

Effects of alkyl chain length and anion size on thermal and structural properties for 1-alkyl-3-methylimidazolium hexafluoro complex salts ($C_x\text{MImAF}_6$, $x = 14, 16$ and 18 ; $A = \text{P, As, Sb, Nb}$ and Ta)[†]

Fei Xu, Kazuhiko Matsumoto* and Rika Hagiwara

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A series of 1-alkyl-3-methylimidazolium hexafluoro complex salts ($C_x\text{MImAF}_6$, $x = 14, 16$ and 18 , $A = \text{P, As, Sb, Nb}$ and Ta) have been characterized by thermal analysis, X-ray diffraction and polarized optical microscopy. A liquid crystalline mesophase is observed for all the $C_{16}\text{MIm}$ and $C_{18}\text{MIm}$ salts. The $C_{14}\text{MIm}^+$ cation gives a liquid crystalline mesophase only with PF_6^- . The temperature range of the liquid crystalline mesophase increases with an increase in alkyl chain length or with decrease in anion size. Single-crystal X-ray diffraction revealed that all the $C_{18}\text{MImAF}_6$ salts ($A = \text{P, As, Sb, Nb}$ and Ta) are isostructural with each other in the crystalline phase and have a layered structure. The interdigitated alkyl chain of the cation has a bent shape like a spoon near the imidazolium ring in the crystalline phase at -100 °C and is tilted with respect to the sheets of the imidazolium headgroups and anions. An increase of temperature increases the ratio of an all-*trans* conformation to the bent conformation in the crystalline phase. X-ray diffraction and polarized optical microscopy suggested that the liquid crystalline mesophase has a smectic A_2 structure. The interlayer distance increases with a decrease in the anion size since the smaller anion has a stronger coulombic interaction with the imidazolium headgroup, resulting in the decrease of the interdigitated part to give a larger layer spacing.

Introduction

Ionic liquid crystals (ILCs) are composed of only ionic species and have anisotropic structural organizations.¹ This makes them attractive as one-dimensional^{2–4} or two-dimensional^{5–7} ion-conduction materials to move a specific ion, as well as anisotropic reaction media. Ionic liquids are attracting more and more attention as functional materials because of their unique characteristics such as wide liquid temperature range, negligible vapor pressure and non-flammability.⁸ Because of the widespread use of imidazolium-based ionic liquids with low melting points and low viscosities, imidazolium-based ILCs are frequently studied.⁹ Thermal behavior of ILCs based on imidazolium cations with functional groups depends on the number of mesogenic units, mesogenic promoter and the counteranion.¹⁰ Although a variety of functional groups, such as a cholesterol group, were coupled with the imidazolium cation to form liquid crystalline

mesophases,¹⁰ ILCs based on an imidazolium cation with a simple alkyl chain are common in previous reports which examine the effects of the alkyl chain and the anion on the physical properties. A series of 1-alkyl-3-methylimidazolium cations ($C_x\text{MIm}^+$) with long alkyl chains were combined with various anions such as chloride (Cl^-),¹¹ bromide (Br^-),¹² tetrachlorometallate (MCl_4^- , $M = \text{Co}$ and Ni),¹¹ trifluoromethylsulfonate ($\text{OSO}_2\text{CF}_3^-$),¹² tetrafluoroborate (BF_4^-)¹³ and hexafluorophosphate (PF_6^-).¹⁴ The temperature range of the mesophase observed for these salts increases with increasing alkyl chain length, although the alkyl chain length where the liquid crystalline mesophase appears depends on the anionic species.

Although the $C_x\text{MImPF}_6$ -type ILCs were studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray diffraction (XRD),¹⁴ other $C_x\text{MImAF}_6$ ($\text{AF}_6^- = \text{hexafluoro complex anion}$) ILCs were not. Liquid crystalline mesophase appears with $x = 14$ in the case of $C_x\text{MImPF}_6$ and the temperature range of the mesophase rapidly increases with increase in x . The cations of $C_{12}\text{MImPF}_6$ and $C_{14}\text{MImPF}_6$ in the crystalline phase show a “spoon-like” shape with the alkyl chains interdigitated to form nonpolar layers, separating the polar layers made up of imidazolium headgroups and anions.^{14–16} In this study, a series of $C_x\text{MImAF}_6$ salts ($x = 14, 16$ and 18 , $A = \text{P, As, Sb, Nb}$ and Ta) were synthesized and characterized by DSC, POM and XRD to systematically investigate effects of the alkyl chain length and anion size on their thermal and structural properties.

Graduate School of Energy Science, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan. E-mail: k-matsumoto@energy.kyoto-u.ac.jp

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Table 1 Summary of DSC for $C_x\text{MImAF}_6$ ($x = 14, 16$ and 18 , $A = \text{P, As, Sb, Nb}$ and Ta)

x	A	Transition ^a	$T/^\circ\text{C}$	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
14	P	cryst-iso	65.1	33.1	97.8
		cryst-SmA ₂ ^b	67.4	36.5	107.3
		SmA ₂ -iso ^b	73.0	0.4	1.3
	As	cryst-iso	64.8	34.0	100.7
	Sb	cryst-iso	56.8	32.4	98.2
	Nb	cryst-iso	56.0	31.4	95.6
16	P	cryst-SmA ₂	75.2	30.1	86.4
		SmA ₂ -iso	124.8	0.5	1.3
	As	cryst-SmA ₂	74.8	36.5	105.0
		SmA ₂ -iso	104.3	0.6	1.5
	Sb	cryst-SmA ₂	67.5	33.1	97.3
		SmA ₂ -iso	77.0	0.4	1.2
18	P	cryst-SmA ₂	66.9	33.0	97.2
		SmA ₂ -iso	77.0	0.5	1.3
	Ta	cryst-SmA ₂	66.3	33.0	97.3
		SmA ₂ -iso	75.5	0.4	1.2
	As	cryst-SmA ₂	79.9	47.5	134.6
		SmA ₂ -iso	164.0	1.1	2.6
Sb	cryst-SmA ₂	78.1	46.3	131.9	
	SmA ₂ -iso	142.8	0.9	2.2	
Nb	cryst-SmA ₂	74.5	36.8	106.0	
	SmA ₂ -iso	117.9	0.7	1.7	
Ta	cryst-SmA ₂	74.2	31.3	90.1	
	SmA ₂ -iso	116.9	0.7	1.9	
	Ta	cryst-SmA ₂	74.0	36.7	105.8
		SmA ₂ -iso	115.4	0.7	1.8

^a A scan rate of 5 °C min⁻¹ was used. The abbreviations, cryst, iso and SmA₂ denote crystal, isotropic liquid and smectic A₂ liquid crystal, respectively. ^b These transitions were determined from DSC recorded at 0.5 °C min⁻¹.

