Inorganic Chemistry

Article

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EXAFS Study into the Speciation of Metal Salts Dissolved in Ionic Liquids and Deep Eutectic Solvents

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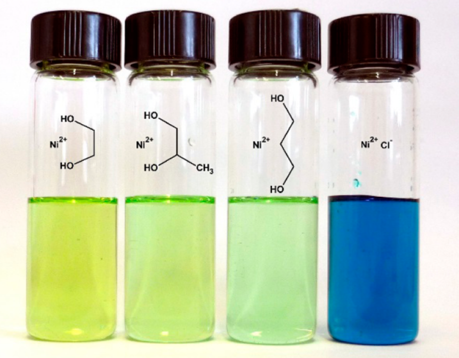

ABSTRACT: The speciation of metals in solution controls their reactivity, and this is extremely pertinent in the area of metal salts dissolved in ionic liquids. In the current study, the speciation of 25 metal salts is investigated in four deep eutectic solvents (DESs) and five imidazolium-based ionic liquids using extended X-ray absorption fine structure. It is shown that in diol-based DESs M^I ions form $[MCl_2]^-$ and $[MCl_3]^{2-}$ complexes, while all M^{II} ions form $[MCl_4]^{2-}$ complexes, with the exception of Ni^{II}, which exhibits a very unusual coordination by glycol molecules. This was also found in the X-ray crystal structure of the compound $[Ni(phen)_2(eg)]Cl_2 \cdot 2eg$ (eg = ethylene glycol). In a urea-based DES, either pure chloro or chloro−oxo coordination is observed. In $[C_6mim][Cl]$ pure chloro complexation is also observed, but coordination numbers are smaller (typically 3), which can be explained by the long alkyl chain of the cation. In $[C_2mim][SCN]$ metal ions are entirely coordinated by thiocyanate, either through the N or the S atom, depending on the hardness of the metal ion according to the hard-soft acid-base principle. With weaker coordinating anions, mixed coordination between solvent and solute anions is observed. The effect of hydrate or added water on speciation is insignificant for the diol-based DESs and small in other liquids with intermediate or strong ligands. One of the main findings of this study is that, with respect to metal speciation, there is no fundamental difference between deep eutectic solvents and classic ionic liquids.

■ INTRODUCTION

The ability to process metals using ionic liquids, so-called ionometallurgy, is of growing interest, fueled by an ability to control speciation and redox properties. Many aspects of metal digestion, deposition, cementation, and ion extraction have been studied in different media, and the use of ionic liquids has been shown to be applicable to the recycling of transition metal oxides and lanthanides.[1,2]

Most studies have concentrated on the extraction of metals from aqueous solution using ionic liquids (ILs) with discrete anions.[3] Other groups have used deep eutectic solvents (DESs), which are a mixture of hydrogen bond donors with quaternary ammonium salts, to extract metals from complex matrices.[1,4]

Speciation is known to control key aspects of metal processing and electrochemical behavior, such as solubility and redox potentials. In aqueous solution, undesirable reagents, such as cyanide, commonly have to be used to give metal ions the required redox properties,[5] due to domination of the speciation by aquo-complexes, whereas in ILs and DESs there is some evidence that speciation is governed by the anionic component of the liquid.

The speciation of metals in ILs has been probed with a variety of techniques, including fast atom bombardment mass spectroscopy (FAB-MS), NMR, ultraviolet−visible (UV−vis), and vibrational spectroscopy, neutron spectroscopy, and extended X-ray absorption fine structure (EXAFS).[6,7] However, there are much fewer speciation studies in DESs than in traditional ionic liquids, and comparison between the two classes of ionic solvents has not been made.[8,9]

In the current study we analyze 25 metal salts in four DESs and five imidazolium-based ILs. By using EXAFS to determine speciation, an *in situ* analysis of the species of interest can be made, without destruction of the sample or breakdown of the solution species.

■ EXPERIMENTAL SECTION

All DESs were made by the method described in previous publications.[10,11] Mixtures were made with 1 mol equiv. of choline chloride and 2 mol equiv. of either 1,2-ethanediol (ethylene glycol (eg)), 1,2-propanediol (propylene glycol), 1,3-propanediol, or urea.

The imidazolium ILs, namely, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_2mim][NTf_2]$, 1-hexyl-3-methylimidazolium chloride $[C_6mim][Cl]$, 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate $[C_2mim][FAP]$,

Received: April 10, 2014
Published: June 5, 2014

Table 1. Nominal Energies for the Different X-ray Absorption Edges under Investigation

edge	*E*, (eV)	edge	*E*, (eV)	edge	*E*, (eV)
chromium-K	5989	nickel-K	8333	gold-L_{III}	11 919
manganese-K	6539	copper-K	8979	palladium-K	24 350
iron-K	7112	zinc-K	9659	silver-K	25 514
cobalt-K	7709	platinum-L_{III}	11 564	tin-K	29 200

1-butyl-3-methylimidazolium tetrafluoroborate [C_4mim][BF_4], and 1-ethyl-3-methylimidazolium thiocyanate [C_2mim][SCN] were obtained from Merck, dried under vacuum overnight, and handled in a glovebox.

EXAFS was carried out using the following X-ray sources: BESSY II (KMC-2 beamline) for Cu in DES, ESRF (BM26A beamline) for Ni and Cr in DESs, and Diamond Light Source (B18 beamline) for all other samples. Measurements were carried out at the absorption edges shown in Table 1 using a double crystal Si(111) monochromator for Cr, Mn, Fe, Co, Ni, Cu, Zn, Pt, and Au and a double crystal Si(311) monochromator for Pd, Ag, and Sn. A nine-element Ge solid-state detector (BM26A operating on seven elements) in total fluorescence yield mode was used for the liquid samples. Solid references were measured with ion chamber detectors in transmission mode.

The samples were kept in a static flat Perspex sample holder with a sample chamber of 15 × 8 mm, at 1.5 mm thick, with 40 μm thick Kapton foil windows. The X-ray beam size varied, depending on the beamline used, but was generally kept as large as possible to minimize radiation damage. In particular, beam sizes were 200 × 250 μm at Diamond, 2 to 4 × 0.3 mm at ESRF, and 250 × 600 μm at BESSY II. The sample was aligned at approximately 55° with respect to the X-ray beam, with the fluorescence detector positioned perpendicular to the beam to minimize any elastic scattering signals. Two to three spectra were recorded in step scan mode, or eight spectra were recorded in quick EXAFS mode. These were subsequently summed, calibrated, and background subtracted using the program Athena.[12] EXAFS spectra were fitted using EXCURV[13] to calculate interatomic distances and their root-mean-square variations (σ^2). Electron scattering parameters were calculated and used to determine the type and number of coordinating atoms, using the Hedin–Lundqvist potential.[14] Uncertainties in the fitted parameters, are quoted to two standard deviations.

