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Metal Chelate Formation Using a Task-Specific Ionic Liquid

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An imidazolium-based task-specific ionic liquid containing an ethylaminediacetic acid moiety readily results in the formation of 2:1 octahedral chelate complexes with aqueous Co^{2+}, Ni^{2+}, and Cu^{2+}.

Ionic liquids are now viable alternatives to conventional solvents in a variety of applications. Ionic liquids have seen considerable use as solvents in synthetic applications, catalysis, electrochemistry, and liquid−liquid extractions.[1] In addition to attractive solvent properties (e.g., tunable polarity, viscosity), ionic liquids have also been touted as *green solvents*.[2] The inherently very low vapor pressure and nonflammability of many ionic liquids make these solvents more environmentally favored. Attention is now being given to such issues as the toxicity and biodegradability of ionic liquids so that they may yet be more attractive alternatives to conventional solvents.[3] However, ionic liquids may exert their most useful benefits via their unique solvent properties and also through their potential as *designer solvents* and in separations.

Ionic liquids that have been "designed" to perform a desired function are referred to as task-specific ionic liquids (TSILs).[4] TSILs that perform a variety of functions ranging from those that act as a catalyst and reactant[5] to those that are specifically designed to sequester CO$_2$ gas have been prepared.[6] As alluded to above, ionic liquids have also been used to extract a variety of chemical species from the solution phase. Of particular interest is the ability of TSILs to extract metal ions from aqueous solutions.[4,7] In this context, TSILs containing thiourea moieties have shown some promise in the removal of Cd and Hg ions from aqueous solutions.[4] However, the precise nature of the complexation in these systems remains unknown. This means that elaboration of the coordinating abilities of the ionic liquids has not yet been accomplished, particularly as a means to improve their ability to sequester metals. The specificity of these TSILs for different metal ions was also not investigated to a great extent. In a related study, ionic liquids containing crown ethers and calixarene−crown ethers have also been used to extract metal ions from solution.[7] In these systems, the ionic liquids were observed to parallel the behavior of conventional solvents except that the ionic liquids played a more active role in ion-exchange processes.

Other systems have been reported in which metal chelate complexes involving ionic liquids were formed. For example, the copper(I) chelate complex $\{[HC(3,5\text{-}Me_2pz)_3]Cu(NCMe)\}BF_4$ has been prepared in the ionic liquid solvent $[bmim]PF_6$ and used as a catalyst for the transfer of $:CHCO_2Et$ units to saturated and unsaturated substrates.[8] A dirhodium(II) carboxylate complex containing an imidazolium moiety tethered to the carboxylate was reported to be a useful catalyst in cyclopropanation reactions conducted in ionic liquid solvents.[9] No X-ray crystal structures of any of these metal complexes have been reported.

Hence, we report herein our preliminary results describing the design, synthesis, and X-ray crystal structural analysis of a metal chelate complex prepared from an imidazolium-based TSIL that contains an ethylaminediacetic acid (EDA) as a chelating moiety (Scheme 1). The generation of the dibasic dicarboxylate ion from *tert*-butyl-2-[2-(*tert*-butoxy)-2-oxoethyl][2-(1-methyl-1*H*-imidazol-3-ium-3-yl)ethyl]aminoacetate hexafluorophosphate, $[t\text{-}Bu_2EDA\text{-}mim]^+\ PF_6^-$ (**1**), readily resulted in the formation of an ionic liquid that

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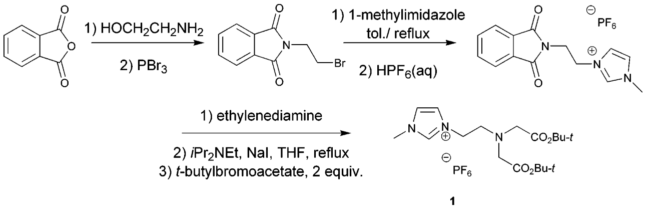
Scheme 1. Synthesis of [*t*-Bu$_2$EDA-mim]$^+$PF$_6^-$ (**1**)



complexes Cu^{2+} ions. This complexing ability was realized from a 2:1 octahedral complex involving aqueous Cu^{2+} (**2**) (Figure 1). An X-ray structural analysis of the resulting metal complex confirms the chelating ability of the TSIL.