Results and discussion

Thermal properties

All the obtained salts are white hydrophobic solids at room temperature and only $C_x\text{MImNbF}_6$ is gradually hydrolyzed in air even at room temperature. The AF_6^- anion is best identified by IR and Raman spectroscopy (Experimental section and Fig. S1–S6†).¹⁷ Table 1 summarizes the DSC data (phase transition

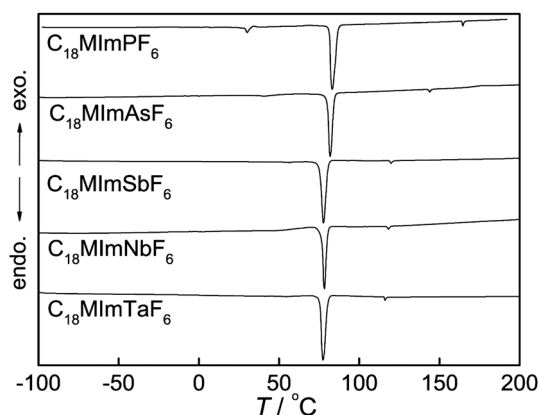


Fig. 1 Differential scanning calorimetric curves (heating process) for $C_{18}\text{MImAF}_6$ ($A = \text{P, As, Sb, Nb}$ and Ta).

temperature, ΔH and ΔS) for all the $C_x\text{MImAF}_6$ salts. Fig. 1 shows the DSC curves of $C_{18}\text{MImAF}_6$. Two endothermic peaks are observed in all the cases. The peaks at the lower and higher temperatures correspond to the melting point (from crystal to liquid crystal) and the clearing point (from liquid crystal to isotropic liquid), respectively. The relatively large ΔH (and thus ΔS) on melting indicates a large structural change, namely, the break-up of a three-dimensionally ordered crystal lattice. The small ΔH (and thus ΔS) on clearing is mainly caused by the break-up of van der Waals interactions between the alkyl chains, which is reflected in the increase of ΔH (and thus ΔS) for clearing with the increase in x for the same anion. Similar phenomena are also observed for ILCs of $C_x\text{MImCl}$, $C_x\text{MImBr}$, $C_x\text{MImBF}_4$ and $C_x\text{MIm}(\text{FH})_2\text{F}$.^{12–14,18} Either a small peak ($C_{18}\text{MImPF}_6$) or a broad peak ($C_{18}\text{MImAF}_6$, $A = \text{As, Sb, Nb}$ and Ta) is observed in the crystalline phase below the melting point, which is probably ascribed to a conformational change of the alkyl chains (see the section of crystal structures below). An endothermic peak corresponding to the clearing point is also observed in the thermograms of $C_{16}\text{MImAF}_6$ (Fig. S11, ESI†), proving all the $C_{16}\text{MImAF}_6$ salts give liquid crystalline mesophases, although the temperature range of liquid crystal is quite narrow (~ 10 °C) for $C_{16}\text{MImSbF}_6$, $C_{16}\text{MImNbF}_6$ and $C_{16}\text{MImTaF}_6$. The clearing point was not observed for $C_{14}\text{MImAF}_6$ (Fig. S10, ESI†) in the heating process at a scan rate of 5 °C min⁻¹. It is noteworthy that a small exothermic peak was observed for $C_{14}\text{MImPF}_6$ at 69.7 °C during the cooling process (Fig. 2). This transition temperature is nearly the same as that for the melting in the heating process and they seem to overlap. The lower scan rate of 0.5 °C min⁻¹ confirmed the liquid crystalline mesophase (Fig. 2, inset) although the transition temperature was slightly lower than those reported in the previous work.¹⁴ The other four $C_{14}\text{MImAF}_6$ ($A = \text{As, Sb, Nb}$ and Ta) salts did not exhibit liquid crystalline mesophase even during the cooling process.

Fig. 3 shows the melting and clearing points of $C_x\text{MImAF}_6$ as a function of the carbon number x and the radius of the central atom of AF_6^- .¹⁹ Both the melting and clearing points increase with the increase in x or the decrease in the size of the anion. The larger temperature dependence of the clearing point than that of the melting point results in an increase in the temperature

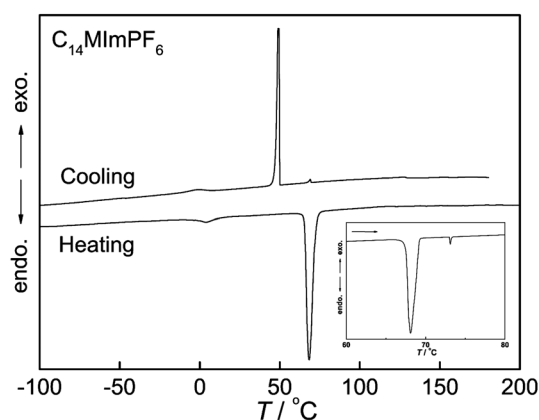


Fig. 2 Differential scanning calorimetric curves of heating and cooling processes for $C_{14}\text{MImPF}_6$ at 5 °C min⁻¹ and heating process at 0.5 °C min⁻¹ (inset).

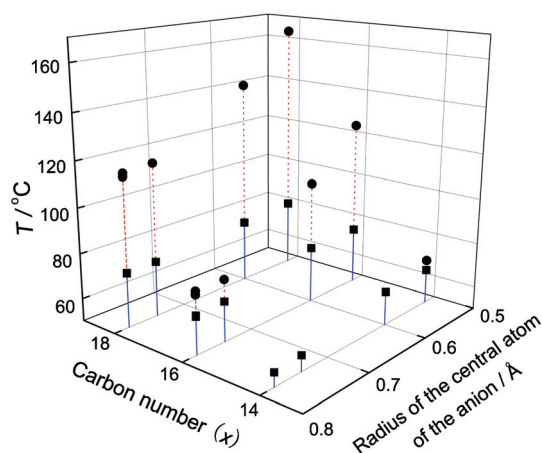


Fig. 3 Melting points (■) and clearing points (●) observed in the DSC thermogram of $C_x\text{MImAF}_6$ ($x = 14, 16$ and 18 , $A = \text{P, As, Sb, Nb}$ and Ta).

