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1-Ethyl-3-methylimidazolium Based Ionic Liquids Containing Cyano Groups: Synthesis, Characterization, and Crystal Structure

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New 1-ethyl-3-methylimidazolium (EMI) salts [EMI][$C(CN)_3$] and [EMI][$Ag(CN)_2$] were prepared and characterized. The $C(CN)_3$ salt has a melting point at –11 °C and shows a low viscosity (18 cP) and a high ionic conductivity (1.8×10^{-2} S cm^{-1}) at room temperature. This conductivity is less than that of [EMI][$N(CN)_2$] salt (2.7×10^{-2} S cm^{-1}), possibly due to the larger molecular weight of the anion. The first EMI salt containing Ag(I) complexes [EMI][$Ag(CN)_2$] has a higher melting point of 73 °C. In the crystal, the C–H$\cdots\pi$ interionic interactions between cations construct zigzag chains in the cationic two-dimensional layer. Close Ag$\cdot\cdot$Ag interionic contacts of 3.226(1) Å were observed in the one-dimensional anionic chain, and the relatively high melting point among the EMI salts with a monoanion appears to be governed essentially by these direct Ag$\cdots$Ag interactions.

Introduction

Room temperature (RT) ionic liquids have been an area of interest both for fundamental reasons, associated with their negligible vapor pressure, high ionic conductivity, wide electrochemical window, and excellent thermal and chemical stabilities, as well as for their application in a variety of electrochemical device fields.[1−4] One of the severest barriers to these applications is the relatively high viscosity of ionic liquids compared to those of organic solvents.[5] The high viscosity leads to the reduction of the reaction rate for organic synthesis and the reduction of the diffusion rate of the redox species. Thus, the current search for new and more versatile ionic liquids is driven, in part, by the need for materials with low viscosity. The most fluid ionic liquids have been usually composed of 1-ethyl-3-methylimidazolium (EMI) cations, and some EMI molten salts have been reported with low RT viscosity: 4.85 cP for the fluoride/hydrofluoric acid (1:2.3),[6] 18 cP for the tetrachloroaluminate [$AlCl_4$],[7] 21 cP for the dicyanamide [$N(CN)_2$],[8] 25 cP for the 2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide [$(CF_3SO_2)(CF_3CO)N$],[9] 28 cP for the bis(trifluoromethylsulfonyl)imide [$(CF_3SO_2)_2N$],[10] and so on. In the present paper, we report on a new EMI-based RT ionic liquid with tricyanomethanide [$C(CN)_3$] and compare its properties with those of the known $N(CN)_2$ salt.[8] On the basis of 13 EMI-based RT ionic liquids, including the present $C(CN)_3$ and $N(CN)_2$ salts, the relationship between the formula weight, density, viscosity, and conductivity is experimentally verified. A new salt containing heavy-metal complexes [EMI]-[$Ag(CN)_2$], which is the first characterized EMI salt contain-

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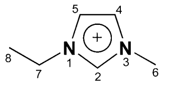
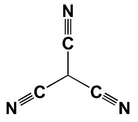
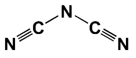
ing complexes of silver, was isolated from an [EMI]I/AgCN aqueous solution and structurally characterized.



EMI$^+$



C(CN)$_3^-$



N(CN)$_2^-$

Ag(CN)$_2^-$

Experimental Section

Materials. Silver salts AgX (X = C(CN)$_3$ and N(CN)$_2$) were prepared by the metathesis of corresponding alkali salts (K[C(CN)$_3$] and Na[N(CN)$_2$]) with AgNO$_3$ in the dark in distilled water. The monoanions including cyano groups have been extensively used as a counteranion for organic (super)conductors,[11] and it has been known that the transport and superconducting properties are very sensitive to impurities in the starting salts.[12] In this work, therefore, the alkali salts were recrystallized from distilled ethanol prior to use. [EMI]I was synthesized according to the reported procedure.[13] All manipulations for the preparation of the EMI salts were carried out either under an inert atmosphere of helium gas in a glovebox with the rigid exclusion of air and moisture (H_2O, $O_2 < 1$ ppm) or under an argon flow. Solvents were distilled prior to use.