To obtain crystals suitable for analysis, a solution of $NiCl_2$ (10 mM) and 1,10-phenanthroline (20 mM) dissolved in the ethylene glycol-based DES was heated at 40 °C until a purple crystalline precipitation was observed. Crystallographic data was collected using a Bruker APEX 2000 CCD diffractometer. The data was corrected for Lorentz and polarization effects and empirical absorption corrections applied. The structure was solved by direct methods and structure refinement was based on full-matrix least-squares F^2, using employed SHELXTL version 6.10.[15] Hydrogen atoms were included in calculated positions ($C-H$ = 0.96 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 U_{eq} for methyl H atoms and 1.2 U_{eq} for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters.

■ RESULTS AND DISCUSSION

Speciation in DESs. The speciation of various metal salts was investigated in deep eutectic solvents formed from choline chloride and a hydrogen bond donor (HBD) in a 1:2 ratio. Ethylene glycol (1,2-ethanediol), propylene glycol (1,2-propanediol), 1,3-propanediol, and urea were used as HBDs. Metal salts were dissolved at concentrations of 0.1 M in these solvents, and EXAFS were recorded at room temperature in fluorescence mode. The formation of the copper, zinc, and silver species in these media has been reported previously and discussed in the context of other analytical methods.[16−19]

EXAFS gives a very uniform picture for the metal(II) chloride salts in the three diol-based DESs: with the exception of nickel, they all form tetrachloro complexes (Table 2). All bond lengths were found to be within ±0.05 Å of the sum of the ionic radii according to the Shannon table.[20] These results are also consistent with data published by other authors on chlorometallate ionic liquids,[21−37] and these have recently been comparatively reviewed by Estager et al.[7] The dilute solutions (0.1 mol dm^{-3}) used in the current study can be regarded as the strongly Lewis basic border of these systems.[38]

Tetrachloro species for a range of d-block MCl_2 salts have also been reported in Lewis-basic, that is, excess chloride, imidazolium chloride-based melts via techniques such as EXAFS,[21,25] X-ray crystallography,[26] UV–vis spectroscopy,[27] Raman spectroscopy[28] and XPS.[29] Tetrachloro species for cobalt and manganese were also suggested by Dent et al. for binary molten salt melts of 1-methyl-3-ethylimidazolium chloride [C_2mim]$_2$[MCl_4] with [C_2mim][Cl-$AlCl_3$] under Lewis-basic conditions (low molar ratio of $AlCl_3$).[39]

For the urea-based liquid, the metal coordination is still dominated by chloride for the ions of the late transition metals (Table 2). For the earlier transition metals, Cr, Mn, Fe, and to some extent Co, the first coordination consists of lighter atoms, that is, O or N originating from water or urea. The Fourier transforms of some spectra (cited as footnote *e* in Table 2) exhibit further electron density at distances of 3 to 5 Å, indicating a multiatom ligand such as urea. However, these parts of the EXAFS could not be included in a stable fit, probably because it originates from too many overlapping scattering signals. The fast decay of the EXAFS amplitude with *k* in the urea-based compared to the glycol-based liquid, for example, for manganese (Figure 1), confirms that the first coordination shell contains light atoms.

The speciation of three metal(I) chloride salts, namely, AgCl, AuCl, and CuCl, were also studied in the diol- and urea-based DESs. In all cases, chloride species were observed (Table 3). In all samples investigated, a single peak was visible in the Fourier transform of the EXAFS, with an electron density suggesting the presence of two to three chloride atoms at a distance consistent with the sum of the ionic radii. For copper, the coordination number was refined to 2.4 and 2.5 in the ethylene glycol- and the urea-based DES, respectively, which can be interpreted as a mixture of $[CuCl_2]^-$ and $[CuCl_3]^{2-}$ species.

Silver also forms a mixture of $[AgCl_2]^-$ and $[AgCl_3]^{2-}$ in both diol-based DESs. Similar behavior is known for AgCl in an aqueous solution that contains high chloride concentrations.[40] In the urea-based DESs only $[AgCl_3]^{2-}$ was found, which is unexpected because this solvent has the lowest chloride activity.[17] For AuCl a dichloro-complex was found for the ethylene glycol- and the urea-based DES, which is also consistent with the chemistry in aqueous chloride-rich solutions.[41]

To understand the effect that hydrate water or added water molecules have on the speciation, the EXAFS of samples containing several hydrated salts were recorded in DES media and compared to their anhydrous analogues. EXAFS showed identical coordination for both cases, within the statistical errors. Hydrate water is hence replaced by chloride ions upon dissolution of the salt hydrate. This is consistent with

Table 2. EXAFS Fits of 100 mM Solutions of Metal Chloride (Hydrate) Salts in Deep Eutectic Solvents

