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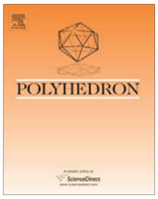

Ambient temperature imidazolium-based ionic liquids with tetrachloronickelate(II) anions

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Deep blue tetrachloronickelate(II) salts of 1-alkyl-3-methylimidazolium cations $[C_n\text{mim}]^+$ with intermediate chain lengths ($n = 5$, 7, 8 and an $n = 4/6$ mixture) have been prepared from imidazolium chlorides and $NiCl_2$. They are liquid at ambient temperatures (ca. 20 °C) and above, and display viscosities and thermal stability comparable to related $[BF_4]^-$ compounds. The similarities may reflect the compensating effects of the dinegative charge of the $[NiCl_4]^{2-}$ ion and its larger size.

1. Introduction

In the past several decades, the chemistry of room temperature ionic liquids (RTILs) has expanded markedly as these compounds have become better understood and more broadly applied in academic and commercial settings [1]. Their unique properties, including large liquid temperature ranges, negligible vapor pressure, and adjustable viscosity and basicity, have stimulated uses as 'designer solvents' [2–4], in electrochemistry [5–7], and in catalysis [8]. A substantial part of their attractiveness stems from the discovery of air- and moisture-stable RTILs with main group anions such as $[PF_6]^-$ [9], $[BF_4]^-$ [10], $[(CF_3SO_2)_2N]^-$ [11], and $[CF_3SO_2]^-$ [11]. Metal-containing anions from across the periodic table have also been incorporated into ionic liquids, and they also can possess air- and moisture-stability; among these are zinc, tin, and iron-containing $[MCl_x]^-$ anions associated with various choline-derived cations [12]. In comparison with commonly used main group monoanions, metal-containing anions offer the possibility of more highly charged species (e.g., $[LnX_6]^{3-}$) [13] and additional variations in geometries (e.g., tetrahedral and square planar $[MX_4]^{2-}$ species) [14–16].

Nickel-based anions have a long history of use in ionic liquids. Osteryoung investigated the solubility of $NiCl_2$ in chloroaluminate melts, and determined that the predominant nickel containing species was $[NiCl_4]^{2-}$, although several additional ions were also detected [17]. Imidazolium-based Ni-containing salts $[C_n\text{mim}]_2[NiCl_4]$ ($n = 2$ (mp = 92–93 °C) [18]; 4 (mp = 55–58 °C) [15]; 12–18 (mp = 50–75 °C) [19]) were later prepared by other workers; crystal structures for the compounds with $n = 2$ and 4 demonstrated the existence of extensive cation-anion hydrogen-bonding. Pyridinium-based Ni-containing salts $[C_n\text{py}]_2[NiCl_4]$ ($n = 12$, 14, 16, 18) were investigated by Seddon and coworkers, who found all of them to be mesogenic solids with melting points ranging from 80–88 °C [19]. Abbott found that a choline-derived nickel chloride salt had a melting point above 100 °C [12]; it thus falls outside the conventional definition of RTILs (mp < 100 °C) [20].

In a search for nickel-containing ionic liquids that would be fluid at ambient temperatures (ca. ⩾ 20 °C), and which might be useful in film formation or electrochemical applications [5], we have investigated the use of imidizolium cations with pendant alkyl chains of intermediate length, roughly C_5–C_{10}. This region has been previously identified as one in which compounds with low melting points are often found, as the hydrogen bonding that contributes to the high melting points of $[C_{(n \leqslant 4)}\text{mim}]$-based RTILs is disrupted, but the dispersion forces between longer chains that cause $[C_{(n \geqslant 10)}\text{mim}]$-based compounds to exhibit mesogenic characteristics have yet to become dominant [9,10].

In this work we outline the synthesis of several imidazolium RTILs that incorporate tetrachloronickelate anions and are liquid at 25 °C. The composition, viscosity and thermal behavior of these compounds was investigated.

2. Results and discussion

2.1. Synthesis of compounds

The mixture of the alkyl imidazolium chlorides with hydrated nickel(II) chloride results in dark blue liquids containing the $[NiCl_4]^{2-}$ anion (Eq. (1)).

