced in a

non-centrosymmetric environment with some p -character mixing. It is difficult to deduce, according to this transition, the structural configuration of preponderant $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ ($n = 4, 5$ and 6) species in $0.55 \text{ mol}\cdot\text{kg}^{-1} \text{ Cl}^-$ solution. However, we observed a significant increase in the intensity of the pre-edge peak in high Cl^- concentration solution, indicating that a large structural change occurs in these systems.

The intensity growth of the shoulder on the low energy side of the white line at 8986 eV stands for the $1s \rightarrow 4p$ transition [35] and serves as evidence of the formation of metal/halide ion-pairs [34]. Furthermore, the transition is more intense for 4-coordinate complexes, especially those with a pure square planar geometry. Fig. 2c shows the XANES spectra of two solid standards, $(\text{NEt}_4)_2[\text{CuCl}_4]_{(\text{s})}$ and $\text{CuCl}_2\cdot 2\text{H}_2\text{O}_{(\text{s})}$ [36]. The crystal structure of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}_{(\text{s})}$ is a square planar configuration with D_{2h} point symmetry [35] and the strong $1s \rightarrow 4p$ transition converts the absorption shoulder into a sharp bulge. In the case of $(\text{NEt}_4)_2[\text{CuCl}_4]_{(\text{s})}$, the $[\text{CuCl}_4]$ unit is a distorted tetrahedron (D_{2d} point symmetry) [37], and its spectra with a weak shoulder are more analogous to the experimentally observed feature of Cu^{2+} in high Cl^- concentration solution, suggesting that the structure of $[\text{CuCl}_4]^{2-}$ in such systems is tetrahedral. In addition, it should be noted that the XANES spectra in the concentrated chloride solutions show no significant change between the ~ 15 and $\sim 16 \text{ mol}\cdot\text{kg}^{-1} \text{ Cl}^-$ (Fig. 2b), indicating that the tetrahedral $[\text{CuCl}_4]^{2-}$ species predominates in both solution. This is consistent with the result of the thermodynamic modeling, which predicts that $[\text{CuCl}_4]^{2-}$ species accounts for 80% of Cu(II) even in $15 \text{ mol}\cdot\text{kg}^{-1} \text{ Cl}^-$ solution, as shown in Fig. 1.

The filtered R-space and q -space spectra as a function of salinity are shown in Fig. 3. The added LiCl resulted in systematic changes for both spectra, as indicated by

the arrows. With increasing chloride ion concentration, the position of the main peak in R-space spectra gradually moves to larger R and the wavenumbers of the oscillations shift with increased intensity of the oscillation in q -space spectra, which not only indicates an increase of bond length from the central Cu^{2+} to neighboring ligands but also a drastic structural change caused by the progressive replacement of H_2O by Cl^- around Cu^{2+} within the first coordination shell. The spectra for the solutions with ~ 15 to $\sim 16 \text{ mol}\cdot\text{kg}^{-1}$ Cl^- also almost overlap in both spaces.

Based on the discussion above, $[\text{CuCl}_4]^{2-}$ with a distorted tetrahedral configuration is the most likely (dominant) species in higher salinity solutions, while the corresponding 4-coordinated $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ species in the lowest Cl^- concentration solution seems to be excluded.

3.2. Ab initio XANES simulation

3.2.1. First end-member: Cu(II) in the dilute Cl^- solution

Most previous studies [32, 38, 39] have concluded that $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ complexes with four-, five- and six-fold coordination configurations, as shown in Scheme 1, are possible species in dilute aqueous Cu(II) solutions. The calculated XANES spectra of these complexes are plotted in Fig. 4 along with experimental spectrum of $0.55 \text{ mol}\cdot\text{kg}^{-1}$ Cl^- solution where the $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ species predominates in ambient conditions. The Cu-O distance taken from results of MXAN with square pyramidal five-fold coordination configuration [32] leads to a very good agreement in the relative amplitude and position of all the features of the calculated and experimental spectra, as shown in Fig. 4b. Although the calculated spectra of four-fold coordination with square planar and distorted tetrahedron configurations also reproduced well features C, D and E of the experimental spectra (Fig. 4a), the small bump or shoulder at the absorption edge and the strong intensity of the pre-edge peak eliminated the

