

Crystal and liquid crystalline polymorphism in 1-alkyl-3-methylimidazolium tetrachloropalladate(II) salts

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1-Alkyl-3-methylimidazolium tetrachloropalladate(II) salts ($[C_n\text{-mim}]_2[\text{PdCl}_4]$, $n = 10, 12, 14, 16, 18$) containing a single, linear alkyl-chain substituent on the cation have been synthesised and their behaviour characterised by differential scanning calorimetry, polarising optical microscopy and small-angle X-ray scattering. The salts display thermotropic polymorphism, exhibiting both crystal-crystal transitions and, for $n = 14-18$, the formation of a thermotropic smectic liquid crystalline phase.

Introduction

Amphiphilic ionic salts have many applications beyond their use as surfactants.¹ Most studies have focused on the solid state structure of these materials; current areas of interest include templating mesoporous materials,² the formation of ordered films³ and as ionic liquid crystals.⁴ By incorporating metal-containing groups into the salts, ionic metallomesogens⁵ can be formed, which offer the potential to develop materials with novel properties (for example, polarisability, redox behaviour, chirality and magnetism) into 1- and 2-dimensionally structured materials.⁶ Metal-containing moieties can be introduced as either the mesogenic unit⁷ or as the counter ion.^{8,9}

Room temperature ionic liquids, comprising an organic cation and a weakly coordinating anion,¹⁰ are of current interest as solvents for clean, green chemical synthesis,¹¹ in separation technology¹² and in the preparation of new materials.¹³ Such ionic liquids are usually 1-alkyl-3-methylimidazolium salts, with an ethyl- or butyl-substituent on the cation. By increasing the amphiphilic character of the cation through substitution with longer, linear alkyl groups, ionic liquid crystals may be obtained¹⁴ with mesomorphic properties that resemble those of the related and well known *N*-alkylammonium salts¹⁵ and aromatic heterocyclic systems,^{8,16,17} which form lamellar phases with a smectic bilayer structure.¹⁵ The salts studied exhibit many of the properties of the ionic liquids, and include a degree of orientational order which may make them viable as ordered media for catalysis.¹⁸

We have studied a wide range of 1-alkyl-3-methylimidazolium ($[C_n\text{-mim}]^+$) salts with metal-containing anions ($[\text{NiCl}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$, etc.): the salts have relatively low melting points, close to room temperature¹⁹ when the alkyl-chain length is small ($n < 10$), and display liquid crystal mesomorphism when $n > 12$.¹⁴ As part of an on-going investigation of these metallate salts^{20,21} and their role as catalysts in ionic liquid systems, we have prepared and studied

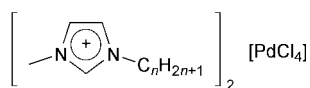


Fig. 1 1-Alkyl-3-methylimidazolium tetrachloropalladate(II) salts, $[C_n\text{-mim}]_2[\text{PdCl}_4]$ ($n = 10, 12, 14, 16, 18$).

the properties of 1-alkyl-3-methylimidazolium tetrachloropalladate(II) salts, $[C_n\text{-mim}]_2[\text{PdCl}_4]$ ($n = 10-18$, see Fig. 1) as a function of alkyl-chain length. These salts have been shown to act as catalysts or catalyst precursors when dissolved in ionic liquid solvents for the hydrodimerisation of butadiene²² and for the Heck coupling reaction.²¹ The crystal structures of the short alkyl-chain salts, $[C_2\text{-mim}]_2[\text{PdCl}_4]$ ²³ and $[C_4\text{-mim}]_2[\text{PdCl}_4]$ ²² have recently been reported and the related, mesomorphic *N*-alkylpyridinium tetrahalopalladate(II) salts,^{8,24} have also been described.

Experimental

All reagents and solvents were obtained from Aldrich and used as received except for 1-methylimidazole, which was distilled under reduced pressure from calcium hydride prior to use. Microanalyses were performed by A.S.E.P. (Queen's University of Belfast). Infrared spectra were recorded as Nujol mulls between KBr plates using a Perkin Elmer 1600 and a BioRad FTS-185 infrared spectrometer. ¹H and ¹³C NMR spectra in CDCl₃ solution were recorded on a Bruker WM500 spectrometer, relative to tetramethylsilane as an internal standard, at room temperature.