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$$2[C_n\text{mim}]Cl + NiCl_2(H_2O)_6 \rightarrow 2[C_n\text{mim}]_2[NiCl_4] + 6H_2O \qquad (1)$$

The water can be removed by heating under vacuum. When $n = 5$, the originally mobile liquid forms an opaque aqua-colored gel after several days at room temperature. When $n = 7$ or 8, or for the mixed cation species with $n = 4$, $n = 6$, the compounds remain transparent blue liquids indefinitely. The previously described $[C_2mim]^+$ and $[C_4mim]^+$ salts of $[NiCl_4]^{2-}$, in contrast, have melting points of 92–93 °C [18] and 56 °C [15], respectively [21]. The salts reported here are hygroscopic, and deliberate addition of water causes them to turn green, but the blue color will be regenerated on heating under vacuum.

2.2. Viscosity measurements

The viscosities of the nickelate salts were measured from 23–60 °C (the exact range varied with the cation), and the available viscosities closest to 25, 30 and 40 °C are given in Table 1. Not surprisingly, the two longer-chained salts with $[C_7mim]^+$ and $[C_8mim]^+$ cations have higher viscosities at a given temperature than do those with shorter chains; e.g., the viscosity of the $[C_8mim]^+$ salt is between 40% and 60% greater than for the $[C_5mim]^+$ analogue. Below 30 °C, the viscosity of the mixed $[C_4mim][C_6mim][NiCl_4]$ species (which could be considered to have an "average" chain length of C_5) tracks closely with that of the single-chained $[C_5mim]_2[NiCl_4]$ salt. Above that temperature, the viscosities start to diverge, and values for the mixed imidazolium salt stay roughly 15% below that of the single. The effect of mixed cations on the viscosities of ionic liquids is not well studied (cf. the relative rarity of viscosity measurements in systems with mixed anions [12,22,23]), so that it is not clear how typical the behavior of $[C_4mim][C_6mim][NiCl_4]$ is.

Table 1
Representative values for substituted imidazolium $[NiCl_4]^{2-}$, $[PF_6]^-$, $[BF_4]^-$ salts.

Ionic liquid	*T* (°C)	*η* (cP)	Ref.
$[C_5mim]_2[NiCl_4]$	24.9	125	This work
$[C_5mim]_2[NiCl_4]$	30.2	76	This work
$[C_5mim]_2[NiCl_4]$	40.2	33	This work
$[C_7mim]_2[NiCl_4]$	26.3	178	This work
$[C_7mim]_2[NiCl_4]$	30.1	116	This work
$[C_7mim]2[NiCl_4]$	40.0	49	This work
$[C_8mim]2[NiCl_4]$	27.7	144	This work
$[C_8mim]2[NiCl_4]$	30.2	109	This work
$[C_8mim]2[NiCl_4]$	40.0	50	This work
$[C_8mim][PF_6]$	30	452	[24]
$[C_8mim][BF4]$	30	82	[25]
$[C_4mim][C_6mim][NiCl_4]$	25.1	122	This work
$[C_4mim][C_6mim][NiCl_4]$	30.0	70	This work
$[C_4mim][C_6mim][NiCl_4]$	40.0	30	This work
$[C_4mim][PF_6]$	30	204	[24]
$[C_4mim][BF_4]$	30	91.4	[24]
$[C_6mim][PF_6]$	30	363	[24]
$[C_6mim][BF_4]$	30	177	[24]

Although the data are still limited, at similar temperatures the $[NiCl_4]^{2-}$ salts appear to have viscosities considerably less than that observed for $[PF_6]^-$ salts, and similar to or slightly greater than $[BF_4]^-$ salts [24,25]. The last point is somewhat surprising, considering that the dianionic charge on the $[NiCl_4]^{2-}$ ion might be expected to strengthen coulombic attractions and hence to increase viscosity. On the other hand, the larger size of $[NiCl_4]^{2-}$ compared to $[BF_4]^-$ (with effective radii of ca. 2.9 Å versus 2.1 Å, respectively) [26] should weaken such interactions, and serve as a compensating influence. It is worth noting that the viscosity of the mixed $[C_4mim][C_6mim][NiCl_4]$ salt is comparable to that of $[C_4mim]_2$-$[BF_4]$, underscoring the potential viscosity lowering ability of mixed cations.

