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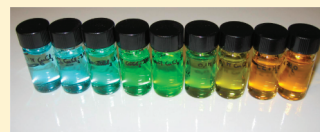
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Speciation of Copper(II) Complexes in an Ionic Liquid Based on Choline Chloride and in Choline Chloride/Water Mixtures

Peter De Vreese,[†] Neil R. Brooks,[‡] Kristof Van Hecke,^{‡,§} Luc Van Meervelt,[‡] Edward Matthijs,[†] Koen Binnemans,^{*,‡} and Rik Van Deun^{*,§}[†]Department of Industrial Engineering, Katholieke Hogeschool Sint-Lieven, Gebroeders Desmetstraat 1, B-9000 Gent, Belgium[‡]Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F P.O. Box 2404, B-3001 Heverlee, Belgium[§]Department of Inorganic and Physical Chemistry, Universiteit Gent, Krijgslaan 281 - Building S3, B-9000 Gent, Belgium

S Supporting Information

ABSTRACT: A deep-eutectic solvent with the properties of an ionic liquid is formed when choline chloride is mixed with copper(II) chloride dihydrate in a 1:2 molar ratio. EXAFS and UV–vis–near-IR optical absorption spectroscopy have been used to compare the coordination sphere of the cupric ion in this ionic liquid with that of the cupric ion in solutions of 0.1 M of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in solvents with varying molar ratios of choline chloride and water. The EXAFS data show that species with three chloride ions and one water molecule coordinated to the cupric ion as well as species with two chloride molecules and two water molecules coordinated to the cupric ion are present in the ionic liquid. On the other hand, a fully hydrated copper(II) ion is formed in an aqueous solution free of choline chloride, and the tetrachlorocuprate(II) complex forms in aqueous choline chloride solutions with more than 50 wt % of choline chloride. In solutions with between 0 and 50 wt % of choline chloride, mixed chloro–aquo complexes occur. Upon standing at room temperature, crystals of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and of $\text{Cu}(\text{choline})\text{Cl}_3$ formed in the ionic liquid. $\text{Cu}(\text{choline})\text{Cl}_3$ is the first example of a choline cation coordinating to a transition-metal ion. Crystals of $[\text{choline}]_3[\text{CuCl}_4][\text{Cl}]$ and of $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$ were also synthesized from molecular or ionic liquid solvents, and their crystal structures were determined.



■ INTRODUCTION

Choline chloride is a crystalline solid with a melting point of 302 °C, but it can form low-melting eutectic mixtures with hydrogen donor compounds (e.g., urea, acetamide, malonic acid, citric acid, ethylene glycol, ...).^{1–3} For instance, a mixture of choline chloride and urea in a 1:2 molar ratio has a freezing point of 12 °C. Such mixtures are often called *deep-eutectic solvents* or *eutectic-based ionic liquids*. The classification of these mixtures as ionic liquids is debated, because they partially contain neutral molecules (albeit strongly associated with the chloride ions). However, these solvents have properties that are very reminiscent of those of genuine ionic liquids.⁴ In this respect, the deep-eutectic solvents are comparable with the acidic chloroaluminate ionic liquids that contain an excess of molecular AlCl_3 .⁵ The choline-based ionic liquids have been used as electrolytes for the electrodeposition of metals,^{6,7} as media for the synthesis of inorganic materials,^{8,9} or as solvents for organic reactions.^{10,11} They can solubilize many different metal salts or metal oxides.^{12–15} Mixtures of choline chloride with some metal chlorides, e.g. ZnCl_2 and SnCl_2 , can be liquid at room temperature.^{16–18} The number of metal chlorides that can be used to form such ionic liquids is limited, and the metal chlorides need to be strong Lewis acids, which can form complexes with the Lewis basic chloride ions. On the other hand, choline chloride is able to generate ionic liquids upon mixing with a variety of hydrated metal chloride salts, such as $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$.^{19,20} An ionic liquid is formed when choline chloride is mixed with copper(II)

chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) in a 1:2 molar ratio. Copper-containing deep-eutectic ionic liquids are of interest for the electrodeposition of copper or its alloys.^{21–23} A recent paper on the coordination environment of copper(II) ions in mixtures of the ionic liquid 1-ethyl-3-methylimidazolium chloride and water shows that different types of copper(II) complexes are formed depending on the molar ratio of the chloride ionic liquid.²⁴

This paper reports on the coordination chemistry of copper in the ionic liquid based on choline chloride and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. EXAFS (extended X-ray absorption fine structure) and UV–vis absorption spectroscopy have been used to probe the environment of the cupric ion in this medium. The results are compared with the chemistry of copper in 0.1 M solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in solvent mixtures of water and choline chloride in different molar ratios. It will be shown that a gradual change from the hexaaquacopper(II) complex to the tetrachlorocuprate(II) complex occurs with increasing choline chloride concentration. The choline chloride/ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ionic liquid represents an intermediate case with coordination of both chloro and aqua ligands to the cupric ion.

■ EXPERIMENTAL SECTION

Preparation of Samples. Choline chloride (99%) was purchased from Acros Organics, and copper(II) chloride dihydrate, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (extra pure), was obtained from Merck. The chemicals were used as received, without further purification. The ionic liquid choline

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bis(trifluoromethylsulfonyl)imide was prepared according to a literature procedure.²⁵ A 1:2 molar mixture of choline chloride and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was prepared by mixing the appropriate amounts at 70 °C until a dark solution was obtained. Diffraction-quality crystals of $\text{Cu}(\text{choline})\text{Cl}_3$ were formed in the ionic liquid after a couple of days. Diffraction-quality crystals of $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$ were formed in the ionic liquid exposed to air after a period of a couple of days. The concentration of Cu^{2+} in this ionic liquid was calculated to be 4.5 mol L^{-1} . A series of choline chloride/water mixtures (27, 39, 49, 62, 73, 84, 95, and 100 wt % of water) was prepared by dissolving choline chloride in Millipore water. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was weighed for each solution so that a final concentration of 0.1 mol L^{-1} of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was obtained.

$[\text{choline}]_3[\text{CuCl}_4][\text{Cl}]$ was synthesized in bulk by the following method: choline bis(trifluoromethylsulfonyl)imide (1.880 g, 5.57 mmol) and choline chloride (0.595 g, 4.26 mmol) were heated together to 70 °C, and then copper(II) bis(trifluoromethylsulfonyl)imide tetrahydrate (0.297 g, 0.426 mmol) was added and the mixture stirred for 10 min and then allowed to cool to room temperature. Ethanol (10 mL) was added and the solid removed by filtration, washed with ethanol (10 mL), and dried in vacuo to give $[\text{choline}]_3[\text{CuCl}_4][\text{Cl}]$ (0.218 g, 0.394 mmol, 92.4%). Mp: 76 °C. Anal. Found: C, 32.8; H, 7.0; N, 7.3. Calcd for $\text{C}_{15}\text{H}_{42}\text{Cl}_5\text{CuN}_3\text{O}_3$: C, 32.6; H, 7.6; N, 7.6. IR: ν/cm^{-1} 3027, 2963, 1633, 1476, 1417, 1350, 1281, 1236, 1202, 1134, 1082, 1052, 1005, 952, 925, 865. Diffraction-quality crystals of $[\text{choline}]_3[\text{CuCl}_4][\text{Cl}]$ were grown by layering a solution of $[\text{choline}][\text{Cl}]$ in ethanol on top of a solution of $\text{Cu}(\text{Tf}_2\text{N})_2$ in the ionic liquid $[\text{choline}][\text{Tf}_2\text{N}]$ and allowing the two solutions to diffuse together over the period of a couple of days.

Spectroscopic Measurements. UV–vis–near-IR optical absorption spectra were measured on a Cary Varian 5000 spectrophotometer, controlled by Cary WinUV Scan Application software version 3.00. Measurements were taken from 1500 to 250 nm in 1 mm and 0.01 mm quartz cuvettes (suprasil) at a scan speed of 300 nm/min with a spectral bandwidth of 2 nm.