Methods. FT-IR spectra were recorded with a Perkin-Elmer 1000 series spectrophotometer in the region 400−4000 cm^{-1} as hexachlorobutadiene mulls between sodium chloride plates. This allows the C−H stretching vibrations to be observed. Glass transition temperature (T_g, onset of the heat capacity change), crystallization temperature (T_c, onset of the exothermic peak), solid−solid transition temperature (T_{s-s}, onset of the exothermic peak), melting temperature (T_m, onset of the endothermic peak), and decomposition temperature (T_d) were determined from differential scanning calorimetry (DSC) thermograms during the heating scans (10 °C min^{-1} heating rate) on a Shimadzu DSC-60 instrument equipped with nitrogen cryostatic cooling, and the temperature was calibrated by water and indium. Density values were approximately obtained by measuring the weight of the sample in a 1 cm^3 pycnometer held in the glovebox. The estimated density for the [EMI]BF$_4$ molten salt (1.28 g cm^{-3}) is essentially the same as that reported previously.[14] Viscosities were measured using a cone-type Tokyo Keiki rotational viscometer VISCONIC ED. Conductance measurements were performed in a two platinum electrode conductivity cell (cell constant is 45 cm^{-1}, which was determined by 5×10^{-2}, 1×10^{-1}, and 5×10^{-1} M aqueous potassium chloride solutions), using an Agilent Technologies impedance analyzer 4294A over a frequency range of 40 Hz to 110 MHz. The conductance of the samples was determined from the first real axis touchdown point in the Cole−Cole plot of the impedance data. For the electrochemical characterization, the cyclic voltammetry measurements were performed using an ALS electrochemical analyzer 650A. Working and counter electrodes were platinum, the reference electrode was Ag/AgCl, and the scan rate was 50 mV s^{-1}. X-ray diffraction data were collected on an imaging plate type diffractometer (Mac Science DIP-2020K) with graphite monochromated Mo Kα radiation. A colorless plate crystal of [EMI][Ag(CN)$_2$] was mounted and sealed in a quartz capillary in a glovebox. Crystal structures were solved by direct method (SIR92) and refined by the full-matrix least-squares method on *F* (SHELXL-93).[15] The position of the hydrogen atoms was determined assuming an sp^3 configuration with a C−H distance of 1.0 Å.

Table 1. Properties of [EMI]X Salts[a]

X	T_g/°C	T_c/°C	T_{s-s}/°C	T_m/°C	T_d/°C	d/g cm^{-3} (20 °C)	η/cP (22 °C)	σ/S cm^{-1} (20 °C)
C(CN)$_3$	−95	−60	−31	−11	ca. 240	1.11	18	1.8×10^{-2}
N(CN)$_2$	−90	−54	*b*	−12	ca. 240	1.08	17	2.7×10^{-2}
Ag(CN)$_2$	*b*	*b*	*b*	73	ca. 270	*c*	*c*	*c*

[a] T_g = glass transition temperature, T_c = crystallization temperature, T_{s-s} = solid−solid transition temperature, T_m = melting point, T_d = decomposition temperature, d = density, η = viscosity, σ = ionic conductivity. [b] Not observed. [c] Not measured.

Synthesis of [EMI][C(CN)$_3$]. A slight excess of Ag[C(CN)$_3$] (1.0×10^{-2} mol) and [EMI]I (8.6×10^{-3} mol) were dissolved in distilled water (200 cm^3). The resulting suspension was stirred overnight in the dark at RT and filtered to remove any trace of AgI and unreacted Ag[C(CN)$_3$]. Evaporation of the filtrate was performed under vacuum at RT, and the water was collected with liquid nitrogen traps. After a week, a transparent melt was obtained. Yield: 83%. Anal. Calcd for $C_{10}H_{11}N_5$: C, 59.69; H, 5.51; N, 34.80; I, 0.00%. Found: C, 59.80; H, 5.60; N, 35.09; I, 0.00%.