range of the liquid crystalline mesophase with an increase in x or a decrease in the size of anion. The increase of melting point against x can be explained by an increase of the van der Waals interactions between the alkyl chains, which leads to clearer separation of polar (imidazolium headgroup and anion) and non-polar (long alkyl chain) regions.¹³ When the size of AF_6^- is changed with a fixed cationic structure, the difference in temperature dependence of melting and clearing points reflects the strength of the interaction between the imidazolium headgroup and the anion. These trends suggest both the van der Waals interaction between the alkyl chains and the electrostatic interaction between the cation and anion have an effect to stabilize the liquid crystalline mesophase. This also explains the phenomenon

that the alkyl chain length where liquid crystalline mesophases are observed depends on the anionic species in the cases of $C_x\text{MIm}$ salts.^{11–14,18} Compared with symmetric N,N' -dialkylimidazolium salts with long alkyl chains, $C_x\text{MIm}$ salts show different thermal behavior, probably due to the weaker van der Waals interactions based on the different number of long alkyl chains.^{20–22} For PF_6^- salts, both the melting and clearing points decrease by introducing another long alkyl chain (melting and clearing points of $\text{C}_{16}\text{MImPF}_6$ are 75.2 and 124.8 °C and melting and clearing points of $\text{C}_{16}\text{C}_{16}\text{ImPF}_6$ are 61.3 and 103.3 °C).²² Another example, PdCl_4^{2-} salts, gives a different trend; melting and clearing points decrease and increase respectively, by introducing another long alkyl chain (melting and clearing points of $(\text{C}_{16}\text{MIm})_2(\text{PdCl}_4)$ are 124 and 190 °C and melting and clearing points of $(\text{C}_{16}\text{C}_{16}\text{Im})_2\text{PdCl}_4$ are 94.9 and 214.6 °C).^{20,21}

Structural properties

The five kinds of $\text{C}_{18}\text{MImAF}_6$ salts are isostructural with each other since the cation with a long alkyl chain dominates crystal packing, although a slight increase in cell volume is observed with increasing anion size. This is in contrast with a series of EMIm salts, where the PF_6^- , AsF_6^- and SbF_6^- salts belong to a monoclinic cell (space group: $P2_1/c$) and the NbF_6^- and TaF_6^- salts belong to an orthorhombic cell (space group: $P2_12_12_1$).²³ The crystal structure of $\text{C}_{18}\text{MImTaF}_6$ at -100 °C, which is shown in Fig. 4, is described as a typical case. The packing mode of $\text{C}_{18}\text{MImAF}_6$ is described as a layered structure of polar and non-polar domains. The sheets consisting of the imidazolium headgroups and TaF_6^- anions (polar domains) are separated by interdigitated alkyl chains (non-polar domains) tilted relative to the polar domain (Fig. 4(a)). The polar domain is made of a

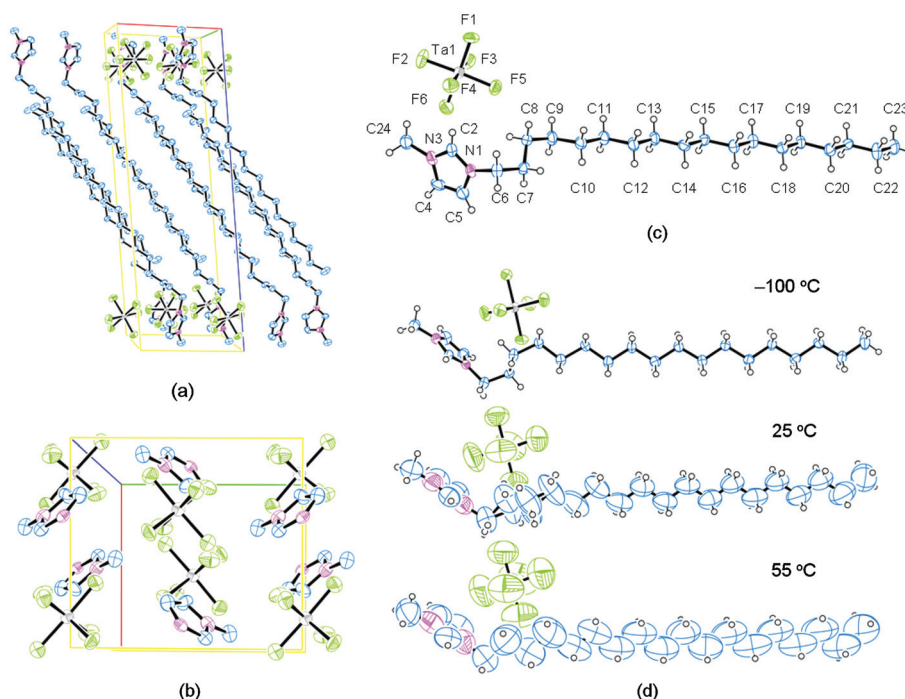


Fig. 4 Crystal structure of $\text{C}_{18}\text{MImTaF}_6$. (a) Packing diagram at -100 °C, (b) configuration of the imidazolium headgroup and TaF_6^- in the polar region at -100 °C, (c) asymmetric unit with atom numbering scheme at -100 °C, (d) structures of $\text{C}_{18}\text{MIm}^+$ and TaF_6^- at $-100, 25$ and 55 °C.

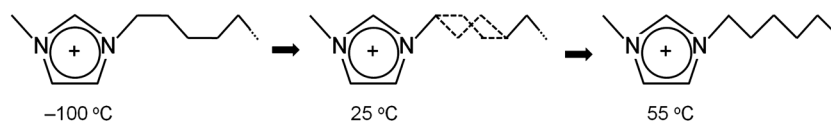


Fig. 5 Schematic drawing of structural changes for the octadecyl chain of $C_{18}MImAF_6$ at -100 , 25 and 55 °C.

double layer of a NaCl-type ion configuration, where one of the two layers is not lying on the other in the ideal manner for a NaCl-type structure (Fig. 4(b)). The alkyl chain keeps a *trans* conformation from C8 to C23 and is bent near the imidazolium ring like a spoon (Fig. 4(c) and (d)), as was reported for $C_{12}MImPF_6$ and $C_{14}MImPF_6$.^{14–15}

