



## Copper ionic liquids: Examining the role of the anion in determining physical and electrochemical properties

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### ABSTRACT

Five new copper(II)-based ionic liquids and three crystalline compounds have been synthesized in order to further understand the role of the anion in determining their physicochemical properties. Materials were prepared with combinations of three different anions (2-ethylhexanoate (EHN), tetrafluoroborate ( $\text{BF}_4^-$ ), and triflate (OTf)) and six-coordinate Cu(II) cations. The complexes that contain at least one  $\text{BF}_4^-$  anion consistently displayed both the highest specific conductivity and electrochemical reversibility. The presence of one OTf anion (in combination with one EHN or  $\text{BF}_4^-$ ) facilitates the formation of crystalline materials. Single crystal X-ray diffraction studies were completed on two of the mixed anion compounds. The results show that both ethanolamine (EA) and diethanolamine (DEA) chelate to the Cu(II) centers in a highly distorted tetragonal geometry. The properties of the ionic liquid with the overall lowest viscosity and highest conductivity and electrochemical reversibility ( $\text{Cu}(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_6(\text{BF}_4)_2$ , **4**) were studied as a function of temperature. The viscosity decreases with increasing temperature, but at 45 °C (over three hours) there is a loss of two EA ligands to form a more viscous four-coordinate complex. Cyclic voltammetry of **4** reveals a quasi-reversible Cu(II)/Cu(I) reduction wave that shifts to more positive potentials with increasing temperature.

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### 1. Introduction

Ionic liquids (ILs) containing transition metal elements (MetILs) are of interest in both basic science and applied energy technologies [1–22]. Their high thermal stabilities, negligible vapor pressures, and wide electrochemical windows make them attractive for applications ranging from separations and synthesis to catalysis and electrochemistry [23–32]. Recently, we (and others) reported ionic liquids containing a first-row transition metal coordination cation (cobalt [22], copper [14,15,21,33], iron [34,35], manganese [21,33], nickel [22], or zinc [6,33]) and weakly pairing monovalent anion(s) (such as  $\text{BF}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ , or  $\text{PF}_6^-$ ). Although some of their physicochemical properties (including viscosity, conductivity, and electrochemical reversibility) can be systematically altered by ligand and anion choice, there is still a need to understand how the anion might be used to more finely tailor their chemistry [36]. This is particularly true given there are at least two anions per coordination cation in all of the materials we have prepared to date. In order to study ion pairing in MetILs more closely, we now report syntheses of new Cu(II)-based complexes containing two different anions in the same ionic liquid. The presence of mixed anions in the ionic liquids appears to facilitate both the

reversible reduction (and subsequent re-oxidation) of the cupric center as well as promote crystallization of the resulting material when triflate ( $\text{CF}_3\text{SO}_3^-$ ) is present. In addition, we have also prepared a new copper ionic liquid with two tetrafluoroborate ( $\text{BF}_4^-$ ) anions that demonstrates the highest electrochemical reversibility, lowest viscosity and highest conductivity of any cupric ionic liquid we have reported to date. The results elucidate a trend for weaker ion pairing leading to higher electrochemical reversibility, lower viscosity and higher conductivity.

### 2. Experimental

#### 2.1. General method

All starting materials were purchased from Sigma–Aldrich or Alfa Aesar. Infrared spectra were recorded on a Thermo Nicolet iS10 FT-IR equipped with a Smart Orbit (Diamond) ATR accessory. Elemental analyses were performed by Galbraith Laboratories, Inc. Water content was measured using a Mettler Toledo C20 coulometric Karl Fischer titrator. Viscosity measurements were performed on a Brookfield DV-II+ Pro viscometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on TA Instruments Q600 and Q2000, respectively. A Thermo Nicolet iZ10 was used to interface the iS10 FT-IR to the TA Instruments Q600. Magnetic susceptibility measurements were

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**Table 1**  
Crystal data and structure refinement for **5** and **9**.