	metal salt	X^a	N^b	r,^{c} (Å)	fit index	proposed species		metal salt	X	N	r, (Å)	fit index	proposed species
1,2-ethanediol	$CoCl_2$	Cl	4.0(2)	2.282(3)	2.2%	$[CoCl_4]^{2-}$	1,2-proanediol	$CoCl_2$	Cl	3.9(1)	2.284(2)	1.6%	$[CoCl_4]^{2-}$
	$CoCl_2·6H_2O$	Cl	3.9(1)	2.282(2)	1.5%	$[CoCl_4]^{2-}$		$PdCl_2$	Cl	4.1(2)	2.315(3)	2.3%	$[PdCl_4]^{2-}$
	$CrCl_3·6H_2O$	OCl	1.9(5)3.3(6)	1.97(1)2.262(6)	3.8%	$[CrCl_4(OD)_2]^{-d}$		$PtCl_2$	Cl	4.1(3)	2.307(4)	4.5%	$[PtCl_4]^{2-}$
	$CrCl_3·6H_2O$ + $20H_2O$	OCl	3.7(5)1.5(4)	1.97(1)2.26(1)	5.2%	$[CrCl_2(OD)_4]^+$	1,3-proanediol	$CoCl_2$	Cl	3.9(1)	2.281(2)	1.6%	$[CoCl_4]^{2-}$
	$CuCl_2$[19]	Cl	3.7(2)	2.252(5)	4.5%	$[CuCl_4]^{2-}$		$FeCl_2$	Cl	3.9(2)	2.318(4)	3.4%	$[FeCl_4]^{2-}$
	$CuCl_2·2H_2O$	Cl	3.6(3)	2.250(5)	6.2%	$[CuCl_4]^{2-}$		$MnCl_2$	Cl	3.9(4)	2.373(6)	7.4%	$[MnCl_4]^{2-}$
	$FeCl_2$	Cl	3.8(2)	2.313(3)	2.9%	$[FeCl_4]^{2-}$		$PdCl_2$	Cl	4.1(2)	2.314(3)	2.3%	$[PdCl_4]^{2-}$
	$FeCl_2·4H_2O$	Cl	3.8(2)	2.312(3)	2.5%	$[FeCl_4]^{2-}$		$PtCl_2$	Cl	4.0(3)	2.306(4)	4.5%	$[PtCl_4]^{2-}$
	$MnCl_2$	Cl	3.8(2)	2.369(3)	3.0%	$[MnCl_4]^{2-}$	urea	$CoCl_2{}^e$	OCl	0.9(2)2.5(2)	2.01(1)2.258(3)	2.9%	$[CoCl_3(OD)]^{-d}$
	$MnCl_2·4H_2O$	Cl	3.9(2)	2.370(3)	3.2%	$[MnCl_4]^{2-}$		$CrCl_3·6H_2O$	O	6.1(5)	1.976(7)	5.7%	$[Cr(OD)_6]^{3+}$
	$PdCl_2$	Cl	4.0(2)	2.313(3)	1.5%	$[PdCl_4]^{2-}$		$CuCl_2$	Cl	3.9(3)	2.239(7)	6.4%	$[CuCl_4]^{2-}$
	$PtCl_2$	Cl	3.9(2)	2.309(4)	4.7%	$[PtCl_4]^{2-}$		$CuCl_2·2H_2O$	Cl	3.8(3)	2.233(6)	4.9%	$[CuCl_4]^{2-}$
	$SnCl_2·2H_2O^f$	Cl	4.2(3)	2.482(7)	5.6%	$[SnCl_4]^{2-}$		$FeCl_2{}^e$	O	4.8(4)	2.08(1)	6.8%	$[Fe(OD)_5]^{2+d}$
	$ZnCl_2{}^f$	Cl	4.3(2)	2.278(4)	2.5%	$[ZnCl_4]^{2-}$		$MnCl_2{}^e$	O	5.9(5)	2.16(1)	11.8%	$[Mn(OD)_6]^{2+}$
								$PdCl_2$	Cl	3.9(2)	2.313(4)	3.2%	$[PdCl_4]^{2-}$
								$PtCl_2{}^e$	Cl	4.7(5)	2.29 (1)	10.0%	$[PtCl_4]^{2-}$

[a] X = type of atom. [b] N = number of atoms. [c] r = distance from X-ray absorber. [d] OD = oxygen bond donor (e.g., water, ethylene glycol, urea). [e] For this solution, additional signal was seen in the FT between 3 and 5 Å. [f] The concentration of $SnCl_2·2H_2O$ was 50 mM, and that of $ZnCl_2$ was 300 mM.

observations made in UV–vis spectra of $CuCl_2$ and $CuCl_2·2H_2O$, which exhibited almost identical spectra.[16] A study by De Vreese et al. found that for choline chloride–$CuCl_2·2H_2O$ mixtures, it was necessary to add 49% w/w water to the solution to cause a change in speciation from pure chloride to a mixed speciation.[33] Li et al. studied the effect of water on the speciation of $CuCl_2$ in the imidazolium-based IL [C_2mim][Cl] and also observed a chloride coordination of 3.7(2) atoms.[32] The first notable change from chloride to oxygen was also seen at 40% w/w water.

On the other hand, $CrCl_3·6H_2O$, the only trivalent ion under investigation and commonly found in octahedral coordination, retained two hydrate water molecules in the first coordination shell when dissolved in the ethylene glycol-based liquid. Addition of 5% w/w water changed the speciation from $[Cr(H_2O)_2Cl_4]^{2-}$ to $[Cr(H_2O)_4Cl_2]^+$. This is a significant discovery because electrochemical deposition kinetics can be substantially different from anionic compared to cationic complexes. A similar effect was observed in chlorochromate(III) ionic liquids when the ratio of organic to inorganic chloride salt was varied.[42]

To explore the effect of solute anions, various silver and copper salts, namely, sulfate, nitrate, oxide, thiocyanate, and perchlorate, were dissolved in diol-based DESs. The metal speciation was again largely identical to the chloride salts (Table 4). Minor deviations occurred only for silver oxide, where the first coordination shell is still dominated by chloride but may contain a small fraction of oxygen donor ligands. This has been discussed in detail in an earlier publication.[18]

Overall, the information gathered for DESs suggests that metals in similar oxidation states will have similar speciation in a DES environment. For instance, the M^I salts all appear to have $[MCl_2]^-$ coordination, mixed with a small amount of $[MCl_3]^{2-}$, and the M^{II} salts show a consistent $[MCl_4]^{2-}$ coordination. Cr^{III} on the other hand formed mixed chloro–aquo complexes with a coordination number of 6. Metal speciation was dominated by the solvent anion. With the exception of chromium, solute anions, hydrate water, and added water had no or only minor effects in the diol-based liquids. Even strong ligands, such as thiocyanate, are replaced by the solvent. In the urea-based DES, water and/or urea was found in the first coordination shell of some ions, particularly with the earlier transition metals.

Nickel in DESs: A Special Case. The speciation of nickel chloride in DESs stood out from the speciation of the other metal salts. Instead of forming a simple tetrachloro complex, nickel was found to be coordinated by oxygen donors, and chelation was observed for the glycol-based DESs (Table 5). The data for nickel chloride in the imidazolium-based IL [C_6mim][Cl] is discussed in contrast below.

In the Fourier transform of the EXAFS of nickel chloride, sulfate, and nitrate in the ethylene glycol-based DES, two peaks were observed. There were no strong multiple scattering peaks, indicating that there are no linear ligands with two or more atoms. The first peak at ca. 2.1 Å could be fitted with six oxygen donor atoms. The second peak appeared as a shoulder on the main peak at ca. 2.9 Å (Figure 2), which is a typical metal–carbon distance for a chelate ligand with hydrocarbon backbone, forming a five-membered ring. Therefore, a second coordination shell with carbon atoms was introduced and could be refined to a coordination number of 5(2). The error on the coordination number is large but not unexpected, considering the overlap of the signal with the first coordination shell. On the basis of these data, Ni^{II} in the ethylene glycol-based DES is coordinated by three ethylene glycol molecules $[Ni(eg)_3]^{2+}$,

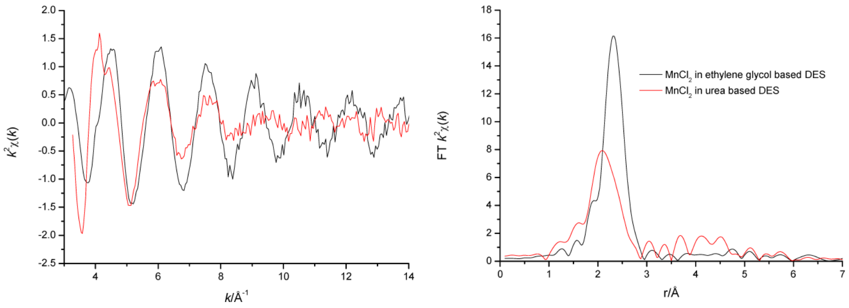

Figure 1. EXAFS (left) and Fourier transform (right) of 100 mM $MnCl_2$ in ethylene glycol-based (black) and urea-based (red) DESs.