EXAFS. EXAFS measurements were carried out either in transmission or fluorescence mode using a Si(111) double crystal monochromator on the Dutch–Belgian Beamline (DUBBLE, BM26 A) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France).^{26,27} Higher harmonics were rejected by Si mirrors (suppression factor about 1000). The copper K-edge spectra were collected using Oxford Instruments ionization chambers, filled with a gas mixture containing N_2 (70%)/He (30%) for the first ionization chamber at a pressure of 1 bar and Ar (12%)/He (88%) for the second ionization chamber at the same pressure.

Data were collected in equidistant k steps of 0.05 \AA^{-1} up to $k = 15 \text{ \AA}^{-1}$. A copper metal foil (first inflection point at 8979 eV) was used for energy calibration. EXAFS data extraction and data fitting was performed using the program EXAFSPAK²⁸ and the Artemis suite.²⁹ Theoretical phase and amplitude functions were calculated using FEFF 8.2 using the crystal structures of copper(II) chloride dihydrate³⁰ and copper(II) perchlorate hexahydrate.³¹ Polyethylene sample holders with a path length of 8 mm were used for liquid samples. Solid samples were mixed with boron nitride and pressed into a pellet with approximately 1 mm of thickness. For the highly concentrated ionic liquid sample (4.5 M $\text{Cu}(\text{II})$), a homemade brass sample holder with Kapton windows was used, in which the path length could be varied by using Teflon spacers with variable thicknesses.

Standard deviations on the fitted parameters are given in parentheses. However, it should be noted that these values can by no means be considered as the real errors on the obtained values, as also other errors have to be taken into account, such as systematic errors and correlation effects, which are much more difficult to estimate. This means that the real errors can be considerably larger than this standard deviation (which only indicates how much the parameters can vary without degrading the quality of the fit). General errors on coordination numbers of single shells are estimated to be on the order of 10–15%, and for closely spaced, highly correlated shells such as the Cu–O and Cu–Cl shells in the mixed water/chloride samples, this error can be as large as 25%. This means that a reported

coordination number of 3.58(9) can, from the point of view of an experienced EXAFS user, be easily interpreted as a 4-fold coordination, even though the actual standard deviation on the value is much lower. Errors in distances are usually quite small, usually on the order of $\pm 0.01 \text{ \AA}$, as this is something that EXAFS can determine very accurately. Debye–Waller factors σ^2 are strongly correlated with the coordination number in the EXAFS formula; therefore, errors on the Debye–Waller factors can also range between 10 and 25%. A more general idea of the goodness of the fit is given by the “weighted F factor”, a parameter generated by the EXAFSPAK software package, representing χ^2 weighted by the magnitude of the data and typically lying between 0.30 and 0.10 for a reasonable to good fit.

Electrochemical Measurements. Voltammograms were recorded on an Autolab PGSTAT12 potentiostat (Ecochemie) controlled by NOVA 1.5 software, which was also used to process the data. Prior to each experiment, samples were deaerated by purging for 5 min with nitrogen gas. A three-electrode setup was used. A platinum-disk electrode (diameter 1 mm) was polished subsequently with 15 and 3 μm diamond slurry and 0.05 μm alumina (Buehler) on a polishing cloth (BASi). Afterward, the electrode was rinsed with Millipore water and ethanol and subsequently dried. A reference electrode with 0.010 mol L^{-1} AgNO_3 (“Pur”, Merck) and 0.100 mol L^{-1} Kryptofix22 (>99%, Merck) in acetonitrile (for HPLC, Acros Organics) was used in a BASi nonaqueous reference kit. The counter electrode was a DSA titanium grid coated with $\text{IrO}_2/\text{RuO}_2$ (Magnet Special Anodes BV). All measurements were performed at 25.0 ± 0.1 °C controlled by a thermostatic bath (rms Lauda).

Crystallography. Crystals of $[\text{choline}][\text{CuCl}_4][\text{Cl}]$, $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$, and $\text{Cu}(\text{choline})\text{Cl}_3$ suitable for single-crystal X-ray diffraction, were mounted on a nylon loop attached to a copper pin and placed in the cold nitrogen gas stream of a Bruker SMART 6000 diffractometer at 100(2) K using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Absorption corrections were applied by using SADABS.³² All structures were solved by using direct methods and refined by the full-matrix least-squares procedure in SHELXL.³³ The program OLEX2 was also used in refinement and making pictures.³⁴ H atoms on carbon atoms were placed in calculated positions or, for CH_3 groups, placed on the basis of the difference electron density around the CH_3 group and refined using a riding model. For all structures the H atoms of O–H were found in the difference map and were allowed to freely refine in $\text{Cu}(\text{choline})\text{Cl}_3$ and $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$, while in $[\text{choline}]_3[\text{CuCl}_4][\text{Cl}]$ the O–H distances were fixed to 0.84 \AA . The thermal parameters were linked to parent O atoms. In the structure of $[\text{choline}]_3[\text{CuCl}_4][\text{Cl}]$ there was space group ambiguity between $Pnma$ and $Pna2_1$, which are indistinguishable on the basis of systematic absences, and disorder of one of the choline cations and of one of the Cl atoms. In space group $Pnma$ a choline cation is disordered over a mirror plane, which is a symmetry it does not possess. Attempts to model this disorder were unsuccessful, and the R value remained over 10%, with several high residual difference electron density peaks. The disorder could be modeled to a reasonable standard in space group $Pna2_1$, but it was felt that the space group $Pnma$ was the true representation of the structure; therefore, $Pnma$ was chosen and the difference electron density related to the disordered choline was removed using the SQUEEZE function in the Platon software.³⁵ One of the Cl atoms in the CuCl_4 anion was also disordered, with the greater disorder part equaling 87.6(6) % of the total occupancy. In the structure of $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$, the oxygen atom on one choline cation is disordered. After studying difference electron density maps and checking the diffraction pattern for missed symmetry, it could be seen this was a dynamic disorder, and this disorder was treated by refining the atom in two positions. Restraints were applied to keep the C–O bond lengths and the thermal parameters the same in the two disorder parts. CCDC 872005–872007 contain supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K., fax +44-1223-336033, or e-mail deposit@ccdc.cam.ac.uk).

Crystal Data for $[\text{choline}]_3[\text{CuCl}_4][\text{Cl}]$: $\text{C}_{15}\text{H}_{42}\text{Cl}_5\text{CuN}_3\text{O}_3$, $M_r = 553.31$, orthorhombic, $a = 18.0697(8) \text{ \AA}$, $b = 12.2968(6) \text{ \AA}$, $c =$



Figure 1. Color changes of Cu^{2+} solutions (0.1 mol L^{-1}) in choline chloride/water mixtures with varying water content. The water content decreases from 100 wt % at the left (blue sample) to 27 wt % at the right (yellow sample).

11.5544(8) Å, $V = 2567.4(2) \text{ Å}^3$, $T = 100(2) \text{ K}$, space group $Pnma$ (No. 62), $Z = 4$, $\mu(\text{Cu K}\alpha) = 6.151 \text{ mm}^{-1}$, 20 425 reflections measured, 2339 unique ($R_{\text{int}} = 0.0774$), which were used in all calculations. The final R indexes ($I \geq 2\sigma(I)$) were $R1 = 0.0569$ and $wR2 = 0.1315$ and on all data were $R1 = 0.0634$ and $wR2 = 0.1351$.