The TSIL used in this study was derived from an α,ω-haloamine. The α,ω-haloamine required for the synthetic route was protected as an *N*-(2-bromoethyl)phthalimide prepared by a one-pot, two-step procedure using the condensation between 2-aminoethanol and phthalic anhydride followed by bromination with PBr$_3$.[10] 1-Methylimidazole was then quaternized with *N*-(2-bromoethyl)phthalimide, resulting in the formation of the quaternary bromide salt in 40% yield. The water-soluble quaternary bromide was subjected to an anion-exchange reaction (metathesis) with an aqueous solution of HPF$_6$, resulting in the formation of an imidazolium salt with a phthaloyl group on the side chain and PF$_6^-$ as the counteranion in a 98% yield.[11] Use of the hexafluorophosphate salts enabled much easier isolation of intermediate and final products of this synthetic sequence than did other common salts such as tetrafluoroborate or halide salts. This has been attributed to the decreased water solubility of the hexafluorophosphate salts.

This hexafluorophosphate salt was then subjected to deprotection of the phthaloyl group with ethylenediamine in 1-butanol at 90 °C for 24 h,[12] to result in the formation of the imidazolium salt carrying an amino group in the side chain, namely, 1-(2′-aminoethyl)-3-methylimidazolium hexafluorophosphate. The amino-functionalized imidazolium salt was then subjected to base-promoted *N*,*N*-dialkylation using 2 equiv of *tert*-butylbromoacetate so as to afford the aminediacetic acid in the form of a diester derivative, **1**, in a 13% overall yield based on *N*-(2-bromoethyl)phthalimide.

Our next task was to form metal complexes between the new TSIL containing the free aminediacetic acid moiety and a metal cation. Although it is anticipated that the TSIL will form chelate complexes with a wide variety of metal cations, we chose metals that displayed colored solutions so that we could easily track the presence of the metal throughout the complex formation and subsequent crystallization. Hence, we sought to form complexes using Co^{2+} (red), Ni^{2+} (green), and Cu^{2+} (blue). It was first necessary to deprotect the aminediacetic acid moiety through deesterification of the di-*tert*-butyl ester **1**. This was best accomplished by reacting a dichloromethane solution of compound **1** with trifluoroacetic acid, TFA (Scheme 2).[13] Once the deesterification was complete, the solvent and unreacted TFA were removed under vacuum to afford a syrupy liquid. The addition of an aqueous solution of an appropriate metal halide salt [i.e., CuCl$_2$(aq)] followed by careful adjustment of the pH using aqueous ammonia resulted in the formation of an octahedral complex Cu(EDA-mim)$_2$, **2** (Figure 1). Single crystals of **2**$\cdot$2H$_2$O were obtained upon slow evaporation from an aqueous solution.[14,15]

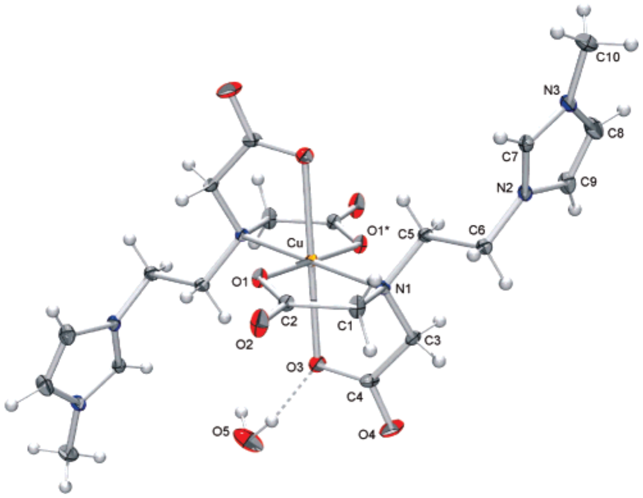
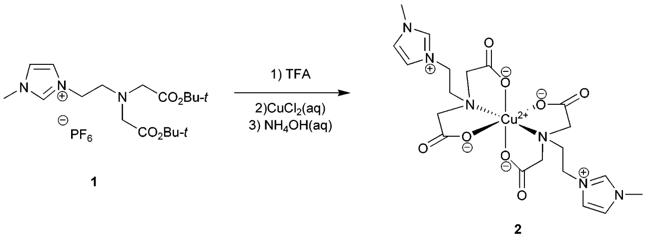