Crystal structures were also determined at 25 and 55 °C for all the five $C_{18}MImAF_6$ salts (see Fig. 4(d) for the asymmetric unit). Although the overall cation–anion configurations at -100 , 25 and 55 °C are similar to each other, the carbon atoms in the octadecyl chain are significantly disordered near the imidazolium ring at 25 and 55 °C and it was hard to solve the structure completely. The atomic displacement parameters become large as the temperature increases, especially for the C7, C8, C9 and C10 atoms. Although a slight sign of disordering was observed for the fluorine atoms in AF_6^- , the structure of AF_6^- was solved as a non-disordered octahedron in this study. Although a similar structural change was reported for $C_{14}MImPF_6$ between -98 and 27 °C, the present diffraction studies at 25 and 55 °C propose a more detailed model. The best model obtained is shown as a schematic illustration in Fig. 5. The octadecyl chain which has a bent conformation at -100 °C adopts an all-*trans* conformation at 55 °C, whereas the electron density map obtained at 25 °C suggests mixing of the all-*trans* and bent conformations. This result suggests that the *trans* conformation is preferred near the melting point and the ratio of the *trans* conformation to the bent conformation becomes larger as the temperature increases. The solid–solid phase transition observed in the crystalline phase seems to result from such structural changes. It is notable that the ratios of the two conformers at 25 °C are different in the five cases and the solid–solid transition temperature is dependent on the anion size. Packing of the ions at low temperatures is tighter than those at or above room temperature, which is reflected in the increase in tilt angle of the alkyl chains with regard to the polar sheet. Since the imidazolium head groups and the anions are connected by ionic interactions in the polar sheet and the alkyl chains are connected with each other by van der Waals interactions in the nonpolar sheet, such an increase of tilt angle leads to a conformation change of C7, C8, C9 and C10 atoms.

Sharper changes of some cell parameters, especially β , are observed between 25 and 55 °C (Tables S1 and S2, ESI†) compared with those between -100 and 25 °C, which are in good accordance with the crystal–crystal phase transition temperatures observed from the DSC results. Comparison of the crystal structures between $C_{12}MImPF_6$, $C_{14}MImPF_6$ and $C_{18}MImPF_6$ also gives interesting information on cell parameters (note: the data collection temperatures are -150 °C for $C_{12}MImPF_6$,¹⁴ -98 °C for $C_{14}MImPF_6$ ¹⁵ and -100 °C for $C_{18}MImPF_6$). The a and b cell parameters, corresponding to cation–cation (or anion–anion) distances within the NaCl-type layer, do not show a significant change, whereas the c cell parameter increases as the alkyl chain length increases (Fig. 6) and the alkyl–alkyl interdigitated part

always roughly starts from C9 regardless of the alkyl chain length. The difference in the overlapped alkyl chain length (12.947 Å, 15.497 Å and 20.617 Å for $x = 12$, 14 and 18 , Table S3, ESI†) directly corresponds to the number of the methylene group added.

Fig. 7 shows the cell parameters (a , b and c) of $C_{18}MImAF_6$ ($A = P, As, Sb, Nb$ and Ta) at -100 °C. On increasing the anion size, the a parameter shows a very small change and the b parameter slightly increases, leading to an increase of the area in the ionic sheets. The c parameter remains nearly constant for the PF_6 , AsF_6 and SbF_6 salts and becomes smaller for the NbF_6 and TaF_6 salts, in spite of the larger sizes of NbF_6^- and TaF_6^- . The value of $c \times \sin\beta$, which is the distance between the layers, decreases with increasing anion size (Table S4, ESI†), with the

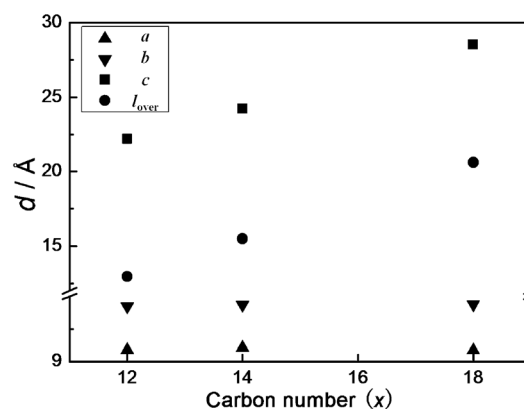


Fig. 6 Cell parameters (a , b and c) for $C_{12}MImPF_6$, $C_{14}MImPF_6$ and $C_{18}MImPF_6$. The overlapped alkyl chain length (l_{over}) is also plotted (see Table S3† for calculation of l_{over}). Data collection temperature: -150 °C for $C_{12}MImPF_6$,¹⁴ -98 °C for $C_{14}MImPF_6$ ¹⁵ and -100 °C for $C_{18}MImPF_6$ (present study).

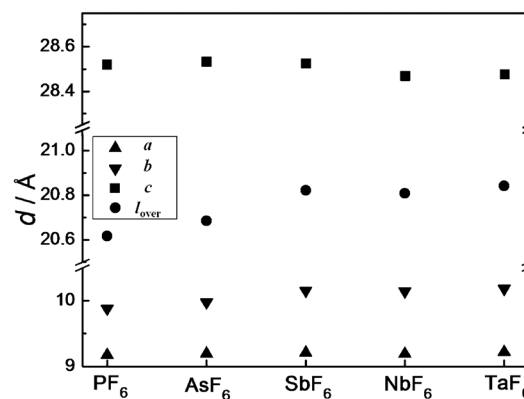


Fig. 7 Cell parameters (a , b and c) for $C_{18}MImAF_6$ ($A = P, As, Sb, Nb$ and Ta) at -100 °C. The overlapped alkyl chain length (l_{over}) is also plotted (see Table S4† for calculation of l_{over}).

only exception of SbF_6^- . The overlapped alkyl chain length also increases with increasing anion size (Fig. 7 and Table S4, ESI†). This observation means the alkyl chains interdigitate more deeply as the anion becomes larger, which is probably due to the weaker cation–anion interaction and the larger alkyl chain inter-spacing caused by the larger anion.

Table 2 lists C–H...F interactions for $\text{C}_{18}\text{MimTaF}_6$. All F atoms are involved in short contacts (below the sum of van der Waals radii) with H atoms of the imidazolium ring (F1, F2, F3 and F5), or those of the alkyl side-chains (F1, F4, F6). Bifurcation of the C–H...F bonds is observed for H atoms (H2 and H4) which interact with two F atoms (F1 and F5, F1 and F2, respectively) of TaF_6^- . Similar phenomena were also observed for the other $\text{C}_{18}\text{MimAF}_6$ salts (A = P, As, Sb and Nb).