Synthesis of [EMI][N(CN)$_2$]. A transparent melt was prepared by the procedure described above for the C(CN)$_3$ salt except that Ag[N(CN)$_2$] was used instead of Ag[C(CN)$_3$]. Yield: 81%. Anal. Calcd for $C_8H_{11}N_5$: C, 54.22; H, 6.26; N, 39.52; I, 0.00%. Found: C, 54.48; H, 6.17; N, 39.73; I, 0.00%. This procedure is essentially the same as that reported previously by MacFarlane et al.[8]

Synthesis of [EMI][Ag(CN)$_2$]. A slight excess of AgCN (1.29×10^{-2} mol) and [EMI]I (1.10×10^{-2} mol) were dissolved in distilled water (30 cm^3), and the resulting suspension was stirred overnight in the dark at RT. Filtration and evaporation under vacuum for a week at RT gave colorless polycrystals including unreacted [EMI]I, which was removed by recrystallization from acetonitrile/ethyl acetate (1:13). Yield (after recrystallization): ca. 20%. Anal. Calcd for $C_8H_{11}N_4Ag_1$: C, 35.45; H, 4.09; N, 20.67; I, 0.00%. Found: C, 35.26; H, 4.04; N, 20.90; I, 0.00%. While the RT ionic liquids [EMI][C(CN)$_3$] and [EMI][N(CN)$_2$] are highly hygroscopic, the [EMI][Ag(CN)$_2$] crystals are not as hygroscopic as the C(CN)$_3$ and N(CN)$_2$ melts.

Results and Discussion

Thermal Property. Some properties of the salts prepared in this work are summarized in Table 1. In the C(CN)$_3$ molten salts, the quenched phase is glass forming, and the glass transition temperature measured upon heating is −95 °C. The exotherms at −60 and −31 °C are associated with the crystallization and solid−solid transition, respectively, and the salt subsequently melts at −11 °C and decomposes at ca. 240 °C, providing a wide liquid range. The N(CN)$_2$ salt we prepared has a melting point of −12 °C, which substantially exceeds the temperature reported previously by

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Table 2. Infrared Spectral Data of [EMI]X Salts above 3000 cm^{-1}

X	νC(4)−H and νC(5)−H	νC(2)−H	νC(2)−H···anion
C(CN)$_3$	3153m	3115s	
N(CN)$_2$	3149m	3106s	
Ag(CN)$_2$	3151m	3109m	3068m

MacFarlane et al. (−21 °C).[8] The [EMI][N(CN)$_2$] melt dissolving 3%(w/w) of [EMI]Cl shows an additional endothermic DSC peak with onset temperature of −20 °C, and the intensity of the signal weakens as the content of the [EMI]Cl decreases. This result strongly indicates that the inherent melting point of the N(CN)$_2$ salt is −12 °C.[16] The reported lower melting point may be caused by some impurity which also results in the deviation of the elemental analyses (C, 52.7; H, 6.3; N, 38.6%) from the calculated values (C, 54.22; H, 6.26; N, 39.52%).

In the case of the Ag(CN)$_2$ salt, the melting event was observed at 73 °C, which is significantly higher than those of the C(CN)$_3$ and N(CN)$_2$ salts. On further heating, the transparent melt decomposes at ca. 270 °C. It is noted that a few well-characterized EMI salts with a monoanionic complex containing metal center, [EMI][AlX$_4$] (T_m: 7 °C for X = Cl,[7] ca. 50 °C for X = Br[17]), [EMI][CuCl$_2$] (T_m < RT),[18] [EMI][AuCl$_4$] (T_m: 58 °C),[19,20] and [EMI][InCl$_4$] (T_m: 33 °C),[21] have lower melting points than that of the Ag(CN)$_2$ salt.