Plots of the complete data sets (Fig. 1) indicate slightly non-Arrhenius behavior for the ionic liquids at higher temperatures. Nevertheless, a fit of the data to an Arrhenius-like equation that expresses the energy of activation for viscous flow (Eq. (2)),

$$\eta = \eta_0 e^{E_\eta/RT} \qquad (2)$$

for which E_η is the energy of action for viscous flow, and η_0 is a constant, is very good for all four liquids ($r^2 > 0.99$). The E_η values (Table 2) cluster around 65–69 kJ mol^{-1}, without an obvious correlation with the chain length. These are near the value of 55.7 kJ mol^{-1} determined for the RTIL $[choline][Zn_2Cl_5]$ [12], but are roughly four times higher than the average of 17 ± 3 kJ mol^{-1} found for various RTILs with more common anions ($[BF_4]^-$, $[PF_6]^-$, $[Tf_2N]^-$, $[Tf_2C]^-$), even when the cations are hydroxy-substituted, and thus capable of engaging in hydrogen bonding [27].

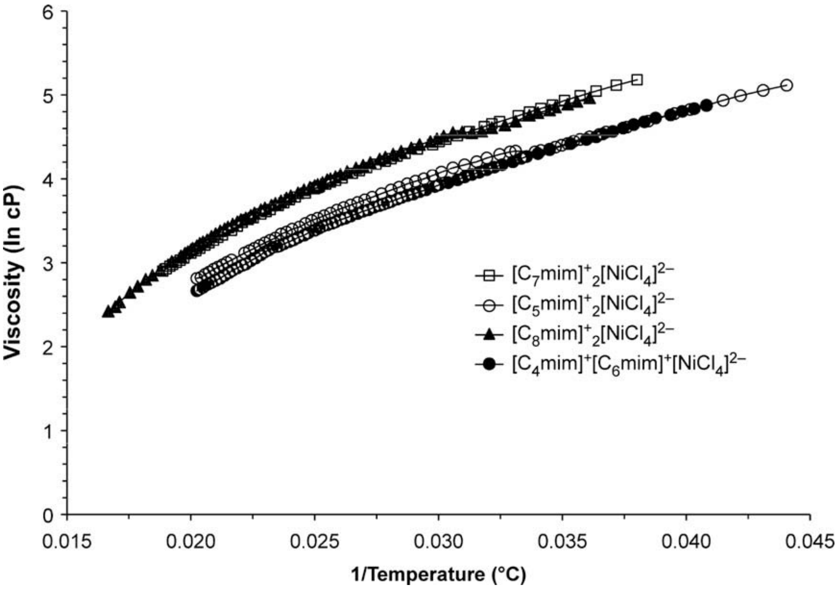

Fig. 1. Viscosity of imidazolium $[NiCl_4]^{2-}$ salts as a function of temperature.

Table 2
Energy of activation for viscous flow of tetrachloronickelate salts.

Compound	$E\eta$ (kJ mol^{-1})	r^2
$[C_5mim]_2[NiCl_4]$	65.6	0.997
$[C_7mim]_2[NiCl_4]$	67.8	0.998
$[C_8mim]_2[NiCl_4]$	64.6	0.995
$[C_4mim][C_6mim][NiCl_4]$	68.7	0.996

2.3. Thermal behavior

The thermal stabilities of imidazolium salts have been studied under various conditions, and have been found to have more dependence on anion type than cation size [24]. The three single-chain $[C_nmim]_2[NiCl_4]$ salts were investigated with scanning TGA, and all were found to decompose in a similar, multistep manner. A TGA scan for $[C_7mim]_2[NiCl_4]$ is presented in Fig. 2. Onset of decomposition (2% weight loss) under N_2 occurs just above 300 °C, and approximately two-thirds of the mass is gone by 430 °C, which corresponds to the loss of both imidazolium cations. Such volatilization temperatures are typical for imidazolium salts [28], but determination of the exact temperature and rate at which decomposition occurs is a non-trivial matter [29]. With imidazolium salts, whether decomposition occurs in a single or in multiple steps varies with the anion; $[C_1mim][PF_6]$ decomposes in a single step, for example, but $[C_1mim][BF_4]$ (like the tetrachloronickelate liquids) does so in several steps [30].