Optical observations were made by heated-stage polarising optical microscopy (POM) using an Olympus BX50 microscope equipped with a Linkam TH600 hot stage and TP92 temperature controller. The phase transition temperatures were determined by differential scanning calorimetry (DSC) using a Perkin Elmer Pyris 1 DSC equipped with cryostat cooling using 5–10 mg samples and operating with a scanning rate of 5 °C min⁻¹ on both heating and cooling cycles.

Small angle X-ray scattering (SAXS) experiments were carried out at the SRS in Daresbury, UK, on beamline 8.2. Data were obtained from powdered samples in sealed 1 mm glass Lindemann tubes using a monochromated (1.54 Å) X-ray beam. A multiwire quadrant detector was used with a camera length of 0.95 m, effective range 8–190 Å. Heating was achieved using a Linkam hot stage. The detector was calibrated using silver behenate.²⁵ The samples were heated and cooled at 6 °C min⁻¹ and data were collected in 12 s frames. Data reduction and analysis, correcting for background scattering,

Table 1 Compounds synthesised with % yield and relevant micro-analytical data

Salt	Yield (%)	Analysis found (calc.)		
		C	H	N
[C ₁₀ -mim] ₂ [PdCl ₄]	84	48.21 (48.39)	7.81 (7.83)	8.08 (8.06)
[C ₁₂ -mim] ₂ [PdCl ₄]	78	51.32 (51.17)	8.43 (8.32)	7.44 (7.46)
[C ₁₄ -mim] ₂ [PdCl ₄]	75	53.32 (53.57)	8.88 (8.74)	6.86 (6.94)
[C ₁₆ -mim] ₂ [PdCl ₄]	76	55.66 (55.65)	9.37 (9.11)	6.45 (6.49)
[C ₁₈ -mim] ₂ [PdCl ₄]	81	57.66 (57.48)	9.68 (9.43)	6.09 (6.09)

transmission and detector response, were carried out using XOTOKO.²⁶

The tetrachloropalladate(II) salts were prepared in high yields (see Table 1) on reaction of palladium(II) chloride with two equivalents of the respective 1-alkyl-3-methylimidazolium chloride[†] salt under reflux in acetonitrile using the method employed by Dupont and co-workers previously for the preparation of [C₄-mim]₂[PdCl₄]²² and Neve *et al.* for long chain *N*-alkylpyridinium tetrahalopalladate(II) salts.⁸ The procedure was identical in each case, and is described below for [C₁₂-mim]₂[PdCl₄] as a representative example. All salts were characterised using infrared, ¹H and ¹³C NMR spectroscopy, CHN analysis and differential scanning calorimetry. The palladium-containing salts prepared, yields and CHN analyses are shown in Table 1.

1-Dodecyl-3-methylimidazolium tetrachloropalladate(II), [C₁₂-mim]₂[PdCl₄]

1-Dodecyl-3-methylimidazolium chloride (2.32 g, 8.1 mmol) was dissolved in acetonitrile (80 cm³). Palladium(II) chloride (0.71 g, 4.0 mmol) was added to the solution and the mixture was heated at reflux under dinitrogen for 3 h. The hot solution was filtered and the reaction mixture was concentrated to *ca.* half-volume under reduced pressure. Cooling to room temperature afforded orange-brown microcrystals of [C₁₂-mim]₂[PdCl₄] (2.35 g, 78%). $\nu_{\max}/\text{cm}^{-1}$ 3133, 3093 (s, aromatic C–H stretch), 2927, 2850 (s, aliphatic C–H stretch), 1746 (w), 1626 (w), 1561, 1470 (s, symmetric ring stretch), 1430, 1377, 1360, 1336 (m), 1161 (s), 1099 (m), 846, 830, 753, 720 (m), 623 (s); $\delta_{\text{H}}/\text{ppm}$ (CDCl₃) 10.08 (1H, s), 7.76 (1H, s), 7.51 (1H, s), 4.44 (2H, t, *J* 7.35 Hz), 4.29 (3H, s), 1.91 (2H, m), 1.27 (18H, m), 0.85 (3H, t, *J* 6.9 Hz); $\delta_{\text{C}}/\text{ppm}$ (CDCl₃) 137.69 (C₂), 123.81, 121.86 (C_{4/5}), 50.30 (N-CH₂), 37.29 (N-CH₃), 31.87, 30.42, 29.59, 29.53, 29.41, 29.30, 29.07, 26.31, 22.64, 14.08 (-CH₃).

