Ionic Liquids Based on $FeCl_3$ and $FeCl_2$. Raman Scattering and ab Initio Calculations

Melissa S. Sitze, Eric R. Schreiter, Eric V. Patterson, and R. Griffith Freeman*

Division of Science, Truman State University, 100 East Normal, Kirksville, Missouri 63501

Received September 14, 2000

We have prepared ionic liquids by mixing either iron(II) chloride or iron(III) chloride with 1-butyl-3-methylimidazolium chloride (BMIC). Iron(II) chloride forms ionic liquids from a mole ratio of 1 $FeCl_2$/3 BMIC to almost 1 $FeCl_2$/1 BMIC. Both Raman scattering and ab initio calculations indicate that $FeCl_4^{2-}$ is the predominant iron-containing species in these liquids. Iron(III) chloride forms ionic liquids from a mole ratio of 1 $FeCl_3$/1.9 BMIC to 1.7 $FeCl_3$/1 BMIC. When BMIC is in excess, Raman scattering indicates the presence of $FeCl_4^-$. When $FeCl_3$ is in excess, $Fe_2Cl_7^-$ begins to appear and the amount of $Fe_2Cl_7^-$ increases with increasing amounts of $FeCl_3$. Ionic liquids were also prepared from a mixture of $FeCl_2$ and $FeCl_3$ and are discussed. Finally, we have used both Hartree−Fock and density functional theory methods to compute the optimized structures and vibrational spectra for these species. An analysis of the results using an all-electron basis set, 6-31G*, as well as two different effective core potential basis sets, LANL2DZ and CEP-31G is presented.

Introduction

Ionic liquids, which for the purpose of this paper means ionic compounds that are liquid at ambient temperatures, are a class of compounds that are being studied extensively because of their unusual physical properties. The earliest report of an ionic liquid at room temperature was a mixture of ethylpyridinium bromide and aluminum chloride that was used for the deposition of aluminum.[1] These authors were also the first to provide experimental evidence for the formation of a tetrahaloaluminate anion in this type of system. The initial interest in ionic liquids (which were then more often referred to as room temperature molten salts) was due to their use as solvents for electrochemical studies. In particular, the introduction of the aluminum chloride/dialkylimidazolium chloride systems made it possible to obtain very large potential windows for electrochemical studies.[2] One specific example of the versatility of these solvents is the fact that the combination of aluminum chloride and 1-ethyl-3-methylimidazolium chloride (EMIC) forms room temperature liquids from a ratio of 2 $AlCl_3$/1 EMIC to 1 $AlCl_3$/2 EMIC. When the mole ratio exceeds 1/1 in favor of $AlCl_3$, the complex anion $Al_2Cl_7^-$ forms and the solvent is Lewis acidic. When there is an excess of dialkylimidazolium chloride, free Cl^- exists and the solution is basic in the Lewis sense. In fact, free $AlCl_3$ is not found in significant amounts in these liquids. Aluminum has been observed as $AlCl_4^-$ and $Al_2Cl_7^-$, and higher order complexes have been hypothesized.

The most useful of the unusual properties of these solvents may be the fact that they have very low vapor pressures. Thus, they have great potential as "green" solvents for industrial processes.[3] This potential is being explored vigorously as recent publications hint at their use in many typical chemical reactions. It has been shown that liquid/liquid extractions may be carried out with one of the phases being an ionic liquid.[4] Freidel−Crafts reactions have been carried out with both organic[5] and organometallic substrates.[6]

There have been numerous studies in which transition metal chlorides were placed in ionic liquids for a variety of purposes, and this field was reviewed in 1988.[7] Osteryoung and coworkers have investigated the behavior of molybdenum[8] and titanium[9] chlorides in chloroaluminate/EMIC ionic liquids. Hussey and colleagues have investigated nickel and iron,[10] copper,[11] molybdenum,[12] and niobium[13] chlorides. Uranium[14] chlorides have also been studied. In all of these cases electrochemical techniques were the primary methods of characterization. However, visible absorption spectrometry was often used as well. More recently, crystal structures of a number of solids formed from transition metal chlorides and dialkylimidazolium chloride have been reported. The structures of $[emim]_2[CoCl_4]$ (emim = 1-ethyl-3-methylimidazolium) and $[emim]_2[NiCl_4]$[15] were obtained in order to provide information that might help decipher the solution structure of the ionic liquids. Additionally, the crystal structures of the salts $[emim]_2[PdCl_4]$,[16] $[emim][AuCl_4]$, and $[bmim][AuCl_4]$ have been reported.[17] However,

---

* Corresponding author: Griff Freeman, SurroMed, Inc., 2375 Garcia Ave., Mountain View, CA 94043. E-mail: gfreeman@surromed.com.

(1) Hurley, F. H.; Thomas P. Wier, J. *J. Electrochem. Soc.* **1951**, *98*, 203−206.

(2) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263−1264.

(3) Seddon, K. R. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351−356.

(4) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. *Chem. Commun.* **1998**, 1765−1766.

(5) Adams, C. J.; Earle, M. J.; Roberts, G.; Seddon, K. R. *Chem. Commun.* **1998**, 2097−2098.