Continued heating of $[C_7mim]_2[NiCl_4]$ eventually leads to a constant weight near 690 °C, with a residual mass of 14%. This value does not correspond to the presence of completely reduced nickel or nickel chloride alone. To investigate this point further, a sample of $[C_7mim]_2[NiCl_4]$ was placed in a tube furnace at 700 °C for 1 h under N_2. After the sample cooled, powder XRD analysis on the resulting metallic-appearing film indicated the presence of both elemental nickel and $NiCl_2$; given this information, the residual weight in the TGA experiment corresponds to a Ni:$NiCl_2$ ratio of 3:1. Other modifications to the anion could make the decomposition to nickel alone more likely [31].

2.4. Conclusions

The strategy of using imidiazolium cations with intermediate chain lengths to produce ambient temperature ionic liquids is successful with $[NiCl_4]^{2-}$ anions. Despite the latters' dinegative charge, the viscosity and thermal properties of the resulting liquids are similar to related $[BF_4]^-$-based species. The nickelate-based liquids could provide useful substrates for electrochemical studies and metal deposition reactions.

3. Experimental

3.1. General considerations

Organic and inorganic starting materials were reagent grade from Acros or Strem Chemical and used as received. The preparation of 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$), 1-pentyl-3-methylimidazolium chloride ($[C_5mim]Cl$), 1-hexyl-3-methylimidazolium chloride ($[C_6mim]Cl$), 1-heptyl-3-methylimidazolium chloride ($[C_7mim]Cl$), and 1-octyl-3-methylimidazolium chloride ($[C_8mim]Cl$) followed literature procedures [32].

Viscosity data were obtained on a Cambridge Applied Systems Viscolab 400 Viscometer fitted with heating tape. All thermal measurements were carried out on an Instrument Specialist TGA-1000 instrument. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory, Desert Analytics (Tucson, AZ), or at the Micro-Mass Facility, University of California, Berkeley (Berkeley, CA).

3.2. Preparation of bis(1-pentyl-3-methylimidazolium) tetrachloronickelate(II), $[C_5mim]_2[NiCl_4]$

1-Pentyl-3-methylimidazolium chloride (5.26 g, 27.9 mmol) and $NiCl_2(H_2O)_6$ (3.31 g, 13.9 mmol) were placed in a 50 mL round bottom flask equipped with a magnetic stirring bar. The flask was flushed with N_2 and the reaction was allowed to stir at 80 °C for 18 h. The reaction was removed from heat and allowed to cool to room temperature. The solution was dried under vacuum at 95 °C to afford a dark blue liquid (6.24 g, 88%). *Anal.* Calc. for $C_{18}H_{34}Cl_4N_4Ni$: C, 42.64; H, 6.76; N, 11.05. Found: C, 39.31; H, 6.38; N, 10.19%. Although individual percentage values are low, the C:H:N values are in nearly exact molar ratios (18.0:34.8:4.0), suggesting that combustion was incomplete.

3.3. Preparation of bis(1-heptyl-3-methylimidazolium) tetrachloronickelate(II), $[C_7mim]_2[NiCl_4]$

1-Heptyl-3-methylimidazolium chloride (4.29 g, 19.8 mmol) and $NiCl_2(H_2O)_6$ (2.35 g, 9.89 mmol) were placed in a 100 mL