All the salts were collected as microcrystalline powders (*n*=10–14) or thin orange-brown plates (*n*=16,18) upon concentration and cooling the reaction mixture. All efforts to obtain crystals suitable for single crystal X-ray structure analysis proved unsuccessful.

The salts obtained were solvent-free and could be stored indefinitely in air. Spectroscopic methods confirmed the presence of the organic cation; the infrared spectra (4000–650 cm⁻¹) displayed characteristic bands from the imidazolium cation and confirm the purity of the salts by the absence of both $\nu(\text{C}\equiv\text{N})$ stretching bands, which would indicate the presence of acetonitrile co-crystallised with the salt, and bands due to water. The spectroscopic data did not change significantly between the different salts, except in the relative intensity of bands related to the alkyl-chain -CH₂ groups.

[†]1-Alkyl-3-methylimidazolium chlorides were prepared by alkylation of 1-methylimidazole with the corresponding chloroalkane and were recrystallised from 1,1,1-trichloroethane yielding crystalline solids which were collected by filtration and stored under nitrogen.

Results

Thermal data

The thermal properties of the salts were investigated using hot-stage polarising optical microscopy and DSC. Transition temperatures and assignments are shown in Table 2 from the temperature peak positions to the nearest degree from the first and second heating cycles, and are shown graphically in Fig. 2.

All the reported salts (*n*=10, 12, 14, 16, 18) showed thermotropic polymorphism; for *n*=10 and 12, the salts only displayed solid–solid transitions whereas the longer-chain salts (*n*=14–18) also exhibited a liquid crystalline phase before clearing to isotropic liquids. Similar enthalpies were calculated for all the crystal–crystal and crystal–isotropic/mesophase transitions as shown by the similar endotherms in Fig. 3 for [C₁₄-mim]₂[PdCl₄] and summarised in Table 2.

In all cases, except *n*=18, an initial crystal–crystal transition is observed by DSC between 55 and 80 °C. This transition is not reversible, but is reproducible for independently prepared samples. On further heating, all the salts (*n*=10–18) show a reversible crystal–crystal transition, observed using both DSC and optical microscopy between 70–111 °C (see Fig. 2). The salts, *n*=10 and 12, melt from the Cr'' phase to the isotropic liquid whereas the higher homologues (*n*=14–18) show an enantiotropic liquid crystalline phase on melting from Cr''. These reversible transitions (*i.e.* Cr'–Cr'', Cr''–isotropic and Cr''–mesophase) are confirmed by polarising optical microscopy. The Cr'–Cr'' transition is observed under crossed polarisers as a colour change from predominantly yellow to a deep red; there is no indication of a change in the macroscopic structure of the crystallites. A viscous mesophase is observed following the melting transition, and is characterised by extensive homeotropic, pseudoisotropic regions and low birefringence oily streaks on deformation of the mesophase. This is indicative of a smectic A mesophase (S_A).²⁷

The tetradecyl-substituted salt (*n*=14) clears from the liquid crystalline phase to an isotropic liquid, whereas the higher homologues (*n*=16, 18) show extensive decomposition associated with the clearing transition, with the deposition of palladium-containing solids. However, if the decomposition temperature is not reached, then all the lower temperature transitions are fully reversible, with the exception of the initial crystal–crystal transition as noted above. It is worth noting that the temperatures of all the solid–solid transitions vary only slightly with *n*, whereas the clearing point is strongly dependent on *n*.

