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Physical trends and structural features in organic salts of the thiocyanate anion

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A new series of ionic liquids based on the thiocyanate anion has been prepared. Incorporation of this anion with an imidazolium, tetraalkylammonium or pyrrolidinium cation produces ionic liquids with advantageously low melting points and good thermal stability. The low temperature phase behaviour of the salts has been investigated using differential scanning calorimetry and multiple solid phases have been observed. The electrochemical windows of representative imidazolium and pyrrolidinium species have been investigated by cyclic voltammetry and determined to be 2.4 and 3.5 V, respectively. In addition, the solid-state structure of *N*,*N*-dimethylpyrrolidinium thiocyanate has been determined by X-ray crystallography. This is the first reported structure of a pyrrolidinium thiocyanate species and shows a layered structure with linear thiocyanate groups having bond lengths comparable to those observed in similar SCN^--containing species.

Introduction

The field of ionic liquids has been rapidly expanding in the last decade, largely driven by an interest in these species as potentially greener replacements for traditional molecular solvents. The range of potential applications of these systems is also expanding and the bulk of the research in the field of ionic liquids is dedicated to finding new applications for a small number of the well-established ionic liquids, such as 1-butyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate. Such applications include, amongst others, a large number of catalytic reactions[1] and liquid–liquid separations,[2] where the ionic liquid is used in combination with an organic solvent in a biphasic operation. Alternatively, incorporation of the ionic liquid into membranes[3] or onto solid supports[4] has been reported and applications even extend to the use of ionic liquids for the solvation of radioactive material[5] and electrochemical applications such as solar cells and actuators.[6] However, in addition to investigations into the potential uses of existing compounds, there exists a significant need for the identification of new ionic liquids. It is well known that combinations of different anions and cations provide ionic liquids with vastly differing characteristics. For instance, a decrease in viscosity, as seen for the bis(trifluoromethanesulfonyl)amide and dicyanamide ionic liquids,[7,8] makes handling easier and, thus, mechanical processes which are important industrially, such as filtration, are made simpler and utilisation of the ionic liquid as a solvent becomes more viable. Investigations into the physico-chemical properties of each new ionic liquid increase our understanding of these systems and will ultimately allow prediction of properties and selection of the best species for each application, thereby bringing the idea of designer solvents a step closer to reality.

As part of the drive to discover new and potentially useful ionic liquids, we report the use of the thiocyanate anion in combination with imidazolium, pyrrolidinium and tetraalkylammonium cations to produce ionic liquids, the majority of which are liquid at room temperature. Known quaternary ammonium thiocyanates, *e.g.* tetrabutylammonium thiocyanate, a well-established, commercially available electrolyte, generally have melting points which are too high for convenient use as solvents for most laboratory or industrial applications (*e.g.* 120–123 °C for tetrabutylammonium thiocyanate). It is interesting that the melting point of tetrabutylammonium tetrafluoroborate is some 40 °C higher than the thiocyanate analogue. Indeed, several inorganic thiocyanates are lower melting than the corresponding BF_4^- and PF_6^- species, suggesting that viable ionic liquid thiocyanates may be a possibility. Although there have been several reports of thiocyanate species in the literature, such as tetrabutylammonium thiocyanate,[9] particularly regarding their use in solar cells,[10] application of this anion to the synthesis of room temperature ionic liquids has not been undertaken.

Experimental

The various alkyl iodides (Aldrich/BDH/Fluka), Pr^iOH (BDH), potassium thiocyanate (Unilab) and 1-methylpyrrolidine (Aldrich) were used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 MHz spectrometer in d_6-DMSO with tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer FTIR 1600 instrument. Solid samples were examined as KBr discs, ~5% w/w, while liquid samples were examined between sodium chloride plates. Electrospray mass spectroscopy was carried out on a Micromass Platform for samples dissolved in a 1 : 1 (v/v) methanol–water mixture. Electrochemistry was carried out under a nitrogen atmosphere (in a drybox) using a Maclab potentiostat, and Maclab software. Electrodes included a glassy carbon working electrode, a platinum wire counter electrode and a silver wire pseudo-reference electrode. Samples were dried overnight in a vacuum oven at <0.1 atm, 50 °C before analysis. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-7 calibrated with *p*-nitrotoluene (51.64 °C) and cyclohexane (−87.06 and 6.54 °C). For consistency, the abbreviations previously used to describe the pyrrolidinium and ammonium cation are used here, where P = pyrrolidinium and N = ammonium, with a subscript to indicate the number of carbons in the linear alkyl chain substituent. Emi indicates the 1-ethyl-3-methylimidazolium cation.

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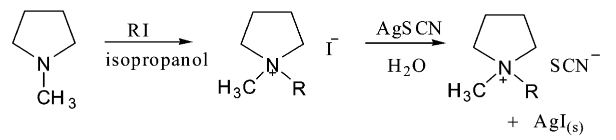

Scheme 1 Synthesis of the pyrrolidinium thiocyanate ionic liquids.