Table 3. EXAFS Fits of a Range of Metal(I) Chloride Salts in Deep Eutectic Solvents

	metal salt	X[a]	N[b]	r,[c] (Å)	fit index	proposed species
1,2-ethanediol	AgCl[9,18]	Cl	2.5(2)	2.484(7)	4.3%	$[AgCl_2]^-$ and $[AgCl_3]^{2-}$
	AuCl	Cl	1.9(2)	2.262(6)	5.5%	$[AuCl_2]^-$
	CuCl	Cl	2.4(2)	2.190(9)	8.1%	$[CuCl_2]^-$ and $[CuCl_3]^{2-}$
1,2-proanediol	AgCl	Cl	2.4(2)	2.486(6)	4.2%	$[AgCl_2]^-$ and $[AgCl_3]^{2-}$
	AuCl	Cl	1.8(1)	2.265(6)	6.8%	$[AuCl_2]^-$
urea	AgCl	Cl	2.9(3)	2.525(8)	7.0%	$[AgCl_3]^{2-}$
	CuCl	Cl	2.5(2)	2.224(7)	7.6%	$[CuCl_2]^-$ and $[CuCl_3]^{2-}$

[a]X = type of atom. [b]N = number of atoms. [c]r = distance from X-ray absorber.

Table 4. EXAFS Fits of 100 mM Solutions of a Range of Metal Salts in Deep Eutectic Solvents

	metal salt	X[a]	N[b]	r,[c] (Å)	fit index	proposed species
1,2-ethanediol	Ag_2O[18]	Cl	2.1(2)	2.490(7)	6.4%	$[AgCl_2]^-$
	$AgNO_3$[18]	Cl	2.6(2)	2.482(6)	4.6%	$[AgCl_2]^-$ and $[AgCl_3]^{2-}$
	AgAc	Cl	2.4(2)	2.485(7)	6.6%	$[AgCl_2]^-$ and $[AgCl_3]^{2-}$
	CuSCN	Cl	2.6(3)	2.211(9)	9.6%	$[CuCl_2]^-$ and $[CuCl_3]^{2-}$
	$CuSO_4{\cdot}5H_2O$	Cl	3.8(3)	2.252(7)	8.3%	$[CuCl_4]^{2-}$
	$Cu(ClO_4)_2{\cdot}6H_2O$	Cl	4.0(3)	2.252(6)	7.5%	$[CuCl_4]^{2-}$
1,2-proanediol	$AgNO_3$	Cl	2.4(2)	2.484(5)	3.7%	$[AgCl_2]^-$ and $[AgCl_3]^{2-}$
	AgAc	ClAg	2.0(1) 2.1(3)	2.479(5)2.822(8)	2.7%	complex species

[a]X = type of atom. [b]N = number of atoms. [c]r = distance from X-ray absorber.

with the glycol acting as chelate ligands (Figure 2). This is unusual because ethylene glycol is not expected to be a good ligand in its protonated form, and deprotonation is very unlikely given its pK_a of 14.22.[43] To further confirm this unconventional speciation we recorded EXAFS with other hydrogen bond donors and tried to crystallize Ni complexes from these solvents for XRD analysis.

The EXAFS experiment was therefore repeated in DESs using 1,2-propanediol (propylene glycol) and 1,3-propanediol as hydrogen bond donors, respectively. This was based on the rationale that both glycols should have similar coordinating properties, while 1,3-propanediol would not have an appropriate bite angle to form a similar chelate complex. As expected, the EXAFS of the propylene glycol solution could be refined to a model similar to the one in the ethylene glycol solution. In the 1,3-propanediol solution, nickel was still coordinated by six oxygen atoms. The Fourier transform indicated further electron density at greater distances from the metal center, but there was no sharp peak (Figure 2). Hence, we conclude that 1,3-propanediol is only acting as a monodentate ligand, with the rest of the molecule being much less ordered than in the chelate ligands ethylene glycol and propylene glycol.

Similar to aqueous solutions, the oxygen donor (OD)-bound Ni^{II} forms green solutions in DESs, with the color varying slightly for the different hydrogen bond donors. In contrast, the nickel complex in $[C_6mim][Cl]$ is deep blue, indicating chloride coordination (see below). The glycol-based DESs were also seen to exhibit thermochromism, with the color of the solution becoming more prominently blue with increasing temperature. This effect has been described by other authors for different nickel-containing ILs and DESs.[44,45]

From the solutions described above, nickel–ethylene glycol complexes did not form crystals large enough for XRD. However, upon addition of phenanthroline ligands, crystals could be prepared and analyzed with single-crystal XRD. The overall formula was found to be $[Ni(phen)_2(eg)]Cl_2{\cdot}2eg$ (phen = phenanthroline; eg = ethylene glycol) with two formula units per unit cell crystallizing in the triclinic space group $P\bar{1}$ (Table 6). The crystal structure contains one ethylene glycol and two phenanthroline moieties bound to the metal center (Figure 3) and lends credence to the speciation proposed in Table 5. The Ni–O bond length was found to be 2.078 Å, which is consistent with the EXAFS results. The orientation of the phenanthroline ligands may allow for π-stacking between pairs of ligands along the crystallographic a- and b-axis, respectively. Importantly, chloride is not found in the nickel coordination shell, and the formula unit calculated from the crystal structure demands that ethylene glycol is bound in its neutral form, that is, with oxygen atoms protonated.

Table 5. EXAFS Fits of 100 mM Solutions of Nickel Chloride Hexahydrate in a Range of DES Environments

metal salt	HBD	X[a]	N^b	r,[c] (Å)	fit index	proposed species
$NiCl_2·6H_2O$	1,2-ethanediol	OC	5.8(3) 5(2)	2.084(5) 2.89(3)	6.1%	$[Ni(OD)_3]^{2+d,e}$
$NiCl_2·6H_2O$	1,2-propanediol	OC	5.6(4) 7(2)	2.067(5) 2.86(3)	5.6%	$[Ni(OD)_3]^{2+e}$
$NiCl_2·6H_2O$	1,3-propanediol	O	6.0(4)	2.059(7)	6.6%	$[Ni(OD)_6]^{2+}$
$NiSO_4·6H_2O$	1,2-ethanediol	OC	5.4(4) 5(2)	2.081(5) 2.91(3)	5.6%	$[Ni(OD)_3]^{2+e}$
$Ni(NO_3)_2·6H_2O$	1,2-ethanediol	OC	5.1(5) 5(2)	2.097(7) 2.92(4)	7.7%	$[Ni(OD)_3]^{2+e}$

[a] X = type of atom. [b] N = number of atoms. [c] r = distance from X-ray absorber. [d] OD = oxygen bond donor (e.g., water, ethylene glycol, 1,2-propanediol, 1,3-propanediol). [e] Chelate complex.