Small angle X-ray scattering data

From the polarising optical microscopy, the appearance of the mesophase indicates that for each mesomorphic salt, the liquid crystal phase has the same symmetry and is a smectic A phase. To confirm this assignment and to gain a better understanding of the temperature dependence of the structural changes, the thermal behaviour of the salts has been studied by variable temperature small-angle X-ray scattering.

All the salts display a similar sequence of phase changes, with corresponding discontinuous changes in the positions of the peaks (see Table 3) in SAXS patterns. The changes in the diffraction pattern for [C₁₄-mim]₂[PdCl₄] are described below as a representative example (see Fig. 4 and 5). Fig. 4 shows the time-resolved SAXS data obtained for [C₁₄-mim]₂[PdCl₄] during the heating and cooling cycle (ramp rate 6 °C min⁻¹, data collected in 12 s frames). Intensity is plotted against temperature and the scattering angle 2θ where $\lambda = 1.54 \text{ \AA}$. The lamellar layer spacing is given by $d = \lambda/2\sin\theta$ from the Bragg equation, where 2θ is the position of the first order diffraction peak.

From the SAXS pattern, it can be seen that the room temperature crystalline phase of [C₁₄-mim]₂[PdCl₄] exhibits a

Table 2 Transition temperatures ($T/^\circ\text{C}$) for $[\text{C}_n\text{-mim}]_2[\text{PdCl}_4]$ salts (enthalpy/ kJ mol^{-1} in parentheses) determined by DSC from the first and second (italics) heating cycles. For the salts with $n=16, 18$, data from the second heating cycle were collected after heating to 170°C on the first cycle

n	Cr	Cr'	Cr''	S_A	Iso
10	• 58 (14.6)	• 72 (11.2)	• 93 (11.9)		•
	•	• 71 (12.7)	• 91 (11.4)		•
12	• 65 (19.3)	• 91 (22.2)	• 111 (18.2)		•
	•	• 91 (20.9)	• 111 (17.6)		•
14	• 78 (16.1)	• 100 (18.8)	• 123 (16.1)	• 175 (0.4)	•
	•	• 100 (15.6)	• 119 (11.1)	• 176 (0.4)	•
16	• 77 (30.5)	• 108 (36.2)	• 126 (25.2)	• 190 (dec)	•
	•	• 106 (33.6)	• 124 (22.6)	• 190 (dec)	•
18	•	• 111 (38.4)	• 123 (21.8)	• 192 (dec)	•
	•	• 111 (37.1)	• 122 (18.7)	• 192 (dec)	•

lamellar structure with a periodicity of 52.1 \AA (Fig. 5a), characterised by two strong diffraction peaks (001, 002) in the small angle region. Both peaks have approximately the same intensities. The weaker peak at *ca.* 8.25° in 2θ , which corresponds to 10.6 \AA , is associated with the $[\text{PdCl}_4]^{2-}$ to $[\text{PdCl}_4]^{2-}$ anion correlation distance.^{8,24} This phase is stable and shows no temperature dependence until 78°C . Above 78°C , the irreversible transition described above, occurs. The high temperature phase (Cr') has a significantly smaller layer spacing (35.2 \AA) than Cr, characterised by a single, intense peak (001) in the small angle region and a shift in the peak associated with the anion–anion correlation distance from 10.6 \AA to 8.7 \AA . At 100°C , the salt undergoes a crystal–crystal transition to the Cr'' phase, indicated by a small increase in the layer spacing to 37.2 \AA and loss of the higher angle reflection. Melting to the liquid crystal S_A phase at 123°C is accompanied by a contraction in the layer spacing to 30.3 \AA , with a marked decrease in intensity and broadening of the 001 peak. As shown by the DSC, the two higher phase transitions (Cr'–Cr'' and Cr''– S_A) are fully reversible on cooling. As described above, the small angle diffraction peaks correspond to an ordered layered structure. The decrease in the layer spacing on forming the liquid crystalline phase is indicative of alkyl-chain melting and, in combination with the texture observed by POM, supports the assignment of the phase as smectic A.²⁷