(6) Stark, A.; MacLean, B. L.; Singer, R. D. *J. Chem. Soc., Dalton Trans.* **1999**, 63−66.

(7) Hussey, C. L. *Pure Appl. Chem.* **1988**, *60*, 1763−1772.

(8) Carlin, R. T.; Osteryoung, R. A. *Inorg. Chem.* **1988**, *27*, 1482−1488.

(9) Carlin, R. T.; Osteryoung, R. A.; Wilkes, J. S.; Rovang, J. *Inorg. Chem.* **1990**, *29*, 3003−3009.

(10) Laher, T. M.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 4079−4083.

(11) Laher, T. M.; Hussey, C. L. *Inorg. Chem.* **1983**, *22*, 3247−3251.

(12) Barnard, P. A.; Sun, I.-W.; Hussey, C. L. *Inorg. Chem.* **1990**, *29*, 3670−3674.

(13) Quigley, R.; Barnard, P. A.; Hussey, C. L.; Seddon, K. R. *Inorg. Chem.* **1992**, *31*, 1255−1261.

(14) Anderson, C. J.; Deakin, M. R.; Choppin, G.; D'Olieslager, W.; Heerman, L.; Pruett, D. J. *Inorg. Chem.* **1991**, *30*, 4013−4016.

(15) Hitchcock, P. B.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1993**, 2639−2643.

(16) Ortwerth, M. F.; Wyzlic, M. J.; Baughman, R. G. *Acta Crystallogr.* **1998**, *C54*, 1594−1596.

10.1021/ic001042r CCC: $20.00

despite considerable interest in the behavior of transition metal chlorides dissolved in chloroaluminate ionic liquids, only limited work has been published on ionic liquids where the chloroaluminate has been replaced by an alternative chlorometalate.

In 1990 Scheffler and Thomson reported the preparation of ionic liquids from a variety of metal chlorides (AgCl, CuCl, LiCl, $CdCl_2$, $CuCl_2$, $SnCl_2$, $ZnCl_2$, $LaCl_3$, YCl_3, $SnCl_4$, and $TiCl_4$, all mixed with EMIC).[18] This report presented extensive information about the liquidous range as well as NMR chemical shift as a function of composition, but offered little other characterization. In addition to this, a patent has been issued on the use of ionic liquids based on K, Ca, Li, Al, Mg, Zn, and Fe halides and alkylpyridinium halides as electrolytes in batteries.[19] Finally, there has also been one report of the physical characterization of CuCl-based ionic liquids (viscosities and densities).[20]

We are interested in the structures of the ions present in these ionic liquids. It has been clearly established that both $AlCl_4^-$ and $Al_2Cl_7^-$ can be present in the chloroaluminate ionic liquids. The amount of each depends on the ratio of $AlCl_3$ to dialkylimidazolium, and the two species have been clearly identified via Raman scattering,[21] as well as other techniques. Our previous work with ionic liquids containing $AuCl_3$ has demonstrated that while $AuCl_4^-$ is present there is no experimental evidence for the formation of $Au_2Cl_7^-$. This occurs despite the fact that ab initio (gas phase) calculations indicate that $Au_2Cl_7^-$ should be more stable than the combination of $AuCl_3$ and $AuCl_4^-$.[22]

Herein we report the results of our studies on ionic liquids prepared from either Fe(III) chloride or Fe(II) chloride and 1-butyl-3-methylimidazolium chloride (BMIC). Raman scattering results indicate that $FeCl_3$ behaves much like $AlCl_3$, forming first $FeCl_4^-$ and then $Fe_2Cl_7^-$ when the ratio of $FeCl_3$ to BMIC exceeds 1/1. $FeCl_2$ reacts with BMIC when the ratio of metal to BMIC is less than 1/1. This is most likely due to the fact that $FeCl_4^{2-}$ is formed instead of species such as $Fe_2Cl_5^-$.

In addition, we report on the performance of basis sets employing effective core potentials to predict vibrational frequencies for these species. Of special interest for ionic liquids containing Fe(II) or Fe(III) is that unrestricted Hartree−Fock computations carried out with the CEP-31G basis set give results that are comparable to those carried out using density functional theory (B3LYP) and the 6-31G* basis set, a combination that is much more computationally expensive.

Experimental Section

Materials. Anhydrous $FeCl_2$ and $FeCl_3$ were purchased from Aldrich, opened in the glovebox, and used without further purification. 1-Methylimidazole and 1-chlorobutane were also purchased from Aldrich and used as received. 1-Butyl-3-methylimidazolium chloride (BMIC) was prepared via literature methods.[23]

The ionic liquids were prepared by direct mixing of the metal chloride and BMIC in an N_2-atmosphere glovebox. Those liquids prepared with $FeCl_3$ formed rapidly with stirring. Reactions with $FeCl_2$ were much slower, and these samples were usually heated to accelerate mixing.