Synthesis and characterisation

The iodide salts of the respective cations were prepared using literature methods.[11,12]

Silver thiocyanate was precipitated by mixing aqueous solutions of silver nitrate and potassium thiocyanate (1 : 1 mole ratio), washed well with water to remove any unreacted reagents and used immediately. An aqueous solution of the iodide was added to an aqueous slurry of the excess silver thiocyanate (Scheme 1) and the solution heated gently with stirring for 1 h. Silver iodide was removed by filtration and the water removed from the filtrate under vacuum. To ensure complete removal of silver salts from the product, dichloromethane or acetonitrile was added and the solution was cooled in a refrigerator or freezer for a day, before filtration and removal of the solvent to give the clean product. Removal of Ag^+ and I^- was confirmed using mass spectroscopy, a technique with detection sensitivity previously ascertained to be below 0.5% w/w for Ag^+ and I^-.[8]

***N*,*N*-Dimethylpyrrolidinium thiocyanate ($P_{11}SCN$, 1).** AgSCN (0.98 g, 5.8 mmol) and $P_{11}I$ (1.00 g, 4.4 mmol) gave **1** as a white solid; yield 93%. IR (KBr disc): 3441s (br), 3019s, 2966s [ν(C–H)], 2792m, 2053vs [ν(SCN)], 1645m, 1554w, 1470s [ν(C–H)], 1361vw, 1320m, 1304m [ν(C–N)], 1275m [ν(C–N)], 1248m, 1120w, 1047w, 1001s, 975m, 932s, 815m, 743m, 932s, 815m, 743m, 577m, 470m, 426w cm^{-1}. ^1H NMR (300 MHz, d_6-DMSO) δ (ppm): 2.09 (m, 2 × CH_2), 3.07 (s, 2 × CH_3), 3.44 (t, 2 × CH_2). ^{13}C NMR (75 MHz, d_6-DMSO) δ (ppm): 21.3 (CH_2), 50.9 (CH_3), 64.8 (CH_2). Electrospray MS: ES^+ *m*/*z* 100 (100%, $P_{11}{}^+$); ES^- *m*/*z* 58 (100%, SCN^-).

Crystal data: $C_7H_{14}N_2S$, $M = 158.26$, monoclinic, $a = 8.4101(2)$, $b = 7.8090(2)$, $c = 13.6228(5)$ Å, $U = 865.1(3)$ Å^3, $T = 123(2)$ K, space group $P2(1)/c$, $Z = 4$, absorption coefficient = 0.305 mm^{-1}, 12 646 reflections measured, 2133 unique ($R_{int} = 0.0482$), R_1 (R_w) [$I > 2\sigma(I)$] = 0.0355 (0.0854), R_1 (R_w) (all data) = 0.0641 (0.0967).

CCDC reference number 192429.

See http://www.rsc.org/suppdata/jm/b2/b208372h/ for crystallographic data in CIF or other electronic format.

***N*-Ethyl-*N*-methylpyrrolidinium thiocyanate ($P_{12}SCN$, 2).** AgSCN (2.34 g, 14 mmol) and $P_{12}I$ (3.25 g, 13.5 mmol) gave **2** as a pale orange solid; yield 94%. IR (KBr disc): 3449s(br), 2982m [ν(C–H)], 2803w, 2057vs [ν(SCN)], 1640w, 1544vw, 1463m [ν(C–H)], 1385m [ν(C–N)], 1303vw, 1235vw, 1113w, 1033m, 998m, 936m, 810w, 739w, 583m cm^{-1}. ^1H NMR (300 MHz, d_6-DMSO) δ (ppm): 1.27 (t, CH_3), 2.07 (t, 2 × CH_2), 2.95 (s, CH_3), 3.36 (q, CH_2), 3.42 (m, 2 × CH_2). ^{13}C NMR (75 MHz, d_6-DMSO) δ (ppm): 7.8 (CH_3), 20.1 (CH_2), 45.9 (CH_3), 57.4 (CH_2), 61.9 (CH_2), 129.3 (SCN). Electrospray MS: ES^+ *m*/*z* 114 (100%, $P_{12}{}^+$); ES^- *m*/*z* 230 {5%, $[P_{12}(SCN)_2]^-$}, 58 (100%, SCN^-).