Discussion

All these palladium-containing salts ($[\text{C}_n\text{-mim}]_2[\text{PdCl}_4]$, $n=10\text{--}18$) are polymorphic, exhibiting reversible and irreversible solid–solid and liquid crystalline transitions. The melting points are generally higher than those observed for monovalent

1-alkyl-3-methylimidazolium salts with simple inorganic anions (Cl^- , $[\text{BF}_4]^-$, $[\text{PF}_6]^-$ etc.) but are comparable with those obtained for other divalent tetrachlorometallate salts ($[\text{CoCl}_4]^{2-}$ or $[\text{NiCl}_4]^{2-}$). The general trends follow those found for other ionic liquid crystals, especially those containing cationic mesogenic units. A greater degree of crystal–crystal polymorphism is found for the tetrachloropalladate(II) salts than is found for 1-alkyl-3-methylimidazolium salts with simple inorganic anions.^{9,14}

The layer spacing in the Cr phase at room temperature for $n=10\text{--}16$ is, in each case, approximately twice the molecular length (L) of the fully extended cation (for $n=14$; $d=52.1 \text{ \AA}$ and $L=26 \text{ \AA}$, based on molecular models), and is therefore likely to indicate a lamellar, bilayer structure with no alkyl-chain interdigitation.

The large decrease in the periodic unit ($\sim 30\%$) to give a layer spacing of $d \approx 1.5 L$, following the first heating transition is clearly a result of a significant crystalline rearrangement and is likely to be the result of the alkyl-chains tilting relative to the layer normal, or becoming interdigitated. This rearrangement also causes the $[\text{PdCl}_4]^{2-}\text{--}[\text{PdCl}_4]^{2-}$ correlation distance to decrease. In the published X-ray crystal structures of amphiphilic dialkylimidazolium salts^{14,17} the alkyl-chains are both interdigitated and tilted from the layer normal. It is likely that both are present in Cr' given that the layer spacings determined for the S_A phases are only slightly larger than the length of the imidazolium cation, which indicates that the mesophase contains fully interdigitated alkyl-chains.

For all salts ($n=10\text{--}18$), the reversible crystal–crystal transition (Cr'–Cr'') has the largest enthalpy (calculated from DSC measurements), indicating a large change in structure. However, this transition is characterised by only a small increase in the interlayer spacing ($\sim 5\%$) and loss of $[\text{PdCl}_4]^{2-}\text{--}[\text{PdCl}_4]^{2-}$ correlation. The large enthalpy change on the

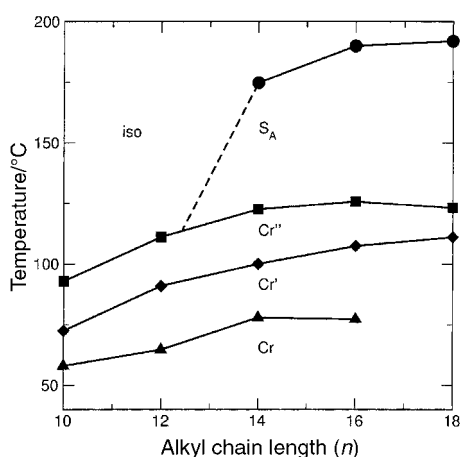


Fig. 2 Phase behaviour of 1-alkyl-3-methylimidazolium tetrachloropalladate(II) salts, $[\text{C}_n\text{-mim}]_2[\text{PdCl}_4]$ ($n=10\text{--}18$), on heating as a function of alkyl-chain length (n); showing melting point (■) and clearing point (●) for the liquid crystalline examples, and reversible (◆) and irreversible (▲) crystal–crystal transitions.

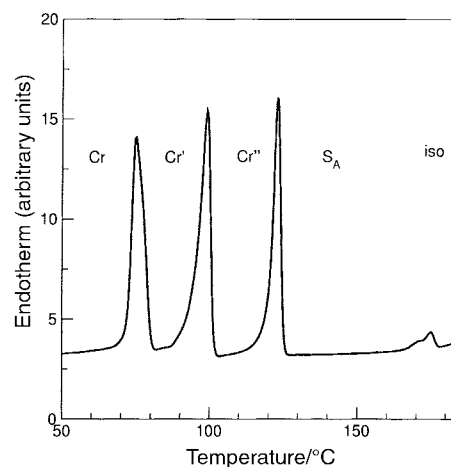


Fig. 3 DSC of $[\text{C}_{14}\text{-mim}]_2[\text{PdCl}_4]$ recorded at $10^\circ\text{C min}^{-1}$ between 50 and 190°C in the first heating cycle showing Cr, Cr', Cr'', S_A and isotropic phase regions.