Raman Scattering. Laser excitation was provided by a HeNe laser (Research ElectroOptics) and was passed through a laser line filter and a cylindrical lens and focused onto a NMR tube containing the sample. The laser power at the sample was approximately 15 mW. Scattered light was collected at about 30° from the excitation beam, collimated, passed through a superholographic notch filter (Kaiser HSNF-633-1.0), and focused onto a Spex270M monochromator. The light was dispersed via either a 1200 lines/mm or 1800 lines/mm grating and detected via a liquid-nitrogen-cooled CCD. Spectral positions were calibrated by reference to spectra of $CDCl_3$ that were collected either immediately before or immediately after the ionic liquid samples. In some cases, signal spikes due to "cosmic rays" were removed either by smoothing the entire spectrum or by inspection.

Computational Methods. Geometries of all species were optimized using both unrestricted Hartree−Fock (UHF) and unrestricted density functional theories. The density functional used comprised the gradient-corrected hybrid exchange functional of Becke[24] and the gradient-corrected correlation functional of Lee, Yang, and Parr,[25] collectively denoted UB3LYP. Three basis sets were chosen for this study: 6-31G*,[26−31] LANL2DZ,[32−35] and CEP-31G,[36−38] the latter two being effective core potential bases while the first is an all-electron basis. The CEP-31G basis is referred to often in the literature as the SBKJ basis.

All geometries were optimized within appropriate symmetry constraints (see discussion). For the Fe(III) species, only the high-spin sextet states were considered, while the analogous quintet Fe(II) states were studied. Frequency calculations were carried out to classify each stationary point (i.e., zero imaginary modes for each minimum or one imaginary mode for each transition state). HyperChem was used to visualize the vibrational modes. All calculations were carried out using either Gaussian98W or Gaussian 98.[39]

Results and Discussion

Ionic Liquids with $FeCl_3$. At room temperature, iron(III) chloride forms ionic liquids with BMIC from a composition of 1/1.9 ($FeCl_3$/BMIC) to 1.7/1. Figure 1 shows the Raman spectrum of the liquid containing an $FeCl_3$/BMIC ratio of 1/1.5. It is typical of those liquids where the ratio of $FeCl_3$/BMIC is less than or equal to 1. The features at 120, 333, and 384 cm^{-1}

---

(17) Hasan, M.; Kozhevnikov, I. V.; Siddiqui, M. R. H.; Steiner, A.; Winterton, N. *Inorg. Chem.* **1999**, *38*, 5637−5641.
(18) Scheffler, T. B.; Thomson, M. S. In *Seventh International Conference on Molten Salts*; The Electrochemical Society, Inc.: Montreal, Quebec, Canada, 1990; pp 281−289.
(19) Koura, N.; Takama, N. Jpn. Kokai Tokkyo Koho JP, 1989.
(20) Bolkan, S. A.; Yoke, J. T. *J. Chem. Eng. Data* **1986**, *31*, 194−197.
(21) Takahashi, S.; Curtiss, L. A.; Gosztola, D.; Koura, N.; Saboungi, M.-L. *Inorg. Chem.* **1995**, *34*, 2990−2993.
(22) Schreiter, E. R.; Stevens, J. E.; Ortwerth, M. F.; Freeman, R. G. *Inorg. Chem.* **1999**, *38*, 3935−3937.
(23) Suarez, P. A. Z.; Einloft, S.; Dullius, J. E. L.; Souza, R. F. d.; Dupont, J. *J. Chim. Phys.* **1998**, *95*, 1626−1639.
(24) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(25) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.
(26) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728.
(27) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261.
(28) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209−214.
(29) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163−168.
(30) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−222.
(31) Binning, R. C.; Curtis, L. A. *J. Comput. Chem.* **1990**, *11*, 1206−1216.
(32) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1976; Vol. 3, p 1.
(33) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283.
(34) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−293.
(35) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310.
(36) Stevens, W.; Basch, H.; Krauss, J. *J. Chem. Phys.* **1984**, *81*, 6026−6033.
(37) Stevens, W. J.; Krauss, M.; Basch, J.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612−630.
(38) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555−5565.
(39) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; J. A. Montgomery, J.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, M. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. In revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

Table 1. Experimental and Calculated Vibrations for Fe(III) Species[a]

$FeCl_3$ (D_{3h})

	UHF			UB3LYP			
	6-31G*	LANL2DZ	CEP31G	6-31G*	LANL2DZ	CEP31G	Bach et al.[41]
energy	−2640.87315	−166.84140	−166.73664	−2644.31434	−168.39092	−168.24405	−2642.16521
R	2.166	2.227	2.214	2.139	2.210	2.188	2.105
E′	120 (2.2)	102	113	88 (A_2')	76	86 (A_2')	108
A_2''	125 (0.0)	115	128	108 (E′)	91*	99 (E′)	113
A_1'	380 (7.6)	343	360	363	320	344	399
E′	480 (0.02)	463	449	463	435*	449	513

$FeCl_4^-$ (T_d)

	UHF			UB3LYP			
	6-31G*	LANL2DZ	CEP31G	6-31G*	LANL2DZ	CEP31G	expt[45]
energy	−3100.53586	−181.75114	−181.60434	−3104.70059	−183.54031	−183.35905	
R	2.258	2.315	2.300	2.230	2.289	2.272	
E	103 (1.9)	95	96	99	90	94	114
T_2	147 (1.2)	135	138	133	118	124	136
A_1	334 (6.0)	314	319	320	296	307	330
T_2	386 (0.03)	388	384	370	365	367	378

