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(54) **Title:** SYNTHESIS OF NON-CYCLIC AMIDE AND THIOAMIDE BASED IONIC LIQUIDS

(57) **Abstract:** Non-cyclic amide or thioamide based ionic liquids and methods of making them are disclosed.



WO 2017/011232 A1

SYNTHESIS OF NON-CYCLIC AMIDE AND THIOAMIDE BASED IONIC LIQUIDS

STATEMENT OF PRIORITY

5 This application claims priority to U.S. Provisional Application No. 62/190952 which was filed July 10, 2015, the contents of which are hereby incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

10 Ionic liquids are of interest to industry because of their wide range of applications, including use as solvents and catalysts. Ionic liquids are salts comprised of cations and anions which typically melt below 100°C.

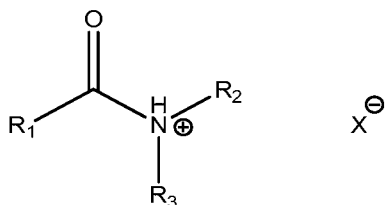
15 Ionic liquids are described in US Patent Nos. 4,764,440, 5,104,840, and 5,824,832, for example. The properties vary extensively for different ionic liquids, and the use of ionic liquids depends on the properties of a given ionic liquid. Depending on the organic cation of the ionic liquid and the anion, the ionic liquid can have very different properties.

 However, the cost of ionic liquids has limited the widespread adoption of ionic liquids.

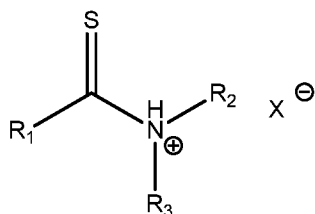
 There is a need for lower cost ionic liquids and for methods of making them.

20 SUMMARY OF THE INVENTION

 One aspect of the invention is a non-cyclic amide or thioamide based ionic liquid. In one embodiment, the non-cyclic amide or thioamide based ionic liquid comprises a cation and an anion and has the formula:

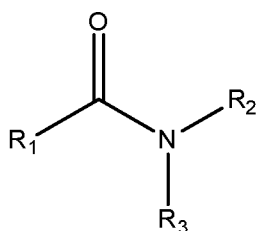


or

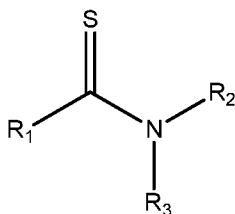


wherein R_1 , R_2 , and R_3 are independently selected from hydrogen, halide, a $C_1 - C_{12}$ alkyl group, a $C_1 - C_{12}$ alkenyl group, a $C_4 - C_{12}$ cycloalkyl group, a $C_4 - C_{12}$ cycloalkenyl group, an aryl group, a substituted $C_1 - C_{12}$ alkyl group, a substituted $C_1 - C_{12}$ alkenyl group, a substituted $C_4 - C_{12}$ cycloalkyl group, a substituted $C_4 - C_{12}$ cycloalkenyl group, a substituted aryl group, a $C_2 - C_{12}$ ether group, or a silyl group; or wherein R_1 is selected from hydrogen, halide, a $C_1 - C_{12}$ alkyl group, a $C_1 - C_{12}$ alkenyl group, a $C_4 - C_{12}$ cycloalkyl group, a $C_4 - C_{12}$ cycloalkenyl group, an aryl group, a substituted $C_1 - C_{12}$ alkyl group, a substituted $C_1 - C_{12}$ alkenyl group, a substituted $C_4 - C_{12}$ cycloalkyl group, a substituted $C_4 - C_{12}$ cycloalkenyl group, a substituted aryl group, a $C_2 - C_{12}$ ether group, or a silyl group, and R_2 and R_3 form a $C_4 - C_{12}$ cycloalkyl group, a $C_4 - C_{12}$ cycloalkenyl group, a substituted $C_4 - C_{12}$ cycloalkyl group, or a substituted $C_4 - C_{12}$ cycloalkenyl group; and X^- is an anion.

Another aspect of the invention is a method of making a non-cyclic amide or thioamide based ionic liquid. In one embodiment, the method includes reacting a non-cyclic amide or thioamide having a general formula:



or



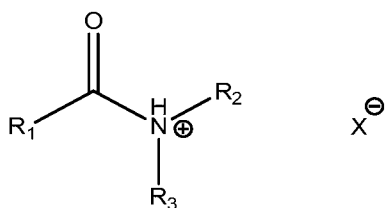
5 with a Brønsted acid HX to form an amidium or thioamidium halide reaction product. The amidium or thioamidium halide reaction product can optionally be reacted with a metal halide to form an amidium or thioamidium halometallate reaction product. R₁, R₂, and R₃ are independently selected from hydrogen, halide, a C₁ – C₁₂alkyl group, a C₁ – C₁₂alkenyl group, a C₄ – C₁₂cycloalkyl group, a C₄ – C₁₂cycloalkenyl group, an aryl group, a substituted C₁ – C₁₂alkyl group, a substituted C₁ – C₁₂alkenyl group, a substituted C₄ – C₁₂cycloalkyl group, a substituted C₄ – C₁₂cycloalkenyl group, a substituted aryl group, a C₂ – C₁₂ether group, or a silyl group; or wherein R₁ is selected from hydrogen, halide, a C₁ – C₁₂alkyl group, a C₁ – C₁₂alkenyl group, a cycloalkyl C₄ – C₁₂group, a C₄ – C₁₂cycloalkenyl group, an aryl group, a substituted C₁ – C₁₂alkyl group, a substituted C₁ – C₁₂alkenyl group, a substituted C₄ – C₁₂cycloalkyl group, a substituted C₄ – C₁₂cycloalkenyl group, a substituted aryl group, a C₂ – C₁₂ether group, or a silyl group, and R₂ and R₃ form a C₄ – C₁₂cycloalkyl group, a C₄ – C₁₂cycloalkenyl group, a substituted C₄ – C₁₂cycloalkyl group, or a substituted C₄ – C₁₂cycloalkenyl group.

