Structure and magnetic behavior of transition metal based ionic liquids†

Rico E. Del Sesto,*[a] T. Mark McCleskey,[a] Anthony K. Burrell,[a] Gary A. Baker,[b] Joe D. Thompson,[c] Brian L. Scott,[a] John S. Wilkes[d] and Peg Williams[d]

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A series of ionic liquids containing different paramagnetic anions have been prepared and all show paramagnetic behavior with potential applications for magnetic and electrochromic switching as well as novel magnetic transport; also, the tetraalkylphosphonium-based ionic liquids reveal anomalous magnetic behavior.

Ionic liquids with anions containing transition metal complexes were among the earliest developed room temperature ionic liquids (RTILs).[1] The magnetic behavior of these paramagnetic materials has been largely ignored until recently, with more magnet-responsive and exotic transition metal complexes being introduced into RTILs.[2] As liquids, it was generally assumed that the metal centers remained isolated, lacking long-range interaction(s) and communication. As such, these RTILs are not expected to exhibit ordered magnetic behavior, as no strong mechanism for magnetic exchange between the paramagnetic metal centers exists, with the possible exception of formation of small clusters such as dimers.[1,3]

As solutions of their components, RTILs with transition metal centers are attractive candidates for magnetic liquids and magnetorheological fluids, because they contain high effective concentrations of metal centers. Additionally, they have the desirable properties of low volatility under ambient (as well as elevated) temperature, control over hydrophilicity *via* cation and/or anion modification, and electrical conductivity. Their intrinsic conductivity, combined with a large electrochemical window, augments the potential for utilizing the electrochromic behavior resulting from integration of a metal center. RTILs are also transparent, a further advantage over conventional ferrofluids which are opaque colloidal dispersions of magnetic particles in a viscous (and often flammable organic) liquid carrier.

Reported structures of some ionic liquids with transition metal halide anions, such as $[MCl_4]^{z-}$, show isolated tetrahedral anions, a lack of metal-bridging halides, and large distances between nearest neighboring metal centers.[4] Most of these salts reported contain the popular imidazolium cations and are solid at room temperature due to an extensive hydrogen-bonding network, with the exception of room temperature liquid $FeCl_4^-$ salts.

We report on several transition metal based RTILs synthesized by reaction of trihexyl(tetradecyl)phosphonium [PR_4], 1-decyl-3-methylimidazolium [C10mim], or 1-butyl-3-methylimidazolium [C4mim] halides with the corresponding metal halides, or metathesis with alkali salts of metal-based anions. Utilizing large and bulky tetraalkylphosphonium cations leads to liquids with all transition metal anions studied. These reactions were performed neat at temperatures sufficient to ensure that the organic halide was molten to start, or with the addition of small volumes of water or $CHCl_3$ to ensure efficient mixing.

RTILs utilizing the imidazolium cation have been previously reported containing metal halide anions, *e.g.*, $Al_xCl_y^-$, $FeCl_4^-$, $MnCl_4^{2-}$.[1b] One significant disadvantage to the imidazolium cation is that the 2-position of the imidazolium ring has a relatively acidic proton, making the cation a fairly strong hydrogen bond donor, particularly in the presence of metal halide anions. This is observed in several of the reported crystal structures,[1] yielding extended network structures of cations and anions and discouraging formation of RTILs. We have observed this hydrogen bonding motif in the [C4mim]$_2$[$MnBr_4$] salt synthesized from the aqueous-phase reaction of [C4mim]Br with $MnBr_2$. The result is a room temperature solid which exhibits H-bonding between the Br and the imidazolium C2 proton, with a Br···H distance of 2.78 Å, as illustrated in Fig. 1.‡

The tetraalkylphosphonium cation lacks acidic protons, preventing the establishment of hydrogen bonded networks seen in the imidazolium salts. The large trihexyl(tetradecyl)phosphonium cation is thus nearly ideal for formation of transition metal ion containing RTILs, as the bulky cation is not conducive to crystallization.

Reaction of trihexyl(tetradecyl)phosphonium chloride [PR_4]Cl with $FeCl_3$, $CoCl_2$, $MnCl_2$ or $GdCl_3$ all yield the corresponding

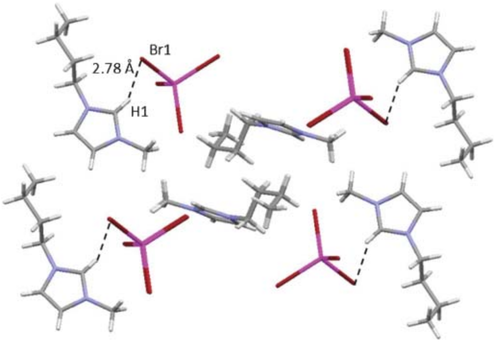

Fig. 1 Structural view of [C4mim]$_2$[$MnBr_4$].

