Selective alkaline stripping of metal ions after solvent extraction by basestable 1,2,3-triazolium ionic liquids

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Supplementary information

Synthetic section:

p-Nitrophenyl azide

p-Nitroaniline (28.1 g, 203 mmol) was suspended in a mixture of water (240 mL), 37% HCl solution (60 mL) and methanol (60 mL). This mixture was cooled to -5 °C, after which a solution of NaNO₂ (16.6 g in 40 mL of water) was added dropwise. This was allowed to stir for 40 min at -5 °C, causing a yellow precipitate to develop. Subsequently, a solution of NaN₃ (16.0 g in 40 mL of water) was added dropwise at -5 °C. This was accompanied by the formation of nitrogen gas and precipitation of the product. The released gasses were washed in a NaOH solution of approximately 10 wt%. The solution was finally allowed to stir overnight at room temperature. To isolate the desired product, the mixture was extracted with two 200 mL portions of dichloromethane. After evaporation, the product was collected as a yellow powder in a yield of 90% (29.880 g).

¹H NMR (400 MHz, $CDCl_3$, δ /ppm): 8.27 (d, 2H, J= 9.0 Hz, H in ortho to nitro), 7.16 (d, 2H, J = 9.0 Hz, H in ortho to azide).

5-Ethyl-1-(2-ethylhexyl)-4-methyl-1,2,3-triazole



Fig. S1: Structure and allocations of hydrogen atoms in 5-ethyl-1-(2-ethylhexyl)-4-methyltriazole.

A flask was charged with *p*-nitrophenyl azide (9.03 g, 55.0 mmol), 3-pentanone (8.11 mL, 76.8 mmol), 2-ethylhexylamine (12.58 mL, 76.80 mmol) and acetic acid (0.941 mL, 16.5 mmol). The mixture was stirred for 3 days at 65 °C in toluene (60 mL). After cooling, the mixture was washed with 10% NaH₂PO₄ (2x 100 mL) to remove the excess of 2-ethylhexylamine. The organic layer was then dried with MgSO₄ and solvents were evaporated off. Distilled water (65 mL) and 37% HCl solution (25 mL) were added and the mixture was cooled to -5 °C. A solution of NaNO₂ (4.50 g, 65.2 mmol) in water (11 mL) was added dropwise. The reaction mixture was allowed to stir at -5 °C for 1 h. The aqueous layer was diluted by the addition of 10% monobasic phosphate solution (100 mL) and separated off. The organic phase was washed with water (50 mL) and dried with MgSO₄. Solvents were evaporated, giving a brown oil in a yield of 70% (8.571 g).

¹H NMR (300 MHz, CDCl₃, δ /ppm): 4.07 ppm (d, 2H, J = 7.5 Hz, H1), 2.62 (q, 2H, J = 7.5 Hz, H9), 2.29 (s, 3H, H11), 1.91 (m, 1H, H2), 1.24 (m, 11H, H3+H5+H6+H7+H10), 0.89 (2t, 6H, H4+H8). Hydrogen allocations for the proton NMR spectrum are shown in Fig. S1. ¹³C NMR (δ /ppm, 75 MHz, CDCl₃): 140.01 (sp²-C), 134.41 (sp²-C), 51.63 (N-CH₂), 40.05 (CH), 30.42 (CH₂), 28.51 (CH₂), 23.69 (CH₂), 22.92 (CH₂), 16.08 (CH₃ or CH₂), 14.01 (2 CH₃), 13.28 (CH₃ or CH₂), 10.51 (CH₃), 10.48 (CH₃). FT-IR (v/cm⁻¹): 2959, 2930, 2873 (sp³C-H), 1596, 1527, 1459 (C=C and N=N stretch), 1342, 1241, 1108, 1046, 855, 754 (fingerprint region).

3,5-Diethyl-1-(2-ethylhexyl)-4-methyl-1,2,3-triazolium iodide [T1][I]



Fig. S2: Structure and allocations of hydrogen atoms in 3,5-diethyl-1-(2-ethylhexyl)-4-methyltriazolium iodide.

5-Ethyl-1-(2-ethylhexyl)-4-methyltriazole (1.97 g, 8.81 mmol), iodoethane (2.42 mL, 26.4 mmol) and acetone (10 mL) were combined in a flask. The mixture was heated and stirred at 55 °C for 19 h. Acetone and the excess of iodoethane were evaporated under reduced pressure. The resulting liquid was washed with 5 mL of heptane at 100 °C to remove trace impurities. Phase separation was aided by cooling to -30 °C. The purified product was collected as a brown oil in a yield of 62% (2.056 g).