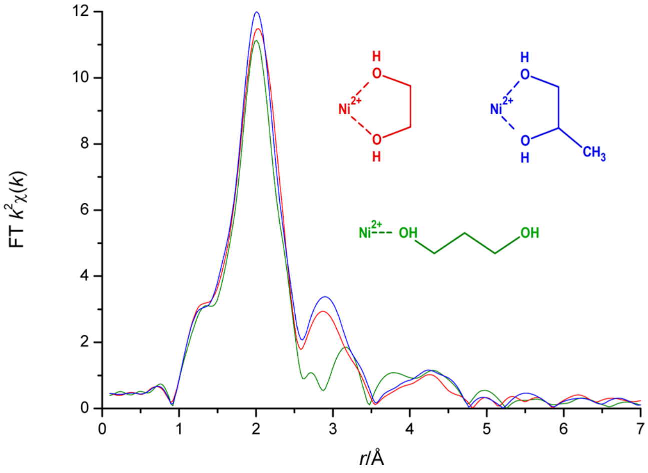

Figure 2. Fourier transform of the EXAFS data for solutions of $NiCl_2·6H_2O$ in ethylene glycol- (red), 1,2-propanediol- (blue), and 1,3-propanediol-based (green) DESs.

These data show that the hydrogen bond donor component of DESs can play a significant role in the coordination of metal ions in solution and that in these exceptional cases, the contribution from the anionic components is not the sole governing factor for metal speciation in DES media. Importantly, nickel forms cationic complexes in DESs at room temperature, while at elevated temperature[44,45] and in imidazolium chlorides anionic complexes are formed. We have previously postulated that because the reduction potential is below the potential of zero charge it should be beneficial to produce cationic metal-containing species as these will then dominate the double layer adjacent to the electrode surface and should make electroreduction easier.[46]

Table 6. Crystallographic Data for $[Ni(phen)_2(en)]Cl_2·2eg$

empirical formula		$C_{30}H_{34}Cl_2N_4NiO_6$
crystal system		triclinic
space group		$P\bar{1}$
unit cell dimensions	a	12.133(3) Å
	b	12.283(3) Å
	c	13.281(3) Å
	α	63.674(4)°
	β	63.441(4)°
	γ	60.698(5)°
volume		1478.5(6) $Å^3$
Z		2
density (calculated)		1.519 g/cm^3
absorption coefficient		0.888/mm
R_{int}		0.1073
absorption correction		empirical
goodness-of-fit on F^2		0.887
final R indices [$I > 2\sigma(I)$]	R1	0.0725
	wR2	0.1295
R indices (all data)	R1	0.1242
	wR2	0.1458
largest diff. peak and hole		0.870 and −0.571 e/$Å^3$

Speciation in Imidazolium-Based Ionic Liquids. By using imidazolium-based ILs, the effect of the solvent cation can be explored. Further, these liquids are commercially available with a large range of anions and are, hence, good candidates to study the effects of the solvent anions compared to the effect of anions from the solute. We have chosen 1-hexyl-3-methylimidazolium chloride $[C_6mim][Cl]$ as a direct comparison for chloride-based DESs and 1-ethyl-3-methylimidazolium thiocyanate $[C_2mim][SCN]$, as well as 1-butyl-3-methylimidazolium

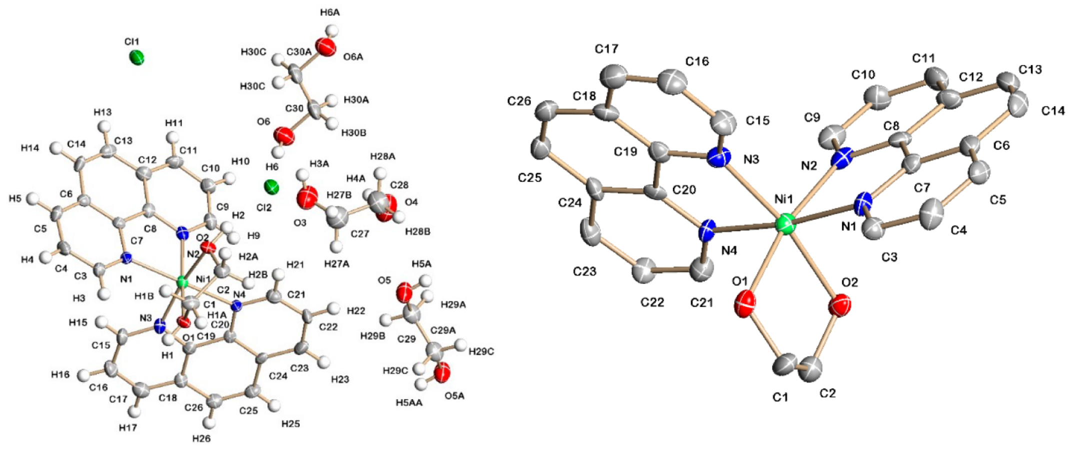

Figure 3. Crystal structure of $[Ni(phen)_2(eg)]Cl_2·2eg$ with hydrogen atoms included (left) and omitted (right). Displacement ellipsoids represent 50% probability.

Table 7. EXAFS Data Fits for 100 mM Solutions of Metal Salts in $[C_6mim][Cl]$

metal salt	X[a]	N[b]	r,[c] (Å)	fit index	proposed species	metal salt	X	N	r, (Å)	fit index	proposed species
$CrCl_3 \cdot 6H_2O$	OCl	2.0(4)3.5(5)	2.08(2)2.369(6)	6.5%	$[CrCl_4(H_2O)_2]^-$	$CrCl_3 \cdot 6H_2O + H_2O$	OCl	3.7(6)2.0(6)	2.00(1)2.31(1)	9.1%	$[CrCl_2(H_2O)_4]^+$
$CuAc_2 \cdot H_2O$	Cl	3.2(2)	2.226(5)	3.3%	$[CuCl_3]^-$	$CuAc_2 \cdot H_2O + H_2O$	Cl	2.9(2)	2.184(5)	3.2%	$[CuCl_3]^-$
$CuCl_2 \cdot 2H_2O$	Cl	3.1(1)	2.230(4)	2.7%	$[CuCl_3]^-$	$CuCl_2 \cdot 2H_2O + H_2O$	Cl	3.0(2)	2.195(5)	3.5%	$[CuCl_3]^-$
$CuSO_4 \cdot 5H_2O$	Cl	3.2(2)	2.224(5)	3.9%	$[CuCl_3]^-$	$CuSO_4 \cdot 5H_2O + H_2O$	Cl	2.8(1)	2.190(4)	3.2%	$[CuCl_3]^-$
$NiAc_2 \cdot 4H_2O$	Cl	3.0(2)	2.259(6)	4.3%	$[NiCl_3]^-$	$NiAc_2 \cdot 4H_2O + H_2O$	OCl	3.7(4)3(2)	2.070(7)2.44(4)	5.9%	$[NiCl_2(OD)_4]^{2-d}$
$NiCl_2 \cdot 6H_2O$	Cl	3.3(3)	2.272(6)	8.1%	$[NiCl_3]^-$	$NiCl_2 \cdot 6H_2O + H_2O$	OCl	2.4(3)2.9(5)	2.03(1)2.261(7)	4.9%	$[NiCl_3(H_2O)_3]^-$