Crystal Data for $\text{Cu}(\text{choline})\text{Cl}_3$: $\text{C}_5\text{H}_{14}\text{Cl}_3\text{CuNO}$, $M_r = 274.06$, monoclinic, $a = 7.9847(4) \text{ Å}$, $b = 7.8230(4) \text{ Å}$, $c = 16.5567(7) \text{ Å}$, $\beta = 90.829(3)^\circ$, $V = 1034.10(9) \text{ Å}^3$, $T = 100(2) \text{ K}$, space group Pc (No. 7), $Z = 4$, $\mu(\text{Cu K}\alpha) = 9.719 \text{ mm}^{-1}$, 13 501 reflections measured, 3900 unique ($R_{\text{int}} = 0.0623$), which were used in all calculations. The final R indexes ($I \geq 2\sigma(I)$) were $R1 = 0.0357$ and $wR2 = 0.0741$ and on all data were $R1 = 0.0376$ and $wR2 = 0.0749$.

Crystal Data for $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$: $\text{C}_{20}\text{H}_{56}\text{Cl}_{10}\text{Cu}_4\text{N}_4\text{O}_5$, $M_r = 1041.39$, monoclinic, $a = 22.4693(12) \text{ Å}$, $b = 10.2874(6) \text{ Å}$, $c = 18.5663(11) \text{ Å}$, $\beta = 113.551(3)^\circ$, $V = 3934.1(4) \text{ Å}^3$, $T = 100(2) \text{ K}$, space group $C2/c$ (No. 15), $Z = 4$, $\mu(\text{Cu K}\alpha) = 8.981 \text{ mm}^{-1}$, 13 421 reflections measured, 3463 unique ($R_{\text{int}} = 0.1164$), which were used in all calculations. The final R indexes ($I \geq 2\sigma(I)$) were $R1 = 0.0658$ and $wR2 = 0.1716$ and on all data were $R1 = 0.0805$ and $wR2 = 0.1821$.

RESULTS AND DISCUSSION

Absorption Spectroscopy. The color of the aqueous Cu^{2+} solutions (concentration 0.1 mol L^{-1}) changed gradually from pale blue, over green and greenish yellow to yellow with increasing concentrations of choline chloride (Figure 1). The blue color is indicative for the fully hydrated Cu^{2+} ion and the yellow color for the $[\text{CuCl}_4]^{2-}$ ion, whereas the intermediate yellowish green and green colors point to a mixed chloro-aquo complex or to a mixture of different complexes. The choline chloride– $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ionic liquid has a very dark green-brown color, due to the much higher Cu^{2+} concentration (4.5 mol L^{-1}) compared to the aqueous solutions (0.1 mol L^{-1}). The green-brown color gives an indication that mixed chloro copper complexes are present in the ionic liquid, rather than the tetrachlorocuprate(II) complex, $[\text{CuCl}_4]^{2-}$.

In order to get more quantitative information on the optical properties of the solutions, UV–vis–near-IR absorption spectra were recorded (Figures 2–4). The absorption spectra consist of two parts. In the ultraviolet–visible region between 200 and 500 nm, intense charge-transfer bands can be observed, whereas the weaker d–d ligand-field transition (of the d^9 electronic configuration of Cu^{2+}) is absorbing in the red and near-infrared region between 600 and 1400 nm.³⁶ The tail of the broad d–d transition extends to wavelengths longer than 1400 nm, but it cannot be measured due to overlap with the very intense overtones of the OH vibrations of water. The intense charge-transfer transitions are more sensitive to changes in the local environment of the copper(II) ion than is the d–d transition. The charge-transfer transitions of the choline chloride $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ionic liquid could not be measured,

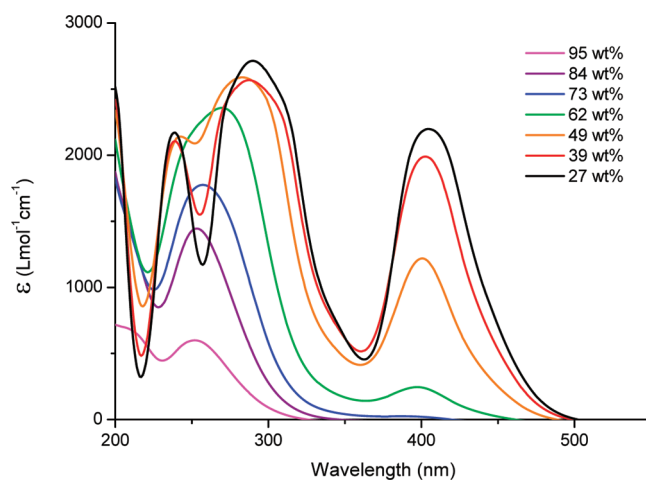


Figure 2. UV–vis absorption spectra of a 0.1 mol L^{-1} solution of Cu^{2+} in solvent mixtures of choline chloride and water (compositions expressed in wt % of H_2O).

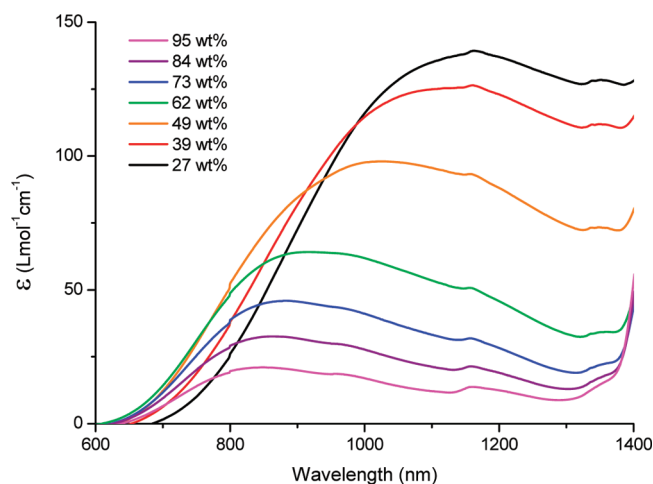


Figure 3. Near-IR absorption spectra of a 0.1 mol L^{-1} solution of Cu^{2+} in solvent mixtures of choline chloride and water (compositions expressed in wt % of H_2O).

because the light absorption was too strong, even when a cuvette with a path length of only 0.01 mm was used. Dilution of the sample was not an option, because the copper(II) ion is an integral part of the ionic liquid and dilution with a solvent would change the speciation.

In the sample with 27 wt % of water, three maxima are observed in the UV–vis part of the absorption spectrum: at 405

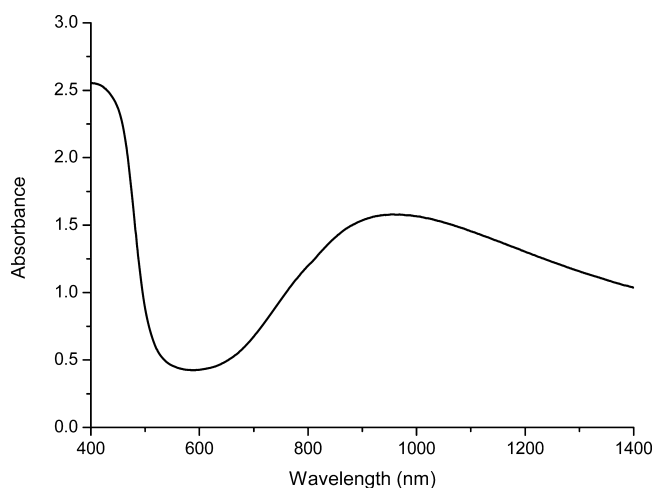


Figure 4. UV-vis-near-IR absorption spectrum of the ionic liquid choline chloride- $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1:2 molar ratio) at room temperature. Because the spectrum has been measured on a thin liquid film with a large uncertainty in the optical path length, the spectrum is displayed in absorbance values instead of molar absorptivities.

nm ($\epsilon = 2200 \text{ L mol}^{-1} \text{ cm}^{-1}$), 291 nm ($\epsilon = 3000 \text{ L mol}^{-1} \text{ cm}^{-1}$), and 231 nm ($\epsilon = 2150 \text{ L mol}^{-1} \text{ cm}^{-1}$). Comparison of this spectrum with that of CuCl_2 dissolved in 1-ethyl-3-methylimidazolium chloride/water mixtures²⁴ shows that the nature of the organic cation has a marked influence on the relative intensities of the charge-transfer bands. With increasing water content, the absorption maximum at 405 nm gradually shifts to the blue and decreases in intensity, whereas the absorption maxima at 291 and 231 nm move closer together and finally merge into a single peak at 257 nm (when the water content of the sample is increased to 73 wt %). A further increase of the water content leads to a small blue shift of this absorption band and a sharp increase in intensity. In the sample with 100 wt % of water, this absorption band is located at 250 nm ($\epsilon = 600 \text{ L mol}^{-1} \text{ cm}^{-1}$). The absorption band at 405 nm can be attributed to the $[\text{CuCl}_4]^{2-}$ complex.^{24,37} Because light is absorbed in the blue spectral region, this absorption band is responsible for the typical yellow color of $[\text{CuCl}_4]^{2-}$ solutions. The gradual disappearance of this peak with increasing water content means that the concentration of the $[\text{CuCl}_4]^{2-}$ species gradually decreases until eventually no $[\text{CuCl}_4]^{2-}$ species are left in solution. The absorption peak at 250 nm in the 100 wt % water sample is indicative of the fully hydrated Cu^{2+} ion.