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[a] *Materials Chemistry, MPA-MC, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. E-mail: ricod@lanl.gov*
[b] *Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*
[c] *Condensed Matter and Thermal Physics, MPA-10, Los Alamos National Laboratory, Los Alamos, NM 87545, USA*
[d] *Department of Chemistry, United States Air Force Academy, USAFA, CO 80840, USA*

† Electronic supplementary information (ESI) available: Synthesis details, FT-IR spectra, cyclic voltammetry and magnetic susceptibility measurements, and videos of the paramagnetic ionic liquids in water. See DOI: 10.1039/b711189d

Table 1 Summary of physical, electrochemical, and magnetic properties of selected transition metal based RTILs

Cation	Anion	FW	T_g/°C (K)	E_{ox}/V[a]	E_{red}/V[a]	χT/emu K mol^{-1} [b]	θ/K[c]
$[PR_4]^{+}$ [d]	$[FeCl_4]^-$	681.51	−71 (202)	+0.58	−0.20	4.34	−0.8
	$[CoCl_4]^{2-}$	1168.46	−68 (205)	+1.50	+0.85	2.48	−3.7
	$[MnCl_4]^{2-}$	1164.46	−69 (204)	+1.60	+0.60	4.22	−0.1
	$[Co(NCS)_4]^{2-}$	1258.97	−72 (201)	—	—	2.06	−0.2
	$[GdCl_6]^{3-}$	1821.53	Below RT[e]	—	—	7.72	−0.1
$[C10mim]^+$	$[FeCl_4]^-$	421.03	−81 (192)	—	—	4.01	−3.3
$[C4mim]^+$	$[MnBr_4]^{2-}$	652.99	Below RT[e]	—	—	4.26	−0.8

[a] As measured at identical currents for both oxidation and reduction. [b] Measured at 300 K and H = 0.1 T. [c] (±1 K). [d] $[PR_4]^+$ = trihexyl(tetradecyl)phosphonium. [e] Not measured.

RTILs; their properties are summarized in Table 1. Typically, the metal halide starting material, as either the anhydrous or hydrated salt, is added directly to the PR_4Cl in the absence of solvent. To ensure efficient mixing, the neat solution may be heated, or a $CHCl_3$–water mixture (1 : 1, v/v) can be added to dissolve the corresponding starting materials, with the resulting $[PR_4]_x[MCl_y]$ RTIL being extracted into the organic layer (water is necessary only for the imidazolium salts). When the hydrated metal halide salts are added to the PR_4Cl neat, one can visually observe the elimination of water which forms a separate layer. For example, reaction of dry $[PR_4]Cl$ with the purple solid $CoCl_2\cdot 4H_2O$ (octahedral symmetry) gradually yields a blue $[PR_4]_2[CoCl_4]$ (tetrahedral symmetry) RTIL, while water droplets spontaneously phase separate from the RTIL layer—essentially dehydrating the metal chloride upon incorporation into the extremely hydrophobic phosphonium salt. This is evident in the IR spectra for all of the $[PR_4]_x[MCl_y]$ RTILs which show no evidence for water (see Fig. S1 in the ESI†). In contrast, the reaction of the more hydrophilic imidazolium halides with $MnBr_2\cdot xH_2O$ and $FeCl_3\cdot xH_2O$ typically result in two layers, with each RTIL layer associated with a different degree of overall hydration, based on IR findings (Fig. S2).†

The metal halide anions exist as discrete MCl_x^{z-} anions, which is evident in the Raman spectra of the $[PR_4][FeCl_4]$, $[PR_4]_2[CoCl_4]$ and $[PR_4]_2[MnCl_4]$ salts, Fig. 2.[4] The $[PR_4][FeCl_4]$ spectrum shows one clean peak at 335 cm^{-1} that has been previously assigned to tetrahedral $FeCl_4^-$. For comparison, [C10mim]Cl also yields a liquid for the corresponding $[FeCl_4]^-$ salt, but not with other metal halides. Due to the wide electrochemical window of the $[PR_4]^+$ based RTILs, the reductions and/or oxidations of the metal centers in the RTILs are readily accessible. The synthesized RTILs display chemically irreversible behavior associated with the geometry changes anticipated for the corresponding changes in oxidation state. For example, as shown in Fig. S3,† $[PR_4]_2[CoCl_4]$ is irreversibly oxidized at 1.5 V *vs.* Ag/AgCl as the geometry is altered from tetrahedral (Co^{2+}) to octahedral (Co^{3+}). Selected oxidation and reduction potentials for several members of this novel class of RTIL are given in Table 1.

The transition metal based RTILs display simple paramagnetic behavior over most of the temperature range of 50–350 K, and room temperature χT values correspond well with their respective spin states (that is, 4.22 emu K mol^{-1} for the $S = 5/2$ $[PR_4]_2[MnCl_4]$ salt compares with the expected value of 4.375 emu K mol^{-1}). All RTILs show very weak antiferromagnetic interactions as seen in the Curie–Weiss θ values in Table 1, which range from −0.1 to −3.7 K (−0.4 to −2.8 cm^{-1}), confirming the lack of any cluster formation in solution. In the $[PR_4]$ salts, however, there is a noticeable deviation between field cooled (FC) and zero-field cooled (ZFC) samples around 250 K, Fig. 3. The deviation is not very significant, and it is not likely a result of electronic state

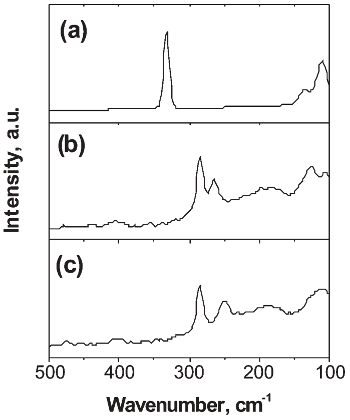

Fig. 2 Raman spectra of (a) $[PR_4][FeCl_4]$ (b) $[PR_4]_2[CoCl_4]$ and (c) $[PR_4]_2[MnCl_4]$.