DETAILED DESCRIPTION OF THE INVENTION

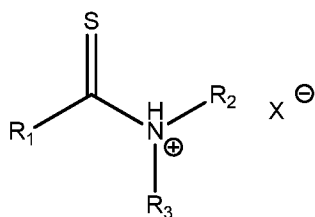
20 The present invention provides non-cyclic amide or thioamide based ionic liquids. The non-cyclic amide or thioamide based ionic liquids can be produced by reacting a non-cyclic amide or thioamide with a strong acid. In some embodiments, the reaction product

of the non-cyclic amide or thioamide and the strong acid is reacted with a metal halide. By non-cyclic amide or thioamide based ionic liquids, we mean ionic liquids in which the amide or thioamide bond in the cation is not contained in a cyclic structure. However, the cation can contain cyclic structures in other parts of the cation.

- 5 The non-cyclic amide or thioamide based ionic liquid comprises a cation and an anion and has the general formula:



or

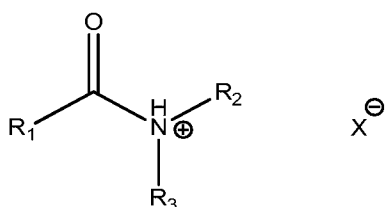


- wherein R₁, R₂, and R₃ are independently selected from hydrogen, halide, a C₁ – C₁₂ alkyl group, a C₁ – C₁₂alkenyl group, a C₄ – C₁₂cycloalkyl group, a C₄ – C₁₂cycloalkenyl group, an aryl group, a substituted C₁ – C₁₂alkyl group, a substituted C₁ – C₁₂alkenyl group, a substituted C₄ – C₁₂cycloalkyl group, a substituted C₄ – C₁₂cycloalkenyl group, a substituted aryl group, a C₂ – C₁₂ether group, or a silyl group; or wherein R₁ is selected from hydrogen, halide, a C₁ – C₁₂alkyl group, a C₁ – C₁₂alkenyl group, a C₄ – C₁₂cycloalkyl group, a C₄ – C₁₂cycloalkenyl group, an aryl group, a substituted C₁ – C₁₂alkyl group, a substituted C₁ – C₁₂alkenyl group, a substituted C₄ – C₁₂cycloalkyl group, a substituted C₄ – C₁₂cycloalkenyl group, a substituted aryl group, a C₂ – C₁₂ether group, or a silyl group, and R₂ and R₃ form a C₄ – C₁₂cycloalkyl group, a C₄ – C₁₂cycloalkenyl group, a

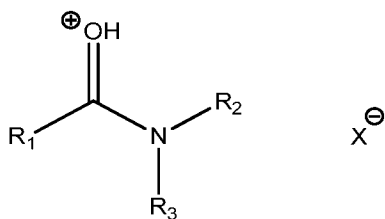
substituted C₄ – C₁₂cycloalkyl group, or a substituted C₄ – C₁₂cycloalkenyl group; and X⁻ is an anion.

By substituted, we mean that the alkyl group, alkenyl group, etc. includes a group including, but not limited to, a halide, such as chloride, bromide, iodide, or fluoride, a C₂ – C₁₂ ether group, a silyl group, a hydroxyl group, a thiol group, a cyano group, a sulfonyl group, an amine group, a nitrile group, a thiocyanate group, or combinations thereof.

Another way to represent



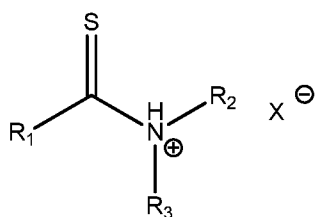
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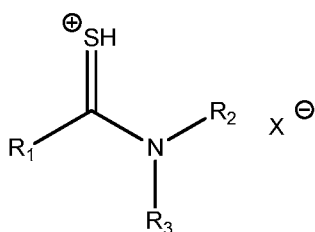
10

We intend both representations to be covered by the first structure.

Another way to represent



is



We intend both representations to be covered by the first structure.

Suitable anions include, but are not limited to carboxylates, nitrates, phosphates, phosphinates, phosphonates, imides, cyanates, borates, sulfates (including bisulfates), sulfonates (including fluoroalkanesulfonates), acetates, halides, halometallates, and combinations thereof. Examples of X^- groups include, but are not limited to, tetrafluoroborate, triflate, trifluoroacetate, chloroacetate, nitrate, hydrogen sulfate, hydrogen phosphate, dicyanoimide, methylsulfonate, and combinations thereof.

In some embodiments, X^- is a halide, such as chloride, bromide, iodide, or fluoride. In some embodiments, when X^- is a halide, the mol ratio of cation to anion is 1:1.