***N*-Propyl-*N*-methylpyrrolidinium thiocyanate ($P_{13}SCN$, 3).** AgSCN (1.81 g, 11 mmol) and $P_{13}I$ (2.55 g, 10 mmol) gave **3** as a pale yellow liquid; yield 96%. IR (KBr disc): 3448m(br), 2973m [ν(C–H)], 2882w, 2058vs [ν(SCN)], 1654w, 1468m [ν(C–H)], 1370vw [ν(C–N)], 1304vw, 1041vw, 1003w, 971w, 939w, 905vw, 434s cm^{-1}. ^1H NMR (300 MHz, d_6-DMSO) δ (ppm): 0.92 (t, CH_3), 1.72 (m, CH_2), 2.08 (t, 2 × CH_2), 2.97 (s, CH_3), 3.24 (q, CH_2), 3.43 (m, 2 × CH_2). ^{13}C NMR (75 MHz, d_6-DMSO) δ (ppm): 10.6 (CH_3), 16.5 (CH_2), 21.1 (CH_2), 47.5 (CH_3), 63.4 (CH_2), 64.5 (s, CH_2), 129.4 (SCN). Electrospray MS: ES^+ *m*/*z* 314 {5%, $[(P_{13})_2SCN]^+$}, 128 (100%, $P_{13}{}^+$); ES^- *m*/*z* 244 {5%, $[P_{13}(SCN)_2]^-$}, 58 (100%, SCN^-).

***N*-Butyl-*N*-methylpyrrolidinium thiocyanate ($P_{14}SCN$, 4).** AgSCN (1.81 g, 11 mmol) and $P_{14}I$ (2.70 g, 10 mmol) gave **4** as a pale yellow liquid; yield 78%. IR (KBr disc): 3442s(br), 2966s [ν(C–H)], 2873m, 2056vs [ν(SCN)], 1642m, 1540vw, 1465s [ν(C–H)], 1380m [ν(C–N)], 1306vw, 1033w, 1002w, 932m, 736w, 458s(br) cm^{-1}. ^1H NMR (300 MHz, d_6-DMSO) δ (ppm): 0.92 (t, CH_3), 1.31 (m, CH_2), 1.67 (m, CH_2), 2.06 (t, 2 × CH_2), 2.96 (s, CH_3), 3.24 (q, CH_2), 3.43 (m, 2 × CH_2). ^{13}C NMR (75 MHz, d_6-DMSO) δ (ppm): 13.8 (CH_3), 19.6 (CH_2), 21.5 (CH_2), 25.3 (CH_2), 47.9 (CH_3), 63.3 (CH_2), 63.8 (CH_2). Electrospray MS: ES^+ *m*/*z* 142 (100%, $P_{14}{}^+$); ES^- 258 {5%, $[P_{14}(SCN)_2]^-$}, 58 (100%, SCN^-).

***N*-Hexyl-*N*-methylpyrrolidinium thiocyanate ($P_{16}SCN$, 5).** AgSCN (1.91 g, 11 mmol) and $P_{16}I$ (2.95 g, 10 mmol) gave **5** as a pale yellow liquid; yield 89%. IR (KBr disc): 3422m(br), 2956s [ν(C–H)], 2930s, 2860m, 2055vs [ν(SCN)], 1643w, 1466s [ν(C–H)], 1376w [ν(C–N)], 1351w, 1305vw, 1193w, 1054w, 995w, 935m, 732m, 472s(br) cm^{-1}. ^1H NMR (300 MHz, d_6-DMSO) δ (ppm): 0.92 (t, CH_3), 1.31 (m, 3 × CH_2), 1.67 (m, CH_2), 2.06 (t, 2 × CH_2), 2.96 (s, CH_3), 3.24 (q, CH_2), 3.43 (m, 2 × CH_2). ^{13}C NMR (75 MHz, d_6-DMSO) δ (ppm): 13.8 (CH_3), 19.7 (CH_2), 21.54 (CH_2), 25.3 (CH_2), 47.9 (CH_3), 63.3 (CH_2), 63.8 (CH_2). Electrospray MS: ES^+ *m*/*z* 170 (100%, $P_{16}{}^+$); ES^- *m*/*z* 58 (100%, SCN^-), 286 {5%, $[P_{16}(SCN)_2]^-$}.

***N*-Hexyl-*N*,*N*,*N*-tributylammonium thiocyanate ($N_{6444}SCN$, 6).** AgSCN (1.91 g, 11 mmol) and $N_{6444}I$ (4.35 g, 11 mmol) gave **6** as a pale yellow liquid; yield 97%. IR (neat liquid): 3456s(br), 2946m [ν(C–H)], 2914m, 2803w, 2057vs [ν(SCN)], 1640w, 1486m [ν(C–H)], 1396w [ν(C–N)], 1305vw, 1164w, 1011w, 903m, 796m cm^{-1}. ^1H NMR (300 MHz, d_6-DMSO) δ (ppm): 0.85 (t, 4 × CH_3), 1.22 (m, 6 × CH_2), 1.56 (m, 4 × CH_2), 3.05 (m, NCH_2), 3.15 (m, 3 × NCH_2). ^{13}C NMR (75 MHz, d_6-DMSO) δ (ppm): 13.0 (CH_3), 18.7 (CH_3), 20.5 (CH_2), 21.4 (CH_2), 21.4 (CH_2), 22.6 (CH_2), 24.5 (CH_2), 24.9 (CH_2), 30.0 (CH_2), 51.35 (CH_2), 57.1 (CH_2). Electrospray MS: ES^+ *m*/*z* 270 (100%, N_{6444}); ES^- *m*/*z* 386 {100%, $[N_{6444}(SCN)_2]^-$}, 58 (48%, SCN^-).