[a] X = type of atom. [b] N = number of atoms. [c] r = distance from X-ray absorber. [d] OD = oxygen bond donor (e.g., water, acetate).

tetrafluoroborate $[C_4mim][BF_4]$, to study anion effects. These liquids were chosen because they are readily available and liquid at room temperature, allowing for facile EXAFS measurements. Imidazolium salts of bis(trifluoromethylsulfonyl)imide $[NTf_2]^-$ and tris(pentafluoroethyl)trifluorophosphate $[FAP]^-$ were also tested. However, the speciation appeared to be very complex, and, due to the poor solubility of the metal salts, the data quality of the EXAFS was insufficient for a meaningful fit. Qualitative comparison of these data to the other ILs suggests that metals mostly retain water coordination.

We studied the speciation of copper, chromium, and nickel salts in $[C_6mim][Cl]$. Copper exhibited pure chloride coordination, irrespective of the solute anion and hydrate water (Table 7). Even the addition of 5% w/w water had no substantial effect on metal speciation. Surprisingly, the coordination number of Cu^{II} was 3 compared to the tetrachloro complexes observed in DESs (see above) and by other authors in $[C_2mim][Cl]$.[32,39] We therefore propose that this is a cation effect: $[C_6mim]^+$ has a longer alkyl chain than $[C_2mim]^+$ and may, hence, favor the formation of complexes with a lower charge, that is, stabilize $[CuCl_3]^-$ rather than $[CuCl_4]^{2-}$.

Interestingly, nickel chloride, which showed coordination with oxygen donor ligands in DESs, has a fully chloride-based shell in $[C_6mim][Cl]$ and forms a deep blue solution (Figure 4). Like copper, the coordination number of nickel is 3, compared to the tetrachloro complexes found in ILs with shorter alkyl chains.[24,25,35] Similarly, XPS studies by License et al. show that nickel in 1:2 $NiCl_2$−$[C_8mim][Cl]$ mixtures is coordinated by 3.3 chloride ions on average.[29] Hence, lower coordination may indeed be facilitated by longer-chain imidazolium cations.

Unlike copper, nickel speciation is susceptible to high water activities: upon the addition of 5% w/w water, oxygen becomes incorporated into the first coordination shell. For nickel chloride, a tricholoro complex with two or three hydrate water molecules is formed. For nickel acetate, the data could be refined to four oxygen atoms and one chloride in the first coordination shell. The Fourier transform exhibits further electron density at 3 to 5 Å, indicating that at least some of the oxygen donors are acetate. Similarly to DESs, dissolution of $CrCl_3 \cdot 6H_2O$ in $[C_6mim][Cl]$ leads to the formation of $[Cr(H_2O)_2Cl_4]^{2-}$. Upon addition of 5% w/w water, $[Cr(H_2O)_4Cl_2]^+$ is formed.

Comparing Cl- with SCN- and BF_4-based ILs demonstrates the great influence of the ligand strength of the solute anion upon speciation. Copper salts dissolved in $[C_2mim][SCN]$ are coordinated by three thiocyanate ions, irrespective of the solute anion (chloride, acetate, sulfate), hydrate water, or added water (Table 8). The Fourier transform for each of these samples displays three main peaks, at ca. 2.0, 3.1, and 4.7 Å, which correspond to the SCN^- ligand,[47] and further signals originating from multiple scattering. The first peak is rather broad and could not be fitted with a shell of only nitrogen or sulfur atoms, but with a mixed N/S coordination. Accordingly, fits with a pure M-SCN or M-NCS were either not stable or yielded fit indices >20%, with irrational Debye−Waller factors. Therefore, we assume that some ligands must bind through the sulfur atom, while others bind through nitrogen. An unconstrained fit would not yield sensible results due to an insufficient data/parameter ratio, resulting in large correlations. The atoms that form a ligand were therefore grouped into two units: one M-SCN and one M-NCS, each to yield one coordination number. All other parameters were allowed to

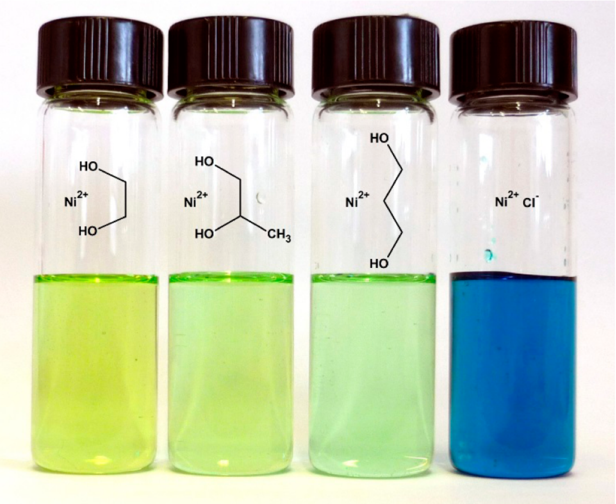

Figure 4. Solutions of $NiCl_2{\cdot}6H_2O$ (100 mM) in DESs using 1,2-ethanediol, 1,2-propanediol, and 1,3-propanediol as a HBD, and in $[C_6mim][Cl]$ (from left to right).

vary freely, resulting in fits of acceptable quality, although some of the errors were relatively large. In all cases copper was coordinated by three $[SCN]^-$ ligands, where two were bound to the metal via the N and one via the S atom.

Chromium EXAFS exhibited features similar to those of the copper spectra but could be refined with five thiocyanate ligands, all binding through nitrogen. According to Pearson's concept of hard and soft acids and bases (HSAB),[48] Cr^{III} and N are classified as hard, S as soft, and Cu^{II} as borderline. The observation that Cr^{III} binds to N while Cu^{II} exhibits mixed S/N coordination in $[C_2mim][SCN]$ is, hence, consistent with the HSAB concept.

