ABSTRACT

The most common organic salts used in our lab to prepare ionic liquids include a variety of imidazolium, pyrrolidinium, or acyclic ammonium cations combined with the $\text{N(SO}_2\text{CF}_3\text{)}_2$ anion. This anion has been found to yield ionic liquids with the best combination of physical properties for routine use in chemical applications. Unfortunately, the coordination chemistry of metal complexes in these solvents is almost completely unknown. This proceedings contribution outlines a series of structural, spectroscopic, and electrochemical studies undertaken to obtain detailed characterization of the primary coordination sphere of electrophilic metal ions dissolved in $\text{N(SO}_2\text{CF}_3\text{)}_2$ based ionic liquids. It is demonstrated that the $\text{N(SO}_2\text{CF}_3\text{)}_2$ anion can behave as a competent ligand, coordinating to electrophilic metal ions through direct M-N or M-O bonds. The consequences of $\text{N(SO}_2\text{CF}_3\text{)}_2$ coordination on the electronic properties and electrochemical behavior of metal species in these novel chemical environments is presented.

INTRODUCTION

The solvent properties of room temperature ionic liquids (RTILs) are of much current interest, based in some part on the curious and unusual liquid state of this class of organic salts. Of more practical import has been the recognition that molecular interactions of dissolved solute species with ionic liquid constituents should directly influence the utility of these solvents in organic synthesis, metal mediated catalysis, chemical separations, and electrochemistry. A number of studies have approached this problem by attempting to determine the polarity of ionic liquids using a variety of spectroscopic probes, which have been previously employed in the study of conventional molecular solvents (1-2). However, Gordon and coworkers have correctly pointed out that “polarity” is actually a complex property composed of many different molecular interactions (3). From a chemical point of view it is generally more useful to appreciate the strength of the Lewis acidity and Lewis basicity for the solvent of interest. This approach is well developed, largely from the work of Victor Gutmann who developed the acceptor number (AN) and donor number (DN) scales to characterize molecular solvents (4-5).

In this paper, the interaction of $\text{N(SO}_2\text{CF}_3\text{)}_2$ based ionic liquids with electrophilic metal ions is studied by direct synthesis of well defined metal salts or actual complexes containing direct M-N or M-O bonds with the anion. These complexes have been
structurally characterized through single crystal X-ray diffraction experiments. The effect of N(SO₂CF₃)₂ coordination on the metal's electronic properties and electrochemical behavior is also reported.

RESULTS AND DISCUSSION

Solvatochromic Copper (II) Complexes

One of the classic probes used to measure Lewis basicity is the solvatochromic Cu(II) complex salt, [Cu(acac)(tmeda)]BPh₄ (1), shown below (acac = acetylacetonate; tmeda = tetramethylethylenediamine) (6-8). This salt exists in the solid state as non-interacting,

![Cu(acac)(tmeda)]BPh₄ (1)

four-coordinate square planar copper cations and tetraphenylborate anions. The solution phase absorbance spectrum of 1 is found to be highly dependent on the Lewis basicity of the particular solvent in which the probe is dissolved. For example, in figure 1 is shown the absorbance spectra of 1 (1 x 10⁻³ M) dissolved in dichloroethane (DCE), nitromethane, 1,3-ethylmethylimidazolium N(SO₂CF₃)₂ (EMI NTf₂), tetrahydrofuran (THF), acetonitrile, ethanol, and dimethylsulfoxide (DMSO).

The absorbance maxima shift from 500 nm for the weakest donor solvent, DCE, to 610 nm for the strongest donor, DMSO. When dissolved in the ionic liquid, EMI NTf₂, the absorbance maxima is observed at 548 nm, in agreement with previous reports for closely related N(SO₂CF₃)₂ based ionic liquids described by Gordon and coworkers (3). This absorbance maximum is consistent with the ionic liquid behaving as a weakly coordinating solvent. Tentatively, the donor number of the ionic liquid can be estimated at about 10, based on this absorbance maximum.

The actual molecular nature of the interaction was determined by preparing the authentic [Cu(acac)(tmeda)]N(SO₂CF₃)₂ (2) complex, which was then structurally characterized. The solid-state structure of 2 is probably relevant to the solution phase structure, indicated by the fact that the absorbance maxima in the solid state (solid-state reflectance) and in ionic liquid solution are both near 550 nm.