1-Ethyl-3-methylimidazolium thiocyanate (emiSCN, 7). AgSCN (1.91g, 11 mmol) and 1-ethyl-3-methylimidazolium iodide (2.61 g, 11 mmol) gave **7** as a pale yellow liquid; yield 81%. IR (neat liquid) 3489m(br), 3150s [ν(C–H)], 3106s, 2988s, 2365w, 2232vs, 2195vs, 2132vs [ν(SCN)], 1637m, 1573s, 1466m [ν(C–H)], 1427w, 1388w, 1131s, 1170s, 1088w, 1030w, 959w, 905m, 844m, 802w, 753m, 701m, 648m, 622s cm^{-1}. ^1H NMR (300 MHz, d_6-DMSO) δ (ppm): 1.42 (t, CH_3), 3.84 (s, NCH_3), 4.19 (q, NCH_2), 7.67 (s, CH) 7.76 (s, CH), 9.10 (s, NCHN). ^{13}C NMR (75 MHz, d_6-DMSO) δ (ppm): 14.5 (CH_3), 35.2 (CH_3), 43.6 (CH_2) 121.4 (CH), 123.0 (CH), SCN and NCHN not observed. Electrospray MS: ES^+ *m*/*z* 111 (100%, emi^+); ES^- *m*/*z* 227 {5%, $[emi(SCN)_2]^-$}, 58 (100%, SCN^-).

Results and discussion

The thiocyanate is a strongly coordinating ion and, as such, the ionic liquids produced with this anion are expected to display similar physical properties to the ionic liquids containing the dicyanamide anion, also a pseudo-halide.[8] The new thiocyanate ionic liquids show good thermal stability, low melting points and electrochemical windows sufficiently wide for a range of electrochemical applications. In addition, they have been found to dissolve some metal thiocyanates in significant quantities. For example, $P_{14}SCN$ will dissolve silver thiocyanate and

$$m(cat^{+}SCN^{-}) + M(SCN)_n \longrightarrow cat[M(SCN)_{n+m}]$$

Scheme 2 General mechanism of metal thiocyanate solvation.

mercury thiocyanate to concentrations above 3 and 2 mol L^{-1}, respectively, and emiSCN will dissolve the same salts to concentrations above 4 and 7 mol L^{-1}, respectively (Scheme 2).

Attempts were made to synthesise the ionic liquids using an anion exchange resin to eliminate the use of silver. The resin can be successfully loaded with the thiocyanate ion by treating it with base, then with aqueous potassium thiocyanate. However, addition of an aqueous solution of the iodide ionic liquid precursor failed to yield completely clean products. Thus, the species analysed below were all synthesised using the silver salt route. Optimisation of the anion exchange resin procedure is ongoing, with a number of different resins being tested, and it is hoped that this will shortly provide a more environmentally friendly route to these new ionic liquids.

Differential scanning calorimetry

The solid phase behaviour of each of the salts was analysed by differential scanning calorimetry (DSC; Fig. 1, Table 1). Some of the salts exhibit multiple solid phases below their melting points. The phase behaviour of the salts is described employing the nomenclature used previously,[13] where phase I denotes the highest temperature crystalline phase, increasing in phase number as the temperature decreases. $P_{11}SCN$ shows a solid–solid transition from phase IV to III at −33 °C. It exists in phase III up to 53 °C, where it appears to undergo two consecutive phase changes from III to II and II to I at 53 and 62 °C, respectively. Following this phase change, a series of low entropy transitions appear between 81 °C and the final melt at 105 °C. This phenomenon is under further investigation. $P_{12}SCN$ shows similar phase behaviour with a low temperature phase change at −67 °C, a large endothermic transition at −15 °C and, finally, a broad continuum of transitions reaching a liquid state at 65 °C. $P_{13}SCN$ displays a low temperature glass transition at −98 °C, followed by a crystallisation at −46 °C, seen as an exothermic transition, followed by slow melting starting at 7 °C. The DSC trace of $P_{14}SCN$ shows only a glass transition, at −74 °C. The crystallisation and melting of the species are not seen in the DSC trace. Further extension of the alkyl substituent chain length to a six carbon chain decreases the glass transition to −89 °C. Again crystalisation of the species is not observed, but the small endothermic transition observed at −5 °C is probably the melting transition. Beyond the propyl subsituent, the glass transition temperature of the salts decreases with increasing chain length, consistent with the general trend observed in the BF_4^- and PF_6^- species. The imidazolium salt, emiSCN, shows a small low temperature glass transition at −89 °C, before undergoing crystallisation at −47 °C and a melt at −6 °C. The DSC trace of the *N*-hexyl-*N*,*N*,*N*-tributylammonium species shows only a glass transition at −58 °C; as for the pyrrolidinium species, crystallisation and melting are not observed.