The d-d transition is much broader than the charge-transfer bands and has an ill-defined maximum. The general trend is that the intensity of the transition decreases and its maximum shifts to shorter wavelengths upon increasing the water content of the choline chloride/water mixtures. For the mixture with 27 wt % of water, the maximum is at 1162 nm ($\epsilon = 140 \text{ L mol}^{-1} \text{ cm}^{-1}$), whereas for the mixture with 100 wt % of water, the maximum is at 837 nm ($\epsilon = 15 \text{ L mol}^{-1} \text{ cm}^{-1}$). This large difference in intensity can be attributed to the fact that the first coordination sphere of the Cu^{2+} ion has no inversion center in the former case (high intensity), whereas it has an inversion center in the latter case (low intensity). These data are consistent with the occurrence of the tetrahedral $[\text{CuCl}_4]^{2-}$ complex in the solutions with a low water content. The d-d transition of the choline chloride- $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ionic liquid has a maximum at 957 nm, which is between the values of the choline chloride/water mixtures with 49 wt % of water (1024

nm) and 62 wt % of water (914 nm). The intensity of the transition is more difficult to determine accurately, because of the large uncertainty in the path length of the 0.01 mm cuvette (30%).

EXAFS Measurements. The copper-containing ionic liquid and the 0.1 mol L^{-1} $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solutions in the solvent systems consisting of varying amounts of choline chloride and water have been studied by EXAFS (extended X-ray absorption fine structure) spectroscopy, in order to determine the number and nature of the atoms in the first coordination sphere of the cupric ion and to determine the atomic distances. In a first step, as a reference, solid $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was mixed with boron nitride (BN), pressed into a pellet, and investigated with Cu K-edge EXAFS spectroscopy. The crystal structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is well-known,³⁰ consisting of two equatorial water molecules at a distance of 1.94 Å and two equatorial chloride ions at a distance of 2.28 Å from the copper(II) ion. There are also two axial chloride ions at 2.93 Å, which belong to a neighboring copper(II) chloride dihydrate entity. The EXAFS spectrum and corresponding Fourier transform signal are shown in Figure 5.

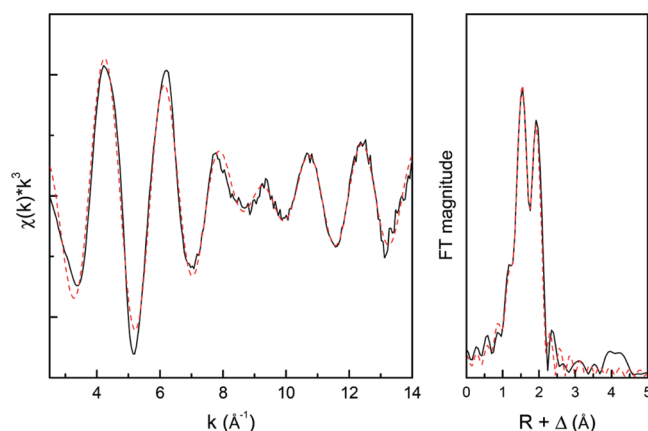


Figure 5. EXAFS spectrum (left) and corresponding Fourier transform (right) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ powder diluted with boron nitride.

Two oxygen atoms (water ligands) at 1.94 Å from the cupric ion, as well as two chloride ions at 2.27 Å, were detected in the EXAFS spectrum. These values correspond very well with the distances observed in the crystal structure. The axial chloride ions could not be observed. The signal at about $R + \Delta = 4 \text{ Å}$ is due to multiple scattering effects and was not included in the fit. The EXAFS structural parameters for solid $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ are summarized in Table 1. Because the coordination numbers are known from the crystal structure, these were fixed during the shell-fitting procedure. The resulting scale factor of 0.815 was taken as fixed in the shell fittings of all the following samples. In a second step, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in water to yield a 0.1

Table 1. EXAFS Structural Parameters for Solid $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and a 0.1 mol L^{-1} Solution in Water

| sample | scattering path | R (Å) | N | σ^2 (Å ²) |
|---|--------------------|----------|----------------|------------------------------|
| solid $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ | Cu-OH ₂ | 1.942(2) | 2 ^a | 0.0026(1) |
| | Cu-Cl | 2.266(2) | 2 ^a | 0.0055(2) |
| $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in H_2O (0.1 mol L^{-1}) ^b | Cu-OH ₂ | 1.953(1) | 4.00(7) | 0.0049(1) |

^aValue fixed during shell-fitting procedure. $\Delta E = 4.2(2) \text{ eV}$. Weighted *F* factor = 0.17. ^b $\Delta E = 0.7(2) \text{ eV}$. Weighted *F* factor = 0.15.

M solution. As there is a very large excess of water molecules compared to chloride ions, it is reasonable to assume that the cupric ion in this solution is completely coordinated by water molecules. Taking the crystal structure of copper(II) perchlorate hexahydrate as a reference,³¹ this would mean that four water molecules are coordinating equatorially, at a distance of 1.95 Å, and two additional water molecules are coordinating axially, at a longer distance (due to a Jahn–Teller distortion) of 2.38 Å. The EXAFS spectrum of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution (0.1 mol L⁻¹) is shown in Figure 6. From this EXAFS

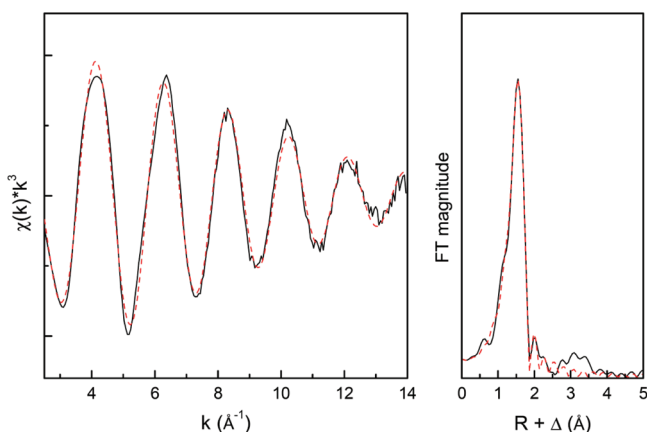


Figure 6. EXAFS spectrum (left) and corresponding Fourier transform (right) of a 0.1 mol L⁻¹ solution of Cu^{2+} in H_2O .

spectrum, it is clear that the Fourier transform signal is dominated by a single shell at $R + \Delta = 1.5$ Å, corresponding to four water molecules at a real distance of 1.95 Å from the cupric ion. No signal at a real distance of 2.38 Å is observed, indicating that the two axial water molecules are less tightly bound and/or fast-exchanged for solvent molecules in water. The signal at $R + \Delta = 3$ –3.5 Å is due to multiple scattering effects and was not included in the fit. The EXAFS data of the fully hydrated Cu^{2+} ion point to four water molecules in the first coordination sphere. It should be noted that the hydration number of the Cu^{2+} ion in aqueous solution is very much debated,^{38–40} with proposals for coordination numbers 4,⁴¹ 5,^{42–44} and 6.^{45,46} Part of the confusion is caused by the fact that octahedral copper(II) complexes show a strongly pronounced Jahn–Teller effect. Basically, the different experimental techniques observe four equatorial water molecules but a varying number of axial ligands. Theoretical calculations show only small energetic differences between the different hydration states.³⁹ The EXAFS structural parameters for the 0.1 mol L⁻¹ solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in water are also summarized in Table 1. From the EXAFS analysis of the two reference samples, one can conclude that a typical copper–water distance is between 1.94 and 1.95 Å, whereas a typical copper–chloride distance is 2.27 Å. These distances were used as starting values in the fitting procedures of the solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in the choline chloride/water mixed solvents but were treated as freely variable parameters, which means that the distances were allowed to change during the fit.