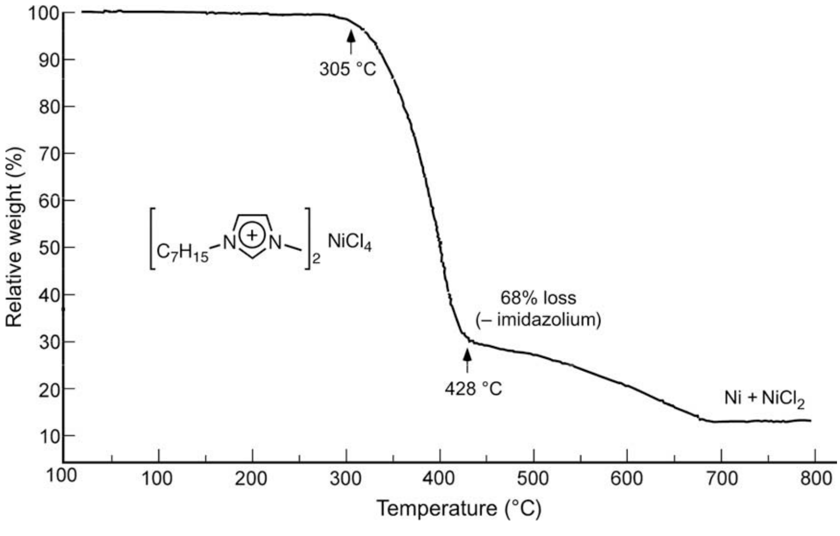

Fig. 2. Thermal behavior of $[C_7mim]_2[NiCl_4]$ under N_2 (20° min^{-1}). The arrow at 305 °C marks the decomposition onset.

round bottom flask equipped with a magnetic stirring bar. The flask was flushed with N_2 and the reaction was allowed to stir at 80 °C for 17 h. The reaction was removed from heat and allowed to cool to room temperature. The solution was dried under vacuum at 95 °C to afford a dark blue liquid (4.65 g, 83%). *Anal.* Calc. for $C_{22}H_{42}Cl_4N_4Ni$: C, 46.93; H, 7.52; N, 9.95. Found: C, 46.04; H, 7.57; N, 9.80%.

3.4. Preparation of bis(1-octyl-3-methylimidazolium) tetrachloronickelate(II), $[C_8mim]_2[NiCl_4]$

1-Octyl-3-methylimidazolium chloride (4.54 g, 19.7 mmol) and $NiCl_2(H_2O)_6$ (2.34 g, 9.84 mmol) were placed in a 100 mL round bottom flask equipped with a magnetic stirring bar. The flask was flushed with N_2 and the reaction was allowed to stir at 90 °C for 9 h. The reaction was removed from heat and allowed to cool to room temperature. The solution was dried under vacuum at 90 °C for 2 h to afford a dark blue liquid (5.17 g, 89%). *Anal.* Calc. for $C_{24}H_{46}Cl_4N_4Ni$: C, 48.72; H, 7.84; N, 9.48. Found: C, 47.91; H, 7.90; N, 9.38%.

3.5. Preparation of (1-butyl-3-methylimidazolium)(1-hexyl-3-methylimidazolium) tetrachloronickelate(II), $[C_4mim][C_6mim][NiCl_4]$

1-Butyl-3-methylimidazolium chloride (2.25 g, 12.9 mmol), 1-hexyl-3-methylimidazolium chloride (2.61 g, 12.9 mmol), and $NiCl_2(H_2O)_6$ (3.06 g, 12.9 mmol) were placed in a 100 mL round bottom flask equipped with a magnetic stirring bar. The flask was flushed with N_2 and the reaction was allowed to stir at 90 °C for 23 h. The reaction was removed from heat and allowed to cool to room temperature. The solution was dried under vacuum at 100 °C to afford a dark blue liquid (5.97 g, 91%).