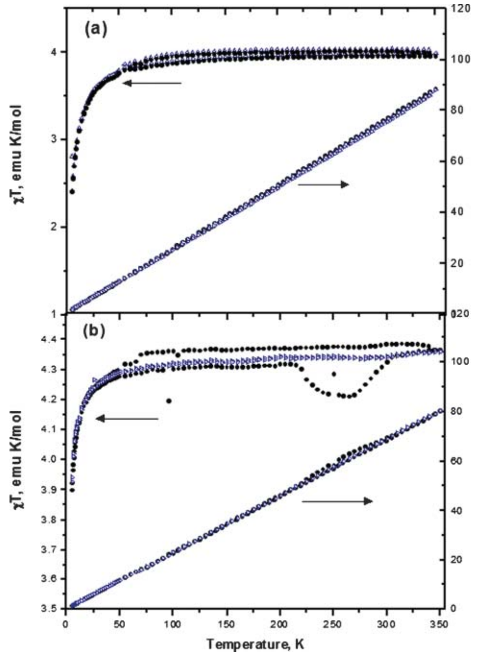

Fig. 3 χT and $1/\chi$ at 1000 G for (a) $[C10mim][FeCl_4]$ and (b) $[PR_4][FeCl_4]$ (△ = slow field cool, ● = rapid field cool).

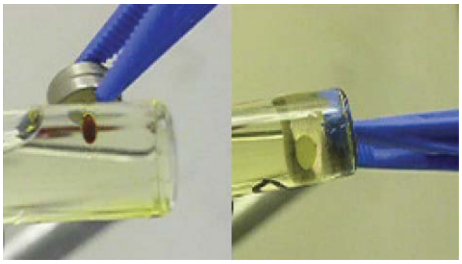

Fig. 4 Response towards a $Nd_2Fe_{14}B$ magnet of [C10mim][$FeCl_4$] (left) and [PR4][$FeCl_4$] (right) ionic liquid droplets in water.

transitions or spin orientation as the anions are all fairly isotropic ($g \approx 2$).

The anomalies in the susceptibility of the [PR_4] salts are reproducible during rapid cooling in ZFC–FC experiments, but disappear when the ZFC–FC experiment is performed with slow cooling from RT. Additionally, the deviations occur in the region of the glass transitions of the PR_4 ionic liquids. Therefore the deviation is likely associated with glass formation during rapid cooling. This reproducible phenomenon is under current investigation to determine its origin. Magnetization studies also show no signs of ordering, with all of the ILs showing saturation at 5 K and 5 T close to their corresponding values.

Though the ionic liquids are simply paramagnetic, they still respond strongly to an applied magnetic field. Droplets of the [C10mim][$FeCl_4$] and [PR4][$FeCl_4$] salts can be added to a vial of water, with which they are initially immiscible. The droplets can then be quite easily manipulated with the application of an external strong magnetic field, such as that from neodymium iron boride, Fig. 4 (a video of these manipulations is in the ESI†). [C10mim][$FeCl_4$] will completely dissolve in the aqueous phase after several hours, whereas [PR_4][$FeCl_4$] droplets remain intact almost indefinitely (over several months). The potential thus exists for using phosphonium-based RTILs for magnetic transport through aqueous systems due to the rapid response to a magnetic field and extreme hydrophobic character. In comparison, a previous report exhibits the movement of diamagnetic bubbles in a paramagnetic ionic liquid.[5] The responses in both cases are likely due to a similar mechanism in which diamagnetic materials are repelled by an applied magnetic field, and paramagnetic materials—in both cases ionic liquid—are attracted to the magnetic field.

In summary, we have prepared several transition metal based RTILs containing imidazolium and phosphonium cations. The materials are redox active and respond to a magnetic field due to the anion's paramagnetic nature.

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Notes and references

‡ Crystal data for [C4mim]$_2$[$MnBr_4$]: $C_{16}H_{30}N_4Br_4Mn$, M = 653.02, monoclinic, a = 15.024(2), b = 9.407(1), c = 18.726(2) Å, β = 112.442(1)°, V = 2446.2(5) Å^3, T = 141 K, space group $C2/c$ (# 15), Z = 4, μ(Mo-Kα) = 1.9 mm^{-1}, 13380 reflections measured, 3019 unique (R_{int} = 0.0491) which were used in all calculations. The final w$R(F^2)$ was 0.0743 (all data). CCDC 655280. For crystallographic data in CIF format see DOI: 10.1039/b711189d

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