¹H NMR (400 MHz, CDCl₃, δ /ppm): 4.66 (q, 2H, J = 7.0 Hz, H12), 4.35 ppm (d, 2H, J = 7.5 Hz, H1), 2.95 (q, 2H, J = 7.5 Hz, H9), 2.68 (s, 3H, H11), 2.03 (m, 1H, H2), 1.68 (t, 3H, J = 7.0 Hz, H13), 1.34 (m, 11H, H3+H5+H6+H7+H10), 0.93 (2t, 6H, H4+H8). Hydrogen allocations for the proton NMR spectrum are shown in Fig. S2. ¹³C NMR (δ /ppm, 100 MHz, CDCl₃): 142.20 (sp²-C), 137.30 (sp²-C), 54.96 & 53.53 (N-CH₂), 47.71 (N-CH₂), 39.40 (CH), 30.97 & 30.16 (CH₂), 28.23 (CH₂), 23.56 (CH₂), 22.79 (CH₂), 17.29 (CH₂), 13.98 (CH₃), 13.79 (CH₃), 12.85 (CH₃), 10.33 (CH₃), 10.17 (CH₃). FT-IR (v/cm⁻¹): 2959, 2929, 2872 (sp³ C-H), 1668, 1595, 1526, 1458 (C=C and N=N stretch), 1327, 1106, 854, 611 (fingerprint region). CHN calculated for C₁₅H₃₀IN₃: C 47.50%, H 7.97%, N 11.08; found: C 47.74, H 7.16, N 11.87.

3,5-diethyl-1-(2-ethylhexyl)-4-methyltriazolium thiocyanate

[T1][SCN]

The triazolium salt [T1][I] (6.0 g, 16 mmol) was equilibrated twice with 25 mL of a 5 M solution of KSCN and washed with 100 mL of water. TXRF with an Yb standard gave an estimated iodide content of 9.93 g/L. This implies a residual iodide content of about 1 wt%.

1-(2-Ethylhexyl)-5-methyl-1,2,3-triazole



Fig. S3: Structure and allocations of hydrogen atoms in 1-(2-ethylhexyl)-5-methyltriazole.

A flask was charged with acetone (12.08 mL, 164.5 mmol), p-nitrophenyl azide (8.97 g, 54.7 mmol), 2ethylhexylamine (12.58 mL, 76.8 mmol) and acetic acid (0.941 mL, 16.5 mmol). This mixture was heated to 55 °C and stirred for 18 h in toluene, using approximately 3 g of 4 Å molecular sieves. The mixture was washed with two 100 mL portions of 10% NaH_2PO_4 solution. A solution of $NaNO_2$ (4.48 g, 64.9 mmol) in water (9 mL) was added dropwise. The reaction mixture was allowed to stir at -5 °C for 40 min. The aqueous layer was separated off. The organic phase was washed with water (100 mL) and dried with MgSO₄. Solvents were evaporated, yielding the product as a dark brown liquid. The product was obtained in a yield of 95% (10.298 g).

¹H NMR (300 MHz, CDCl₃, δ /ppm): 7.43 (s, 1H, H10), 4.12 (m, 2H, H1), 2.62 (s, 3H, H9), 1.90 (m, 1H, H2), 1.29 (m, 8H, H3+H5+H6+H7), 0.89 (m, 6H, H4+H8). Hydrogen allocations for the proton NMR spectrum are shown in Fig. S3. ¹³C NMR (δ /ppm, 75 MHz, CDCl₃): 132.75 (sp²-C), 132.52 (sp²-C), 51.21 (N-CH₂), 40.90 & 39.89 (CH), 30.40 (CH₂), 28.47 (CH₂), 23.67 (CH₂), 22.87 (CH₂), 13.97 (CH₃), 10.46 (CH₃), 8.56 (CH₃).FT-IR (v/cm⁻¹): 3066 (sp₂ C-H), 2959, 2929, 2860 (sp³ C-H), 1593, 1520, 1458 (C=C and N=N stretch), 1238, 1045, 752, 700 (fingerprint region).