$Fe_2Cl_7^-$ (C_2)

	UHF			UB3LYP		
	6-31G*	LANL2DZ	CEP31G	6-31G*	LANL2DZ	CEP31G
energy	−5741.45766	−348.65179	−348.38971	−5749.06380	−351.98439	−351.65042
Δ*E*	−127.6	−155.6	−127.6	−128.4	−139.7	−124.3
B	7 (0.04)	1	7	5	11	1
A	14 (0.00)	8	12	9	12	8
A	29 (0.2)	12	24	29	23	24
B	71 (1.1)	67	68	67	60	64
A	72 (2.0)	67	68	67	62	66
A	79 (1.1)	76	76	74	68	71
B	103 (0.4)	96	98	97	91	94
A	120 (0.8)	105	112	113	102	106
B	127 (2.2)	117	119	117	106	110
A	130 (2.3)	118	121	120	109	111
B	143 (0.3)	133	135	127	117	119
B	144 (0.9)	134	136	131	118	123
A	158 (0.2)	138	147	139	124	129
A	240 (2.2)	213	231	231	222	226
B	279 (0.6)	319	302	281	282	286
B	359 (0.08)	335	343	344	321	332
A	375 (10)	352	360	359	334	347
B	419 (0.08)	412	415	397	384	393
A	420 (0.1)	413	416 (A)	400 (A)	386 (A)	394
B	430 (0.05)	419	424 (A)	409 (A)	393 (A)	402
A	430 (0.1)	419	424 (B)	409 (B)	393 (B)	403

[a] Energy is the total energy reported in hartrees, *R* in angstroms, vibrational frequencies in cm^{-1}. Calculated Raman intensities are in parentheses in the UHF/6-31G* column. In those cases where the symmetry changes it is also noted. $\Delta E = E(Fe_2Cl_7^-) - E(FeCl_3) - E(FeCl_4^-)$, in kJ/mol.

in these mixtures correspond very well with literature values for $FeCl_4^-$ as a solid or in solution.[40] Finding $FeCl_4^-$ in these liquids is not surprising, as it has been reported as the primary Fe-containing species in basic chloroaluminate melts prepared with *N*-*n*-butylpyridinium chloride.[10] However, the peak observed at 223 cm^{-1} does not correspond to a known $FeCl_4^-$ feature. This feature is most likely due to the BMI cation, which is calculated to have a modest feature at 265 cm^{-1}. This assignment is strengthened by the fact that we see a similar feature in the Fe(II) liquids as well (Figure 3 below). Table 1 summarizes the results of ab initio calculations done to predict the vibrational frequencies of $FeCl_3$, $FeCl_4^-$, and $Fe_2Cl_7^-$. Calculations were done with both UHF and UB3LYP methods as well as three basis sets (6-31G*, LANL2DZ, and CEP-31G) in order to establish relationships between our experimental data and predicted values that can be used when investigating more

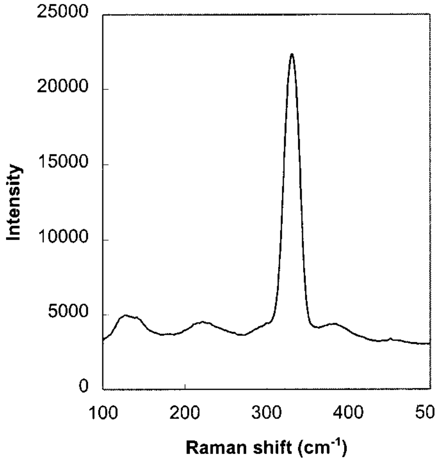


Figure 1. Raman spectrum of ionic liquid prepared from 1/1.5 $FeCl_3$/BMIC.

---

(40) Avery, J. S.; Burbridge, C. D.; Goodgame, D. M. L. *Spectrochim. Acta* **1968**, *24A*, 1721−1726.

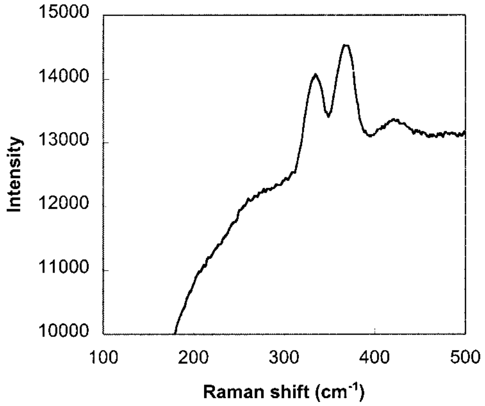
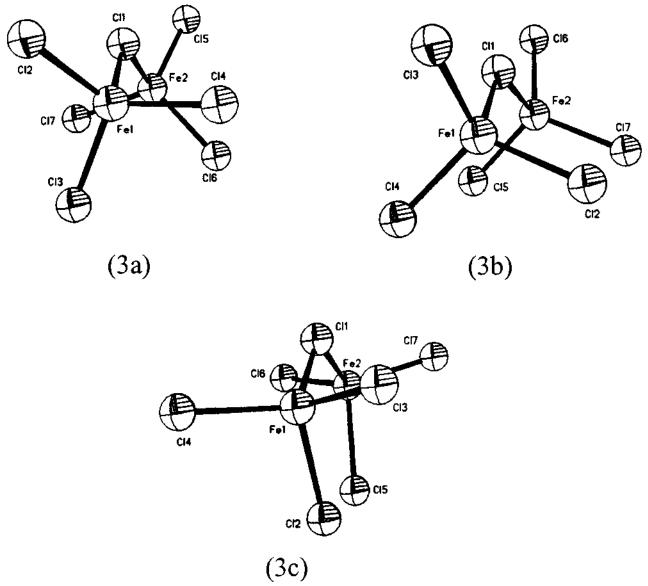