possibility that these configurations are predominant in solution, as observed in section 3.1. It should be noted that the calculated spectrum of a Jahn-Teller distorted octahedron also exhibits good agreement with features D and E of the experimental spectra, however, a subtle energy shift (~ 1.13 eV) of the white line peak to lower energy and that (~ 1.89 eV) of the absorption edge to higher energy, indicated with arrows in Fig. 4c within the first 20 eV, as well as the strong intensity of the pre-edge peak, show poor agreement with experiment. Hence, the present analysis shows the preference of aqueous $[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$ with an equatorial D_{2d} -distorted elongated square-pyramidal geometry, supporting the result previously reported by the MXAN method. This also confirmed that the parameters selected in the FDMNES software are suitable to reproduce the experimental XANES spectra of systems in the present study.

3.2.2. Second end-member: Cu(II) in the highest Cl-bearing solution

Based on the analysis in the section 3.1 and the thermodynamic result (Fig. 1), it is likely that the distorted tetrahedral $[\text{CuCl}_4]^{2-}$ species is preponderant at very high chloride ion concentrations, such as the present end-member solution with up to ~ 16 mol $\cdot\text{kg}^{-1}$ Cl^- . Therefore, mainly this species shall be considered to reproduce the experimental XANES spectra of the current system.

Fig. 5 displays the experimental spectrum of this second end-member, along with the calculated spectrum of the distorted tetrahedral $[\text{CuCl}_4]^{2-}$, whose coordination is obtained from DFT optimization [17], and a regular tetrahedral $[\text{CuCl}_4]^{2-}$. The spectrum obtained using the DFT optimized configuration does not match the features of the experimental spectrum very well. Compared to the experimental spectrum, a red-shift was observed in the calculated absorption bands of 20-100 eV. As observed in Fig. 5, the only agreement is in the spectral features in the pre-edge range and the

weak shoulder at 3.2 eV. As mentioned previously [25, 40], DFT Cu-Cl bond lengths often are too long. Shortening the Cu-Cl distance to 2.25 Å, as derived from the EXAFS analysis of this end-member solution (see Table 2), the energy bands range from 50 to 120 eV in the calculated XANES spectrum, in very good agreement with experiment. However, the difference between the calculated and experimental spectrum lies in the white line peak, where the calculation seems to have a narrower spine. More importantly, the weak shoulder in the experimental spectrum, as indicated by the arrow in the raw and convoluted spectra of Fig. 5, is not reproduced by the calculation when only changing the Cu-Cl distance. These results also suggest that variation of the Cu-Cl distance has minor influence on the calculated features near the white line peak. Hence, the distortion degree in tetrahedral $[\text{CuCl}_4]$, is probably responsible for the varied features. In fact, the effect of the distortion degree on the calculated spectrum has been investigated by Brugger et al. [16], who focused on the three-coordinated Cu(I)-chloride species with a trigonal configuration. However, the $[\text{CuCl}_4]^{2-}$ species with four Cu-Cl bonds in the present work is more complex than their $[\text{CuCl}_3]^{2-}$ with only three Cu-Cl bonds.

To investigate the effect of distortion in the edge region of the spectra, the simple four-coordinated $[\text{CuCl}_4]$ structure model unit with an angle α , defined as the Cu-Cl bond deviation from the mean CuCl_4 equatorial plane and shown in Scheme 2, was tested. The calculated spectra as a function of α , along with the experimental spectrum, are displayed in Fig. 6a. As observed, the features of the calculated spectra between 0-20 eV are very sensitive to the deformation of the $[\text{CuCl}_4]$ model unit. When $\alpha = 0$, corresponding to the $[\text{CuCl}_4]^{2-}$ species with a square planar configuration, the features of the calculated spectrum agree very well with the experiment in the edge region except for the white line peak, where the calculation only has a single peak in the