3-Ethyl-1-(2-ethylhexyl)-4-methyl-1,2,3-triazolium iodide [T2][I]



Fig. S4: Structure and allocations of hydrogen atoms in 3-ethyl-1-(2-ethylhexyl)-5-methyltriazolium iodide.

5-Ethyl-1-(2-ethylhexyl)-4-methyltriazole (1.97 g, 8.81 mmol), iodoethane (2.42 mL, 26.4 mmol) and acetone (10 mL) were combined in a flask. The mixture was heated and stirred at 55 °C for 19 h. Acetone and the excess of iodoethane were evaporated under reduced pressure. The resulting liquid was washed with 5 mL of heptane at 100 °C to remove trace impurities. Phase separation was aided by cooling to -30 °C. The purified product was collected as a brown oil in a yield of 62% (2.056 g).

¹H NMR (400 MHz, CDCl₃, δ /ppm): 9.47 (s, 1H, H10), 4.82 ppm (q, 2H, J = 7.5 Hz, H11), 4.38 (d, 2H, J = 7.0 Hz, H1), 2.66 (s, 3H, H9), 1.99 (m, 1H, H2), 1.71 (t, 3H, J = 7.0 Hz, H12), 1.34 (m, 8H, H3+H5+H6+H7), 0.93 (2t, 6H, H4+H8). Hydrogen allocations for the proton NMR spectrum are shown in Fig. S4. In some batches, a singlet at 2.63 ppm appears, believed to correspond to bound water molecules. ¹³C NMR: (δ /ppm, 75 MHz, CDCl₃): 140.04 (sp₂-C), 130.17 (sp₂-C), 54.77 (N-CH₂), 49.84 (N-CH₂), 40.99 & 39.38 (CH), 30.96 & 30.06 (CH₂), 28.18 (CH₂), 23.50 (CH₂), 22.75 (CH₂), 14.82 (CH₃), 13.93 (CH₃), 10.30 (CH₃), 10.10 (CH₃). FT-IR (v/cm⁻¹): 3119 (sp²C-H), 2959, 2930, 2861 (sp³C-H), 1588, 1518, 1458 (C=C and N=N stretch), 1341, 1176, 1108, 853, 752 (fingerprint region). CHN calculated for C₁₃H₂₆IN₃: C 44.45%, H 7.46%, N 11.96%; found: C 47.73%, H 7.26%, N 11.28%.

3,5-Diethyl-1-(2-ethylhexyl)-4-methyl-1,2,3-triazolium thiocyanate [T2][SCN]

3-Ethyl-1-(2-ethylhexyl)-5-methyltriazolium iodide (13,0 g, 37 mmol) was equilibrated twice with 50 mL of a 5 M solution of KSCN and washed with 100 mL of water. TXRF with an Yb standard gave an estimated iodide content of 24.6 g/L. This implies a residual iodide content was about 2 wt%.

Some signals in ¹³C-NMR spectra are believed to correspond to identical carbon atoms, in separate conformers with slow interconversion.

Additional characterization data:





Fig. S5: TGA trace for [T1][I] (nitrogen flow).



Fig. S6: TGA trace for [T1][SCN] (nitrogen flow).



Fig. S7: TGA trace for [T2][I] (nitrogen flow).



Fig. S8: TGA trace for [T2][SCN] (nitrogen flow).

Densities of the ionic liquids used in extended extraction studies at 60°C:

[T1][I], water saturated: 1.142 g mL⁻¹ at 60 °C

60 mol% [T1][SCN] in [T1][I], water saturated: 1.079 g mL⁻¹ at 60 °C

Extraction data for [T2][I] and [T1][SCN]:



Fig. S9: Extraction of 0.01 M metal ion solutions from chloride media by [T2][I].



Fig. S10: Extraction of 0.01 M metal ion solutions from chloride media by 60 mol% [T2][SCN] in [T1][I].

EXAFS Data:

$[CuCl_2]^-$ in [T2][I]

Scattering path	Ν	r (Å)	σ² (Ų)	
Cu-Cl	2	2.11	0.094	
Cu-Cl1-Cu-Cl2	2	4.22	0.38	
Cu-Cl1-Cl2-Cu	2	4 22	0.38	

Table S1: Scattering paths and bond distances in $[CuCl_2]^-$ as determined by EXAFS.