Infrared Spectroscopy. An infrared spectrum of the EMI molten salts has offered distinctive information about the hydrogen bonds. The dominant peaks observed above 3000 cm^{-1} for the present salts are listed in Table 2. The peak with the highest frequency lies within 3149−3153 cm^{-1} and can be attributed to the stretching mode of the aromatic C(4)−H and C(5)−H bonds of the imidazolium cation. The next highest frequency peak in the range 3106−3115 cm^{-1} is readily assigned to the aromatic C(2)−H stretching mode, owing to its adjacency to both imino nitrogens. The Ag(CN)$_2$ salt exhibits an additional peak at 3068 cm^{-1}, which is indicative of the C−H···anion hydrogen-bonding-type interactions. The observation of this peak seems to be in good agreement with the crystallographic observations (vide infra) and is closely connected with the higher melting point than those of the C(CN)$_3$ and N(CN)$_2$ salts.

Electrochemical Window. The electrochemical properties of the C(CN)$_3$ salt as well as the N(CN)$_2$ salt were investigated at 22 °C (Figure 1), where the voltammogram of the N(CN)$_2$ salt is similar to that reported previously.[8] Both ionic liquids are stable down to quite a low potential around −2 V versus Ag/AgCl. In the oxidation scan, the C(CN)$_3$ and N(CN)$_2$ salts were stable up to ca. +0.9 and +1.3 V, respectively, at which point an irreversible broad wave was observed.

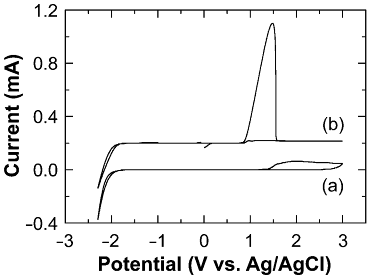

Figure 1. Cyclic voltammograms of (a) [EMI][N(CN)$_2$] and (b) [EMI]-[C(CN)$_3$].

Viscosity. The lowest viscosities of ionic liquids have usually been obtained for melts composed of the EMI cation,[5] and many organic syntheses in the EMI ionic liquids have been reported.[1−4] In the present work, the viscosity (η) of the N(CN)$_2$ salt is 17 cP at 22 °C, which is slightly lower than that reported previously (21 cP at 25 °C).[8] A low viscosity of the C(CN)$_3$ salt, 18 cP at 22 °C, was also observed and is comparable to that of the N(CN)$_2$ salt. For the N(CN)$_2$ salt, it has been reported that acetylation reactions of alcohols and carbohydrates proceed rapidly and in high yield in the molten salt.[22] Thus, the C(CN)$_3$ salt also seems promising as a medium for such organic synthesis and electrolytes.

Conductivity. The N(CN)$_2$ salt is slightly more conductive than the C(CN)$_3$ salt, despite their comparable viscosities and glass transition temperatures. Ionic conductivities (σ) at 20 °C were determined to be 1.8 × 10^{-2} S cm^{-1} for the C(CN)$_3$ salt and 2.7 × 10^{-2} S cm^{-1} for the N(CN)$_2$ salt (estimated error: ±10%). These values are similar to that reported for the most conductive 1:1 EMI salt [EMI][AlCl$_4$] (2.3 × 10^{-2} S cm^{-1} at 25 °C)[7] but still less than the value for non 1:1 salt [EMI]F·2.3(HF) (1.0 × 10^{-1} S cm^{-1} at 25 °C).[6] Walden pointed out that the product $\Lambda\eta$, where Λ is the equivalent conductivity and can be represented by $\sigma M/d$ (M, formula weight of liquid; d, density of liquid), remains constant in a wide range of aqueous solution systems.[23] Figure 2 demonstrates the relationship between η^{-1} and Λ for the 13 EMI-based RT ionic liquids[6,7,10,14,18,25−27] including the present C(CN)$_3$ and N(CN)$_2$ salts. It is evident that the equivalent conductivity increases in proportion to a decrease of the viscosity as expected from the Walden rule, and such a behavior was very recently reported for 9 1-butyl-3-

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(16) We prepared [EMI][N(CN)$_2$] salt using [tetraphenylphosphonium]-[N(CN)$_2$] instead of Na[N(CN)$_2$] as a starting material, since the sodium salt might include a small amount of NaCl even after the simple recrystallization from ethanol (ref 12). The resulting EMI salt has a melting point of −13 °C, which is also higher than the previous value (ref 8).