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References

[1] N.V. Plechkova, K.R. Seddon, Chem. Soc. Rev. 37 (2008) 123.
[2] T. Welton, Chem. Rev. 99 (1999) 2071.
[3] I. Newington, J.M. Perez-Arlandis, T. Welton, Org. Lett. 9 (2007) 5247.
[4] N.V. Plechkova, K.R. Seddon, Ionic liquids: designer solvents for green chemistry, in: A. Perosa, F. Zecchini, P. Tundo (Eds.), Methods and Reagents for Green Chemistry: An Introduction, John Wiley and Sons, Hoboken, NJ, 2007.
[5] M.-J. Deng, I.W. Sun, P.-Y. Chen, J.-K. Chang, W.-T. Tsai, Electrochim. Acta 53 (2008) 5812.
[6] T.-I. Leong, I.W. Sun, M.-J. Deng, C.-M. Wu, P.-Y. Chen, J. Electrochem. Soc. 155 (2008) F55.
[7] D.-X. Zhuang, M.-J. Deng, P.-Y. Chen, I.W. Sun, J. Electrochem. Soc. 155 (2008) D575.
[8] P. Wasserscheid, W. Keim, Angew. Chem., Int. Ed. 39 (2000) 3772.
[9] C.M. Gordon, J.D. Holbrey, A.R. Kennedy, K.R. Seddon, J. Mater. Chem. 8 (1998) 2627.
[10] J.D. Holbrey, K.R. Seddon, J. Chem. Soc., Dalton Trans. (1999) 2133.
[11] P. Bônhote, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168.
[12] A.P. Abbott, G. Capper, D.L. Davies, R. Rasheed, Inorg. Chem. 43 (2004) 3447.
[13] K. Binnemans, Chem. Rev. 107 (2007) 2592.
[14] M.S. Sitze, E.R. Schreiter, E.V. Patterson, R.G. Freeman, Inorg. Chem. 40 (2001) 2298.
[15] C. Zhong, T. Sasaki, A. Jimbo-Kobayashi, E. Fujiwara, A. Kobayashi, M. Tada, Y. Iwasawa, Bull. Chem. Soc. Jpn. 80 (2007) 2365.
[16] R.E.D. Sesto, T.M. McCleskey, A.K. Burrell, G.A. Baker, J.D. Thompson, B.L. Scott, J.S. Wilkes, P. Williams, Chem. Commun. (2008) 447.
[17] R.J. Gale, B. Gilbert, R.A. Osteryoung, Inorg. Chem. 18 (1979) 2723.
[18] P.B. Hitchcock, K.R. Seddon, T. Welton, J. Chem. Soc., Dalton Trans. (1993) 2639.
[19] C.J. Bowlas, D.W. Bruce, K.R. Seddon, Chem. Commun. (1996) 1625.
[20] J.D. Holbrey, R.D. Rogers, Physicochemical properties of ionic liquids: melting points and phase diagrams, in: P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2008.
[21] The melting points of the single-chain liquids were below 0 °C, but attempts to measure the exact temperatures with DSC were unsuccessful.
[22] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Inorg. Chem. 21 (1982) 1263.
[23] J.R. Sanders, E.H. Ward, C.L. Hussey, J. Electrochem. Soc. 133 (1986) 325.
[24] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156.
[25] L.C. Branco, J.N. Rosa, J.J.M. Ramos, C.A.M. Afonso, Chem. Eur. J. 8 (2002) 3671.
[26] D.M.P. Mingos, A.L. Rohl, J. Chem. Soc., Dalton Trans. (1991) 3419.
[27] H. Jin, B. O'Hare, J. Dong, S. Arzhantsev, G.A. Baker, J.F. Wishart, A.J. Benesi, M. Maroncelli, J. Phys. Chem. B 112 (2008) 81.
[28] B.K.M. Chan, N.-H. Chang, M.R. Grimmett, Aust. J. Chem. 30 (1977) 2005.
[29] K.J. Baranyai, G.B. Deacon, D.R. MacFarlane, J.M. Pringle, J.L. Scott, Aust. J. Chem. 57 (2004) 145.
[30] D.M. Blake, L. Moens, D. Rudnicki, H. Pilath, J. Sol. Energy Eng. 128 (2006) 54.
[31] In preliminary experiments, the reaction of 1-heptyl-3-methylimidazolium iodide and NiI_2 was used to prepare $[C_7mim]_2NiI_4$. The dark red liquid was heated to 700 °C for 30 min under N_2. Powder XRD indicated that the residue consisted only of elemental nickel; a Scherrer analysis of peak widths suggested an average particle size of 44 nm.
[32] J.G. Huddleston, R.D. Rogers, Chem. Commun. (1998) 1765.