Fig. 8 shows a polarized optical microscopic (POM) texture of $\text{C}_{18}\text{MimTaF}_6$ which is typical of all the C_xMimAF_6 ILCs (see Figures S12–S14, ESI† for the other salts) and characterized by spontaneous formation of smooth fan-like or focal conic textures. The broken fan-like texture, which is indicative of the smectic C mesophase, was not observed in the liquid crystalline mesophase on cooling from the isotropic phase to the crystalline mesophase. This suggests the absence of the smectic C

mesophase in these systems.^{24–25} These POM results combined with the XRD study later, suggest that the liquid crystalline mesophase of C_xMimAF_6 ILCs is assigned to a smectic A mesophase.^{1,11,13–14,18} Such an enantiotropic smectic A liquid crystalline mesophase was also observed for other 1-alkyl-3-methylimidazolium ILCs in previous reports, since the large cation dominates formation of the smectic layer.^{11–14,18}

Fig. 9 and 10 show the XRD patterns ($2^\circ < 2\theta < 30^\circ$) of the crystalline phase and liquid crystalline mesophase for $\text{C}_{18}\text{MimAF}_6$, respectively. In both the phases, sharp peaks are observed in the low-angle region, indicating formation of layered structures, and no peak was found in the region lower than 2.0° . The similar crystal structures of $\text{C}_{18}\text{MimAF}_6$ result in the similar 2θ -angle for the sharp peaks in the XRD pattern of the crystalline phase (see Figs. S15 and S16, ESI†, for $\text{C}_{14}\text{MimAF}_6$ and $\text{C}_{16}\text{MimAF}_6$). Absence of additional peaks in the high-angle region in the cases of liquid crystals suggests the loss of positional ordering within the layer plane, which fits the characteristics of a smectic A mesophase. Small peaks around 5.0° were observed for $\text{C}_{18}\text{MimAF}_6$ and $\text{C}_{16}\text{MimPF}_6$ and were indexed as the (002) diffraction of the smectic layers (Fig. 10 and S17†). Measurements of the patterns of the liquid crystalline mesophase

Table 2 The C–H...F interaction geometries (Å, °) in $\text{C}_{18}\text{MimTaF}_6$

D–H...A	D–H	H...A	D...A	$\angle D\text{–H...A}$
C2–H2 ^a ...F1	0.930	2.598	2.978	105.07
C4–H4 ^b ...F1	0.930	2.586	3.326	136.80
C24–H24 ^a ...F1	0.960	2.605	3.113	113.35
C4–H4 ^b ...F2	0.930	2.633	3.425	143.32
C5–H5 ^c ...F3	0.930	2.357	3.211	152.51
C6–H6 ^b ...F4	0.970	2.634	3.440	140.65
C8–H8 ^a ...F4	0.970	2.700	3.352	124.96
C23–H23 ^b ...F4	0.960	2.691	3.620	163.06
C2–H2 ^d ...F5	0.930	2.458	3.093	125.59
C6–H6 ^a ...F6	0.970	2.462	3.398	161.92
C7–H7 ^a ...F6	0.970	2.615	3.579	172.15

Symmetry codes: ^a $-1 + x, y, z$. ^b $-x, -y, -z$. ^c $-1 - x, -y, 1 - z$. ^d $-1/2 + x, -1/2 - y, z$. ^e $-1/2 + x, 1/2 - y, z$.

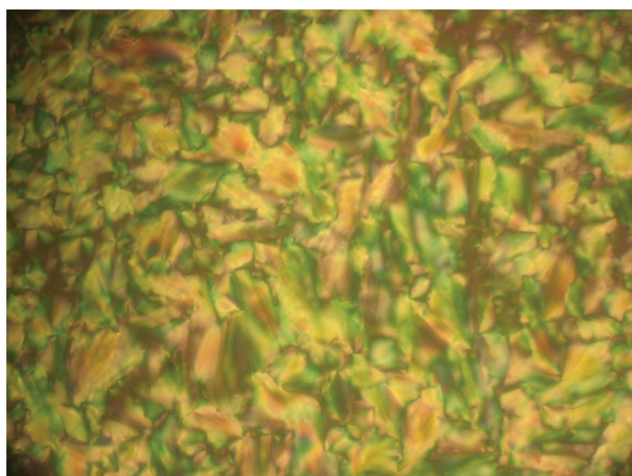


Fig. 8 Polarized optical microscopic texture of $\text{C}_{18}\text{MimTaF}_6$ at 100°C .

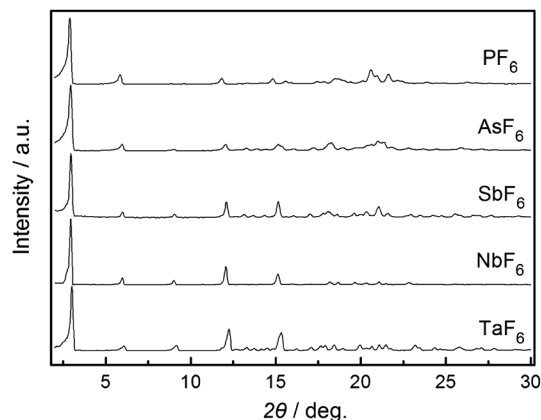


Fig. 9 X-ray diffraction patterns for $\text{C}_{18}\text{MimAF}_6$ (A = P, As, Sb, Nb and Ta) in the crystalline phase (40°C).

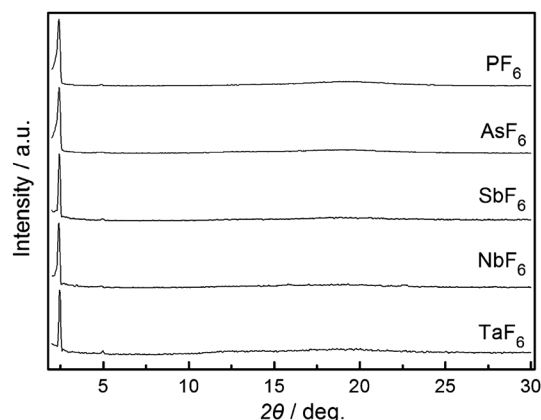


Fig. 10 X-ray diffraction patterns for $\text{C}_{18}\text{MimAF}_6$ (A = P, As, Sb, Nb and Ta) in the liquid crystalline mesophase (100°C).