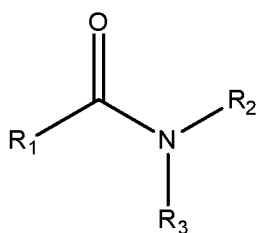
In other embodiments, X^- is a halometallate. In some embodiments, the metal in the halometallate comprises Sn, Al, Zn, Mn, Fe, Ga, Cu, Ni, Co, In, or combinations thereof. In some embodiments, the halide in the halometallate comprises bromide, chloride, iodide, fluoride, or combinations thereof. One or more of the halides (but not all) can be substituted with an -OH group, for example, $\text{Al}_3\text{Cl}_9\text{OH}$. Suitable halometallates include, but are not limited to, AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$, AlCl_3Br^- , $\text{Al}_2\text{Cl}_6\text{Br}^-$, $\text{Al}_3\text{Cl}_9\text{Br}^-$, AlBr_4^- , Al_2Br_7^- , $\text{Al}_3\text{Br}_{10}^-$, GaCl_4^- , Ga_2Cl_7^- , $\text{Ga}_3\text{Cl}_{10}^-$, GaCl_3Br^- , $\text{Ga}_2\text{Cl}_6\text{Br}^-$, $\text{Ga}_3\text{Cl}_9\text{Br}^-$, CuCl_2^- , Cu_2Cl_3^- , Cu_3Cl_4^- , ZnCl_3^- , FeCl_3^- , FeCl_4^- , Fe_3Cl_7^- , InCl_4^- , InCl_5^{2-} , InCl_6^{3-} , or combinations thereof. In some embodiments, when X^- is the halometallate, the mol fraction of metal in the halometallate is in the range of 0.25 to 1.

Suitable cations include, but are not limited to, *N,N*-dimethylacetamidium, acetamidium, carbonyl diamidium, thioamidium, *N*-methylthioacetamidium, *N,N*-dimethylthioacetamidium, *N*-methylacetamidium, *N,N*-dimethylformamidium, benzamidium, *N*-methylbenzamidium, *N,N*-dimethylbenzamidium, or dichloroacetamidium.

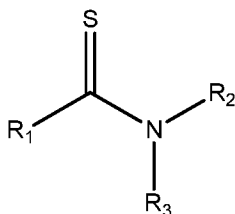
Suitable non-cyclic amide or thioamide based ionic liquids include, but are not limited to, *N,N*-dimethylacetamidium chloride, *N,N*-dimethylacetamidium bromide, *N,N*-

dimethylacetamidium AlCl_4 , *N,N*-dimethylacetamidium Al_2Cl_7 , acetamidium chloride, acetamidium bromide, acetamidium AlCl_4 , acetamidium Al_2Cl_7 , urea chloride, urea bromide, urea AlCl_4 , urea Al_2Cl_7 , thioacetamidium chloride, thioacetamidium bromide, thioacetamidium AlCl_4 , thioacetamidium Al_2Cl_7 , *N*-methylthioacetamidium chloride, *N*-methylthioacetamidium bromide, *N*-methylthioacetamidium AlCl_4 , *N*-methylthioacetamidium Al_2Cl_7 , *N,N*-dimethylthioacetamidium chloride, *N,N*-dimethylthioacetamidium bromide, *N,N*-dimethylthioacetamidium AlCl_4 , *N,N*-dimethylthioacetamidium Al_2Cl_7 , *N*-methylacetamidium chloride, *N*-methylacetamidium bromide, *N*-methylacetamide AlCl_4 , *N*-methylacetamidium Al_2Cl_7 , *N,N*-dimethylformamidium chloride, *N,N*-dimethylformamidium bromide, *N,N*-dimethylformamidium AlCl_4 , or *N,N*-dimethylformamidium Al_2Cl_7 .

The non-cyclic amide or thioamide based ionic liquids can be made by reacting a non-cyclic amide or thioamide having a general formula:



15 or



with a Brønsted acid HX to form an amidium or thioamidium reaction product;

20 wherein R_1 , R_2 , and R_3 are independently selected from hydrogen, halide, a $\text{C}_1 - \text{C}_{12}$ alkyl group, a $\text{C}_1 - \text{C}_{12}$ alkenyl group, a $\text{C}_4 - \text{C}_{12}$ cycloalkyl group, a $\text{C}_4 - \text{C}_{12}$ cycloalkenyl group, an aryl group, a substituted $\text{C}_1 - \text{C}_{12}$ alkyl group, a substituted $\text{C}_1 -$

C₁₂alkenyl group, a substituted C₄ – C₁₂cycloalkyl group, a substituted C₄ – C₁₂cycloalkenyl group, a substituted aryl group, a C₂ – C₁₂ether group, or a silyl group; or wherein R₁ is selected from hydrogen, halide, a C₁ – C₁₂alkyl group, a C₁ – C₁₂alkenyl group, a C₄ – C₁₂cycloalkyl group, a C₄ – C₁₂cycloalkenyl group, an aryl group, a substituted C₁ – C₁₂alkyl group, a substituted C₁ – C₁₂alkenyl group, a substituted C₄ – C₁₂cycloalkyl group, a substituted C₄ – C₁₂cycloalkenyl group, a substituted aryl group, a C₂ – C₁₂ether group, or a silyl group, and R₂ and R₃ form a C₄ – C₁₂cycloalkyl group, a C₄ – C₁₂cycloalkenyl group, a substituted C₄ – C₁₂cycloalkyl group, or a substituted C₄ – C₁₂cycloalkenyl group.

In some embodiments, the non-cyclic amide or thioamide comprises *N,N*-dimethylacetamide, acetamide, urea, thioacetamide, *N*-methylthioacetamide, *N,N*-dimethylthioacetamide, *N*-methylacetamide, *N,N*-dimethylformamide, benzamide, *N*-methylbenzamide, *N,N*-dimethylbenzamide, or dichloroacetamide.