The copper (II) cation exists as a four-coordinate square planar complex containing two oxygen and two nitrogen donor atoms in the coordination sphere (Figure 2). A weak Cu···O interaction is found along the z-axis between the copper atom and one
Figure 1. Absorbance spectra of \([\text{Cu(acac)}(\text{tmeda})]\text{BPh}_4\) (1 x 10^{-1} M) as a function of solvent.

The oxygen atom of the \(\text{N(SO}_2\text{CF}_3\text{)}_2\) ligand. These interactions are observed both above and below the plane of the copper complex, and are related by symmetry, though only one is shown in Figure 2. The weak Cu***O distance is 2.75 Å, compared to shorter (and stronger) Cu–O interactions in related Cu(II) complexes between OH\(_2\) (2.38 Å) (9) or NO\(_3^-\) (2.38–2.41 Å) (10). Consistent with the weak Cu***O interaction in 2, the bond lengths and angles of the \(\text{N(SO}_2\text{CF}_3\text{)}_2\) anion are little perturbed from those found in simple organic salts, where no bonding interaction with the anion is indicated (11).

Figure 2. Ball and stick representation of \([\text{Cu(acac)}(\text{tmeda})]\text{N(SO}_2\text{CF}_3\text{)}_2\) derived from a single crystal X-ray diffraction study.
An Organoiron (II) Complex of N(SO₂CF₃)₂

Treatment of a bright yellow solution of (C₅H₅)Fe(CO)₂Me in EMINTf₂ with HN(SO₂CF₃)₂ rapidly yields a deep red solution from which bubbles of methane are liberated (eqn 1). The new complex, assigned as (C₅H₅)Fe(CO)₂(N(SO₂CF₃)₂) (3) displays unique \( \nu(CO) \) bands in the solution phase IR spectrum shifted to significantly higher energy at 2072 and 2026 cm⁻¹. An identical reaction carried out in CH₂Cl₂ gives the same complex as evidenced by IR spectroscopy. Carbonyl stretching bands in this range compare closely to several known (C₅H₅)Fe(CO)₂X complexes, where X is a weakly coordinating anion such as BF₄ (2072, 1994 cm⁻¹), SbF₆ (2074, 2030 cm⁻¹), ClO₄ (2071, 2009 cm⁻¹) or OSO₂CF₃ (2068, 2017 cm⁻¹) (12). These comparisons support the conclusion that \( \sim\)N(SO₂CF₃)₂ is a weakly donating ligand capable of stabilizing coordinatively unsaturated metal complexes.

Complex 3, prepared in CH₂Cl₂ and isolated upon cooling to −30 °C, yields well formed deep red crystals suitable for X-ray structural analysis. A ball and stick representation of 1 is shown in figure 3. The (C₅H₅)(CO)₂Fe fragment,

![Figure 3](image)

**Figure 3.** Ball and stick representation of (C₅H₅)Fe(CO)₂(N(SO₂CF₃)₂) derived from a single crystal X-ray diffraction study.

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characterized by typical bond lengths and angles, is directly coordinated to the nitrogen atom of the $\text{N(SO}_2\text{CF}_3)_2$ anion with an Fe–N bond length of 2.084(4) Å. The N–S bond lengths in 3 become significantly longer upon nitrogen coordination (N(1)–S(1) and N(1)–S(2) are 1.630(4) and 1.643(4) Å, respectively), compared to the free anion (N–S = 1.56–1.57 Å). Further the S–N–S angle becomes more acute in the complex (117° vs. 125° in the uncoordinated anion). Complex 3 is an extremely rare case of a structurally characterized $\text{N(SO}_2\text{CF}_3)_2$ complex. Only one other example, Cu(CO)$_2$(N(SO$_2$CF$_3$)$_2$), (characterized by similar metrical parameters) has been structurally characterized (13).