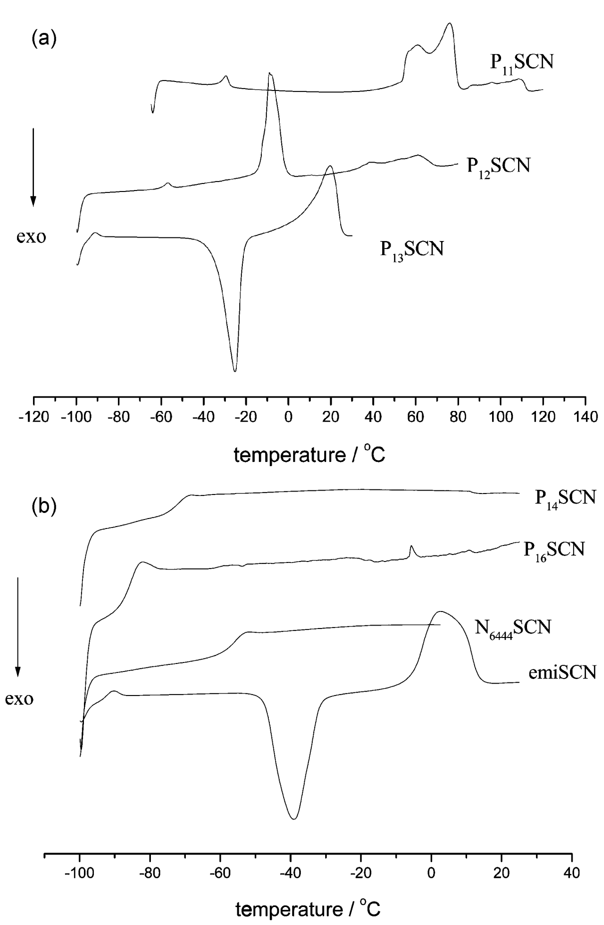

Fig. 1 DSC traces of (a) P_{11}, P_{12} and $P_{13}SCN$, and (b) the P_{14}, P_{16}, N_{6444} and emi thiocyanate ionic liquids. Phase transitions were measured at the onset temperature.

The entropy of fusion of each of the salts is calculated from $\Delta H_f/T_m$ (where ΔH_f is given by the area under the peaks in the DSC trace) and these values are listed in Table 1. Entropies of fusion <20 J K^{-1} mol^{-1} are described as a typical feature of plastic crystal phase behaviour.[14] The transitions observed in the DSC trace of emiSCN and $P_{13}SCN$ are much higher in energy than those of the P_{11} and P_{12} species.

Comparison of the melting points of the thiocyanate salts with those of the tetrafluoroborate and hexafluorophosphate analogues shows a striking effect (Table 2). Utilisation of the thiocyanate anion results in a significant decrease in melting point—as much as 300 °C for the P_{11} species. This reduction

Table 1 Thermal properties of the thiocyanate ionic liquids

Compound	Acronym	$T_g{}^a/°C$	$T_x{}^b/°C$	$T_{s–s}{}^c/°C$	$T_m{}^d/°C$	$\Delta S_f{}^e/J\ K^{-1}\ mol^{-1}$ (±5%)
N,*N*-Dimethylpyrrolidinium thiocyanate	$P_{11}SCN$			−33 53 62	85–105	27.1
N-Ethyl-*N*-methylpyrrolidinium thiocyanate	$P_{12}SCN$			−60 −12 35	65	4.3
N-Propyl-*N*-methylpyrrolidinium thiocyanate	$P_{13}SCN$	−98	−35		7	83.3
N-Butyl-*N*-methylpyrrolidinium thiocyanate	$P_{14}SCN$	−74			—	—
N-Hexyl-*N*-methylpyrrolidinium thiocyanate	$P_{16}SCN$	−89				
N-Hexyl-*N*,*N*,*N*-tributylammonium thiocyanate	$N_{6444}SCN$	−58				
1-Ethyl-3-methylimidazolium thiocyanate	emiSCN	−94	−47		−6	101

[a]Glass transition temperature. [b]Crystallisation temperature. [c]Temperature of solid–solid transition. [d]Melting point. [e]Entropy of fusion.