lower energy position. With a slight increase of the angle α to 8° , the single peak is split in two small peaks at 7.12 and 8.70 eV. Further increase of the distortion angle α to 18° produces a more intense the splitting, and the split peaks approach their experimental positions. In parallel, a bump appears at ~ 15.36 eV, which can be regarded as 1) adding the white line peak width of the calculated spectra and 2) corresponding to feature D (~ 13.25 eV) of the experimental spectrum. However, when the α adds up to 28° and, finally, to 36° (the regular tetrahedral configuration of $[\text{CuCl}_4]^{2-}$), a dramatic change in the edge region of the calculated spectra occurs: (i) a rise in the intensity of the white line peak and the bump at ~ 15.36 eV, as well as a red-shift of their positions; (ii) a shift in the position of the peak at ~ 2.7 eV towards higher energy and, finally, degeneracy with the white line peak. These calculated spectral changes cause the disappearance of the peak at ~ 2.7 eV and a shift in the position of the white line to lower energy, corresponding to experimental features B and C, respectively. As a consequence, the calculated spectrum deviates considerably from experiment. Based on the above analysis, $\alpha = 18^\circ$ seems to be the correct value and the corresponding spectrum is included in Fig. 6b. The calculated raw spectrum using the $[\text{CuCl}_4]$ model with a Cu-Cl distance of 2.25 Å and distortion degree of 18° reproduces almost all features of the experimental spectrum including the subtle bulge (feature D) near the white line peak, although this is smoothed in the convolution spectrum. This model indicates that the $[\text{CuCl}_4]^{2-}$ species has a flattened tetrahedral structure. Such a configuration is found in the solids $\text{Cs}_2[\text{CuCl}_4]_{(\text{s})}$ and $(\text{NEt}_4)_2[\text{CuCl}_4]_{(\text{s})}$, whose XANES spectra [36] are analogous with that of Cu^{2+} in the highest Cl-bearing solution. It should be mentioned that the precise angle cannot be refined by the present methods, due to ignorance of the effect of the second coordination shell and charges, which can also affect to the spectra in pre-edge

regions.

The UV-Vis spectroscopy study by Brugger et al. [3] suggests that the $[\text{CuCl}_5]^{3-}$ species may be present, probably with D_{3h} point group, in very high Cl^- concentration solution ($\sim 15 \text{ mol}\cdot\text{kg}^{-1} \text{ Cl}^-$). Therefore, a trigonal bipyramid geometry with four Cu-Cl bonds of 2.25 Å as a plane (distorted plane, $\alpha = 15^\circ$) and the other one of 2.35 Å at the axial position is used to calculate the XANES spectrum. However, the calculated raw spectrum, as displayed in Fig. 6b, with a rigid white line peak and a bump at 60-80 eV split into double peaks (as indicated with arrows) far deviating from the experimental spectrum, seems to eliminate this species. This result is supported by a recent molecular dynamics study, in which the authors observed that one Cl ligand of $[\text{CuCl}_5]^{3-}$ quickly escapes from the inner coordination sphere of Cu even in $16.32 \text{ mol}\cdot\text{kg}^{-1} \text{ Cl}^-$ solution [41].

Upon replacement of Cl in the axial position by O in the geometry above, forming the $[\text{CuCl}_4\text{O}]$ model, the calculated XANES spectrum reproduces almost all the experimental features, including the weak shoulder at 2.7 eV and the subtle bulge near the white line peak (as indicated with arrows, see Fig. 6b). Such a result seems not to eliminate this species. Furthermore, the calculated spectra as a function of α using the $[\text{CuCl}_3(\text{H}_2\text{O})]^-$ species (not shown) also exhibited a similar evolution as described above for the $[\text{CuCl}_4]^{2-}$ species. This result is not surprising, since H_2O and Cl coordinated to a transition metal often have a similar bond distance [42], resulting in analogous XANES spectral features and making it difficult to distinguish between $\text{Cu}^{2+}\text{-H}_2\text{O}$ and $\text{Cu}^{2+}\text{-Cl}^-$ interactions from the XANES data only. In the next section, the EXAFS refinement is used to further clarify these points.

3.3. EXAFS refinement

EXAFS spectra are sensitive to the coordination environment of the central atom,

such as type and number of bonds of the neighboring atom and their distances. EXAFS spectra analysis is used to provide confirmation of the speciation model derived from the XANES data and to further characterize changes in Cu(II) complexing with salinity. Nevertheless, for most solutions containing at least 2 species with different geometries, the refinements of EXAFS spectra often have an unstable solution due to under determination of structural parameters [16, 43]. Ultimately, we only addressed the EXAFS spectra of the two end-member solutions, i.e., Cu^{2+} in the lowest and highest Cl^- concentration solutions, where one species is predominant.

