Structure and Magnetic Behavior of Transition Metal Based Ionic Liquids

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Supporting Information

Synthesis of transition-metal based RTILs.

[PR₄][FeCl₄], [PR₄][CoCl₄], [PR₄][MnCl₄], [PR₄][GdCl₄]. A solution of the trihexyl(tetradecyl)phosphonium chloride in chloroform or methylene chloride was added to an aqueous solution with the appropriate number of equivalents of the hydrated metal halide salt MClₓH₂O in slight excess. The solution was allowed to stir overnight, after which time the aqueous solutions were nearly colorless, and the organic layer deeply colored. The organic layer was separated, washed several times with water, and the solvent evaporated to yield the viscous room temperature liquids.

[PR₄][Co(NCS)₄] - K₂[Co(NCS)₄] was first prepared by reacting the CoCl₂ with K(NCS) in water. This solution was then used directly for metathesis with a solution of the [PR₄]Cl in methylene chloride. The solution was allowed to stir overnight during which time the aqueous layer became colorless, and the organic layer deeply colored blue. The organic layer was separated, washed several times with water, and the solvent evaporated to yield the viscous room temperature liquid.

[C10mim][FeCl₄], [C4mim]₂[MnBr₄]. The appropriate number of equivalents of the hydrated metal halide was added to the imidazolium halide at 90°C and allowed to stir overnight. Two layers resulted containing different layers of hydration, which could be dehydrated under vacuum at 90°C to yield one layer of a viscous ionic liquid (or pale orange crystals for the [MnBr₄] salt).

Characterization. To measure the magnetic susceptibility, the ionic liquids were degassed by placing under vacuum (< 100 mtorr) at room temeparture for 24 hours. The liquids were then loaded into air-tight delrin holders (Quantum Design) under a nitrogen atmosphere to keep oxygen interference out of the sample. Measurements were performed on a Quantum Design MPMS Magnetometer with SQUID detector. Thermal characterization was carried out using a TA Instruments Q100 DSC and SDT 2960 SDT-TGA. IR spectra were recorded on a Thermo Avatar 360 FT-IR with a MCT detector on a Thermo-Nicolet 470 FTIR with a Raman module.

Fig. S1 IR spectra for [PR₄] based transition metal RTILs.
**Fig. S2** IR spectra top and bottom layers formed in [C10mim][FeCl4].

![IR spectra](image)

**Fig. S3** Cyclic voltammetry for the [PR4]2[CoCl4] ionic liquid neat. Pt working and counter electrodes, Ag/AgO pseudo-reference; scan rate: 100mV/s.

![Cyclic voltammetry](image)
Fig. S4 Magnetic susceptibility for [PR₄]⁺ based RTILs.

Videographs - Ionic liquids in water – see files in Supporting Information