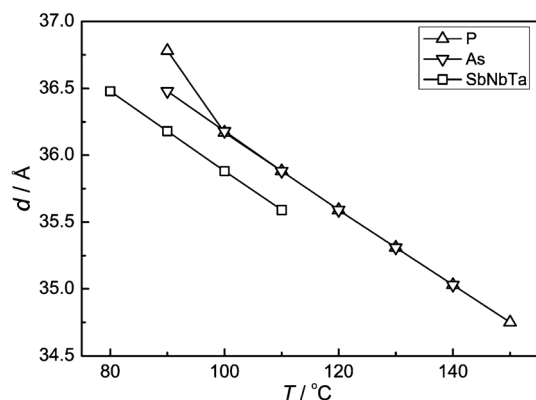


Fig. 11 Layer spacings of $C_{18}MImAF_6$ ($A = P, As, Sb, Nb$ and Ta) in the liquid crystalline mesophase.

were difficult for $C_{16}MImSbF_6$, $C_{16}MImNbF_6$ and $C_{16}MImTaF_6$ due to the relatively narrow temperature range of their mesophases.

Fig. 11 shows the layer spacing (d) of $C_{18}MImAF_6$ in the liquid crystalline mesophase as a function of temperature. The layer spacing d is found to satisfy $l < d < 2l$, where l is the fully extended length of the cation, which indicates an interdigitated bilayer structure is formed in the smectic A liquid crystalline mesophase (smectic A_2).^{12,18} The layer spacing decreases with an increase in temperature, which is also indicative of a smectic A_2 mesophase.^{12,18} To our knowledge, all the 1-alkyl-3-methylimidazolium ILCs known today show the same type of liquid crystalline mesophase of smectic A_2 , since the bulky cation is much larger than the anion and dominates the type of mesophase for such ILCs.^{12–14,18} The layer spacing for PF_6^- and AsF_6^- is larger than that for SbF_6^- , NbF_6^- and TaF_6^- , which can be explained by changes in the cation–anion interactions within the polar region. The bilayer structure interdigitates more deeply with decreasing cation–anion interaction due to the increase of thermal mobility of the cations, leading to a decrease of the layer spacing. An increase of the AF_6^- anion size results in a longer cation–anion distance and weaker cation–anion interactions, which facilitates the interdigitation of the alkyl chains and leads to the smaller layer spacing. The same trend observed in the crystal structure as shown above, also supports this explanation. Similar phenomena were also observed for $C_{16}MImPF_6$ and $C_{16}MImAsF_6$ (Fig. S18, ESI†).

Conclusions

Thermal and structural properties of 1-alkyl-3-methylimidazolium hexafluoro-complex salts, C_xMImAF_6 ($x = 14, 16$ and 18 , $A = P, As, Sb, Nb$ and Ta), were investigated. These salts exhibit a liquid crystalline mesophase with a smectic A structure. The temperature range of the mesophase increases with increasing alkyl chain length or decreasing anion size, suggesting both the van der Waals interactions between the alkyl chains and the electrostatic interaction between the imidazolium headgroup and the anion have an effect on stabilization of the liquid crystalline mesophase. X-ray crystallography revealed that all five $C_{18}MImAF_6$ salts have the same layered structure where the non-polar layers of interdigitated alkyl chains and the polar layers of

the imidazolium headgroup and the anion alternate with each other. The octadecyl chain of $C_{18}MIm^+$ in the $C_{18}MImAF_6$ crystal structure at -100 °C has a bent structure, which changes into a *trans* conformation as temperature increases. The layer spacing (d) in the liquid crystalline mesophases satisfies the relation of $l < d < 2l$ (l is the fully extended length of the cation) and monotonously decreases with increasing temperature, indicative of a smectic A_2 interdigitated bilayer structure. The layer spacing in the mesophase decreases with increasing anion size, due to the decrease of cation–anion interactions within the polar region.

Experimental section

Apparatus and materials

Volatile materials were handled in a vacuum line constructed of SUS316 stainless steel and PFA (tetrafluoroethylene-perfluoro-alkylvinylether copolymer). Nonvolatile materials were handled under a dry Ar atmosphere in a glove box. Acetone (Wako Chemicals, 99.5%) and dichloromethane (Aldrich, 99.8%) were used as purchased. The 1-alkyl-3-methylimidazolium chlorides, C_xMImCl ($x = 14, 16$ and 18), were prepared by reactions of 1-methylimidazole (Aldrich, 99%) and equimolar quantities of the corresponding chloroalkanes (1-chlorotetradecane (Aldrich, 98%), 1-chlorohexadecane (Wako Chemicals, 95%), 1-chlorooctadecane (Wako Chemicals, 95%)) at temperatures between 70 and 100 °C for several days. Purification of the chlorides was performed by dissolving the chloride salts in acetonitrile (dehydrated, Wako Chemicals, 99%) and then precipitating from the solution by adding ethyl acetate (dehydrated, Wako Chemicals, 99.5%). The hexafluoro-complex salts (KPF_6 (Wako Chemicals), $NaAsF_6$ (Aldrich), $KSbF_6$ (Aldrich, 99%)) were used as purchased. Potassium fluoride (Wako chemicals, 99%) was dried under vacuum at 180 °C for a few days before use. Anhydrous HF (Daikin Industries) was dried over K_2NiF_6 prior to use. Niobium pentafluoride (NbF_5 , Aldrich, 99%) and tantalum pentafluoride (TaF_5 , Furuuchi Chemical Corp., 99.5%) were used as purchased. The two potassium salts, $KNbF_6$ and $KTaF_6$, were prepared by the reaction of KF and the corresponding metal pentafluorides in HF according to the previous report.^{23,26} The white powder obtained was dried under dynamic vacuum at 70 °C.

Synthesis of $C_{14}MImPF_6$

The two starting materials, $C_{14}MImCl$ (3.150 g, 10.00 mmol) and KPF_6 (2.024 g, 11.00 mmol), were dissolved in water (30 mL) and the mixture was stirred vigorously overnight. A slight excess of KPF_6 was used for the thorough removal of Cl^- . The solid product was separated from the mixture by centrifugation and the remaining water-soluble species were washed with water several times. Testing for the presence of residual chloride impurities in the water phase with 1 M $AgNO_3$ aqueous solution gave no precipitation of $AgCl$. The product was dried under vacuum at room temperature and then at 80 °C (3.574 g, 8.420 mmol). Anal. Calcd. for $C_{18}H_{35}N_2F_6P_1$: C, 50.94; H, 8.25; N, 6.60; F, 26.89. Found: C, 50.77; H, 8.34; N, 6.72; F, 26.94. Raman (frequency/ cm^{-1} (relative intensity)): 741(s)

(PF₆⁻, ν₁), 566(w) (PF₆⁻, ν₂), 471(m) (PF₆⁻, ν₃). IR (frequency/cm⁻¹ (relative intensity)): 847(w) (PF₆⁻, ν₃), 556(s) (PF₆⁻, ν₄) (see S1–S6† for the vibrational spectra of C_xMImAF₆). Here, s, m and w for relative intensity denote strong, medium and weak, respectively.