Table 2 Comparison of the melting points (°C) of a range of ionic liquids

	Anion				
Cation	BF_4^-[21]	PF_6^-[13]	SCN^-	DCA^-[8]	$TFSA^-$[22]
P_{11}^+	340 (dec)[a]	390 (dec)[a]	105	115	132
P_{12}^+	280	200	65	−10	86
P_{13}^+	64	113	19	−35	12
P_{14}^+	138	70	—[b]	−55	−18
P_{16}^+	—	203	—[b]	−11	—
emi^+	15[23]	62[24]	−6	−21	−15

[a] dec = Decomposition. [b] Melting point below room temperature, but not observed using DSC.

in melting point means that the species with alkyl substituents of three carbon chains or longer now exhibit melting points below room temperature and, as such, their suitability as solvents under ambient conditions and, thus, their range of potential applications is greatly increased.

Thermogravimetric analysis

The thermal stability of the thiocyanate ionic liquids was assessed using thermogravimetric analysis (TGA). Using this technique, the salts were warmed to 110 °C under a nitrogen atmosphere, held at 110 °C for 20 min to ensure any weight loss observed subsequently was not due to water loss, then the temperature was ramped up to 450 °C. The $P_{12}SCN$ and $P_{16}SCN$ salts were analysed as representative examples of the pyrrolidinium family.

Thermal analysis of the thiocyanate salts indicates good thermal stability, perhaps contrary to expectations. The pyrrolidinium salts did not show any weight loss below 225 °C (Fig. 2). This shows comparable stability to the iodide salts, *e.g.* $P_{12}I$ starts to lose weight at 250 °C, indicating that a change in anion to thiocyanate is not overly detrimental to the thermal stability of the species. emiSCN shows similar thermal stability, with weight loss beginning above 237 °C; emiI is thermally stable to 243 °C (Fig. 3).

While the thermal stability of the thiocyanate salts was confirmed as relatively good, the optical stability of the species is less certain. The salts are often yellow or orange in colour and darken on extended exposure to sunlight. The thiocyanate ion is known to dimerise to thiocyanogen $(SCN)_2$ under chemically or electrochemically oxidative conditions in melts, or in solutions of alkali metal thiocyanates.[15] Thiocyanogen is itself unstable and will polymerise to polythiocyanogen $(SCN)_x$, a linear polymer whose structure has only recently been established (Fig. 4).[16]

Both thiocyanogen and polythiocyanogen are known to be photoactive, with exposure to light producing both an electric effect, where the species behaves as a semiconductor, and also, in the case of thiocyanogen, an increase in the rate of polymerisation.[17] It is also interesting to note that the presence of iodine increases the photosensitivity of the polythiocyanogen,[18] a fact that may have implications if the thiocyanate ionic liquids are synthesised from the iodide salt. Indeed the presence of either I_2 or Br_2 is likely to result in the electrochemical oxidation of some of the thiocyanate ion to the polymeric species. However, such species were not observed in the mass spectra of the reported compounds.

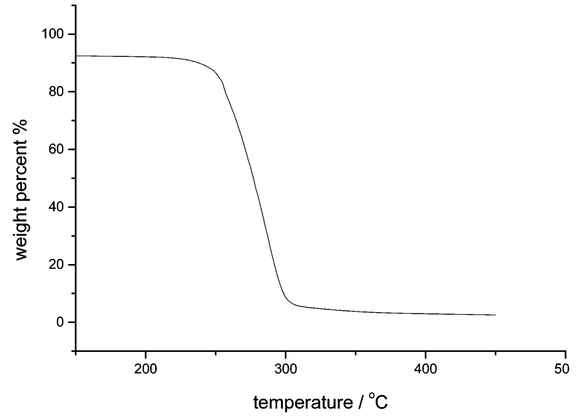

Fig. 2 Thermogravimetric analysis of $P_{16}SCN$.

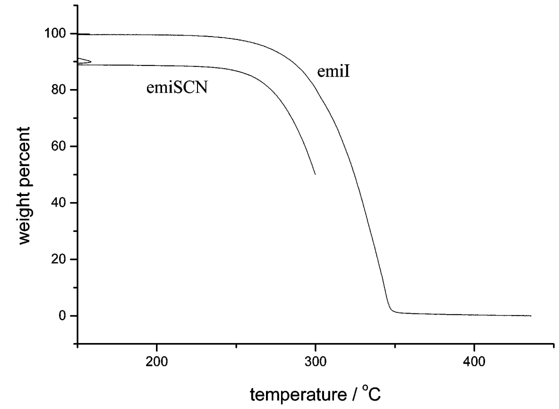

Fig. 3 TGA plots for emiI and emiSCN. Heating of the thiocyanate salts was halted before complete decomposition to avoid the possible formation of any cyanide species.

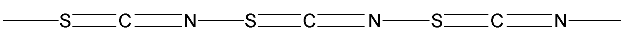

Fig. 4 The structure of polythiocyanogen.

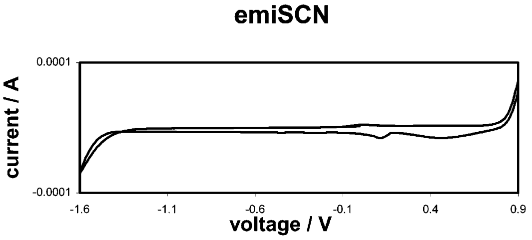

Fig. 5 The cyclic voltammogram of emiSCN.

