Synthesis of an ionic liquid with an iron coordination cation†

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Received 21st May 2010, Accepted 19th July 2010
DOI: 10.1039/c0dt00523a

An iron-based ionic liquid, Fe((OHCH₂CH₂)₂NH)₆(CF₃SO₃)₃, is synthesized in a single-step complexation reaction. Infrared and Raman data suggest NH(CH₂CH₂OH)₂ primarily coordinates to Fe(III) through alcohol groups. The compound has T_g and T_a values of −64 °C and 260 °C, respectively. Cyclic voltammetry reveals quasi-reversible Fe(III)/Fe(II) reduction waves.

Introduction

Room temperature ionic liquids (RTILs) containing transition metal elements are of both considerable intellectual interest and potential utility.¹ The high thermal stabilities and negligible vapor pressures of ionic liquids, coupled with potential value-added properties from transition metals, make them attractive for a wide range of applications.²–⁶ The conventional approach to form an ionic liquid is to employ a large, asymmetric organic cation with anions such as BF₄⁻, PF₆⁻, CF₃SO₃⁻, or (CF₃SO₂)₂N⁻.¹ Recently, a number of RTILs have been reported that contain transition metal-based anions. Examples include compounds containing imidazolium cations with tetrahedral halogenoferrates and phosphoniminate cations with various cobaltates as well as RTILs consisting of either alkyl ammonium, phosphonium, or imidazolium salts of polyoxotungstate clusters.⁷ There are also several liquid transition metal-based cations. Dai has reported RTILs that have Ag(H₂N–R)₂⁺ or Zn(H₂N–R)₂⁺ (R = alkyl group) cations,⁸ and there are also a number of compounds containing ferrocenyl-functionalized cations.⁹ We now report the synthesis of Fe((OHCH₂CH₂)₂NH)₆(CF₃SO₃)₃ (I), a viscous dark red liquid (at 25 °C) containing an iron coordination cation. Complex I is characterized by elemental analysis, viscosity, TGA-DSC, infrared, Raman, and UV-Visible spectroscopy. The electrochemical properties of I are evaluated using cyclic voltammetry and impedance spectroscopy.

Results and discussion

The iron-based ionic liquid Fe((OHCH₂CH₂)₂NH)₆(CF₃SO₃)₃ (I), is obtained by mixing the solid metal salt Fe(CF₃SO₃)₃ with liquid NH(CH₂CH₂OH)₂ in a 1 : 6 stoichiometry. The reaction is exothermic but additional heating is required to drive it to completion. A color change from almost white to red–orange is observed upon heating but additional heating is required to drive it to completion. A color change from almost white to red–orange is observed upon heating.† A DSC measurement of I was also performed using a liquid N₂ quench cooling accessory and the results are shown in Fig. 1b. There is a T_g at −64 °C that is indicative of an amorphous glass reforming a liquid upon heating.⁸

The infrared spectrum of I is shown in Fig. 2a. The infrared bands from 3500–3200 cm⁻¹ and 3100–2700 cm⁻¹ are associated with the alcohol and amine functional groups of NH(CH₂CH₂OH)₂, respectively.⁹ The alcohol and amine bands of I are blue-shifted by approximately 200 cm⁻¹ and 30 cm⁻¹, respectively, relative to NH(CH₂CH₂OH)₂. The observed blue-shifts support the TGA data that indicate NH(CH₂CH₂OH)₂ is coordinated to Fe(III). In addition, the larger blue-shift of the alcohol group relative to the amine indicates that NH(CH₂CH₂OH)₂ preferentially coordinates through the alcohol groups.

The Raman spectra (633 nm laser) of NH(CH₂CH₂OH)₂, I, and Fe(CF₃SO₃)₃ are shown in Fig. 2b. The Fe(CF₃SO₃)₃ symmetrical deformation and stretching frequencies associated with CF₃ (780 cm⁻¹) and SO₃ (1075 cm⁻¹) respectively, are red-shifted in I.† This is consistent with displacement of CF₃SO₃⁻ by NH(CH₂CH₂OH)₂ around the Fe(III) center. In addition, there is a peak in I around 300 cm⁻¹ not associated with either CF₃SO₃⁻ or NH(CH₂CH₂OH)₂. This peak is associated with a Fe–O bond...
due to preferential coordination through the alcohol group of NH(CH2CH2OH)2.

The high optical absorption of 1 prevented the direct acquisition of UV-Vis spectroscopic data. As a result, 1 was dissolved in 1-butyl-3-methyl-imidazolium hexafluoro phosphate (BMI-PF6). A single λmax was observed at 477 nm (Fig. 3a). The position of the λmax at 477 nm, along with value of the extinction coefficient (ε = 63), suggest this peak may be attributed to an iron d-d transition and is consistent with preferential coordination through the alcohol groups. There are no changes to the infrared and Raman difference spectra (subtraction of solvent peaks) of 1 in BMI-PF6, and there is no shift in λmax as a function of the concentration of 1, suggesting that PF6- is not coordinating to Fe(III).