Figure 2. Raman spectrum of an ionic liquid prepared from 1.5/1 $FeCl_3$/BMIC.

complicated structures. The table also includes results from other workers who carried out calculations either at higher levels of theory or with more extensive basis sets.[41] The UHF/6-31G* calculations for the highest energy T_2 and A_1 symmetry vibrations are remarkably close to the measured values for the ionic liquids while the DFT calculations are systematically lower in energy. Switching to one of the effective core potential basis sets generally results in lower vibrational frequencies than those obtained with the all-electron basis set although the change in the T_2 vibration for $FeCl_4^-$ is insignificant. Since the strongest Raman feature predicted for $FeCl_3$ (A_1') is at essentially the same energy as the weak feature found for $FeCl_4^-$, we cannot use our data to rule out the possibility that small amounts of $FeCl_3$ exist in this liquid. Nevertheless, the evidence for $FeCl_4^-$ as the primary iron-containing species in the chloride-rich ionic liquids is quite strong.

Figure 2 shows a typical spectrum obtained when the ratio of $FeCl_3$ to BMIC is greater than 1, in this case 1.5/1. The peak at 333 cm^{-1} is still due to $FeCl_4^-$ with the new features at about 370 and 420 cm^{-1} belonging to $Fe_2Cl_7^-$. The 370 cm^{-1} feature may be assigned to an A symmetry vibration predicted to have a frequency of 375 cm^{-1} and relatively high intensity in the UHF/6-31G* calculations (Table 1). The four vibrational modes predicted to be at higher energy could all lie under the broad feature centered around 420 cm^{-1}. Many of the spectra obtained with excess $FeCl_3$ contain an interfering, broad fluorescence signal of unknown origin. This accounts for the sloping background signal seen in Figure 2. The broad feature centered at approximately 260 cm^{-1} is most likely the A-type vibration from $Fe_2Cl_7^-$ predicted to be at 240 cm^{-1} in the UHF/6-31G* calculations. Together these features provide strong evidence for the formation of $Fe_2Cl_7^-$. This conclusion is also supported by the fact that a Raman peak has been reported at 363 cm^{-1} in high-temperature $FeCl_3$ molten salts and has been assigned to $Fe_2Cl_7^-$ in those systems.[42]



(3a)

(3b)

(3c)

Figure 3. Three energy optimization stationary points for $Fe_2Cl_7^-$ computed at the UB3LYP/CEP-31G level: (a) lowest energy structure, C_2 symmetry; (b) lowest energy C_{2v} structure; (c) high-energy C_{2v} structure.

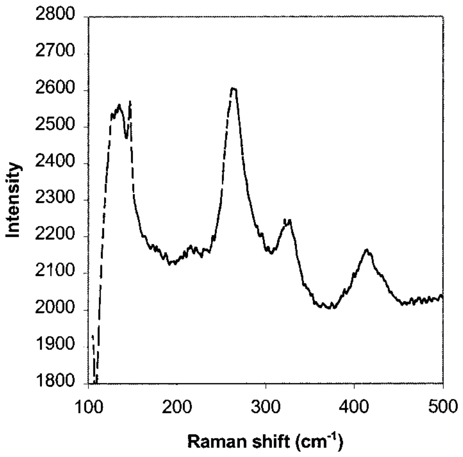


Figure 4. Raman spectrum of an ionic liquid prepared from 1/2 $FeCl_2$/BMIC.

Our calculations find a lowest energy, C_2 structure for $Fe_2Cl_7^-$, see Figure 3. We have also examined the potential energy surface for internal rotation about the bridging Cl−Fe bond in $Fe_2Cl_7^-$. Figure 3 illustrates three of the stationary points found when investigating this rotation. While the C_2 structure (Figure 3a), with opposing Fe−Cl bonds approximately 85° out of the Fe−Cl−Fe plane, is lowest in energy, a C_{2v} structure with two terminal chlorine atoms in the Fe−Cl−Fe plane (Figure 3b) is only 0.6 kJ/mol higher in energy (at the UB3LYP/CEP31G level of theory). However, rotating the chlorine atoms by approximately 60° (Figure 3c) gives the other C_{2v} structure that is much higher in energy, 380 kJ/mol, due to steric crowding caused by two of the chlorine atoms that are only 2.79 Å apart. Both C_{2v} structures are transition states primarily found by rotating around the bridging Cl−Fe bonds rather than isolated minima.