Table 3 Interlayer spacing ($d/\text{\AA}$) of the crystalline and smectic phases of $[\text{C}_n\text{-mim}]_2[\text{PdCl}_4]$ salts at given temperatures, $T/^\circ\text{C}$

n	$T/^\circ\text{C}$	$d/\text{\AA}(\text{Cr})$	$d/\text{\AA}(\text{Cr}')$	$d/\text{\AA}(\text{Cr}'')$	$d/\text{\AA}(\text{S}_A)$
10	50	39.0			
	65		24.3		
	80			25.5	
12	50	47.1			
	85		31.9		
	95			33.0	
14	50	50.1			
	85		35.2		
	110			37.2	
16 ^a	140				30.3
	50	55.8	37.6		
	85		37.6		
18	110			39.9	
	140				33.2
	50		41.1		
	120			43.4	
	140				35.4

^aBiphasic, contains both Cr and Cr'.

transition is likely to be the result of anion disordering, indicated by the loss of the anion–anion correlation peak and corresponds to breaking of C–H...[PdCl₄] hydrogen bonds on heating.

The initial Cr–Cr' transition was not observable by POM, despite the significant change in the d -spacing determined from the SAXS data. The Cr'–Cr'' transition was observed as a colour change in the salts from yellow to red and may be associated with the changes in the *in-plane* [PdCl₄]²⁻ to [PdCl₄]²⁻ correlation and local structure.

The two, non-mesomorphic salts ($n=10, 12$) display the same changes in layer spacing for the Cr–Cr' and Cr'–liquid transitions. In the longest alkyl-chain salt ($n=18$) the initial phase observed is the Cr' phase *i.e.* no initial irreversible transition. For $n=16$, the salt contains both Cr and Cr' phases initially. The layer spacings for each phase region as a function of n are shown in Fig. 6; the monotonic increase in d with n confirms the correlation of the phases between the salts and shows the identification of the initial structure of $n=18$ as the Cr' phase observed in the other salts.

The stability of the lower temperature crystal phase (Cr) with respect to the Cr' phase decreases with increasing chain length. Based on the crystal structures and data from X-ray powder diffraction¹⁴ and thin-film reflectivity studies,²⁸ the periodic layer-spacings for most amphiphilic 1-alkyl-3-methylimidazolium salts have values where $2L > d > L$. The initial crystalline phase (Cr) identified for the palladium salts ($n=10$ – 16) may therefore be considered as unusual and is clearly formed as a function of the crystal growth process from solution as distinct

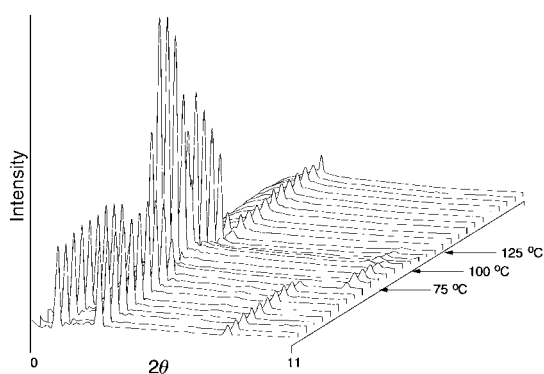


Fig. 4 Time resolved relief diagram of SAXS data obtained for the melting and recrystallisation cycle (heating and cooling at 6°C min^{-1}) for $[\text{C}_{14}\text{-mim}]_2[\text{PdCl}_4]$. Intensity is plotted against temperature and the scattering angle 2θ ($\lambda=1.54 \text{\AA}$).