Synthesis of C₁₆MImPF₆

The same procedure as for C₁₄MImPF₆ was used. Anal. Calcd. for C₂₀H₃₉N₂F₆P₁: C, 53.10; H, 8.63; N, 6.19; F, 25.22. Found: C, 52.98; H, 8.55; N, 6.35; F, 25.44. Raman (frequency/cm⁻¹ (relative intensity)): 742(s) (PF₆⁻, ν₁), 565(w) (PF₆⁻, ν₂), 471(m) (PF₆⁻, ν₃). IR (frequency/cm⁻¹ (relative intensity)): 847(w) (PF₆⁻, ν₃), 554(s) (PF₆⁻, ν₄).

Synthesis of C₁₈MImPF₆

The same procedure as for C₁₄MImPF₆ was used. Anal. Calcd. for C₂₂H₄₃N₂F₆P₁: C, 55.00; H, 8.96; N, 5.83; F, 23.75. Found: C, 54.76; H, 9.01; N, 5.94; F, 23.67. Raman (frequency/cm⁻¹ (relative intensity)): 741(s) (PF₆⁻, ν₁), 568(w) (PF₆⁻, ν₂), 471(m) (PF₆⁻, ν₃). IR (frequency/cm⁻¹ (relative intensity)): 845(w) (PF₆⁻, ν₃), 554(s) (PF₆⁻, ν₄).

Synthesis of C₁₄MImAsF₆

The same procedure as for C₁₄MImPF₆ was used. Anal. Calcd. for C₁₈H₃₅N₂F₆As₁: C, 46.15; H, 7.48; N, 5.98; F, 24.36. Found: C, 46.06; H, 7.42; N, 5.96; F, 24.18. Raman (frequency/cm⁻¹ (relative intensity)): 678(s) (AsF₆⁻, ν₁), 575(w) (AsF₆⁻, ν₂), 368(m) (AsF₆⁻, ν₃). IR (frequency/cm⁻¹ (relative intensity)): 693(m) (AsF₆⁻, ν₃).

Synthesis of C₁₆MImAsF₆

The same procedure as for C₁₄MImPF₆ was used. Anal. Calcd. for C₂₀H₃₉N₂F₆As₁: C, 48.39; H, 7.86; N, 5.65; F, 22.98. Found: C, 48.36; H, 7.65; N, 5.68; F, 23.21. Raman (frequency/cm⁻¹ (relative intensity)): 678(s) (AsF₆⁻, ν₁), 573(w) (AsF₆⁻, ν₂), 369(m) (AsF₆⁻, ν₃). IR (frequency/cm⁻¹ (relative intensity)): 695(m) (AsF₆⁻, ν₃).

Synthesis of C₁₈MImAsF₆

The same procedure as for C₁₄MImPF₆ was used. Anal. Calcd. for C₂₂H₄₃N₂F₆As₁: C, 50.38; H, 8.21; N, 5.34; F, 21.76. Found: C, 50.09; H, 8.20; N, 5.37; F, 21.74. Raman (frequency/cm⁻¹ (relative intensity)): 678(s) (AsF₆⁻, ν₁), 573(w) (AsF₆⁻, ν₂), 368(m) (AsF₆⁻, ν₃). IR (frequency/cm⁻¹ (relative intensity)): 698(s) (AsF₆⁻, ν₃).

Synthesis of C₁₄MImSbF₆

The same procedure as for C₁₄MImPF₆ was unsuccessful for the synthesis of C₁₄MImSbF₆ since addition of C₁₄MImCl and KSbF₆ into water gave a gel-like solution, making the separation of the product difficult. Instead of this method, the following procedure was used for the SbF₆ salts; the two starting materials,

C₁₄MImCl (3.150 g, 10.00 mmol) and KSbF₆ (2.886 g, 10.50 mmol), were dissolved in 30 mL of acetone and the mixture was stirred vigorously overnight. The solution was separated from the mixture by centrifugation and the acetone was removed under vacuum at room temperature. Testing for the presence of residual chloride impurities with a 1 M AgNO₃ aqueous solution gave no precipitation of AgCl. The product was dissolved in 20 mL of dichloromethane and the mixture was stirred vigorously overnight. The dichloromethane solution was separated from the precipitate (probably the potassium salt) by centrifugation and dichloromethane was removed under vacuum at room temperature initially and then at 80 °C for 3 days. Anal. Calcd. for C₁₈H₃₅N₂F₆Sb₁: C, 41.94; H, 6.80; N, 5.44; F, 22.14. Found: C, 41.84; H, 6.76; N, 5.44; F, 21.94. Raman (frequency/cm⁻¹ (relative intensity)): 645(s) (SbF₆⁻, ν₁), 280(m) (SbF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 654(m) (SbF₆⁻, ν₃).

Synthesis of C₁₆MImSbF₆

The same procedure as for C₁₄MImSbF₆ was used. Anal. Calcd. for C₂₀H₃₉N₂F₆Sb₁: C, 44.20; H, 7.18; N, 5.16; F, 20.99. Found: C, 44.20; H, 7.14; N, 5.25; F, 20.88. Raman (frequency/cm⁻¹ (relative intensity)): 645(s) (SbF₆⁻, ν₁), 570(w) (SbF₆⁻, ν₂), 280(m) (SbF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 656(m) (SbF₆⁻, ν₃).

Synthesis of C₁₈MImSbF₆

The same procedure as for C₁₄MImSbF₆ was used. Anal. Calcd. for C₂₂H₄₃N₂F₆Sb₁: C, 46.23; H, 7.53; N, 4.90; F, 19.96. Found: C, 46.07; H, 7.37; N, 4.86; F, 19.72. Raman (frequency/cm⁻¹ (relative intensity)): 645(s) (SbF₆⁻, ν₁), 571(w) (SbF₆⁻, ν₂), 280(m) (SbF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 654(m) (SbF₆⁻, ν₃).