Ionic Liquids with $FeCl_2$. In contrast to $FeCl_3$, room temperature ionic liquids cannot be prepared with $FeCl_2$ to BMIC ratios greater than 1/1. Thus we do not expect to observe species such as $Fe_2Cl_5^-$, which would be analogous to $Fe_2Cl_7^-$ that is seen in the $FeCl_3$ melts. It is quite possible that these species could be prepared in melts at somewhat higher temperatures, but we did not investigate this possibility. We have been able to prepare ionic liquids from a 1/1 ($FeCl_2$/BMIC) to a 1/3 ratio. Figure 4 shows the Raman spectrum of an ionic liquid with a 1/2 $FeCl_2$/BMIC ratio. The large peak at 265 cm^{-1} is most likely due to the A_1 vibration of $FeCl_4^{2-}$, calculated to be at approximately 230 cm^{-1} (Table 2). This assignment is consistent with the literature in which the A_1 feature has been

---

(41) Bach, R. D.; Shobe, D. S.; Schlegel, H. B.; Nagel, C. J. *J. Phys. Chem.* **1996**, *100*, 8770−8776.

(42) Papatheodorou, G. N.; Voyiatzis, G. A. *Chem. Phys. Lett.* **1999**, *303*, 151−156.

Table 2. Experimental and Calculated Vibrations for Fe(II) Species[a]

$FeCl_2$ ($D_{\infty h}$)

	UHF			UB3LYP			
	6-31G*	LANL2DZ	CEP31G	6-31G*	LANL2DZ	CEP31G	Bach et al.[41]
energy	−2181.38047	−152.18022	−152.05068	−2184.08387	153.43883	−153.30540	−2182.47090
R	2.194	2.258	2.254	2.117	2.192	2.195	2.129
Π_u	87 (0.0)	93	87	73	85	70	86
$\Sigma^+{}_g$	327 (5.7)	314	321	353	324	326	362
$\Sigma^+{}_u$	489 (0.0)	498	468	514	512	476	528

$FeCl_3^-$ (D_{3h})

	UHF			UB3LYP			Bach et al.[41]
	6-31G*	LANL2DZ	CEP31G	6-31G*	LANL2DZ	CEP31G	
energy	−2641.03152	−167.05971	−166.89479	−2644.46148	−168.57028	−168.40504	−2641.62948
R	2.320	2.368	2.355	2.244	2.303	2.292	2.260
E′	102 (1.1)	98	98	96	93	92	95
A_2''	127 (0.0)	118	121	123	112	111	123
A_1'	279 (2.9)	276	273	292	279	280	283
E′	353 (0.1)	362	348	370	367	358	370

$FeCl_4^{2-}$ (D_{2d})

	UHF			UB3LYP		
	6-31G*	LANL2DZ	CEP31G	6-31G*	LANL2DZ	CEP31G
energy	−3100.50125	−181.77393	−181.57357	−3104.64307	−183.52257	−183.32490
Δ*E*	−180.7	−243.9	−143.9	−143.5	−227.2	−124.1
R	2.467	2.489	2.494	2.407	2.435	2.440
B_1	52 (0.01)	36	31	50 (A_1)	69 (A_1)	63 (A_1)
A_1	69 (1.0)	75	70	87 (B_1)	92 (B_1)	87 (B_1)
B_2	117 (0.9)	116	112	113	106	101
E	120 (0.9)	120	116	114	114	109
A_1	226 (1.8)	236	223	217 (B_2)	236	222 (B_2)
B_2	228 (0.02)	266	234	230 (A_1)	254	225 (A_1)
E	247 (0.05)	279	252	247 (E)	282	256 (E)

[a] Energy is the total energy reported in hartrees, *R* in angstroms, vibrational frequencies in cm^{-1}. Calculated Raman intensities are in parentheses in the UHF/6-31G* column. In those cases where the symmetry changes, it is also noted. $\Delta E = E(FeCl_4^{2-}) - E(FeCl_2) - 2E(Cl^-)$, in kJ/mol.

reported at 266 cm^{-1} in the solid $[(CH_3CH_2)_4N]_2FeCl_4$.[40] Although $FeCl_3^-$ is calculated to have a strong feature at about 280 cm^{-1}, the general tendency is for these calculations to underestimate vibrational frequencies rather than overestimate them. If the feature at 265 cm^{-1} is the A_1 vibration for $FeCl_4^{2-}$, then we have two higher energy vibrational modes predicted for $FeCl_4^{2-}$ that might be observed. However, neither should have large Raman scattering intensity, and they are both predicted to appear at much lower energy than what is actually observed. The features at 325 and 415 cm^{-1} are both due to the BMI cation. We have verified this by collecting the Raman spectrum of an aqueous solution of BMIC. The other large feature, near the edge of our ability to reliably acquire data, falls around 110−120 cm^{-1} and is probably due to a combination of the lower energy B_2 and E vibrational modes from $FeCl_4^{2-}$.

In ionic liquids with larger amounts of BMIC (1/2 and 1/3, see Supporting Information) an increase in the fluorescence background makes assigning precise peak intensities difficult. In general, the peaks due to BMI^+ appear to be increasing in intensity relative to $FeCl_4^{2-}$ and the ratio of the two BMI^+ peaks remains relatively constant. In summary, the only iron-containing species that we observe in these ionic liquids is $FeCl_4^{2-}$.