Due to the relationship of the observed paths, their degeneracies were fixed as equal during fitting of the model, as were their absorption edge energies (8981 eV). The Debye-Waller factors were 53.8 and 55.8 for the first and last two paths, respectively. The low value of the absorption edge indicates that copper is present in the +I oxidation state.¹



Fig. S11: background-corrected X-ray absorption edge for [T2][I] loaded with CuCl₂, showing the absorption edge at <8985 keV, indicating the presence of a Cu(I) species.¹



Fig. S12: Experimental and model EXAFS functions of the $[CuCl_2]^-$ complex anion.



Fig. S13: Experimental and model pseudo-radial distribution functions of the $[CuCl_2]^-$ complex anion.

[Ni(H₂O)₆]²⁺ in [T2][I]

Scattering path	N	r (Å)	σ² (Ų)	
Ni-O-Ni	6	2.05	0.29	
Ni-O-Ni-O-Ni	6	4.10	1.1	
Ni-O-O-Ni	6	4.10	1.1	

Table S2: Scattering paths and bond distances in $[Ni(H_2O)_6]^{2+}$ as determined by EXAFS.

Due to the relationship of the observed paths, their degeneracies were set as equal during fitting of the model. The Debye-Waller factor was 71.3 for all paths.



Fig. S14: Experimental and model EXAFS functions of the $[Ni(H_2O)_6]^{2+}$ complex cation.



Fig. S15: Experimental and model pseudo-radial distribution functions of the $[Ni(H_2O)_6]^{2+}$ complex cation.

Raman spectroscopy of stripped [T2][I] samples

Samples of [T2][I] were equilibrated with 0.1 M CuCl₂ (1 mL aqueous phase and 150 mg ionic liquid) by shaking at 60 °C for 1 h at 2500 rpm. The aqueous phase was discarded and 1 mL of a reducing solution was added. Three solutions were evaluated: 0.1 M oxalic acid (a), 0.1 M sodium dithionite $(Na_2S_2O_4, b)$ and 0.25 M Na_2S (c). The mixture was again shaken for equilibration. The aqueous phase was discarded and the ionic liquid was dissolved in 2 mL (samples a and b) or 4 mL (sample c) of DCM. Raman spectroscopy was performed on a Bruker RAMII FT-Raman module with the source operating at 100 mW. The spectra shown in Fig. S12 clearly show the absence of the characteristic vibrational band of the triiodide ion in samples b and c, located between 110 and 115 cm⁻¹, while this band was still present in sample a. Thus, both sulfide and dithionite are effective in the reduction of I_3^- to I^- , while oxalic acid is ineffective. No precipitate of S_8 was present after reduction. It is therefore assumed that sulfur is oxidized to S(IV) as H_2SO_3 .



Fig. S16: Raman spectra of [T2][I] dissolved in DCM after treatment with oxalic acid (a), sodium dithionite (b) and sodium sulfide (c).

¹H NMR Spectra of synthesized compounds:

5-ethyl-1-(2-ethylhexyl)-4-methyltriazole



Fig. S17: Proton NMR of 5-ethyl-1-(2-ethylhexyl)-4-methyltriazole.





Fig. S18: Proton NMR of 3,5-diethyl-1-(2-ethylhexyl)-4-methyltriazolium iodide.

1-(2-ethylhexyl)-5-methyltriazole



Fig. S19: Proton NMR of 1-(2-ethylhexyl)-5-methyltriazole.

3-ethyl-1-(2-ethylhexyl)-5-methyltriazolium iodide [T2][I]



Fig. S20: Proton NMR of 3-ethyl-1-(2-ethylhexyl)-5-methyltriazolium iodide.

¹³C NMR Spectra of synthesized compounds:

5-ethyl-1-(2-ethylhexyl)-4-methyltriazole



Fig. S21: Carbon-13 NMR of 5-ethyl-1-(2-ethylhexyl)-4-methyltriazole.

3,5-diethyl-1-(2-ethylhexyl)-4-methyltriazolium iodide [T1][I]



Fig. S22: Carbon-13 NMR of 3,5-diethyl-1-(2-ethylhexyl)-4-methyltriazolium iodide.



Fig. S23: Carbon-13 NMR of 1-(2-ethylhexyl)-5-methyltriazole.





Fig. S24: Carbon-13 NMR of 3-ethyl-1-(2-ethylhexyl)-5-methyltriazolium iodide.

References:

1 A. Gaur, B. D. Shrivastava and S. K. Joshi, J. Phys. Conf. Ser., 2009, **190**, 12084.