Cyclic voltammetry

The cyclic voltammogram of emiSCN (Fig. 5) shows that the species is electrochemically stable down to −1.4 V and up to 0.8 V *vs.* Ag/Ag^+. This is a small electrochemical window compared to those of other ionic liquids such as $bmiPF_6$, largely due to the electrochemical instability of the anion. This is thought to be related to the pseudohalide behaviour of the anion, oxidation producing the neutral dimeric species $(SCN)_2$, as discussed above. A change of cation to pyrrolidinium results in an increase in the size of the electrochemical window (Fig. 6), with the cation electrochemically stable down to −2.7 V, although the anion stability remains unchanged. However, even the imidazolium thiocyanate salt displays an

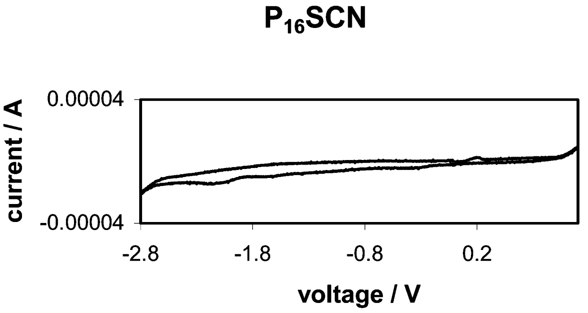

Fig. 6 The cyclic voltammogram of $P_{16}SCN$.

electrochemical window large enough to be effective for a range of electrochemical applications and the low melting points of the thiocyanate salts is a further benefit for such applications. Future work will include conductivity measurements and investigations into the electrochemical and ion conduction applications of these new ionic liquids.

Crystal structure of $P_{11}SCN$

In an attempt to investigate the structural arrangement of the cations and anions within the solid-state structure of the pyrrolidinium thiocyanate materials, the crystal structure of $P_{11}SCN$ was analysed. This is the first reported structure of a pyrrolidinium thiocyanate compound.

Crystals of the compound were formed as colourless needles on cooling a dichloromethane solution at approximately −20 °C and analysis at 123 K revealed discrete cation and anion pairs [Fig. 7(a)] with a linear [178.9(1)°] thiocyanate anion. The unit cell is composed of eight anions and eight cations, and each thiocyanate anion is surrounded by eight pyrrolidinium cations. Interaction of the cation and anion was assessed by counting close-contact distances between atoms that lie within the sum of their van der Waals radii, *i.e.* C–H···N interactions less than 2.7 Å and C–H···S interactions less than 3.05 Å. Using these criteria, there are four close contacts between the pyrrolidinium hydrogens and the thiocyanate nitrogen atom, but only two to the sulfur atom (Table 3). Two of the C–H···N interactions are to ring hydrogens and two are to hydrogens on the methyl groups. The packing arrangement within the structure [Fig. 7(b)] shows a layered structure, with the thiocyanate anion aligned alternately SCN then NCS along the *c* axis. The shortest anion to anion N–S interaction is 4.633 Å in length, which is significantly longer than the sum of the van der Waals radii. The S–C–N bond lengths are comparable to those reported for structures containing similar, uncoordinated thiocyanate anions.[19]

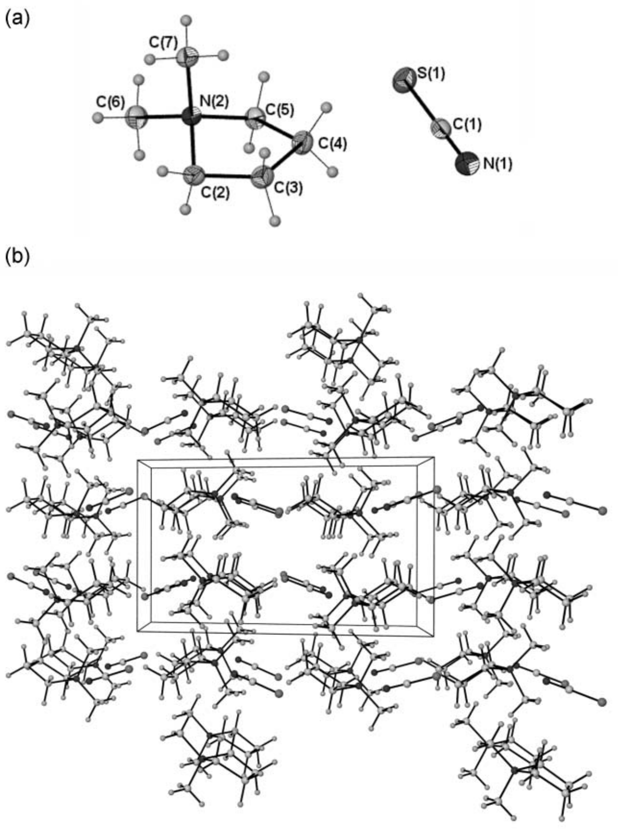

Fig. 7 (a) The discrete ion pair in $P_{11}SCN$ (30% thermal ellipsoids). (b) Packing arrangement within $P_{11}SCN$ viewed along the *a* axis.