Mixed Melts Containing Both $FeCl_2$ and $FeCl_3$. We have prepared a few liquids that contain iron in both the II and III oxidation states. Figure 5 shows the Raman spectra for liquids prepared with different amounts of iron(III) chloride. The predominant feature is the strong $FeCl_4^-$ peak at 333 cm^{-1}. The size of this peak increases consistently as the amount of $FeCl_3$ increases. The smaller peak at 265 cm^{-1} is most likely the A_1 vibration for $FeCl_4^{2-}$. In the expanded spectrum, it is possible to see both the weaker T_2 symmetry vibration (385 cm^{-1}) from $FeCl_4^-$ and the 415 cm^{-1} feature from BMIC; and we see an increase in the relative size of the 385 cm^{-1} feature, compared to the 415 cm^{-1} feature, as the amount of $FeCl_3$ increases. We have not observed any peaks that could be due to $Fe_2Cl_7^-$ in the mixed oxidation state liquids. The 1.7 $FeCl_3$/1 $FeCl_2$/3 BMIC mixture had to be warmed somewhat to produce a clear liquid. This composition probably presents the upper limit of the amount of $FeCl_3$ that can be dissolved in a 1 $FeCl_2$/3 BMIC ionic liquid and may actually be somewhat beyond the limit that can be dissolved at room temperature.

A Comparison of Computational Results. While the computational methods that we employed are primarily designed to provide information about gas-phase species, they can still provide insight into ionic liquid chemistry. Reviews of the use of both ab initio[43] and density functional methods[44] for the prediction of electronic structures of transition metal complexes have recently appeared. We endeavor to use computational results to help us decipher the Raman spectra that we obtain and eventually to model the interactions between anions such as $FeCl_4^-$ and the 1-butyl-3-methylimidazolium cation. The

---

(43) Martin, C. H.; Zerner, M. C. In *Inorganic Electronic Structure and Spectroscopy*; Solomon, E. I., Lever, A. B. P., Eds.; John Wiley & Sons: New York, 1999; Vol. 1, pp 555−658.

(44) Li, J.; Noodleman, L.; Case, D. A. In *Inorganic Electronic Structure and Spectroscopy*; Solomon, E. I., Lever, A. B. P., Eds.; John Wiley & Sons: New York, 1999; Vol. 1, pp 661−724.

(45) Nakamoto, K. *Infrared and Raman Scattering of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.

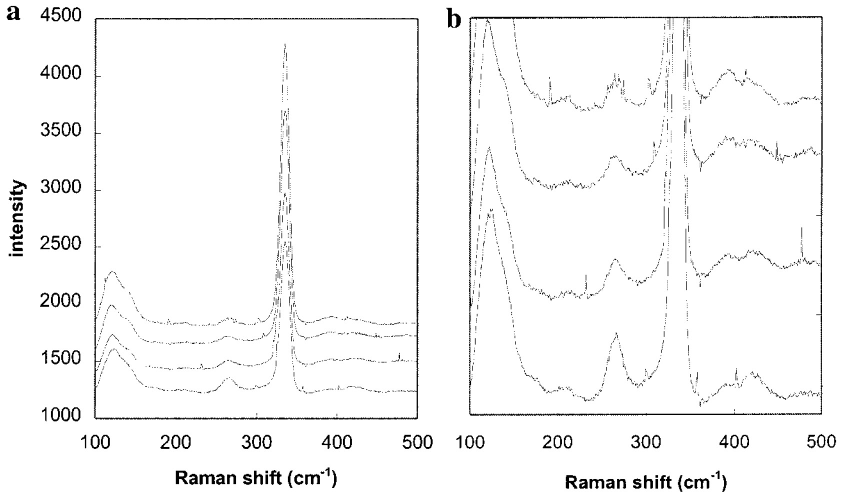


Figure 5. Raman spectra of ionic liquids prepared from $FeCl_3$, $FeCl_2$, and BMIC. Spectra were separated by 200 counts for increased visibility. From bottom to top (a and b): 0.64 $FeCl_3$/1 $FeCl_2$/3 BMIC, 1.2 $FeCl_3$/1 $FeCl_2$/3 BMIC, 1.5 $FeCl_3$/1 $FeCl_2$/3 BMIC, 1.7 $FeCl_3$/1 $FeCl_2$/3 BMIC. 1800 lines/mm grating. The intensity axis on plot b is magnified by approximately 4.4.

ability to use ECP basis sets for these calculations will be very important as these calculations will involve a large number of atoms.