In some embodiments, the Brønsted acid HX is at least one of hydrochloric acid, hydrobromic acid, hydroiodic acid, sulfuric acid, nitric acid, phosphoric acid, tetrafluoroboric acid, sulfonic acid, triflic acid, toluenesulfonic acid dihaloacetic acid, and trihaloacetic acid.

The mol ratio of the non-cyclic amide or thioamide to the Brønsted acid HX is typically 1:1.

The non-cyclic amide or thioamide is reacted with the Brønsted acid HX with or without a solvent. Suitable solvents include, but are not limited to, water, alcohols, such as methanol or ethanol, dichloromethane, chloroform, or toluene.

The reaction can be performed at room temperature and atmospheric pressure. Higher or lower temperatures and/or pressures could be used, if desired.

The reaction time to form the non-cyclic amidium or thioamidium reaction product is generally in the range of 1 min to 1 hr.

In some embodiments, the anion is a halide, and the non-cyclic amidium or thioamidium reaction product is a non-cyclic amidium or thioamidium halide reaction product. In some embodiments, the non-cyclic amidium or thioamidium halide reaction product is reacted with a metal halide to form an amidium or thioamidium halometallate reaction product.

In some embodiments, the mol ratio of the cation to the metal in the halometallate or of the amidium halide reaction product to the metal halide is typically in a range of 1:0.8 to 1:2.2, or 1:1 to 1:2.2, or in 1:1.2 to 1:2.2, or 1:1.4 to 1:2.2, or 1:1.16 to 1:2.2. The ratio may be affected by the specific cation used and the synthesis temperature.

5 In some embodiments, the metal of the metal halide comprises Sn, Al, Zn, Mn, Fe, Ga, Cu, Ni, Co, In, or combinations thereof. Suitable metal halides include, but are not limited to, AlCl_3 , AlCl_2Br , AlBr_3 , GaCl_3 , GaCl_2Br , CuCl_3 , FeCl_3 , or InCl_3 . In some embodiments, one or more (but not all) of the halide can be substituted with an $-\text{OH}$ group.

10 The amidium or thioamidium halide reaction product can be reacted with the metal halide in the presence of a solvent. Suitable solvents include, but are not limited to, dichloromethane, chloroform, toluene, or benzene. Protic solvents are not desirable for this reaction because they could react with the metal halide.

The ratio of the metal to the halide in the halometallate is less than the ratio of metal atoms to halide atoms in the neutral metal halide. That is, the metal: halide ratio is less than 1: X, where X is the valence of the metal. For example, the ratio of metal to halide in Al_2Cl_7^- is 2:7, whereas the ratio of AlCl_3 is 1:3.

15

The halide in the Brønsted acid HX can be the same as the halide in the metal halide, or it can be different.

20 The reaction of the amidium or thioamidium halide reaction product and the metal halide can be performed at room temperature and atmospheric pressure. Higher or lower temperatures and/or pressures could be used, if desired.

The reaction time to form the non-cyclic amidium or thioamidium halometallate is generally in the range of 1 min to 24 hr. The reaction time is affected by whether a solvent is used in the reaction with solvents increasing the rate of reaction.

25 The reaction of the amidium or thioamidium halide reaction product and the metal halide typically takes place under an inert atmosphere, such as nitrogen, argon, and the like.

The reactions (non-cyclic amide or thioamide with the Brønsted acid HX and/or amidium or thioamidium halide reaction product with the metal halide) may be

practiced in laboratory scale experiments through full scale commercial operations. The process may be operated in batch, continuous, or semi-continuous mode.

Examples

Synthesis of *N,N*-Dimethylacetamidium Chloride

5 An HCl in ethanol solution (1.25M, 35 mL, 43.8 mmol) was added to *N,N*-dimethylacetamide (3.55 g, 40.2 mmol) at room temperature. After stirring for 1 h, the volatiles were removed at 50°C under reduced pressure to yield a white solid. Yield: 4.87 g, 98%. ¹H NMR (500 MHz, CDCl₃): 2.51 (s, 3H), 3.14 (s, 6H), 15.58 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): 18.19, 38.67, 174.83.

10 Synthesis of *N,N*-Dimethylacetamidium Chloroaluminate

 Under a nitrogen atmosphere, aluminum trichloride was slowly added to *N,N*-dimethylacetamidium chloride. Upon addition of the aluminum chloride with stirring, the mixture began to liquefy. The mixture was stirred 1.67 h with stirring until the material was completely liquefied. Yield: 11.2 g, 90.3%. ¹H NMR (500 MHz, CDCl₃): 2.55 (s, 3H), 3.34
15 (d, 6H). ¹³C NMR (125 MHz, CDCl₃): 21.27, 39.39, 40.77, 173.02.

Alkylation Experiment

 In a nitrogen atmosphere, *N,N*-dimethylacetamidium chloroaluminate was loaded into a 300 ml autoclave containing a baffle. Prior to loading, the autoclave and baffle had been dried for several hours above 100°C. The number of acid sites in the ionic liquid
20 was adjusted to optimize the performance by addition of 2-chlorobutane. (The number of acid sites could be adjusted by changing the catalyst loading or by changing the amount of acid or acid precursor added.) The autoclave was charged with 80 g isobutane and pressurized with 3.4 MPa (g) (500psig) of nitrogen. The contents were stirred at 1600 rpm, and 8 g 2-butene
25 was added over time (118.72 mL/h) at room temperature. After 8 min, the reaction mixture was allowed to settle and the liquid product was sampled directly from the autoclave. The sample was passed through a silica column then analyzed by gas chromatography. The results are shown Table 1.