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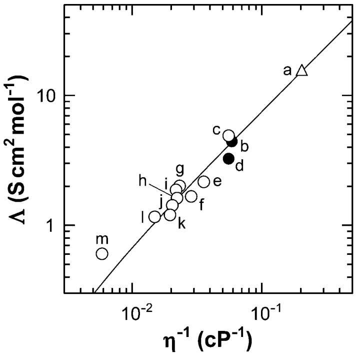

Figure 2. A plot of the equivalent conductivity against the reciprocal of the viscosity for [EMI]X ionic liquids with melting point below RT (X = (a) F•2.3(HF),[6] (b) $N(CN)_2$, (c) $AlCl_4$,[7] (d) $C(CN)_3$, (e) $(CF_3SO_2)_2N$,[10,25] (f) CF_3CO_2,[25] (g) BF_4,[10,14] (h) CF_3SO_3,[25] (i) $CuCl_2$,[18] (j) NbF_6,[26] (k) TaF_6,[26] (l) SbF_6,[27] and (m) WF_7[27]). Data were collected in the temperature range 20−26 °C. An open triangle (△) represents a non 1:1 molten salt, and closed circles (●) represent the molten salts prepared in this paper. A solid line (—) is the least-squares fit to the data (r = 0.994).

Table 3. Crystallographic Data for [EMI][$Ag(CN)_2$]

compd	[EMI][$Ag(CN)_2$]
empirical formula	$C_8H_{11}N_4Ag_1$
fw	271.07
cryst syst	orthorhombic
space group	*Pbca*
a, Å	6.4370(2)
b, Å	17.745(1)
c, Å	19.076(1)
V, Å^3	2178.9(2)
Z	8
d_c, g cm^{-1}	1.653
λ, Å	0.71073
μ, mm^{-1}	1.80
criterion for obsd reflns	$F_o \geq 3\sigma(F_o)$
no. of intensity measd	1666
no. of refined params	118
GOF on F	1.866
R	0.059
R_w	0.102

methylimidazolium (BMI) molten salts by Angell et al.[24] and 26 *N,N′*-dialkylimidazolium molten salts including 3 EMI melts by Hagiwara et al.[28] Since the molar concentration d/M does not change largely in the case of the EMI-based ionic liquids, it appears that the ionic conductivity is also inversely proportional to the viscosity. Of particular importance is that the Λ and σ values are prone to increase as the molecular weight of the anions decreases, and thus, the high conductivities observed for the $C(CN)_3$ and $N(CN)_2$ salts are reasonable.

Crystal Structure. The crystallographic data for the $Ag(CN)_2$ salt are given in Table 3. The structure contains one crystallographically independent EMI cation and $Ag(CN)_2$ anion. EMI cations form a two-dimensional layer in the *ab* plane, and the layers are separated from each other in the *c* direction by the $Ag(CN)_2$ anions. Within the layer, the cations are linked to each other by C−H⋯π interactions[29] between one methyl carbon C(8) and the imidazolium ring of another cation to form one-dimensional zigzag chains along the *a*-axis (Figure 3). The distance between the methyl carbon and the center of imidazolium ring is estimated to be ca. 3.6 Å, which is in excellent agreement with the value expected for the lowest benzene⋯ethane interaction.[30] A close interionic C(2)−H⋯N(cyano) contact with linear anionic complexes was found to be 3.19(1) Å (the sum of van der Waals (vdW) radii is 3.75 Å[31]) involving the imidazolium ring-bound hydrogen (Figure 4), suggesting the presence of a hydrogen bond, as expected from infrared spectroscopy. In addition, a close N(cyano)⋯cation interaction was observed, as seen in Figure 4. The interionic