Figure 1. ORTEP perspective of the octahedral Cu^{2+} complex Cu(EDA-mim)$_2$ (**2**). Selected interatomic distances (Å) and angles (deg): Cu−O1 1.936(1), Cu−O3 2.382(1), Cu−N1 2.064(1), O5⋯O3 2.813(2), O5⋯O4^{ii} 2.956(3); O1−Cu−O1^{i} 180, O3−Cu−O3^{i} 180, N1−Cu−N1^{i} 180, O1−Cu−O3 88.3(1), O1−Cu−N1 86.5(1), O3−Cu−N1 76.3(1). Symmetry operator: i, $-x$, $-y$, $-z+1$; ii, $-x-0.5$, $y-0.5$, z.

Scheme 2. Synthesis of Cu[EDA-mim]$_2$ (**2**)



The octahedral complex, which sits around a crystallographic center of inversion, features a 2:1 ratio of the chelating TSIL-based ligand to Cu^{2+} with two unidentate carboxylate ligands in axial positions and two other unidentate carboxylate ligands occupying equatorial positions in a trans configuration. The remaining coordination sites in the octahedral complex are occupied by two equatorial amine ligands. Because the ligand used to chelate the metal is a novel zwitterionic imidazolium ethylaminedicarboxylate ligand with a 1− overall charge, the resulting complex is overall neutral. Thus, a counterion is neither required nor observed for this chelate complex. It is likely that the hexafluorophosphate ion was removed as NH$_4$PF$_6$(aq) during the formation of the complex (see experimental section). The octahedral complex

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and included water molecules assemble via O−H⋯O hydrogen bonds to form a two-dimensional structure.

A particularly interesting feature of the X-ray structure is that the alkyl substituents on the imidazolium rings are oriented away from, rather than toward or wrapped around, the center of the complex. The position of the alkyl groups has enabled us to rationally "re-design" the TSIL ligand to contain a longer alkyl chain, *n*-butyl. Lengthening the alkyl chain renders the complexes formed with Co^{2+}, Ni^{2+}, or Cu^{2+} more hydrophobic and also soluble in 1-butanol. Whereas the complexes derived from **1** are water-soluble and 1-butanol-insoluble, we have determined that those prepared from a derivative containing a butyl chain in the 1 position of the imidazolium ring are soluble in 1-butanol. The formation of these 2:1 complexes using the C4 derivatives has been confirmed using electrospray ionization mass spectrometry (ESI-MS). Yet, other analogues derived from *tert*-butyl{(*tert*-butoxycarbonyl)[3-(**1-decyl**-1*H*-imidazol-3-ium-3-yl)propyl]-amino}methanoate (i.e., the 1-decyl analogue of **1**) have allowed metal ions to be removed directly from aqueous phases with separation into a phase containing the 2:1 complexes. We have subsequently used these TSILs to extract Co^{2+}, Ni^{2+}, or Cu^{2+} from aqueous solutions and are currently investigating the efficiency of these extractions by analyzing the aqueous supernatants by way of inductively coupled plasma MS (ICP-MS). The results of these studies along with details of other complexes currently under investigation will be disclosed in a subsequent full account in due course.

In summary, we have shown that imidazolium-based TSILs containing ethylaminediacetic acid moieties form metal chelate complexes. The presence of the ethylaminediacetic acid moiety presents the possibility that metals may be selectively and perhaps reversibly complexed through careful control of the pH. Recognizing that the majority of ionic liquids are prepared via quarternization of N- or P-containing compounds, we envisage being able to readily extend this methodology to TSILs derived from tetraalkylammonium, pyridinium, pyrollidinium, and phosphonium salts. We are investigating these classes of ionic liquids concurrently with those mentioned herein with the intent of preparing TSILs with desirable solubility and recyclability properties, which should enable these TSILs to be used as recyclable extractants for metal ions of environmental and academic interest.

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Supporting Information Available: General information, experimental procedures for the synthesis of products at each step, characterization data and ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR, MS, and ESI-MS of intermediates and **1** and **2**, references, and X-ray data for compound **2** (Cu^{2+} complex). This material is available free of charge via the Internet at http://pubs.acs.org.

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