The groupings below include all isomers having the same carbon number. The % butenes conversion was calculated using $100 - (\text{the weight of butenes in the product} / \text{the weight of butenes added})$. RONC is the Research Octane Number Calculated. TMP/DMH is the weight ratio of trimethylpentanes to dimethylhexanes in the product. The

5 %Selectivity is $(\text{wt\% of that paraffin}) / (\text{sum of wt\% of the C}_5 \text{ and larger products formed})$. The yield is $(\text{the mass of C}_5 \text{ and larger products formed}) / (\text{the mass of the C}_4 \text{ olefin added})$.

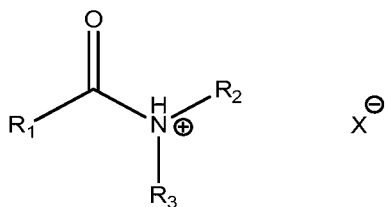
Table 1

	3.8 g <i>N,N</i>-dimethylacetamidium chloroaluminate+ 0.466 g 2-chlorobutane
Mol ratio cation:mol Al:chlorobutane	1:1.8:0.4
Vol% IL	1.9
Reaction Time	8 min
i/o (mol ratio)	7.9
Butenes Conversion (%)	95.2
RONC	95.0
%Sel C8	73.7
%Sel C9	11.6
%Sel C5-7	14.7
TMP/DMH	13.9
Yield (C5+/C4=)	2.19

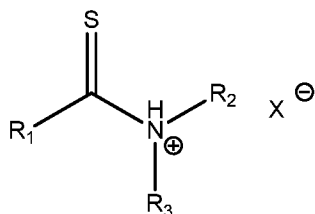
SPECIFIC EMBODIMENTS

While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

A first embodiment of the invention is a non-cyclic amide or thioamide based ionic liquid comprising a cation and an anion, the ionic liquid having a formula



or



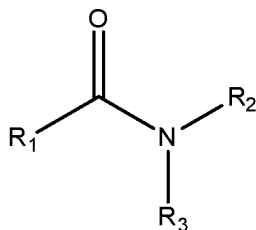
wherein R₁, R₂, and R₃ are independently selected from hydrogen, halide, a C₁ – C₁₂ alkyl group, a C₁ – C₁₂ alkenyl group, a C₄ – C₁₂ cycloalkyl group, a C₄ – C₁₂ cycloalkenyl group, an aryl group, a substituted C₁ – C₁₂ alkyl group, a substituted C₁ – C₁₂ alkenyl group, a substituted C₄ – C₁₂ cycloalkyl group, a substituted C₄ – C₁₂ cycloalkenyl group, a substituted aryl group, a C₂ – C₁₂ ether group, or a silyl group; or wherein R₁ is selected from hydrogen, halide, a C₁ – C₁₂ alkyl group, a C₁ – C₁₂ alkenyl group, a C₄ – C₁₂ cycloalkyl group, a C₄ – C₁₂ cycloalkenyl group, an aryl group, a substituted C₁ – C₁₂ alkyl group, a substituted C₁ – C₁₂ alkenyl group, a substituted C₄ – C₁₂ cycloalkyl group, a substituted C₄ – C₁₂ cycloalkenyl group, a substituted aryl group, a C₂ – C₁₂ ether group, or a silyl group, and R₂ and R₃ form a C₄ – C₁₂ cycloalkyl group, a C₄ – C₁₂ cycloalkenyl group, a substituted C₄ – C₁₂ cycloalkyl group, or a substituted C₄ – C₁₂ cycloalkenyl group; and X[–] is an anion. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the anion is a carboxylate, a nitrate, a phosphate, a phosphinate, a phosphonate, an imide, a cyanate, a borate, a sulfate, a sulfonate, an acetate, a halide, a halometallate, and combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the anion is the halide and wherein the halide is bromide, chloride, iodide, fluoride, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the anion is the halometallate, wherein the metal in the halometallate comprises Sn, Al, Zn, Mn, Fe, Ga, Cu, Ni, Co, In, or combinations thereof, and wherein the halide in the halometallate comprises bromide, chloride, iodide, fluoride, or combinations thereof, and wherein the halometallate optionally includes an –OH group. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the anion is the halometallate, and

wherein the halometallate comprises AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$, AlCl_3Br^- , $\text{Al}_2\text{Cl}_6\text{Br}^-$, $\text{Al}_3\text{Cl}_9\text{Br}^-$, AlBr_4^- , Al_2Br_7^- , $\text{Al}_3\text{Br}_{10}^-$, GaCl_4^- , Ga_2Cl_7^- , $\text{Ga}_3\text{Cl}_{10}^-$, GaCl_3Br^- , $\text{Ga}_2\text{Cl}_6\text{Br}^-$, $\text{Ga}_3\text{Cl}_9\text{Br}^-$, CuCl_2^- , Cu_2Cl_3^- , Cu_3Cl_4^- , ZnCl_3^- , FeCl_3^- , FeCl_4^- , Fe_3Cl_7^- , InCl_4^- , InCl_5^{2-} , InCl_6^{3-} , or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the cation comprises *N,N*-dimethylacetamidium, acetamidium, carbonyl diamidium, thioamidium, *N*-methylthioacetamidium, *N,N*-dimethylthioacetamidium, *N*-methylacetamidium, *N,N*-dimethylformamidium, benzamidium, *N*-methylbenzamidium, *N,N*-dimethylbenzamidium, or dichloroacetamidium. An embodiment of the invention is one, any or all of prior