Figure 7 shows the EXAFS spectrum and the corresponding Fourier transform signal of a $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution (0.1 mol L⁻¹) in a choline chloride/water mixture with 27 wt % of water. Only one shell is present, corresponding to 3.6 chloride ions at a real distance of 2.24 Å from the copper ion. Including a Cu– H_2O shell in the fit yielded poorer results than leaving it out.

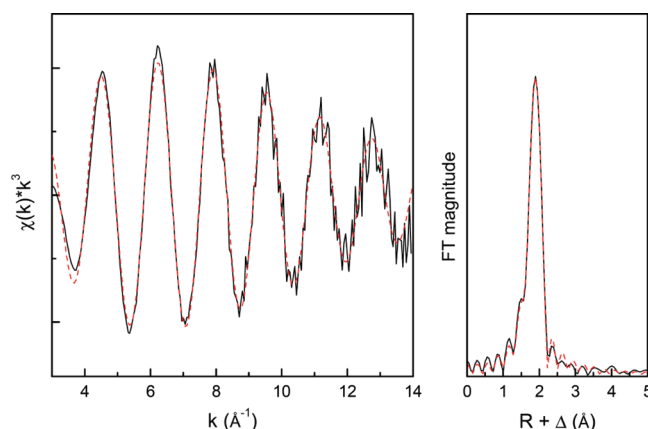


Figure 7. EXAFS spectrum (left) and corresponding Fourier transform (right) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1 mol L⁻¹) dissolved in a solvent mixture consisting of choline chloride (73 wt %) and water (27 wt %).

Thus, it has to be concluded that, from the point of view of EXAFS, this sample contains cupric ions that are nearly completely coordinated by chloride ions. There may be some cupric ions present, which are coordinated by three chloride ions and one additional water molecule (resulting in a Cu–Cl coordination number slightly lower than 4), but the resulting Cu– H_2O shell is too insignificant for EXAFS to identify it. The Fourier transform signal of the EXAFS measurement on a sample with 39 wt % of water is dominated by one shell, corresponding to about four chloride ions coordinated to the cupric ion. Including a Cu– H_2O shell in the fit did not result in improved results. The EXAFS spectra of this sample were noisier than those of the other samples. Due to the poorer data quality of this sample, the results obtained should be interpreted with care. It is not unlikely that the errors in the coordination number are larger; therefore, one can assume that the true coordination of the copper ion here lies between that of the sample with 27 wt % of water and that with 49 wt % of water. In the sample with 49 wt % of water, the Fourier transform signal is dominated by a single peak, but now the best fit is obtained when including not only a Cu–Cl shell but also a Cu– H_2O shell, indicating that with increasing water content the water molecules can enter the coordination sphere of the cupric ion. From the analysis of the EXAFS spectra, it can be concluded that approximately one water molecule and three chloride ions are coordinating to the cupric ion. It has to be pointed out that in cases like this, where coordination of both chloride and water is to be expected, we attempted to fit the EXAFS spectrum with an oxygen shell alone, with both an oxygen and a chloride shell, and with a chloride shell alone. In each of those three cases, the resulting parameters were compared and special attention was paid to the uncertainties on the obtained values, as well as to possibly excessive correlations between certain parameters. Nevertheless, fitting two shells that are so close together almost inevitably leads to very high correlations between the obtained parameters. Fixing e.g. the coordination numbers to reasonable values can then decrease these correlations significantly while keeping most parameters the same. We concluded that the results were realistic when the fits appeared to be stable and when the weighted *F* factor was as small as possible for parameters that showed minimal correlations and error margins. Analysis of the EXAFS spectra of the sample with 62 wt % of water shows that in this case on average two water molecules and two chloride ions are

coordinated to the copper(II) ion. For the samples with 73 and 84 wt % of water, the coordination sphere of the copper(II) is formed by roughly three water molecules and one chloride ion. For the sample with 95 wt % of water, inclusion of a Cu–Cl shell in the fit did not give useful results. One can therefore conclude that the cupric ion is in these circumstances almost completely coordinated by water molecules and that the chloride ions of the added choline chloride can no longer efficiently compete with the water molecules for coordination to the copper(II) ion. The EXAFS results of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solutions (0.1 mol L^{-1}) in the different choline chloride/water mixtures have been summarized in Table 2.

Table 2. EXAFS Structural Parameters for a $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ Solution (0.1 mol L^{-1}) in Choline Chloride/Water Solvent Mixtures

| water content (wt %) | scattering path | R (Å) | N | σ^2 (Å ²) |
|----------------------|--------------------|-----------|----------|------------------------------|
| 27 ^a | Cu–Cl | 2.243(1) | 3.58(9) | 0.0039(2) |
| 39 ^b | Cu–Cl | 2.234(2) | 3.85(18) | 0.0032(3) |
| 49 ^c | Cu–OH ₂ | 1.936(41) | 0.60(53) | 0.0011(42) |
| | Cu–Cl | 2.236(11) | 2.59(51) | 0.0043(13) |
| 62 ^d | Cu–OH ₂ | 1.960(18) | 1.88(55) | 0.0044(12) |
| | Cu–Cl | 2.241(15) | 2.01(60) | 0.0063(20) |
| 73 ^e | Cu–OH ₂ | 1.961(9) | 2.12(25) | 0.0033(6) |
| | Cu–Cl | 2.255(13) | 0.65(25) | 0.0034(25) |
| 84 ^f | Cu–OH ₂ | 1.944(10) | 2.12(27) | 0.0030(6) |
| | Cu–Cl | 2.250(20) | 0.62(32) | 0.0052(40) |
| 95 ^g | Cu–OH ₂ | 1.966(2) | 3.32(8) | 0.0032(2) |

^a $\Delta E = 11.3(3) \text{ eV}$. Weighted F factor = 0.21. ^b $\Delta E = 10.8(4) \text{ eV}$. Weighted F factor = 0.30. ^cCu–OH₂ shell ill-determined when all parameters are varied freely. With the coordination number N fixed to 0.6, R becomes 1.936(7) Å, σ^2 becomes 0.0011(7), and all correlations drop below 0.9. $\Delta E = 9.5(3) \text{ eV}$. Weighted F factor = 0.17. ^dStable fit, but shells are highly correlated when all parameters are varied freely. When the coordination number N is fixed to 2 for both shells, $R_{\text{Cu–O}}$ becomes 1.963(6) Å with $\sigma^2 = 0.0052(6)$ and $R_{\text{Cu–Cl}}$ becomes 2.241(4) Å with $\sigma^2 = 0.0066(4)$. All correlations drop below 0.9. $\Delta E = 9.7(4) \text{ eV}$. Weighted F factor = 0.22. ^eStable fit, but shells are highly correlated when all parameters are varied freely. When coordination numbers are fixed to $N_{\text{OH}_2} = 2.15$ and $N_{\text{Cl}} = 0.65$, $R_{\text{Cu–O}}$ becomes 1.962(3) Å with $\sigma^2 = 0.0034(3)$ and $R_{\text{Cu–Cl}}$ becomes 2.256(6) Å with $\sigma^2 = 0.0035(5)$. All correlations drop below 0.9. $\Delta E = 9.6(4) \text{ eV}$. Weighted F factor = 0.27. ^fStable fit, but shells are highly correlated when all parameters are varied freely. When coordination numbers are fixed to $N_{\text{OH}_2} = 2.15$ and $N_{\text{Cl}} = 0.60$, $R_{\text{Cu–O}}$ becomes 1.944(4) Å with $\sigma^2 = 0.0030(3)$ and $R_{\text{Cu–Cl}}$ becomes 2.251(8) Å with $\sigma^2 = 0.0051(8)$. All correlations drop below 0.9. $\Delta E = 8.4(5) \text{ eV}$. Weighted F factor = 0.24. ^g $\Delta E = 10.1(3) \text{ eV}$. Weighted F factor = 0.22.