	<b>5</b>	<b>9</b>
Empirical formula	C <sub>14</sub> H <sub>42</sub> Cu <sub>2</sub> F <sub>6</sub> N <sub>6</sub> O <sub>13</sub> S <sub>2</sub>	C <sub>18</sub> H <sub>42</sub> Cu <sub>2</sub> F <sub>6</sub> N <sub>4</sub> O <sub>14</sub> S <sub>2</sub>
Formula weight	807.74	843.76
T (K)	193(2)	193(2)
Crystal system/space group	monoclinic/C2/c	triclinic/Pī
a (Å)	21.2337(15)	11.9035(9)
b (Å)	9.0399(6)	12.2224(9)
c (Å)	17.3308(12)	12.9488(9)
α (°)		94.9710(1)
β (°)	107.3570(1)	108.7470(1)
γ (°)		112.6420(1)
V (Å <sup>3</sup> )	3175.2(4)	1598.1(2)
Z	4	2
D <sub>calc</sub> (Mg/m <sup>3</sup> )	1.690	1.753
μ (Mo Kα) (mm <sup>-1</sup> )	1.570	1.564
Goodness-of-fit (GOF) on F <sup>2</sup>	1.036	1.031
R <sub>1</sub> <sup>a</sup> (%) (all data)	2.90 (3.40)	4.01 (4.87)
wR <sub>2</sub> <sup>b</sup> (%) (all data)	7.67 (8.16)	9.40 (10.09)

<sup>a</sup>  $R_1 = \sum |F_o| - |F_c| / \sum |F_o| \times 100$ .<sup>b</sup>  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2} \times 100$ .

made on a Johnson and Matthey MK-1 balance and Pascal's constants were used to apply a diamagnetic correction. Electrochemical (cyclic voltammograms, CVs) and impedance measurements were made as previously described [34]. Temperature control was maintained using a Tenney environmental chamber.

## 2.2. Synthesis studies

### 2.2.1. General procedure for mixed anion compounds

The compounds summarized in Table 2 (Section 3.1) were prepared by mixing a copper salt (with anion 1) with 12 equivalents of NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (ethanolamine, EA) or NH(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> (diethanolamine, DEA) in a 20 mL glass vial. The resulting mixture was heated until a homogeneous blue solution was obtained. Then the second copper salt (with anion 2, in an equal molar amount to the copper salt containing anion 1) was added, and the solution was continually heated (up to 200 °C) until homogeneity was once again obtained. The resulting product was then slowly cooled to room temperature. Elemental analyses were performed on all samples to verify the correct elemental ratios were present.

**Table 2**  
Summary of cupric ionic liquids as a function of anion constitution.

#	Ligand <sup>a</sup>	Anion 1 <sup>b</sup>	Anion 2 <sup>b</sup>	State at 25 °C	T <sub>g</sub> (°C)	σ (mS/cm)	E <sub>1/2</sub> <sup>h</sup> (mV)	ΔE <sup>h</sup> (mV)
<b>1</b>	EA	EHN	EHN	Liquid <sup>c</sup>	-63	0.207	-156	244
<b>2</b>	EA	OTf	OTf	Solid <sup>d</sup>	105 <sup>f</sup>	- <sup>g</sup>	93	158
<b>3</b>	EA	EHN	OTf	Solid <sup>d</sup>	100 <sup>f</sup>	- <sup>g</sup>	93 <sup>i</sup>	158 <sup>i</sup>
<b>4</b>	EA	BF <sub>4</sub>	BF <sub>4</sub>	Liquid	-70	6.80	46	102
<b>5</b>	EA	BF <sub>4</sub>	OTf	Solid <sup>e</sup>	100 <sup>f</sup>	- <sup>g</sup>	118	256
<b>6</b>	EA	BF <sub>4</sub>	EHN	Liquid	-66	0.586	-16	187
<b>7</b>	DEA	EHN	EHN	Liquid <sup>c</sup>	-54	0.014	-149	522
<b>8</b>	DEA	OTf	OTf	Liquid <sup>c</sup>	-65	0.067	-45	566
<b>9</b>	DEA	EHN	OTf	Solid <sup>e</sup>	82 <sup>f</sup>	- <sup>g</sup>	90	507
<b>10</b>	DEA	BF <sub>4</sub>	BF <sub>4</sub>	Liquid	-62	1.05	21	150
<b>11</b>	DEA	BF <sub>4</sub>	OTf	Liquid	-64	0.210	32	159
<b>12</b>	DEA	BF <sub>4</sub>	EHN	Liquid	-67	0.142	-37	201

<sup>a</sup> EA = ethanolamine, DEA = diethanolamine.<sup>b</sup> BF<sub>4</sub> = tetrafluoroborate, EHN = 2-ethylhexanoate, OTf = triflate.<sup>c</sup> Data from Ref. [33].<sup>d</sup> Microcrystalline.<sup>e</sup> Crystalline (single crystal diffraction quality).<sup>f</sup> A T<sub>m</sub> (onset of melting) is observed in place of a T<sub>g</sub>.<sup>g</sup> Data not collected (solid sample).<sup>h</sup> 0.1 M solutions in 1-butyl-3-methyl-imidazolium hexafluorophosphate (BMI-PF<sub>6</sub>) with a glassy carbon (working) electrode (scan rate 50 mV s<sup>-1</sup>).<sup>i</sup> Isolated, microcrystalline material is identical to compound **2** based on infrared spectroscopy and elemental analysis.