For the first end-member solution with $0.5 \text{ mol}\cdot\text{kg}^{-1} \text{ Cl}^-$, the fully hydrated Cu^{2+} complex is the preponderant species with only a small fraction (less than 10%, see Fig. 1) of Cl coordinated to Cu. The result from the *ab initio* XANES simulation in section 3.2.1 suggested that hydrated Cu^{2+} has an elongated square-pyramidal geometry, which is chosen as the original model unit to fit the EXAFS spectrum. The theoretical fitting in k^3 -weight and R-space spectra with the experimental spectra are displayed in Fig. 7 and the extracted results are compiled in Table 2. The distance of the four Cu- O_{eq} (equatorial plane) bonds, $1.956 (\pm 0.003) \text{ \AA}$, agrees with that of previous studies [32]. However, the Cu- O_{ax} distance of $2.40 (\pm 0.03) \text{ \AA}$ is slightly longer than that obtained previously [32, 39, 44], where the authors refined an axial bond distance of 2.35-2.37 $\text{\AA}$ for the $[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$ complex from the pure $\text{Cu}(\text{ClO}_4)_2$ dilute solution, indicating that the bond is possibly perturbed by the small fraction of Cl^- ions. In addition, the obtained Debye-Waller factors of 0.005 for Cu- O_{eq} (axis direction) and 0.037 for Cu- O_{ax} are also close to previously reported values [39]. Using the square planar $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and octahedral $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ structures as the initial model to fit the experimental EXAFS spectrum, the refined statistical errors (χ^2 , 112.3 and 112.4,

respectively) are significantly larger than that obtained from five-coordinated $[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$ complexes (71.7). Hence, the EXAFS refinement agrees with the *ab initio* XANES calculation favoring the five-coordinate structure over the other structures.

The XANES analysis suggested that species with tetrahedral features are dominant in high salinity Cu-containing solution. However, the calculated XANES spectra of the $[\text{CuCl}_4]$ and $[\text{CuCl}_3\text{O}]$ model units as a function of angle α , as well as the trigonal bipyramid $[\text{CuCl}_4\text{O}]$ model, exhibited small differences. Therefore, the spectrum was fitted with these structures. The results are collected in Table 2. Using the $[\text{CuCl}_4]$ unit extracted from the DFT calculation, the fitted average Cu-Cl distance is $2.252 (\pm 0.004) \text{ \AA}$ but with a larger statistical error ($\chi^2 = 307.8$). Upon replacement of Cl by O in the distorted $[\text{CuCl}_4]$ unit, the fit error reduces to 162.5, and finally, the model with 1.32 O ligands and 2.68 Cl ligands is obtained when the sum of the coordination number around Cu(II) is fixed to 4. Varying the number of Cl ligands but fixing the number of O ligands to 1.0, the fitted result shows that the number of Cl ligands is 2.64 with an almost insignificant change in the error ($\chi^2 = 167.2$). We also attempted to use the trigonal bipyramid $[\text{CuCl}_4\text{O}]$ and octahedron $[\text{CuCl}_4\text{O}_2]$ model units as the initial structures to fit the spectra, and the obtained errors are also satisfactory, with χ^2 of 191.8 and 126.8, respectively. Nevertheless, attempting to mix the regular tetrahedron and square planar $[\text{CuCl}_4]$ as model units to fit the EXAFS spectrum, we obtain the lowest statistical error of 93.8 with the final model of 54% square planar + 46% regular tetrahedron, which corresponds to a squashed tetrahedral shape with $\alpha \sim 16^\circ$ and an average Cu-Cl distance of $2.24 (\pm 0.02) \text{ \AA}$. These structural parameters of $[\text{CuCl}_4]$ agree with those of the *ab initio* XANES calculation very well. Although the fitting error of the $[\text{CuCl}_3\text{O}]$ model is also good, as studied by the recent

molecular dynamics simulation [41], where the $[\text{CuCl}_3(\text{H}_2\text{O})]^-$ species is tracked in a 16.32 mol·kg⁻¹ Cl⁻ solution, the $[\text{CuCl}_4]^{2-}$ species with a squashed tetrahedral shape is considered predominant while the $[\text{CuCl}_3(\text{H}_2\text{O})]^-$ species is minor, based on our *ab initio* XANES calculation and EXAFS analysis.