The EXAFS spectrum and corresponding Fourier transform signal of the ionic liquid formed by mixing choline chloride and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in a 1:2 molar ratio are shown in Figure 8. From the EXAFS data analysis results (Table 3), it can be noted that the coordination sphere of the copper(II) ion is intermediate between that of the samples with 49 and 62 wt % of water. This means that the cupric ion probably has a coordination number of four in the ionic liquid, containing three coordinated chloride ions and one coordinated water molecule. These EXAFS data for the ionic liquid are in agreement with the optical absorption spectra in the sense that also in that case the data for the ionic liquid were intermediate between those of the samples with 49 and 62 wt % of water.

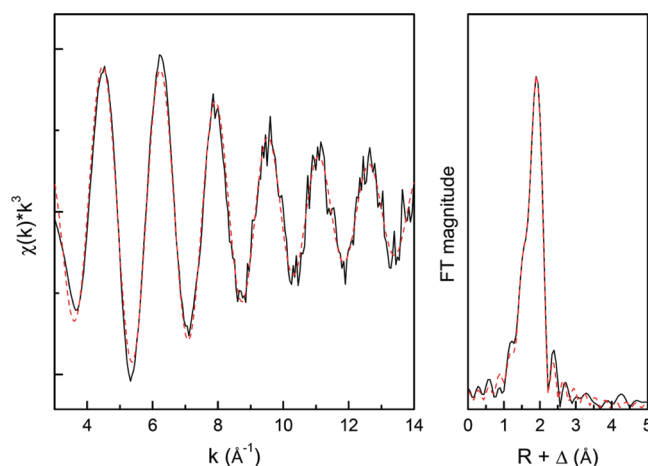


Figure 8. EXAFS spectrum (left) and corresponding Fourier transform (right) of the ionic liquid formed by mixing choline chloride and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in a 1:2 molar ratio.

Table 3. EXAFS Structural Parameters for the Ionic Liquid Formed by Choline Chloride and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in a 1:2 Molar Ratio^a

| scattering path | R (Å) | N | σ^2 (Å ²) |
|--------------------|-----------|----------|------------------------------|
| Cu–OH ₂ | 1.958(15) | 0.80(29) | 0.0020(19) |
| Cu–Cl | 2.250(5) | 2.79(26) | 0.0044(6) |

^aStable fit, but shells are highly correlated when all parameters are varied freely. When coordination numbers are fixed to $N_{\text{OH}_2} = 0.8$ and $N_{\text{Cl}} = 2.8$, $R_{\text{Cu–O}}$ becomes 1.958(5) Å with $\sigma^2 = 0.0020(4)$ and $R_{\text{Cu–Cl}}$ becomes 2.251(1) Å with $\sigma^2 = 0.0044(1)$. All correlations drop below 0.9. $\Delta E = 11.1(2) \text{ eV}$. Weighted F factor = 0.18.

Electrochemistry. Cyclic voltammograms (CVs) were recorded in solutions consisting of choline chloride with 25, 49, 73, and 100 wt % of water, each containing 0.1 mol L^{-1} of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. According to the spectroscopic measurements, the set of solutions spans a range where the tetrachlorocuprate(II) complex is the dominating species, mixed chloro–aquo complexes occur, and Cu^{2+} is fully hydrated. The electrochemical behavior of these mixtures is illustrated in Figures 9 and 10. A significant difference is observed between the CV of the solution without any choline chloride (100 wt % H_2O) and the other 3 CVs. The presence of chloro ligands shifts the deposition potential of copper toward more negative potentials, while at the same time the electroactivity of a Cu(II)/Cu(I) couple can be observed at around 0.35 V versus $0.01 \text{ mol L}^{-1} \text{ Ag}^+ / 0.1 \text{ mol L}^{-1} \text{ Kryptofix22/acetoneitrile}$ in the solutions with 25, 49, and 73 wt % of water. The presence of chloride stabilizes the copper(I) species in solution, which has been described before in aqueous chloride solutions.^{47–49} Relevant data of the Cu(II)/Cu(I) couple in the 25, 49, and 73 wt % choline chloride/water solutions are summarized in Table 4. At high water content ($\geq 73 \text{ wt \%}$ of water) deviation from reversible behavior is large, as illustrated by the ratio of forward and reverse peak current (i_p^r/i_p^f). Also in the case of the 25 and 49 wt % water solutions the i_p^r/i_p^f ratio indicates that the electrochemical behavior is not completely reversible. The higher viscosity of the solutions cannot explain this deviation. Recently, the kinetics of the Cu(II)/Cu(I) couple have been determined as being quasi-reversible as well in a deep-eutectic solvent consisting of choline chloride and ethylene glycol.⁵⁰ These authors found that copper(II) was present predom-

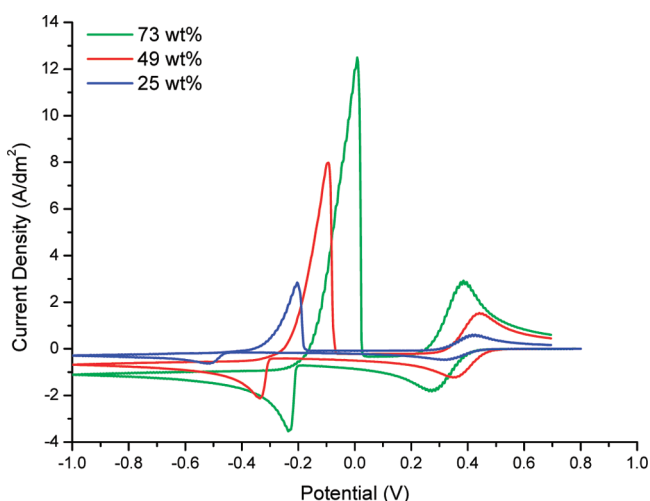


Figure 9. Cyclic voltammograms at 0.100 V s^{-1} of $0.1 \text{ mol L}^{-1} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$ in choline chloride solutions containing 25, 49, and 73 wt % of water: working electrode, Pt disk (diameter 1 mm); reference electrode, $0.01 \text{ mol L}^{-1} \text{ Ag}^+ / 0.1 \text{ M}$ Kryptofix22/acetonitrile; counter electrode, Ti grid coated with $\text{RuO}_2 / \text{IrO}_2$. All measurements were performed at 25°C after a 5 min purge with nitrogen gas.