### 2.2.2. Synthesis of Cu{NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH}<sub>6</sub>[BF<sub>4</sub>]<sub>2</sub> (**4**)

A 0.70 g (3.43 mmol) amount of Cu(BF<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O (water content measured by TGA) was added to a stirring solution of EA (1.26 g, 20.6 mmol) in a 20 mL glass vial, quickly heated, and continuously stirred for approximately 10 min without additional heating. Excess water (introduced from Cu(BF<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O) was removed using 4 Å molecular sieves. IR (ATR, 4000–500 cm<sup>-1</sup>): 3572 (m), 3341 (sh), 3263 (m), 3166 (m), 2945 (m), 2881 (m), 1637 (sh), 1598 (m), 1539 (w), 1458 (m), 1387 (sh), 1361 (w), 1288 (w), 1054 (sh), 1016 (s), 870 (m), 839 (sh), 765 (s), and 668 (w). Anal. Calc.: B, 3.55; C, 23.6; Cu, 10.4; F, 24.9; H, 7.94; N, 13.8. Found: B, 3.48; C, 24.0; Cu, 10.2; F, 24.1; H, 7.90; N, 13.5%. (MW = 603.7 g/mol).

### 2.2.3. Synthesis of Cu{NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH}<sub>2</sub>{NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O}{OH<sub>2</sub>}[CF<sub>3</sub>SO<sub>3</sub>] (**5**)

A 0.282 g (1.38 mmol) sample of Cu(BF<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O was added to a stirring solution of EA (1.01 g, 16.6 mmol) in a 20 mL glass vial and the resulting mixture was quickly heated to obtain homogeneity. Afterwards, a 0.500 g (1.38 mmol) amount of Cu(OTf)<sub>2</sub> (where OTf is CF<sub>3</sub>SO<sub>3</sub>) was added to the heated solution and the solution was again allowed to stir until homogeneity is obtained. The solution was cooled to room temperature and allowed to sit (approximately one week) until diffraction quality crystals were obtained. The same product is obtained when an equal molar quantity of Cu(EHN)<sub>2</sub> (where EHN is 2-ethylhexanoate) is used in place of Cu(BF<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O. IR (ATR, 4000–500 cm<sup>-1</sup>): 3332 (m), 3279 (m), 3174 (m), 2958 (sh), 2934 (m), 2878 (m), 2838 (w), 1665 (sh), 1598 (m), 1551 (m), 1462 (m), 1404 (sh), 1390 (m), 1356 (w), 1337 (sh), 1244 (s), 1224 (s), 1196 (sh), 1160 (s), 1060 (s), 1024 (s), 890 (sh), 876 (m), 852 (sh), 802 (w), 759 (m), 693 (sh), 679 (w), 634 (s), and 573 (m). Anal. Calc.: B, 0; C, 20.4; Cu, 15.4; F, 13.8; H, 5.37; N, 10.2; S, 7.77. Found: B, 0; C, 20.7; Cu, 15.2; F, 13.3; H, 5.38; N, 10.1; S, 7.69%. (MW = 412.9 g/mol).

### 2.2.4. Synthesis of

#### Cu{NH(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>}{NH(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>CH<sub>2</sub>O)}[CF<sub>3</sub>SO<sub>3</sub>] (**9**)

A 0.500 g (1.43 mmol) amount of Cu(EHN)<sub>2</sub> was added to a stirring solution of DEA (1.81 g, 17.2 mmol) in a 20 mL glass vial and the resulting mixture was quickly heated to obtain homogeneity. Afterwards, a 0.517 g (1.43 mmol) sample of Cu(OTf)<sub>2</sub> was added to the heated solution and the solution was again allowed to stir until homogeneity is obtained. The solution was cooled to room

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