

COORDINATION CHEMISTRY AND SPECIATION OF METAL COMPLEXES IN ROOM TEMPERATURE IONIC LIQUIDS

Warren J. Oldham and D. Bridget Williams

Nuclear Materials Technology Division
Mail Stop J-514, Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Room temperature ionic liquids are low melting organic salts generally composed of unsymmetrical organic cations and weakly coordinating anions. While the most commonly used organic cations are 1,3-dialkylimidazolium salts (e.g. Figure 1), MacFarlane and

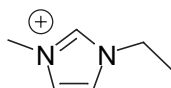


Figure 1. 1,3-ethylmethylimidazolium cation

co-workers have recently demonstrated that N,N-dialkylpyrrolidinium salts also yield low viscosity/high conductivity ionic liquids (Figure 2).¹ This class of ionic

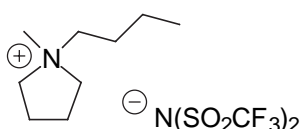
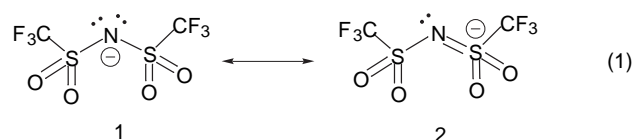


Figure 2. N,N-butylmethylpyrrolidinium bis(trifluoromethanesulfonyl)amide salt

liquids, prepared as the bis(trifluoromethanesulfonyl)amide salt, offers distinct advantages over imidazolium based ionic liquids due to their expanded electrochemical window and improved chemical stability.

Pyrrolidinium- or more generally, quaternary ammonium-based ionic liquids are potentially useful solvents for use in actinide electrorefining due to their robust cathodic stability. While efficient electrochemical plating and stripping of both sodium and potassium metals have been demonstrated in this media, multielectron plating processes appear to be kinetically inhibited at ambient temperature.² In order to more fully understand these issues we have set out to characterize the coordination chemistry and speciation of metal complexes dissolved in bis(trifluoromethanesulfonyl)amide (NTf₂) based ionic liquids.

The coordination chemistry anticipated for the ionic liquids under investigation in this work are related to the electronic structure of ⁻NTf₂. Single crystal X-ray diffraction experiments carried out for organic salts of ⁻NTf₂ reveal short S–O and N–S bond lengths most consistent with resonance structure **2** (eq 1).³



Delocalization of negative charge within the S–N–S core can account for the weak coulombic attraction between the ⁻NTf₂ anion and weakly Lewis acidic organic cations (*i.e.* low lattice energy and low melting points). Although little interaction between ⁻NTf₂ and weak Lewis acids is

indicated by structural studies of organic ⁻NTf₂ salts, the potential of bonding interaction with Lewis acidic metal ions should be considered. Strauss and coworkers employed ⁻NTf₂ as a weakly coordinating anion in the study of nonclassical metal-carbonyl complexes, for which a crystal structure of an ⁻NTf₂ anion coordinated to a copper (I) atom has been reported.⁴ In this case, metrical data obtained for Cu(CO)₂(NTf₂) demonstrates that ⁻NTf₂ coordinates to Cu via nitrogen ligation. Based on this data the ⁻NTf₂ ligand could be considered as an unusual amido type ligand, perhaps similar to ⁻N(C₆F₅)₂ in its coordinating ability.

One of the metal complexes that we have examined in some detail to learn about the coordination environment of ⁻NTf₂ based ionic liquids is the solvatochromic copper(II) salt, [Cu(acac)(tmeda)]NTf₂. A single crystal X-ray diffraction study carried out for this complex demonstrates a short 2.794 Å Cu•••O interaction between a sulfonyl oxygen atom and the square planar Cu complex (Figure 3).

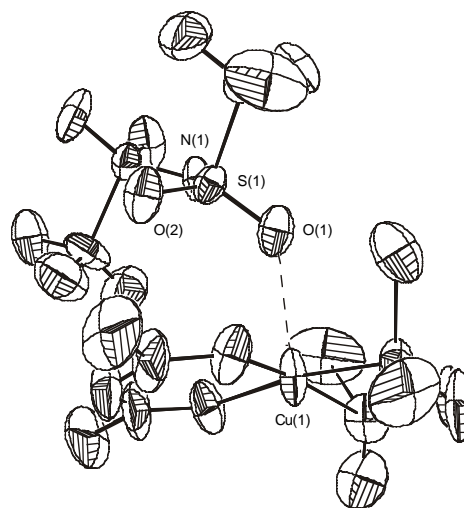


Figure 3. Thermal ellipsoid representation of [Cu(acac)(tmeda)]NTf₂ (acac = acetylacetonate, tmeda = tetramethylethylenediamine).

Examination of the solid state and solution phase UV/vis spectrum suggests that this structure is maintained upon dissolution in the ionic liquid. This example serves to illustrate the range of different ionic liquid/metal interactions that are possible, which in-turn should influence the behavior of metal complexes in solution.

This research was supported by the Laboratory Directed Research and Development (LDRD) program of Los Alamos National Laboratory, operated by the University of California for the U. S. Department of Energy.

- (1) MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. *J. Phys. Chem. B* **1999**, *103*, 4164
- (2) "Development of Room Temperature Ionic Liquids for Applications in Actinide Chemistry" Oldham, W. J., Jr.; Costa, D. A.; Smith, W. H. in *Industrial Applications of Ionic Liquids*, Rogers, R. D., ed., ACS Publications, Washington, D. C., 2001, (in press).
- (3) Golding, J. J.; MacFarlane, D. R.; Spiccia, L.; Forsyth, M.; Skelton, B. W.; White, A. H. *Chem. Comm.* **1998**, 1593.
- (4) Polyakov, O. G.; Ivanova, S. M.; Gaudinski, C. M.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Organometallics* **1999**, *18*, 3769.