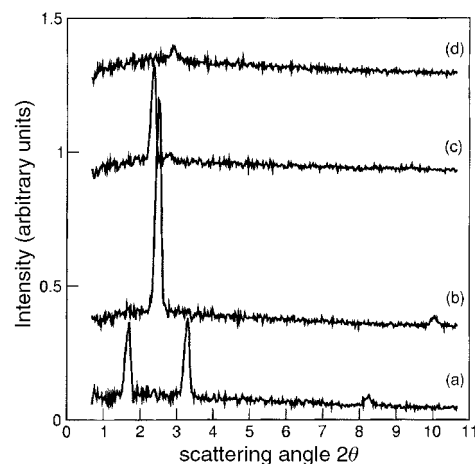


Fig. 5 Variable temperature SAXS patterns of $[\text{C}_{14}\text{-mim}]_2[\text{PdCl}_4]$ from the first heating cycle. (a) $T=50^\circ\text{C}$; (b) $T=85^\circ\text{C}$; (c) $T=110^\circ\text{C}$; (d) $T=140^\circ\text{C}$. Intensity is plotted against the scattering angle 2θ ($\lambda=1.54 \text{\AA}$).

from crystallisation from the melt. As described in the Experimental section, in all cases, solvent was not observed in the crystalline salts (from CHN analysis, ¹H, ¹³C NMR or infrared spectroscopy), this precludes the possibility that the Cr–Cr' transition represents elimination of solvent from the crystals.

The mesomorphic salts ($n=14$ – 18) display a wide mesophase range, compared with the analogous *N*-alkylpyridinium tetrachloropalladate(II) salts⁸ studied by Neve and co-workers. This can be ascribed to the destabilisation of the crystal phases, relative to the *N*-alkylpyridinium salts through reduced packing efficiency which leads to lower melting points and an enhanced mesophase range. It seems likely that both Coulombic and hydrogen-bonding interactions play an important role in stabilisation of the phases formed by these salts and that both structure-building interactions and microphase separation (driven by the *hydrophobic* effect²⁹) have important contributions to the polymorphism observed.

Conclusions

A series of 1-alkyl-3-methylimidazolium tetrachloropalladate(II) salts have been studied. The salts display thermal polymorphism including both crystal–crystal and crystal–liquid crystalline transitions with layered phases in each case. The thermotropic mesophase was identified as a fully

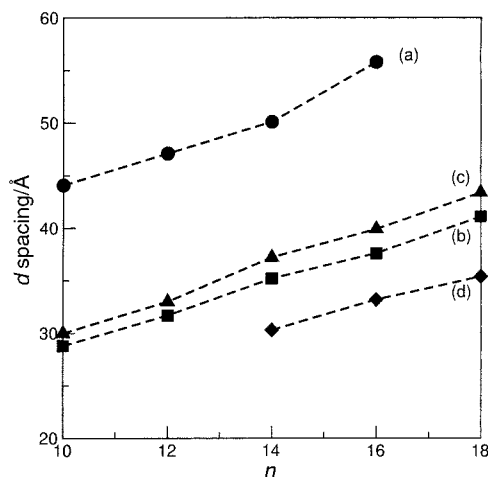


Fig. 6 Layer spacings ($d/\text{\AA}$) as a function of n for the salts $[\text{C}_n\text{-mim}]_2[\text{PdCl}_4]$ in each of the phase regions (a) Cr; (b) Cr'; (c) Cr''; (d) S_A.

interdigitated smectic A phase. The change in layer-spacing in each of the phases has been measured using variable temperature SAXS and indicates that the initial crystalline phase obtained varies with chain-length. The salts with $n = 10$ – 14 have a non-interdigitated bilayer structure, whereas $n = 18$ crystallised with a layered structure containing a significantly lower layer-spacing. The intermediate salt, $n = 16$, crystallised as a mixture of the two phases. The transformation Cr'–Cr'', common to all the salts studied has the highest enthalpy in each case. This transition probably corresponds to the breaking of C–H...[PdCl₄]²⁻ hydrogen bonds on heating. The Cr''–S_A/isotropic transition corresponds to alkyl-chain melting.

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