A comparison of the calculations on the Fe(III) and Fe(II) systems leads to a number of conclusions. First, the molecular geometry for each species is quite reasonable and is independent of the method/basis set used. $FeCl_2$ is linear, $FeCl_3$ and $FeCl_3^-$ are trigonal planar, and $FeCl_4^-$ is tetrahedral while $FeCl_4^{2-}$ is distorted due to the Jahn–Teller effect. All attempts to restrict $FeCl_4^{2-}$ to a tetrahedral geometry result in convergence to transition states, as evidenced by negative vibrational frequencies. $Fe_2Cl_7^-$ adopts a C_2 configuration. The use of effective core potentials (either LANL2DZ or CEP-31G basis sets) leads to longer average bond lengths and generally lower vibrational frequencies than with the use of the 6-31G* basis set. On the other hand, the use of density functional theory produces bonds that are slightly shorter, and frequencies that are somewhat lower than those obtained by the unrestricted Hartree–Fock calculations. One cannot compare total energies computed at different levels of theory. However, relative energies may be compared. Table 1 includes the energy change for the reaction of $FeCl_3$ and $FeCl_4^-$ to form $Fe_2Cl_7^-$. The agreement between the calculations using the 6-31G* and CEP-31G basis sets is quite good, while the LANL2DZ results are several kilojoules/mole different. A similar calculation on the formation of $FeCl_4^{2-}$ from $FeCl_2$ and 2 Cl^- gives results that are a little more varied although the largest differences are again obtained with the LANL2DZ basis set. One interesting result is the close agreement between the calculations carried out at the UB3LYP/6-31G* level, which are the most time expensive, and those carried out using UHF/CEP-31G, which are the least expensive. Our results also fit well with those of Bach et al., who carried out a series of calculations on iron(III) chlorides at the MP2, QCISD, and UB3LYP levels.[41]

Table 3. Experimental and Calculated Vibrational Frequencies for Fe(II), Fe(III), and Al-Based Ionic Liquids

species, experimentally determined freq, sym type	UB3LYP/6-31G*	UHF/CEP-31G
$FeCl_4^-$/332/A_1	320	319
$FeCl_4^-$/384/T_2	370	384
$Fe_2Cl_7^-$/370/A	359	360
$Fe_2Cl_7^-$/420/A	409	424
$FeCl_4^{2-}$/265/A_1	223	223
$AlCl_4^-$/347[a]/A_1	333	315
$AlCl_4^-$/504[a]/A_1	491	475
$Al_2Cl_7^-$/310[a]/A	296	267
$Al_2Cl_7^-$/432[a]/A	423	396
$Al_2Cl_7^-$/566[a]/A	534	515

[a] See ref 21.

It is interesting to look for systematic differences between the most efficient calculations, using UHF and the CEP-31G basis set, and what should be the "best" calculations, using the UB3LYP method and the 6-31G* basis set. We have calculated the energies of 43 vibrational modes (counting degenerate modes only once) of Fe-containing species by both methods. If we somewhat arbitrarily designate any difference of less than 5 cm^{-1} as negligible, 24 out of 43 vibrations are predicted to have essentially the same energy. The difference is greater than 15 cm^{-1} 11 times. Plotting the UHF/CEP-31G data vs the UB3LYP/6-31G* data gives a line with a slope of 0.98 and an intercept of 4.5. Thus, the UHF/CEP-31G calculations tend to slightly overestimate the frequency at low frequencies and to underestimate at higher frequencies. The obvious benefit of carrying out calculations at the UHF/CEP-31G level instead of the UB3LYP/6-31G* level is that it is computationally less expensive. For example, the frequency calculation step takes 50% less time for $Fe_2Cl_7^-$ and more than 90% less time for both $FeCl_4^-$ and $FeCl_4^{2-}$, when using UHF/CEP-31G instead of UB3LYP/6-31G*.

For the purpose of understanding ionic liquids it is also useful to compare the calculated vibrational frequencies to those clearly identified in the ionic liquids. Table 3 briefly summarizes experimental and computational results for the chlorometalate ions present in both aluminum chloride and iron chloride ionic liquids. From this it appears that while the UHF/CEP-31G computations do a very good job with respect to matching the observed Raman features for the iron chlorides, the UB3LYP/6-31G* computations are superior for the aluminum ionic liquids. One likely reason is that the CEP-31G basis set may do a much poorer job representing Al than Fe.

Conclusion

Ionic liquids have been prepared by the direct mixing of iron(II) chloride or iron(III) chloride with 1-butyl-3-methylimidazolium chloride. Ionic liquids have also been prepared from mixtures of the two iron chlorides with 1-butyl-3-methylimidazolium chloride and represent the first ionic liquids reported with mixed oxidation states. $FeCl_4^-$, $FeCl_4^{2-}$, and $Fe_2Cl_7^-$ have been identified in these liquids and all obtain either tetrahedral or distorted tetrahedral geometry around each Fe atom. Calculations using the UHF/CEP-31G method/basis set combination are remarkably useful for studying ionic liquids containing iron chlorides although this combination may not be as good for all metal chlorides.

Acknowledgment. The authors thank Russell G. Baughman for the preparation of Figure 3 and Truman State University for direct support of the research as well as for summer support for E.R.S. and M.S.S.

Supporting Information Available: Cartesian coordinates for all Fe(III) and Fe(II) structures determined by computation. Raman spectra for $FeCl_3$/BMIC at 1.7/1, 1.5/1, 1/1, 1/1.1, 1/1.3, 1/1.5, and 1/1.7 ratios. Raman spectra for $FeCl_2$/BMIC at 1/2 and 1/3 ratios. This material is available free of charge via the Internet at http://pubs.acs.org.

IC001042R