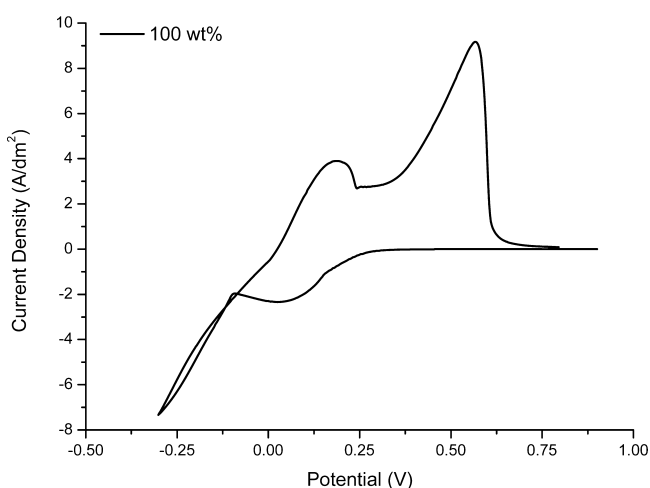


Figure 10. Cyclic voltammogram at 0.100 V s^{-1} of $0.1 \text{ mol L}^{-1} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$ in pure water: working electrode, Pt disk (diameter 1 mm); reference electrode, $0.01 \text{ mol L}^{-1} \text{ Ag}^+ / 0.1 \text{ mol L}^{-1}$ Kryptofix22/acetonitrile; counter electrode, Ti grid coated with $\text{RuO}_2 / \text{IrO}_2$. All measurements were performed at 25°C after a 5 min purge with nitrogen gas.

inantly as $[\text{CuCl}_4]^{2-}$ and Cu(I) as $[\text{CuCl}_3]^{2-}$, as determined with UV–vis spectroscopy. The increasing viscosity can explain

Table 4. Position of the Redox Potential $(E_p^f - E_p^r)/2$, Peak Difference $E_p^f - E_p^r$, and Ratio of Peak Heights i_p^f/i_p^r of the Cu(II)/Cu(I) Couple in Choline Chloride Solutions Containing Different Contents of Water^a

| water content (wt %) | $(E_p^f - E_p^r)/2$ (V) | $E_p^f - E_p^r$ (V) | i_p^f/i_p^r |
|----------------------|-------------------------|---------------------|---------------|
| 73 | 0.329 | 0.112 | 1.606 |
| 49 | 0.400 | 0.083 | 1.2565 |
| 25 | 0.372 | 0.090 | 1.2871 |

^a E_p^f and E_p^r are the peak potentials in forward and reverse sweeps, respectively; i_p^f and i_p^r are the current densities in forward and reverse sweeps.

the shift in potential of the Cu(I)/Cu(0) couple toward more negative potentials on decreasing the water content. Also, a change in liquid junction potential due to this increasing viscosity might cause potential shifts. In 25 wt % of water, electrodeposition starts around -0.47 V vs $0.01 \text{ mol L}^{-1} \text{ Ag}^+ / 0.1 \text{ mol L}^{-1}$ Kryptofix22/acetonitrile. In 49 wt % of water, it is around -0.3 V and -0.2 V in a solution with 73 wt % of water.

Crystal Structures. The ionic liquid choline chloride– $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was synthesized by mixing choline chloride and copper(II) chloride dihydrate in a 1:2 molar ratio and heating the mixture to 70°C . When it was cooled to room temperature, the mixture remained a liquid, but over time crystals formed in the melt. The precipitate consisted mostly of large, nicely formed crystals, of which there were two forms: yellow needles and green blocks. The yellow needles were numerous, and analysis with single-crystal diffraction showed them to be $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The green crystals were less numerous and were found to have the composition Cu(choline)Cl_3 , in which the copper center is coordinated by three Cl^- ions and to one choline cation, bonded through the O atom (Figure 11), meaning that the molecule is a zwitterion. There are two molecules of Cu(choline)Cl_3 in the crystallographic asymmetric unit, both having similar Cu–L bond distances: Cu–Cl = $2.2614(10)$, $2.2739(9)$, $2.2830(10) \text{ \AA}$ and Cu–O = $2.060(3) \text{ \AA}$ and Cu–Cl = $2.2630(10)$, $2.2720(10)$, $2.2838(9) \text{ \AA}$ and Cu–O = $2.052(2) \text{ \AA}$. The coordination geometry of the copper center is slightly distorted square planar (range L–Cu–L: cis, $86.1-97.7^\circ$; trans, $172.7-176.9^\circ$). There are also longer range interactions between the Cu and Cl atoms (Cu–Cl = $2.9747(12)$, $3.0009(12)$, $3.1309(13)$, $3.1873(13) \text{ \AA}$) of adjacent molecules in what would be the apical positions of the square-planar arrangement, but these are much longer than the Cu–Cl bonds (Figure 11). There are also hydrogen bonds between the choline O–H and a Cl atom of an adjacent molecule (Figure 11; H...Cl $2.28(6)$, $2.23(6) \text{ \AA}$, O...Cl $3.054(3)$, $3.055(3) \text{ \AA}$, O–H...Cl $166(5)$, $161(4)^\circ$). A four-coordinate Cu center with the CuCl_3O ligand set is relatively rare, with only 25 examples reported in the Cambridge Structural Database (CSD).⁵¹ What is most remarkable is that this is the first structurally characterized example of the choline cation coordinating to a metal ion.⁵¹ Although this is a solid-state structure, it would be interesting if this kind of metal–choline complex was present in the deep-eutectic mixtures of choline chloride and metal chlorides. However, we found no experimental evidence for it in our study. It was not possible to isolate Cu(choline)Cl_3 as a bulk sample, as it was a minor product; however, it was more than a one-off as 20–30 or more of these crystals could be found in the sample.

If the ionic liquid sample was left exposed to air for a period of a few days, red crystals were found to form in large numbers. X-ray analysis showed these crystals to be $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$, in which an O atom has been extracted from either O_2 or H_2O and formed the center of a complex anion in which it is bonded to four copper atoms (Figure 12; Cu–O = $1.917(3)$, $1.926(3) \text{ \AA}$). There are in addition 10 chlorides, 6 of which make a bidentate bridge (Cu–Cl = $2.3785(15)$ – $2.4362(15) \text{ \AA}$) and 4 are terminally bonded (Cu–Cl = $2.2685(15)$, $2.2460(17) \text{ \AA}$), giving an overall approximately tetrahedral shape. The anion has a 4– charge, and so there are four choline cations per anion, although the anion sits on a crystallographic 2-fold axis so that the asymmetric unit only contains half of the anion and two cations. Two choline cations are hydrogen-bonded to Cl atoms in the anion (Figure

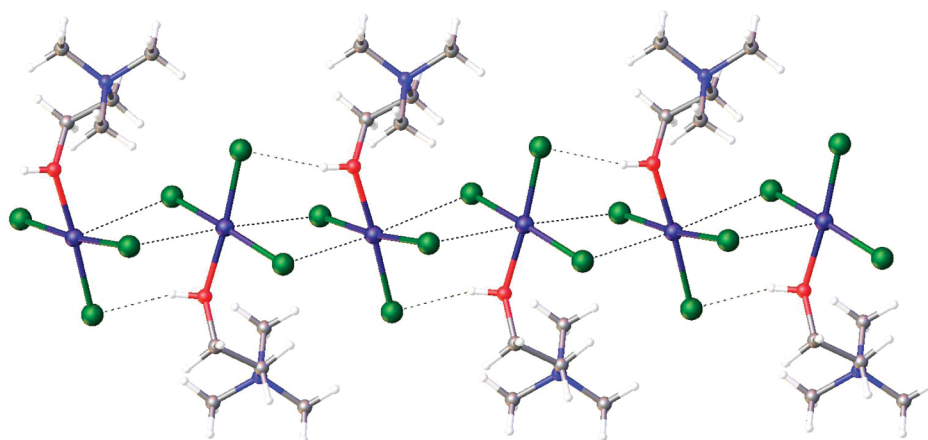


Figure 11. View of the packing in the crystal structure of $\text{Cu}(\text{choline})\text{Cl}_3$, showing the structure of the zwitterions and the one-dimensional chain formed by the long-range $\text{Cu}\cdots\text{Cl}$ interactions and the $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonds (Cu, royal blue; Cl, green; N, blue; O, red; C, gray; H, white).