A Titanocene (IV) Bis(N(SO$_2$CF$_3$)$_2$) Complex

In the second example, a red EMINTf$_2$ solution of (C$_5$H$_5$)$_2$TiCl$_2$ (4) is reacted with two equiv. of AgN(SO$_2$CF$_3$)$_2$ (see eqn 2). After filtration to remove insoluble AgCl, the deep brown ionic liquid solution is probed electrochemically by cyclic voltammetry experiments. Shown in figure 4 is a comparison of the reversible $4^+/3^+$ couples of 4 and the new titanium species assigned as (C$_5$H$_5$)$_2$Ti(N(SO$_2$CF$_3$)$_2$)$_2$ (5). Substitution of the two chloride ligands for two $\text{N(SO}_2\text{CF}_3)_2$ ligands results in a significant shift of the $4^+/3^+$ $E_{1/2}$ value from -1.43 to -0.49 V indicating a strong stabilization of the metal based LUMO of 0.94 V.
Potential (mV)

Figure 4. Cyclic voltammetry curve for Cp₂TiCl₂ (E₁/₂ = -1.43 V) and Cp₂Ti(N(SO₂CF₃)₂)₂ (E₁/₂ = -0.49 V) measured using a standard size Pt working electrode vs. Ag/AgOTf/EMI NTf₂. Fc/Fc⁺ = -0.38 V.

Complex 5 may also be prepared and isolated from benzene solutions upon crystallization with hexane. Single crystals suitable for structural analysis were obtained by slow vapor diffusion of hexane into a concentrated benzene solution at ambient temperature. Figure 5 depicts a ball and stick representation of 5, which illustrates a typical titanocene fragment coordinated to two N(SO₂CF₃)₂ ligands through an unprecedented metal–oxygen binding mode. The titanium–oxygen bond lengths of ca. 2.06 Å are on the short side of normal Ti–O bonds, but are similar to tetravalent Ti–OSO₂CF₃ complexes found in the Cambridge crystallographic database. Furthermore, significant structural changes are observed in the N(SO₂CF₃)₂ ligands compared to the free anion. The S–O bond lengths of the titanium bound oxygen atoms are lengthened to about 1.467 Å compared to the remaining S–O bond lengths, which remain short at about 1.42 Å. The N–S bond lengths also reveal significant distortion indicated by a short (N(1)–S(1) = 1.523(5) Å) and a long (N(1)–S(2) = 1.613(5) Å) distance.
Figure 5. Ball and stick representation of \( \text{Cp}_2\text{Ti}(\text{N(SO}_2\text{CF}_3)\text{)}_2 \) derived from a single crystal X-ray diffraction study.

Interpretation of Structural Data

It has been demonstrated in this paper that the \( \text{N(SO}_2\text{CF}_3)\text{)}_2 \) anion can function as a competent ligand to electrophilic metal complexes. The uncoordinated anion is characterized by short \( N-S \) (1.56–1.57 Å) and short \( S-O \) (1.42 Å) bond lengths, which is consistent with the valence bond resonance structure, B, shown in equation 3. Upon coordination to a metal complex via the nitrogen atom, the \( N-S \) bond lengths increase to about 1.63 Å, indicating an increasing contribution of resonance structure A to the overall valence bond description. However, when coordinated to a metal complex via the oxygen atom, the \( S-O \) bond of the ligated oxygen atom is lengthened to about 1.47 Å and two distinct \( N-S \) bond lengths of 1.52 and 1.61 Å suggest that resonance structure C now becomes an important description of \( \text{N(SO}_2\text{CF}_3)\text{)}_2 \).

\[
\begin{align*}
\text{F}_3\text{SO}_3^+ & \quad \text{N} \quad \text{CF}_3^+ \\
\text{A} & \quad \text{B} & \quad \text{C}
\end{align*}
\]
Although these data indicate that $\text{N(SO}_2\text{CF}_3)_2$ can function as a competent ligand in the absence of a better alternative, it is also found that this anion is a very poor donor. This is most profoundly demonstrated in the $4^+/3^+$ $E_{1/2}$ shift between $\text{Cp}_2\text{TiCl}_2$ and $\text{Cp}_2\text{Ti}(\text{N(SO}_2\text{CF}_3)_2)_2$ in which the $\text{N(SO}_2\text{CF}_3)_2$ complex is nearly 1V more easily reduced (see Figure 4).

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