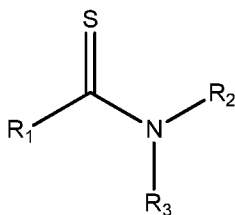
embodiments in this paragraph up through the first embodiment in this paragraph wherein the ionic liquid is *N,N*-dimethylacetamidium chloride, *N,N*-dimethylacetamidium bromide, *N,N*-dimethylacetamidium AlCl_4 , *N,N*-dimethylacetamidium Al_2Cl_7 , acetamidium chloride, acetamidium bromide, acetamidium AlCl_4 , acetamidium Al_2Cl_7 , urea chloride, urea bromide, urea AlCl_4 , urea Al_2Cl_7 , thioacetamidium chloride, thioacetamidium bromide, thioacetamidium AlCl_4 , thioacetamidium Al_2Cl_7 , *N*-methylthioacetamidium chloride, *N*-methylthioacetamidium bromide, *N*-methylthioacetamidium AlCl_4 , *N*-methylthioacetamidium Al_2Cl_7 , *N,N*-dimethylthioacetamidium chloride, *N,N*-dimethylthioacetamidium bromide, *N,N*-dimethylthioacetamidium AlCl_4 , *N,N*-dimethylthioacetamidium Al_2Cl_7 , *N*-methylacetamidium chloride, *N*-methylacetamidium bromide, *N*-methylacetamide AlCl_4 , *N*-methylacetamidium Al_2Cl_7 , *N,N*-dimethylformamidium chloride, *N,N*-dimethylformamidium bromide, *N,N*-dimethylformamidium AlCl_4 , or *N,N*-dimethylformamidium Al_2Cl_7 . An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the anion is a halometallate and wherein a mol ratio cation to the metal in the halometallate is in a range of 10.8 to 12.2. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the anion is the halometallate and wherein a ratio of metal to halide in the halometallate is less than a ratio of the metal to the halide in a neutral metal halide. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the substituted $\text{C}_1 - \text{C}_{12}$ alkyl group, the substituted $\text{C}_1 - \text{C}_{12}$ alkenyl group, the substituted $\text{C}_4 - \text{C}_{12}$ cycloalkyl group, the substituted $\text{C}_4 - \text{C}_{12}$ cycloalkenyl group, or the substituted aryl group is substituted with a halide, a $\text{C}_2 - \text{C}_{12}$ ether group, a silyl group, a hydroxyl group, a

thiol group, a cyano group, a sulfonyl group, an amine group, a nitrile group, a thiocyanate group, or combinations thereof.

A second embodiment of the invention is a method of making a non-cyclic amide or thioamide based ionic liquid comprising reacting a non-cyclic amide or thioamide
 5 having a general formula



or



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with a Brønsted acid HX to form an amidium or thioamidium reaction product wherein R₁, R₂, and R₃ are independently selected from hydrogen, halide, a C₁ – C₁₂ alkyl group, a C₁ – C₁₂ alkenyl group, a C₄ – C₁₂ cycloalkyl group, a C₄ – C₁₂ cycloalkenyl group, an aryl group, a substituted C₁ – C₁₂ alkyl group, a substituted C₁ – C₁₂ alkenyl group, a substituted C₄ – C₁₂ cycloalkyl group, a substituted C₄ – C₁₂ cycloalkenyl group, a substituted aryl group, a C₂ – C₁₂ ether group, or a silyl group; or wherein R₁ is selected from hydrogen, halide, a C₁ – C₁₂ alkyl group, a C₁ – C₁₂ alkenyl group, a C₄ – C₁₂ cycloalkyl group, a C₄ – C₁₂ cycloalkenyl group, an aryl group, a substituted C₁ – C₁₂ alkyl group, a substituted C₁ – C₁₂ alkenyl group, a substituted C₄ – C₁₂ cycloalkyl group, a substituted C₄ – C₁₂ cycloalkenyl group, a substituted aryl group, a C₁ – C₁₂ ether group, or a silyl group, and R₂ and R₃ form a C₄ – C₁₂ cycloalkyl group, a C₄ – C₁₂ cycloalkenyl group, a substituted C₄ –

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C₁₂ cycloalkyl group, or a substituted C₄ – C₁₂ cycloalkenyl group. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the Brønsted acid HX is at least one of hydrochloric acid, hydrobromic acid, hydroiodic acid, sulfuric acid, nitric acid, phosphoric acid, tetrafluoroboric acid, sulfonic acid, triflic acid, toluenesulfonic acid dihaloacetic acid, and trihaloacetic acid. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the Brønsted acid HX is at least one of the hydrochloric acid, the hydrobromic acid, and the hydroiodic acid, and further comprising reacting the amidium or thioamidium reaction product with a metal halide to form an amidium or thioamidium halometallate reaction product. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein a metal of the metal halide comprises Sn, Al, Zn, Mn, Fe, Ga, Cu, Ni, Co, In, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph a mol ratio of the amidium or thioamidium reaction product to the metal halide is in a range of 10.8 to 12.2. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the amidium or thioamidium reaction product is reacted with the metal halide in the presence of a solvent selected from dichloromethane, chloroform toluene, or benzene. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the halide in the Brønsted acid HX is the same as the halide in the metal halide. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the non-cyclic amide or thioamide comprises *N,N*-dimethylacetamide, acetamide, urea, thioacetamide, *N*-methylthioacetamide, *N,N*-dimethylthioacetamide, *N*-methylacetamide, *N,N*-dimethylformamide, benzamide, *N*-methylbenzamide, *N,N*-dimethylbenzamide, or dichloroacetamide. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein a mol ratio of the non-cyclic amide or thioamide to the Brønsted acid HX is 11. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein

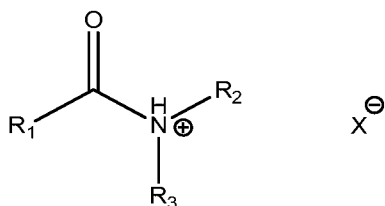
the non-cyclic amide or thioamide is reacted with the Brønsted acid HX in the presence of a solvent.

Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily
5 ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent
10 arrangements included within the scope of the appended claims.

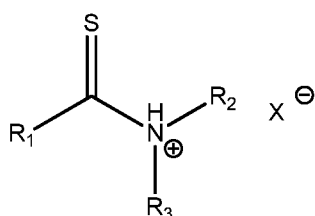
In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

What is claimed:

1. A non-cyclic amide or thioamide based ionic liquid comprising a cation and an anion, the ionic liquid having a formula:



5 or



wherein R_1 , R_2 , and R_3 are independently selected from hydrogen, halide, a $\text{C}_1 - \text{C}_{12}$ alkyl group, a $\text{C}_1 - \text{C}_{12}$ alkenyl group, a $\text{C}_4 - \text{C}_{12}$ cycloalkyl group, a $\text{C}_4 - \text{C}_{12}$ cycloalkenyl group, an aryl group, a substituted $\text{C}_1 - \text{C}_{12}$ alkyl group, a substituted $\text{C}_1 - \text{C}_{12}$ alkenyl group, a substituted $\text{C}_4 - \text{C}_{12}$ cycloalkyl group, a substituted $\text{C}_4 - \text{C}_{12}$ cycloalkenyl group, a substituted aryl group, a $\text{C}_2 - \text{C}_{12}$ ether group, or a silyl group; or wherein R_1 is selected from hydrogen, halide, a $\text{C}_1 - \text{C}_{12}$ alkyl group, a $\text{C}_1 - \text{C}_{12}$ alkenyl group, a $\text{C}_4 - \text{C}_{12}$ cycloalkyl group, a $\text{C}_4 - \text{C}_{12}$ cycloalkenyl group, an aryl group, a substituted $\text{C}_1 - \text{C}_{12}$ alkyl group, a substituted $\text{C}_1 - \text{C}_{12}$ alkenyl group, a substituted $\text{C}_4 - \text{C}_{12}$ cycloalkyl group, a substituted $\text{C}_4 - \text{C}_{12}$ cycloalkenyl group, a substituted aryl group, a $\text{C}_2 - \text{C}_{12}$ ether group, or a silyl group, and R_2 and R_3 form a $\text{C}_4 - \text{C}_{12}$ cycloalkyl group, a $\text{C}_4 - \text{C}_{12}$ cycloalkenyl group, a substituted $\text{C}_4 - \text{C}_{12}$ cycloalkyl group, or a substituted $\text{C}_4 - \text{C}_{12}$ cycloalkenyl group; and X^- is an anion.

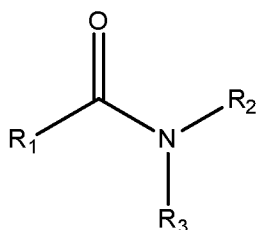
2. The ionic liquid of claim 1 wherein the anion is a carboxylate, a nitrate, a phosphate, a phosphinate, a phosphonate, an imide, a cyanate, a borate, a sulfate, a sulfonate, an acetate, a halide, a halometallate, and combinations thereof.

3. The ionic liquid of any of claims 1-2 wherein the cation comprises *N,N*-dimethylacetamidium, acetamidium, carbonyl diamidium, thioamidium, *N*-methylthioacetamidium, *N,N*-dimethylthioacetamidium, *N*-methylacetamidium, *N,N*-dimethylformamidium, benzamidium, *N*-methylbenzamidium, *N,N*-dimethylbenzamidium, or dichloroacetamidium.

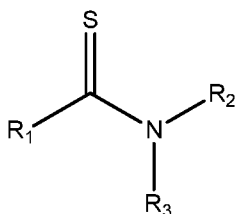
4. The ionic liquid of any of claims 1-2 wherein the substituted C₁ – C₁₂ alkyl group, the substituted C₁ – C₁₂ alkenyl group, the substituted C₄ – C₁₂cycloalkyl group, the substituted C₄ – C₁₂cycloalkenyl group, or the substituted aryl group is substituted with a halide, a C₂ – C₁₂ ether group, a silyl group, a hydroxyl group, a thiol group, a cyano group, a sulfonyl group, an amine group, a nitrile group, a thiocyanate group, or combinations thereof.