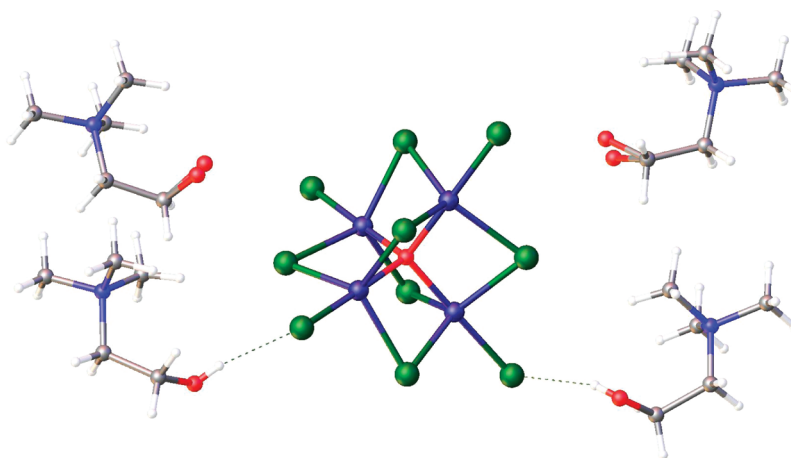


Figure 12. View of the crystal structure of $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$, showing one complete anion and four cations and the hydrogen-bonding interactions between them and the disorder on one of the choline cations (Cu, royal blue; Cl, green; N, blue; O, red; C, gray; H, white).

12; $\text{H}\cdots\text{Cl} = 2.46(7) \text{ \AA}$, $\text{O}\cdots\text{Cl} = 3.167(5) \text{ \AA}$, $\text{O}-\text{H}\cdots\text{Cl} = 160(8)^\circ$, while the oxygen atom on the other cholines is disordered, suggesting there is not a strong hydrogen-bonding interaction. The structure of $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$ has been reported by Wu et al. in a room-temperature determination.⁵² We have improved upon this by collecting data at 100 K and provide the three-dimensional coordinates. $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$ could be isolated in pure form and was found to melt at 180°C , but the liquid started to change color after a few seconds; thus, it does not form a stable ionic liquid.

In order to produce reference compounds for the EXAFS analysis, we attempted to produce crystals of $[\text{choline}]_2[\text{CuCl}_4]$. Following the procedure of White et al.,⁵³ we failed to produce crystals of X-ray quality; however, a small number of crystals of $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$, as described above, were also produced. Part of the problem with the crystallization of $[\text{choline}]_2[\text{CuCl}_4]$ is that it immediately precipitates on formation and is insoluble in most solvents. Thus, we attempted to produce crystals by slow diffusion of the reactants. In this method the two reactants (choline chloride and CuCl_2) were dissolved in different solvents and layered on top of each other; however, again no diffraction-quality single crystals were formed. Finally, another route to the synthesis of $[\text{choline}]_2[\text{CuCl}_4]$ was tried, using an ionic liquid as one of the solvents. For this, $\text{Cu}(\text{Tf}_2\text{N})_2$ was dissolved in choline

bis(trifluoromethylsulfonyl)imide, a solution of choline chloride in ethanol was carefully layered on top, and they were slowly allowed to diffuse together. This produced a yellow precipitate that was presumed to be $[\text{choline}]_2[\text{CuCl}_4]$, and there were diffraction-quality crystals present. However, after structural determination it was found that the yellow product was actually $[\text{choline}]_3[\text{CuCl}_4][\text{Cl}]$, which contains an additional cocrystallized choline chloride cation and anion pair per $[\text{choline}]_2[\text{CuCl}_4]$ unit (Figure 13). The $[\text{CuCl}_4]^{2-}$ anion has a distorted-tetrahedral geometry ($\text{Cu}-\text{Cl} = 2.176(13)-2.2695(18) \text{ \AA}$; $\text{Cl}-\text{Cu}-\text{Cl} = 91.97(18)-157.0(6)^\circ$), and it is involved in two hydrogen bonds to choline cations (Figure 13; $\text{H}\cdots\text{Cl} = 2.46(2) \text{ \AA}$, $\text{O}\cdots\text{Cl} = 3.270(3) \text{ \AA}$, $\text{O}-\text{H}\cdots\text{Cl} = 162(6)^\circ$). There are only 17 examples of crystal structures that contain $[\text{CuCl}_4]^{2-}$ and $[\text{Cl}]^-$ in the same structure; thus, this compound is rare and was a surprise to find in this case.⁵⁰ The compound could then be produced in bulk and was found to have a melting point of 76°C . Above the melting point an ionic liquid exists which has one type of cation but two different anions.

CONCLUSIONS

The spectroscopic measurements (EXAFS and UV-vis-near-IR) on $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ dissolved in choline chloride/water and in the ionic liquid choline chloride- $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (1:2) gave

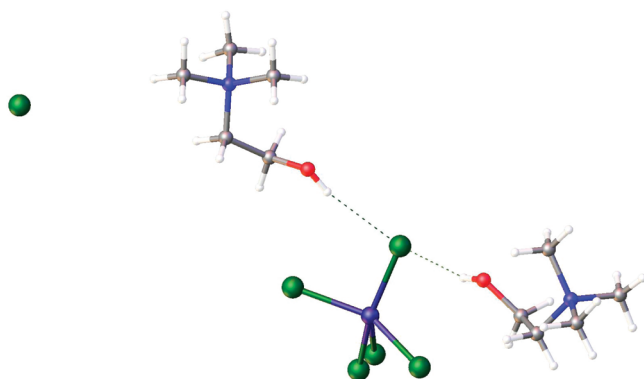


Figure 13. View of the crystal structure of $[\text{choline}]_3[\text{CuCl}_4][\text{Cl}]$, showing the hydrogen bond between $[\text{CuCl}_4]^{2-}$ and two choline cations and the disorder of the $[\text{CuCl}_4]^{2-}$ anion (Cu, royal blue; Cl, green; N, blue; O, red; C, gray; H, white; disordered choline molecule not shown).

consistent results and revealed three different situations for the environment of the cupric ion in binary choline chloride/water mixtures. In the samples with up to 39 wt % of water, the tetrachlorocuprate(II) complex is clearly the dominating species. In samples with more than 95 wt % of water, the cupric ion is fully hydrated. The EXAFS data indicate that four water molecules are coordinated to the cupric ion in this case. These four water molecules are the well-defined equatorial water molecules at about 1.95 Å. There may be loosely bound and/or fast-exchanged axial water molecules present at larger distances, due to the strong Jahn–Teller distortion as a result of the d^9 electronic configuration of Cu^{2+} . However, the literature reports on the coordination number of the hydrated cupric ion (including EXAFS studies) are not consistent. In our case, the EXAFS spectra gave no indication of the presence of axial water molecules. Therefore, we limited ourselves to the well-proven presence of the equatorial water molecules at 1.95 Å. For the choline chloride/water mixtures with an intermediate water content, mixed chloro–aquo complexes or mixtures of different cupric complexes are present. The environment of the Cu^{2+} ion in the ionic liquid choline chloride– $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is similar to that in the choline chloride/water samples with a water content between 49 and 62 wt %. The gradual change from the fully hydrated cupric ion to the complexes of copper(II) that contain chloro ligands induces a shift in the electrodeposition potential of copper toward more negative potentials, while the existence of a Cu(II)/Cu(I) couple can be clearly observed. The electrochemical behavior of this redox couple is not completely reversible. The ionic liquid choline chloride– $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1:2) was found to form crystals of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and Cu(choline)Cl_3 upon standing at room temperature. Furthermore, on exposure to air crystals of $[\text{choline}]_4[\text{Cu}_4\text{Cl}_{10}\text{O}]$ were formed. The compound $[\text{choline}]_3[\text{CuCl}_4][\text{Cl}]$ was also synthesized and found to melt at 76 °C and thus forms an ionic liquid with choline cations and two different anions.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving crystal structure data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Koen.Binnemans@chem.kuleuven.be (K.B.); Rik.VanDeun@ugent.be (R.V.D.).

Notes

The authors declare no competing financial interest.

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