For $CrCl_3{\cdot}6H_2O$ and $CuCl_2{\cdot}2H_2O$ in $[C_4mim][BF_4]$, the Fourier transforms of the EXAFS exhibit a first coordination shell at 2 to 2.5 Å and further electron density between 3 and 5 Å, indicating that at least some of the ligands are $[BF_4]^-$. The first coordination shell could be refined with three Cl and three F atoms for chromium and two Cl and two F atoms for copper. The signal at larger distances could not be included in a stable fit; therefore, it is unknown whether some of the lighter atoms are actually oxygen from water ligands.

For the imidazolium-based ILs, the speciation appeared to be based on the anionic species from the IL and not the anion initially bound to the metal salt. Liquids with weaker coordinating anions than chloride did not dissolve the metal salts very well, resulting in EXAFS data with a poor signal-to-noise ratio. Water may be found in the first coordination shell only for the weaker anion BF_4 and for the hard ion Cr^{III}. By controlling the anionic component of the IL, the speciation of the metal ions in solution can also be controlled.

■ SUMMARY AND CONCLUSIONS

EXAFS methods were used to determine the speciation for 25 metal salts in four deep eutectic solvents (DESs) and five imidazolium-based systems. Dissolution of these salts in diol-based liquids, as well as $[C_6mim][Cl]$, generally produced chloro complexes. Even strong ligands, such as thiocyanate, are replaced by the solvent anion. Exceptions occurred only for Cr^{III}, which showed mixed chloro–aquo coordination, and the rather unusual complexation of Ni^{II} by ethylene glycol. The structure of $[Ni(phen)_2(eg)]Cl_2{\cdot}2eg$ was obtained from crystals grown from the ethylene glycol-based IL and also displays glycol coordination. Most complexes were anionic but some were also cationic, which may be significant for electrodeposition kinetics. In the urea-based liquid, chloride coordination was observed for metal ions, which are soft, and oxygen or mixed coordination was observed for ions, which are hard, according to the HSAB principle. This probably originates from the lower chloride activity in the urea-based liquid. Coordination numbers were surprisingly consistent and depended on the oxidation state of the metal ion: in DESs the M^I salts displayed coordination numbers between 2 and 3, on average. Again with the exception of Ni, the M^{II} salts had a coordination number of 4. In $[C_6mim][Cl]$ the metal ions were typically coordinated by

Table 8. EXAFS Data Fits for 100 mM Solutions of Metal Salts in $[C_2mim][SCN]$ (top) and $[C_4mim][BF_4]$ (bottom)

metal salt	X[a]	N[b]	r,[c] (Å)	X	N	r, (Å)	fit index	proposed species
$CrCl_3{\cdot}6H_2O$	N	5.1(6)	1.99(1)				11.0%	$[Cr(NCS)_6]^{3-}$
	C		3.10(2)					
	S		4.45(5)					
$CuAc_2{\cdot}H_2O$	N	2.0(4)	1.914(9)	S	1.0(4)	2.28(1)	6.9%	$[Cu(NCS)_2(SCN)]^-$
	C		3.03(3)	C		4.06(3)		
	S		4.90(7)	N		5.2(6)		
$CuCl_2{\cdot}2H_2O$	N	2.0(3)	1.913(9)	S	0.9(3)	2.27(1)	5.1%	$[Cu(NCS)_2(SCN)]^-$
	C		3.03(1)	C		3.8(1)		
	S		5.0(2)	N		5.2(4)		
$CuCl_2{\cdot}2H_2O + H_2O$	N	2.0(3)	1.911(8)	S	1.0(4)	2.28(2)	6.6%	$[Cu(NCS)_2(SCN)]^-$
	C		3.02(1)	C		4.05(2)		
	S		4.90(6)	N		5.2(5)		
$CuSO_4{\cdot}5H_2O$	N	2.0(3)	1.908(9)	S	1.0(4)	2.26(3)	6.6%	$[Cu(NCS)_2(SCN)]^-$
	C		3.019(9)	C		4.04(3)		
	S		4.9(1)	N		5.0(5)		
$CrCl_3{\cdot}6H_2O$	F	3.1(4)	1.971(4)				3.8%	$[CrCl_3(H_2O/BF_4)_3]$
	Cl	2.5(3)	2.295(3)					
$CuCl_2{\cdot}2H_2O$	F	1.8(3)	1.95(1)				3.4%	$[CuCl_2(H_2O/BF_4)_2]$
	Cl	2.0(5)	2.14(2)					

[a] X = type of atom. [b] N = number of atoms. [c] r = distance from X-ray absorber.

one less ligand than that in DESs, as well as other imidazolium chlorides known from the literature. This could originate from the lower polarity caused by the long alkyl chain.

With the exception of chromium, solute anions, hydrate water, and added water had no or only minor effects in the diol-based liquids. This is important because it means that any potential applications for these liquids do not need to be carried out in a moisture-free environment.

With solute anions other than chloride, the speciation varies depending on the ligand strength of this anion. In [C_2mim]-[SCN] all metals under investigation were coordinated by thiocyanate ligands, while mixed speciation was observed with the weaker tetrafluoroborate ligand in [C_4mim][BF_4]. Speciation in this liquid was also more susceptible to the addition of water. For even weaker anions, such as [FAP]$^-$ or [NTf_2]$^-$, solubilities for the investigated salts were too low to obtain a signal-to-noise ratio suitable for EXAFS fits. The Fourier transforms do, however, indicate that some of the solvent anions bind to the metal.

In conclusion, speciation and coordination numbers are surprisingly uniform for a wide range of different metals if a strong or intermediate ligand is used as the anionic component of the IL. In these cases, the effect of water on speciation is not significant, up to relatively high water contents. With respect to metal solute speciation, there is no significant difference between deep eutectic solvents and imidazolium ILs.

■ ASSOCIATED CONTENT

Supporting Information

Crystal structure of [Ni(phen)$_2$(eg)]Cl$_2$·2eg in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the teams of Diamond beamline B18, ESRF beamline BM26 (DUBBLE) and BESSY II beamline KMC-2 for beamtime and support.

■ REFERENCES

(1) Abbott, A. P.; Frisch, G.; Hartley, J.; Ryder, K. S. *Green Chem.* **2011**, *13*, 471−481.

(2) Binnemans, K. *Chem. Rev.* **2007**, *107*, 2592−2614.

(3) Dietz, M. L. *Sep. Sci. Technol.* **2006**, *41*, 2047−2063.

(4) Smith, E. L.; Abbott, A. P.; Ryder, K. R. *Chem. Rev.* **2014**, accepted for publication.

(5) Habashi, F. *Hydrometallurgy* **2005**, *79*, 15−22.

(6) Hardacre, C. *Annu. Rev. Mater. Res.* **2005**, *35*, 29−49.