4. Conclusions

The speciation and structure of Cu²⁺ in chloride-containing solutions have been explored at room temperature using synchrotron X-ray absorption spectroscopy. In parallel, *ab initio* XANES calculations of the Cu K-edge XANES spectra of Cu(II) aqua ion and Cu(II)-Cl complexes, considering different structures proposed in the literature or adjusted manually, have been performed. In the lowest Cl⁻ concentration solution, XANES calculations using four-, five- and six-coordinate structures with different distortion degrees suggest that the five-coordinate $[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$ complex is predominant relative to the other two structures, which is consistent with the EXAFS refinement using a CuO₅ model which led the smallest statistical error. By manually adjusting the $[\text{CuCl}_4]^{2-}$ geometry, the features of the calculated XANES spectrum using the squashed tetrahedral $[\text{CuCl}_4]^{2-}$ with an average Cu-Cl bond distance of 2.25 Å and a distortion degree α of ~18° are in close agreement with the experimental spectrum of Cu(II) in the highest Cl-containing solution. This result is also supported by the EXAFS analysis with the mixed model of regular tetrahedron and square planar. The *ab initio* XANES spectrum obtained using trigonal bipyramid $[\text{CuCl}_5]^{3-}$ deviates considerably from experiment and thus this species is eliminated. When using the distorted tetrahedral $[\text{CuCl}_3(\text{H}_2\text{O})]^-$ and trigonal bipyramid $[\text{CuCl}_4(\text{H}_2\text{O})]^{2-}$, spectra analogous to the $[\text{CuCl}_4]^{2-}$ model are obtained. However, these species are considered to be minor in the ~16 mol·kg⁻¹ Cl⁻ solution due to having larger statistical errors than that of $[\text{CuCl}_4]^{2-}$ in the corresponding EXAFS refinements.

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Captions:

Fig. 1 Concentration distribution of individual Cu(II)-chloride species in LiCl solutions at room temperature. Data are re-calculated by BeerOz software [7] using the parameters from ref. [3].

Fig. 2 The Cu K-edge XNAES spectra: a. Cu(II) in 0.55-15.96 mol·kg⁻¹ Cl⁻ solutions at room temperature (Details with enlarged scale are shown in the insets for clarity); b. Cu(II) in 14.97 and 15.96 mol·kg⁻¹ Cl⁻ solutions at room temperature; c. Two solid standards, whose spectra data are extracted from ref. [36] (The gray, green, red and white atoms are Cu, Cl, O and H, respectively).

Fig. 3 Spectral evolution of Cu(II) complexes as a function of salinity: a. Fourier transform EXAFS R-space spectra; b. EXAFS oscillations in *q*-space. The dotted line is the position of Cu-O and Cu-Cl peaks.

Scheme 1 Possible structural configuration of [Cu(H₂O)_{*n*}]²⁺ (*n* = 4, 5 and 6) species. The gray, red and white atoms refer to the Cu, O and H, respectively.

Fig. 4 Experimental XANES spectrum of the end-member complex present at the lowest concentration Cl⁻ solution, compared to the calculated raw and convoluted spectra of octahedral (c), square planar (a), tetrahedral (a) and square pyramidal (b) complexes.

Scheme 2 Distorted tetrahedral [CuCl₄]²⁻ complexes. The gray and green atoms are Cu and Cl, respectively.

Fig. 5 Experimental XANES spectrum of the end-member complex present at the highest Cl⁻ concentration solution, compared to the calculated raw and convoluted spectra of DFT optimized [CuCl₄] configuration and the regular tetrahedral one (*R*_{Cu-Cl} = 2.25 Å), respectively.

Fig. 6 Experimental XANES spectrum of the end-member complex present at the highest concentration Cl⁻ solution compared with the calculated spectra: (a) The raw spectra calculated as a function of *α*; (b) The calculated spectra using different geometry.

Fig. 7 Cu K-edge *k*³-weighted EXAFS spectra (*left*) and the amplitude of Fourier transforms (*right*) for the sample solutions with 0.55 and 16.0 mol·kg⁻¹ Cl⁻ solution. The solid lines represent experimental values and the dashed lines are fitted spectra. The dotted line is the position of Cu-O and Cu-Cl peaks.

Table 1 Composition of Cu(II) solutions for XAS measurement.