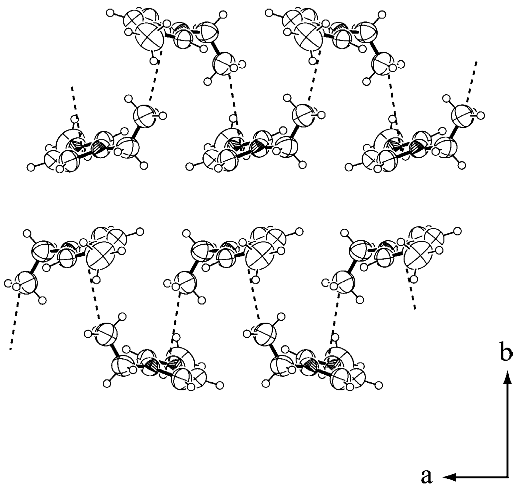

Figure 3. View of a two-dimensional cationic layer in [EMI][$Ag(CN)_2$] viewed along the *c*-axis. Short C−H⋯π interionic contacts are shown by dashed lines (- - -).

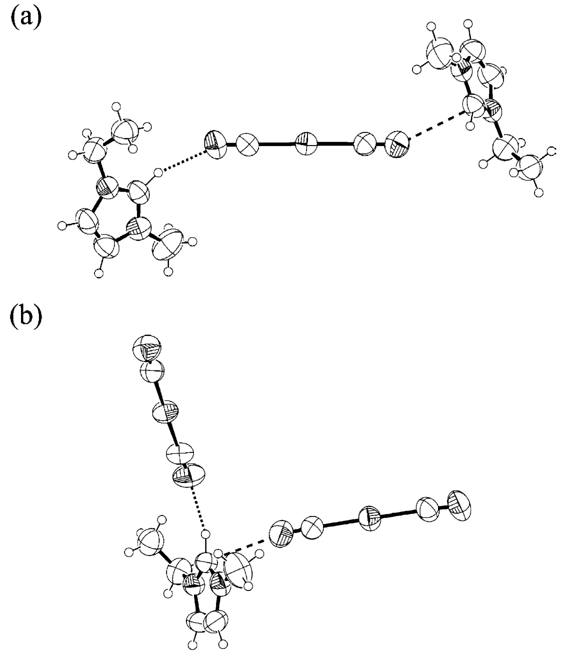

Figure 4. Interionic contacts between EMI cation and $Ag(CN)_2$ anion in [EMI][$Ag(CN)_2$] around (a) $Ag(CN)_2$ anion and (b) EMI cation. Short C(2)−H⋯N(cyano) and N(cyano)⋯C(2) contacts are shown by dotted (⋯) and dashed (- - -) lines, respectively.

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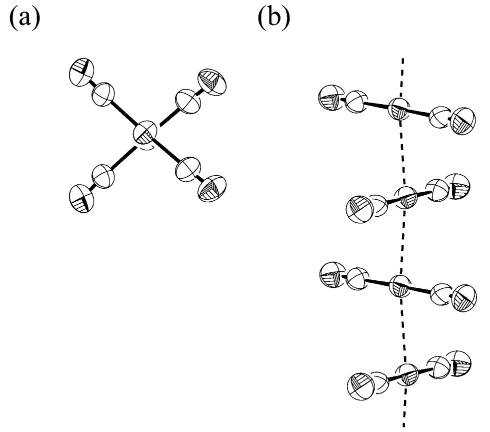

Figure 5. View of a chain of $Ag(CN)_2$ anions in [EMI][$Ag(CN)_2$] (a) along the *a*-axis and (b) perpendicular to the *a*-axis. Short Ag···Ag interionic contacts are shown by dashed lines (- - -).

distance is 3.05(1) Å for N(cyano)···C(2) (the sum of vdW radii is 3.25 Å[31]), and the contact can be attributed to the interionic Coulomb attractive forces.