(7) Estager, J.; Holbrey, J. D.; Swadźba-Kwaśny, M. *Chem. Soc. Rev.* **2014**, *43*, 847−886.

(8) Abbott, A. P.; Frisch, G.; Ryder, K. S. *Annu. Rev. Mater. Res.* **2013**, *43*, 1.1−1.24.

(9) Abbott, A. P.; El Ttaib, K.; Frisch, G.; Ryder, K. S.; Weston, D. *Phys. Chem. Chem. Phys.* **2012**, *14*, 2443−244.

(10) Abbott, A. P.; Boothby, D.; Capper, G.; Davies, D. L.; Rasheed, R. K. *J. Am. Chem. Soc.* **2004**, *126*, 9142−9147.

(11) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajaha, V. *Chem. Commun.* **2003**, 70−71.

(12) Ravel, B.; Newville, M. *J. Synchrotron Radiat.* **2005**, *12*, 537−541.

(13) Tomic, S.; Searle, B. G.; Wander, A.; Harrison, N. M.; Dent, A. J.; Mosselmans, J. F. W.; Inglesfield, J. E. *CCLRC Technical Report DL-TR-2005−001*, **2005**

(14) Gurman, S. J.; Binsted, N.; Ross, I. *J. Phys. C: Solid State Phys.* **1986**, *19*, 1845−1861.

(15) Sheldrick, G. M. *SHELXTL, Version 6.10;* Bruker AXS, Inc.: Masdison, WI, 2000.

(16) Abbott, A. P.; El Ttaib, K.; Frisch, G.; McKenzie, K. J.; Ryder, K. S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4269−4277.

(17) Abbott, A. P.; Barron, J. C.; Frisch, G.; Gurman, S.; Ryder, K. S.; Silva, A. F. *Phys. Chem. Chem. Phys.* **2011**, *13*, 10224−10231.

(18) Abbott, A. P.; Azam, M.; Frisch, G.; Hartley, J.; Ryder, K. S.; Saleem, S. *Phys. Chem. Chem. Phys.* **2013**, *15*, 17314−17323.

(19) Abbott, A. P.; Frisch, G.; Gurman, S. J.; Hillman, A. R.; Hartley, J.; Holyoak, F.; Ryder, K. S. *Chem. Commun.* **2011**, *47*, 10031−10033.

(20) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

(21) Sasaki, T.; Tada, M.; Zhong, C.; Kume, T.; Iwasawa, Y. *J. Mol. Catal. A: Chem.* **2008**, *279*, 200−209.

(22) Pitula, S.; Mudring, A.-V. *Chem.−Eur. J.* **2010**, *16*, 3355−3365.

(23) Sitze, M. S.; Schreiter, E. R.; Patterson, E. V.; Freeman, R. G. *Inorg. Chem.* **2001**, *40*, 2298−2304.

(24) Zhong, C.; Sasaki, T.; Tada, M.; Iwasawa, Y. *J. Catal.* **2006**, *242*, 357−364.

(25) Carmichael, A. J.; Hardacre, C.; Holbrey, J. D.; Nieuwenhuyzen, M.; Seddon, K. R. *Anal. Chem.* **1999**, *71*, 4572−4574.

(26) Zhong, C.; Sasaki, T.; Jimbo-Kobayashi, A.; Fujiwara, E.; Kobayashi, A.; Tada, M.; Iwasawa, Y. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2365−2374.

(27) Schaltin, S.; Nockemann, P.; Thijs, B.; Binnemans, K.; Fransaer, J. *Electrochem. Solid-State Lett.* **2007**, *10*, D104−D107.

(28) Estager, J.; Nockemann, P.; Seddon, K. R.; Swadźba-Kwaśny, M.; Tyrrell, S. *Inorg. Chem.* **2011**, *50*, 5258−5271.

(29) Taylor, A. W.; Men, S.; Clarke, C. J.; Licence, P. *RSC Adv.* **2013**, *3*, 9436−9445.

(30) Di Marco, V. B.; Bombi, G. G. *Mass Spectrom. Rev.* **2006**, *25*, 347−379.

(31) Zhao, D.; Fei, Z.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 15876−15882.

(32) Li, G.; Camaioni, D. M.; Amonette, J. E.; Zhang, Z. C.; Johnson, T. J.; Fulton, J. L. *J. Phys. Chem. B* **2010**, *114*, 12614−12622.

(33) De Vreese, P.; Brooks, N. R.; Van Hecke, K.; Van Meervelt, L.; Matthijs, E.; Binnemans, K.; Van Deun, R. *Inorg. Chem.* **2012**, *51*, 4972−4981.

(34) Taylor, A. W.; F. Qiu, F.; Villar-Garcia, I. J.; Licence, P. *Chem. Commun.* **2009**, 5817−5819.

(35) Neve, F.; Francescangeli, O.; Crispini, A. *Inorg. Chim. Acta* **2002**, *338*, 51−58.

(36) Alves, M. B.; Santos, V. O., Jr; Soares, V. C. D.; Suarez, P. A. Z.; Rubim, J. C. *J. Raman Spectrosc.* **2008**, *39*, 1388−1395.

(37) Currie, M.; Estager, J.; Licence, P.; Men, S.; Nockemann, P.; Seddon, K. R.; Swadźba-Kwaśny, M.; Terrade, C. *Inorg. Chem.* **2013**, *52*, 1710−1721.

(38) Endres, F.; Abbott, A. P.; MacFarlane, D. R. *Electrodpeosition from Ionic Liquids;* Wiley-VCH, Weinheim, Germany, 2008.

(39) Dent, A. J.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Chem. Commun.* **1990**, 315−316.

(40) Barriada, J. L. *TrAC, Trends Anal. Chem.* **2007**, *26*, 809−817.

(41) Gammons, C. H.; Yu, Y.; Williams-Jones, A. E. *Geochim. Cosmochim. Acta* **1997**, *61*, 1971−1983.

(42) Abbott, A. P.; Abbott, P. D.; Al-Barzinjy, A. A.; Frisch, G.; Hartley, J.; Ryder, K. S. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9047−9055.

(43) Lide, D. R. *CRC Handbook of Chemistry and Physics, 85th ed.*, CRC Press, Boca Raton, FL, 2004, Chapter 8.

(44) Wei, X.; Yu, L.; Wang, D.; Jin, X.; Chen, G. Z. *Green Chem.* **2008**, *10*, 296−305.

(45) Gu, C.-D.; Tu, J.-P. *RSC Adv.* **2011**, *1*, 1220−1227.

(46) Abbott, A. P.; McKenzie, K. J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4265−4279.

(47) Kabesova, M.; Dunaj Jurco, M.; Serator, M.; Gazo, J. *Inorg. Chim. Acta* **1976**, *17*, 161−165.

(48) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533−3539.