The specific conductivity of 1 (with < 2 ppm H2O) at 25 °C is 207 mSc m-1. Although this value is similar to a number of conventional ionic liquids,2 it is three orders of magnitude lower than traditional aqueous battery electrolytes such as H2SO4 and KOH.10 The low conductivity of 1 is consistent with the fact that it is highly viscous (4482 cP, see ESI for more information†). The activation energy of conduction, measured from an Arrhenius plot, is 13.1 kcal mol-1. Typical activation energy values for conduction in aqueous and molten metal salts are ~3–5 kcal mol-1.10

The data suggests significant ion pairing is present in 1. In contrast, the conductivity values reported by Dai for the Ag(H2N–R)2+/CF3SO3– RTILs range from 1.70–12.30 mS cm-1 at 24 °C.8 Although the higher charge of Fe(III) versus Ag(I) is an important factor, the results indicate that higher conductivity might be achieved by replacing the CF3SO3– anion of 1 with the more hydrophobic (CF3SO2)2N–.

Cyclic voltammograms (CVs) of 1, performed with a glassy carbon working electrode at four different scan rates, are illustrated in Fig. 3b. The high viscosity and low conductivity of 1 prevented the direct acquisition of electrochemical data. As a result, CV measurements were performed on a 0.011 M solution of 1 in BMI-PF6, and stability was confirmed by UV-Vis measurements. Complex 1 displays several quasi-reversible waves associated with Fe(III)/Fe(II) reduction and oxidation that become more resolved at slower scan rates. To further resolve these peaks, an Osteryoung square wave voltammogram was acquired on 1 (Fig. 3b, inset). The results show there are three waves. One plausible explanation for this behavior is the pendant –CH2CH2OH groups of the NH(CH2CH2OH)2 ligands are coordinating to adjacent Fe(III) centers. This is consistent with the fact that the magnetic susceptibility measurement of 1 at 25 °C shows there is a small amount of antiferromagnetic coupling (measured μeff = 5.78 BM at
A 2.00 g (3.98 mmol) sample of recrystallized Fe(CF₃SO₃)₃ was added to 2.51 g (23.9 mmol) of NH(CH₂CH₂OH)₂ in a 20 mL glass vial, thoroughly mixed for several minutes, and then heated to 115 °C in an oven for 15–20 min. Additional mixing was then performed by ultrasound for 5 min and the solution was again heated to 115 °C for 15–20 min (yield >99.9%). IR (ATR, 4000–5000 cm⁻¹): 3440 (m), 3309 (sh), 3094 (w), 2938 (w), 2862 (m), 1608 (m), 1453 (m), 1273 (sh), 1240 (s), 1224 (s), 1161 (s), 1061 (s), 1024 (s), 811 (m), 760 (m), 635 (s), 574 (m), and 515 (m). Raman spectral data (400–700 nm, in BMI-PF₆): 477 (63). Density: 1.44 ± 0.06 g mL⁻¹. Magnetic susceptibility: µₑₐ₉ = 5.78 BM at 295 K. Anal Calc (%): Fe, 4.48; N, 7.36; C, 5.98; H, 5.78; F, 14.7; Fe, 5.0; S, 8.8. [MW = 1134 g mol⁻¹].

Notes and references
† There are a series of exotherms from 260 °C to 350 °C that correspond to the loss of NH(CH₂CH₂OH)₂ ligands and this is further corroborated by X-ray fluorescence (no change in the Fe : S ratio of a sample heated in an oven to 350 °C). The onset of CF₃SO₃⁻ decomposition is approximately 350 °C, and it is consistent with a decrease in the Fe : S ratio.
§ In order to understand if the isolation of I is fortuitous or if it is the first member of a new family of ionic liquids, we have examined the reaction of other metal salts (including Zn(CF₃SO₃)₂ and Cu(NH₂CH₂CH₂OH)₂(CH₃(CH₂)₃CH(C₂H₅)CO₂)₂) with both NH(CH₂CH₂OH)₂ and NH₂CH₂CH₂OH ligands. To date we have synthesized and characterized three additional liquid materials: Zn(NH₂CH₂CH₂OH)₂(CF₃SO₃)₃, Cu(NH₂CH₂CH₂OH)₂(CH₃(CH₂)₃CH(C₂H₅)CO₂)₃, and Cu(NH₂CH₂CH₂OH)₂(CH₃(CH₂)₃CH(C₂H₅)CO₂)₄. Electrochemical studies of these complexes are presently underway and the results will be reported in due course.