In the $Ag(CN)_2$ anion, the bond angle of C−Ag−C is 178.2(5)°, indicating an almost linear form. Interatomic distances in the anion are 2.056(11) and 2.064(12) Å for Ag−C, and 1.118(16) and 1.125(15) Å for C≡N. The linear $Ag(CN)_2$ anions are oriented in a nearly perpendicular geometry (Figure 5a) with respect to the uniformly spaced neighboring anions along the *a*-axis (Figure 5b). The interionic Ag···Ag distance is 3.226(1) Å, which is significantly shorter than the corresponding vdW distance of 3.44 Å.[31] The shortest Ag···Ag distance has been reported as 3.710 and 3.525 Å in Na[$Ag(CN)_2$][32] and $K_2Na[Ag(CN)_2]_3$,[33] respectively. Crystal structures have also been determined for K[$Ag(CN)_2$],[34] $M[Ag(CN)_2]_2{\cdot}2H_2O$ (M = Ca, Sr),[35] and Rb{Cd[$Ag(CN)_2]_3$},[36] and all these compounds have Ag···Ag distances longer than 3.5 Å. Only Tl[$Ag(CN)_2$] salt, containing a similar stacking pattern of $Ag(CN)_2$ anions, has a shorter Ag···Ag contact (3.110(3) Å)[37] than that of the [EMI][$Ag(CN)_2$] salt.

There have been a small number of spectrochemical and electrochemical studies on EMI salts with a monoanionic complex with metal center, but even fewer reports of structural characterization in the solid state have appeared: [EMI][$AlBr_4$][13c] and [EMI][$AuCl_4$].[19] In both salts, there is no direct metal···metal interionic contact as observed in the $Ag(CN)_2$ salt. In the tetrabromoaluminate salt ($T_m \sim 50$ °C[17]), the tetrahedral geometry of the $AlBr_4$ anion inhibits the Al···Al interionic interaction[13c] as well as in the molten salt [EMI][$AlCl_4$] ($T_m = 8$ °C[7]). That the melting point of the $AlBr_4$ salt is higher than that of the $AlCl_4$ salt is similar to that previously observed for $NaAlX_4$ (X = Cl and Br) systems,[38] and this might be caused by the increased cation···anion Coulomb interactions in the $AlBr_4$ salts. On the other hand, the tetrachloroaurate salt has square planar $AuCl_4$ anions, which are arranged perpendicularly to one another in the salt.[19] This structural feature gives rise to the indirect Au···Au interionic interactions such as the Au···Cl−Au pattern, which is accompanied by the quasioctahedral $AuCl_6$ anions. The melting point far above RT ($T_m = 58$ °C) seems to be related to the indirect Au···Au contacts between the $AuCl_4$ anions. In the case of the $Ag(CN)_2$ salt, there are direct Ag···Ag interionic contacts between silver dicyanides together with the cation−anion and cation−cation interactions, which would be the essential reason for the relatively high melting point (73 °C) among the EMI salts with a monoanion.

Conclusion

A new RT ionic liquid [EMI][$C(CN)_3$] shows a low viscosity (18 cP) at 22 °C and high ionic conductivity (1.8×10^{-2} S cm^{-1}) at 20 °C. The conductivity is less than that of the [EMI][$N(CN)_2$] salt (2.7×10^{-2} S cm^{-1}), possibly due to the larger molecular weight of the anion. On the basis of 13 EMI-based RT ionic liquids including the present $C(CN)_3$ and $N(CN)_2$ salts, it has become apparent that the equivalent conductivity is approximately proportional to the reciprocal of the viscosity as expected from the Walden rule. X-ray crystallography of the [EMI][$Ag(CN)_2$] salt reveals short C−H···π contacts in the two-dimensional cationic layer and short C(2)−H···N(cyano) hydrogen bonding between cation and anion. In addition, significant direct Ag···Ag interactions are seen in the one-dimensional anionic chain, resulting in a relatively high melting point.

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Supporting Information Available: Crystallographic data for [EMI][$Ag(CN)_2$] in CIF format, and DSC and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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