5. A method of making a non-cyclic amide or thioamide based ionic liquid comprising:

reacting a non-cyclic amide or thioamide having a general formula:



or



with a Brønsted acid HX to form an amidium or thioamidium reaction product wherein R₁, R₂, and R₃ are independently selected from hydrogen, halide, a C₁ – C₁₂ alkyl group, a C₁ – C₁₂ alkenyl group, a C₄ – C₁₂cycloalkyl group, a C₄ – C₁₂cycloalkenyl group, an aryl group, a substituted C₁ – C₁₂ alkyl group, a substituted C₁ – C₁₂ alkenyl group, a substituted C₄ – C₁₂cycloalkyl group, a substituted C₄ – C₁₂cycloalkenyl group, a substituted aryl group, a C₂ – C₁₂ ether group, or a silyl group; or wherein R₁ is selected from hydrogen,

halide, a C₁ – C₁₂ alkyl group, a C₁ – C₁₂ alkenyl group, a C₄ – C₁₂cycloalkyl group, a C₄ – C₁₂cycloalkenyl group, an aryl group, a substituted C₁ – C₁₂ alkyl group, a substituted C₁ – C₁₂ alkenyl group, a substituted C₄ – C₁₂cycloalkyl group, a substituted C₄ – C₁₂cycloalkenyl group, a substituted aryl group, a C₁ – C₁₂ ether group, or a silyl group, and R₂ and R₃ form a C₄ – C₁₂cycloalkyl group, a C₄ – C₁₂cycloalkenyl group, a substituted C₄ – C₁₂cycloalkyl group, or a substituted C₄ – C₁₂cycloalkenyl group.

6. The method of claim 5 wherein the Brønsted acid HX is at least one of hydrochloric acid, hydrobromic acid, hydroiodic acid, sulfuric acid, nitric acid, phosphoric acid, tetrafluoroboric acid, sulfonic acid, triflic acid, toluenesulfonic acid dihaloacetic acid, and trihaloacetic acid.

7. The method of any of claims 5-6 wherein the non-cyclic amide or thioamide is reacted with the Brønsted acid HX in the presence of a solvent.

8. The method of any of claims 5-6 wherein the Brønsted acid HX is at least one of the hydrochloric acid, the hydrobromic acid, and the hydroiodic acid, and further comprising reacting the amidium or thioamidium reaction product with a metal halide to form an amidium or thioamidium halometallate reaction product.

9. The method of claim 8 wherein the amidium or thioamidium reaction product is reacted with the metal halide in the presence of a solvent selected from dichloromethane, chloroform toluene, or benzene.

10. The method of any of claims 5-6 wherein the non-cyclic amide or thioamide comprises *N,N*-dimethylacetamide, acetamide, urea, thioacetamide, *N*-methylthioacetamide, *N,N*-dimethylthioacetamide, *N*-methylacetamide, *N,N*-dimethylformamide, benzamide, *N*-methylbenzamide, *N,N*-dimethylbenzamide, or dichloroacetamide.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/041031

A. CLASSIFICATION OF SUBJECT MATTER <i>C07C 233/89 (2006.01)</i> <i>C07C 231/08 (2006.01)</i> <i>C07C 327/38 (2006.01)</i> According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C07C 233/89, 231/08, 327/38 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) STN Online, PatSearch (RUPTO internal), Espacenet, DWPI, PAJ, USPTO, CIPO, Patentscope				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 2010/0224063 A1 (HYUNDAI MOTOR COMPANY et al.) 09.09.2010, abstract, paragraphs [0021], [0024], [0025], [0045] - [0048], [0055] - [0063], [0073], claims 1-3	1-7, 10		
Y		8, 9		
X	US 2013/0012699 A1 (KIA MOTORS CORPORATION et al.) 10.01.2013, abstract, paragraphs [0032] - [0035], [0042] - [0050], [0060], claims 1-3	1-7, 10		
X	US 2011/0229401 A1 (UT-BATTELLE, LLC) 22.09.2011, fig. 1, compounds [DMAcH]H ₂ PO ₄ , paragraphs [0008], [0125], [0151]	1-3, 5-7, 10		
X	KUMLER W.D. Structure of Salts of N,N-Dimethylacetamide and N,N-Di(n)butylacetamide, J. Am. Chem. Soc., 1961, Vol. 83, pp. 4983-4985, abstract, p. 4985, paragraph "Experimental"	1-3, 5-7, 10		
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.				
* Special categories of cited documents: <table border="0"> <tr> <td style="vertical-align: top;"> “A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier document but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed </td> <td style="vertical-align: top;"> “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family </td> </tr> </table>			“A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier document but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family
“A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier document but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family			
Date of the actual completion of the international search 03 October 2016 (03.10.2016)		Date of mailing of the international search report 20 October 2016 (20.10.2016)		
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer O. Zavarzina Telephone No. (495)531-64-81		

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/041031

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BONNER O.D. et al. The Raman spectra of the hydrochloride salts of N-methylacetamide. Spectrochimica Acta, 1966, Vol. 22, pp. 1125-1129, abstract, p. 1125, paragraph "Experimental", lines 1-3, p. 1127-1128, paragraph 3.2	1-3, 5-7, 10
X	SPINNER E. The vibration spectra and structures of the hydrochlorides of urea, thiourea and acetamide. The basic properties of amides and thioamides. Spectrochimica Acta, 1959, pp. 95-109, abstract, p. 96, paragraph "Experimental"	1-3, 5-7, 10
X	COOK Denys. Protonated carbonyl groups. IV. N,N-Dimethylacetamide salts. Canadian Journal of Chemistry, 1964, Vol. 42, pp. 2721-2727, abstract, p. 2722, table 1, p. 2726, paragraph "Experimental"	1-3, 5-7, 10
Y	WO 2010/074835 A2 (CHEVRON U.S.A. INC et al.) 01.07.2010, p. 2, lines 17-34, p. 3, lines 1-26, p. 7, lines 8-15, example 1, claims 1, 2, 8, 9	8, 9
A	Obschaya organicheskaya khimiya, pod red. D. Bartona, W. Ollis. Tom 4, Karbovye kisloty b ikh proizvodnye. Soedineniya fosfora. Moskva "Khimiya" 1983, p. 728, p. 438	1-10