Table 2 Cu(II) K-edge EXAFS parameters refined from the experimental data (Cu²⁺ in 0.55 and 16.0 mol·kg⁻¹ Cl⁻ solutions) using different speciation and structural models.

602 Figures:

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Fig. 1

Fig. 2

Fig. 3

Scheme 1

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Fig. 4

Scheme 2

Fig. 5

Fig. 6

Fig. 7

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Tables:

Table 1

Sample no.	Cu _{tot} (mol·kg ⁻¹)	Cl _{tot} (mol·kg ⁻¹)	Cl/Cu ratio	Ion strength
S1	0.0089	0.5494	61.73	0.5575
S2	0.0238	4.071	171.1	4.093
S3	0.0101	6.001	594.2	6.021
S4	0.0439	7.173	163.4	7.213
S5	0.0499	11.11	222.7	11.16
S6	0.0874	14.97	171.3	15.05
S7	0.0841	15.96	189.8	16.04

Table 2

Sample no.	$\Delta E_0(\text{eV})$	Cu-O interaction			Cu-Cl interaction			k-range	R-range	R-factor	χ^2
		N_{O}	$R_{\text{Cu-O}}(\text{\AA})$	$\sigma_{\text{O}}^2 \times 10^3(\text{\AA}^2)$	N_{Cl}	$R_{\text{Cu-Cl}}(\text{\AA})$	$\sigma_{\text{Cl}}^2 \times 10^3(\text{\AA}^2)$				
S1	-2.43(0.61)	4.0 ^{a,‡}	1.956(0.003)	5.0(0.24)	-	-	-	2-11	1-5	0.0091	71.7
		1.0 ^{a,‡‡}	2.40(0.03)	37.3(24)							
S1 ^{&}	-2.31(0.60)	4.0 ^a	1.962(0.004)	5.1(0.3)	-	-	-	2-11	1-5	0.014	112.3
		4.0 ^{a,‡}	1.951(0.004)	5.2(0.3)							
S1 ^{&&}	-3.70(0.86)	2.0 ^{a,‡‡}	2.51(0.05)	32.4(13)	-	-	-	2-11	1-5	0.014	112.4
S7 [*]	4.78(1.06)	1.0 ^a	2.14(0.06)	6.4(14.6)	4.0 ^a	2.264(0.005)	7.2(1.8)	2-11	1-5	0.011	191.8
S7 [*]	6.56(0.92)	1.0 ^a	2.03(0.02)	0.48(2.7)	2.64(0.43)	2.282(0.009)	4.2(1.7)	2-11	1-5	0.0094	167.2
S7 [*]	7.24(1.95)	1.32 ^b (0.51)	2.06(0.02)	2.9(1.5)	2.68 ^b (0.51)	2.28(0.01)	5.0(0.9)	2-11	1-5	0.0091	162.5
S7 [*]	7.00(1.53)	1.70 ^c (0.41)	2.11(0.01)	6.9(4.3)	3.30 ^c (0.41)	2.269(0.008)	6.7(1.1)	2-11	1-5	0.0083	147.4
S7 [*]	6.65(1.10)	2.11 ^d (0.39)	2.16(0.02)	9.5(11.7)	3.89 ^d (0.39)	2.26(0.01)	7.1(1.6)	2-11	1-5	0.0071	126.8
S7 ^{**}	2.14(0.64)	-	-	-	4.0 ^a	2.252(0.004)	6.6(0.3)	2-11	1-5	0.017	307.8
S7 ^{***}	-7.80(2.69)	-	-	-	4.0 ^a (Td)	2.18(0.02)	6.5(0.9)	2-11	1-5	0.0053	93.8
frac = 0.54	8.35(1.36)	-	-	-	4.0 ^a (SP)	2.29(0.01)	4.8(0.8)				

^a Values are fixed during refinements.^b Sum of number of O and Cl fixed to be equal to 4.^c Sum of number of O and Cl fixed to be equal to 5.^d Sum of number of O and Cl fixed to be equal to 6.[‡] Apical position of square planar.^{‡‡} Axial position.[&] Model unit: square planar.^{&&} Model unit: distorted octahedron.^{*} Model unit: manually adjusted geometry.^{**} Model unit: distorted tetrahedron (DFT opt.).^{***} Model unit: Regular tetrahedron $\times$ (1-frac) + Square planar $\times$ (frac).