Table 3 Close contacts between the pyrrolidinium cation and the thiocyanate anion in the solid-state structure of $P_{11}SCN$

Interaction	Distance/Å
N(1)–H(7B)	2.552
N(1)–H(6B)	2.649
N(1)–H(5B)	2.680
N(1)–H(5A)	2.692
S(1)–H(7C)	3.004
S(1)–H(3B)	3.006

Table 4 Comparison of the three *N*,*N*-dimethylpyrrolidinium species analysed by X-ray crystallography. For the purposes of comparison, a close contact is defined as less than the sum of the van der Waals radii of the two atoms

	M.p./°C	No. of close contacts	Shortest anion–cation distance/Å
$P_{11}I$[13]	250 (dec)	10	3.02(2) (C–H···I)
$P_{11}TFSA$[25]	120	3	2.31(2) (C–H···O)
$P_{11}SCN$	85–105	6	2.55(2) (C–H···N)

Comparison of the solid-state structure of this species with those of the other dimethylpyrrolidinium species that have been characterised by X-ray crystallography allows investigation into the effect of structure on the physical properties, such as melting point. The solid-state structure of $P_{11}I$, $P_{11}TFSA$ and $P_{11}SCN$ have been compared (Table 4), and analysis suggests that there are two main factors that influence the melting point of the compounds, but the relative importance of these is unclear.

The packing of the anion and cation has an effect, as would be expected, with a larger anion such as iodide, which is closer in size to the P_{11} cation, allowing more efficient packing and, thus, producing a higher melting point than the relatively small thiocyanate anion. It is probably also the packing efficiency that is most significantly affected by the utilisation of an asymmetric cation or anion, as recently demonstrated by Matsumoto *et al.*[20] with [2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl) acetamide (CF_3SO_2–N^-–$COCF_3$)], which lowers the melting point of the P_{11} species to 24 °C, compared to 120 °C for $P_{11}TFSA$. However, the effect of the reduced anion weight and less potential hydrogen bond donors should also be considered. The observation that this new anion has the opposite effect on the melting point of the emi species also highlights the complexity of the structure–property relationship.

The second major factor determining the melting points of the species is the degree of anion–cation contact, with respect to both the strength and number of interactions. Within the iodide salt, each anion has ten close contacts to each cation, a reflection of the increased size of the anion, but the length of all of these separations approach the van der Waals limits. By comparison, each TFSA anion within the P_{11}TFSA structure shows only three close contacts to surrounding cations. The separations within this structure are shorter, but still approaching the van der Waals limits for the atoms involved. In comparison, the smaller thiocyanate species displays more interactions, but has a lower melting point, possibly suggesting that the strength and number of the interactions is not sufficient to overcome the effect of poor packing. Thus, analysis of the relationship between the structure and physical properties of these salts shows a fine balance between a number of influencing factors. However, it is evident that the route to low melting point ionic liquids lies in the utilisation of small, asymmetric anions with a diffuse charge to minimise anion–cation interactions.

Solid-state properties

In common with many other pyrrolidinium salts, the thiocyanates have rich thermal behaviour in the solid state, with several phases being displayed in the solid-state region and a substantial fraction of the entropy of the liquid already being present in the phase I state. This has previously been associated with rotator motions of the cation and, in some cases, the anion as well. The SCN^- anion should rotate easily about its long axis, and such a motion may well be present at quite low temperatures. It would not have any significant effect on the crystallographic solution. The remaining solid-state transitions and the low entropy of fusion in the P_{11}SCN and P_{12}SCN cases therefore appear to be associated with motions of the cation, as has been observed in several other salts of these particular cations. emiSCN and P_{13}SCN do not show such behaviour, which may be due to the fact that these compounds supercool and melt at relatively low temperatures, thereby supressing any possible low temperature transitions. The difference in the phase behaviour between the structurally similar emi and P_{12} cations may reflect the lower electrostatic interactions generated by the partially delocalised charge in the emi cation.

Conclusion

Synthesis and analysis of a new species of ionic liquid based on the thiocyanate anion are described, particularly with regard to the pyrrolidinium cation. The ionic liquids produced show particularly low melting points and good thermal stability. The crystal structure of P_{11}SCN is described and shows a linear thiocyanate anion surrounded by eight pyrrolidinium cations. Future work on these new ionic liquids will include further investigation into the phase behaviour of these compounds and measurement of their conductivity across these different phases.

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