Synthesis of C₁₄MImNbF₆

The same procedure as for C₁₄MImSbF₆ was used. Anal. Calcd. for C₁₈H₃₅N₂F₆Nb₁: C, 44.44; H, 7.20; N, 5.76; F, 23.46. Found: C, 44.56; H, 7.37; N, 5.79; F, 23.26. Raman (frequency/cm⁻¹ (relative intensity)): 681(s) (NbF₆⁻, ν₁), 285(m) (NbF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 608(w) (NbF₆⁻, ν₃).

Synthesis of C₁₆MImNbF₆

The same procedure as for C₁₄MImSbF₆ was used. Anal. Calcd. for C₂₀H₃₉N₂F₆Nb₁: C, 46.69; H, 7.59; N, 5.45; F, 22.18. Found: C, 46.90; H, 7.76; N, 5.50; F, 21.92. Raman (frequency/cm⁻¹ (relative intensity)): 681(s) (NbF₆⁻, ν₁), 284(m) (NbF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 604(w) (NbF₆⁻, ν₃).

Synthesis of C₁₈MImNbF₆

The same procedure as for C₁₄MImSbF₆ was used. Anal. Calcd. for C₂₂H₄₃N₂F₆Nb₁: C, 48.71; H, 7.93; N, 5.17; F, 21.03. Found: C, 49.00; H, 8.07; N, 5.26; F, 20.92. Raman (frequency/cm⁻¹ (relative intensity)): 681(s) (NbF₆⁻, ν₁), 285(m) (NbF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 606(m) (NbF₆⁻, ν₃).

Synthesis of C₁₄MImTaF₆

The same procedure as for C₁₄MImSbF₆ was used. Anal. Calcd. for C₁₈H₃₅N₂F₆Ta₁: C, 37.63; H, 6.10; N, 4.88; F, 19.86. Found: C, 37.66; H, 6.02; N, 4.88; F, 19.60. Raman (frequency/cm⁻¹ (relative intensity)): 693(s) (TaF₆⁻, ν₁), 290(m) (TaF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 573(w) (TaF₆⁻, ν₃).

Synthesis of C₁₆MImTaF₆

The same procedure as for C₁₄MImSbF₆ was used. Anal. Calcd. for C₂₀H₃₉N₂F₆Ta₁: C, 39.87; H, 6.48; N, 4.65; F, 18.94. Found: C, 39.70; H, 6.25; N, 4.70; F, 19.09. Raman (frequency/cm⁻¹ (relative intensity)): 693(s) (TaF₆⁻, ν₁), 287(m) (TaF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 575(w) (TaF₆⁻, ν₃).

Synthesis of C₁₈MImTaF₆

The same procedure as for C₁₄MImSbF₆ was used. Anal. Calcd. for C₂₂H₄₃N₂F₆Ta₁: C, 41.90; H, 6.83; N, 4.44; F, 18.10. Found: C, 41.88; H, 6.82; N, 4.50; F, 17.87. Raman (frequency/cm⁻¹ (relative intensity)): 693(s) (TaF₆⁻, ν₁), 287(m) (TaF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 576(m) (TaF₆⁻, ν₃).

Spectroscopic and thermal analyses

Infra-red spectra were obtained by FTS-165 (Bio-Rad Laboratories). The samples were sandwiched between a pair of AgCl windows fixed in a stainless steel airtight cell under dry Ar. Raman spectra were obtained by FTS-175C (Bio-Rad Laboratories) using the 1064 nm line of a Nd:YAG laser as the excitation line. The samples for Raman spectroscopy were loaded in Pyrex glass tubes under dry Ar and sealed with a plastic cap. Thermogravimetric and DSC analyses were performed under a dry Ar gas flow using Shimadzu DTG-60H and Shimadzu

DSC-60, respectively, at a scan rate of 5 °C min⁻¹. The sample was placed in a Ni open cell for TG analysis and in an aluminium sealed cell for DSC analysis. Polarized optical microscopy was carried out using a VHX digital microscope (Keyence, Co.) under cross-polarized light at ×100 magnification. The sample was placed in a transparent cell made of sapphire and covered with a piece of glass substrate. The temperature was controlled by a TS1500 hot stage unit (Japan High Tech Co., Ltd.).

X-Ray diffraction analyses. a. Powder diffraction

X-ray diffraction was performed using a Rigaku Ultima IV diffractometer (Cu-Kα, λ = 1.542 Å). The output power was set as 40 kV–40 mA. The data were recorded in the 2θ ranges of 2–30° (scanning rate of 2° per minute) with a step of 0.02°. The sample was sealed in a vacuum cell. The heating and cooling rate of 5 °C min⁻¹ was used.

b. Single-crystal diffraction

Crystals of C₁₈MImAF₆ (A = P, As, Sb, Nb and Ta) were grown by slow evaporation of the solvent from an acetone (A = P, As, Sb, Ta) or dichloromethane (A = Nb) solution. Suitable crystals of C₁₈MImAF₆ (A = P, As, Sb and Ta) were fixed on a glass rod with perfluoro polyether oil (fomblin YL VAC 06\6) and centered on an X-ray diffractometer (R-axis Rapid II, Rigaku controlled by the program RAPID AUTO 2.40)²⁷ equipped with an imaging plate area detector and graphite-monochromated Mo-Kα radiation (0.71073 Å). The crystal of C₁₈MImNbF₆ was transferred into a quartz capillary (0.5 mm o.d., dried under a vacuum at 500 °C) under a dry Ar atmosphere. The capillary was tentatively plugged with vacuum grease and sealed using an oxygen burner. Data collection was performed at –100, 25 and 55 °C. The measurements consisted of 12 ω scans (130–190°,

Table 3 Summary of crystal data and refinement results for C₁₈MImAF₆ (A = P, As, Sb, Nb and Ta) at –100 °C

	P	As	Sb	Nb	Ta
Formula	C ₂₂ H ₄₃ N ₂ F ₆ P	C ₂₂ H ₄₃ N ₂ F ₆ As	C ₂₂ H ₄₃ N ₂ F ₆ Sb	C ₂₂ H ₄₃ N ₂ F ₆ Nb	C ₂₂ H ₄₃ N ₂ F ₆ Ta
Fw	480.55	524.50	571.34	542.49	630.53
Crystal size/mm	0.80 × 0.30 × 0.05	0.70 × 0.20 × 0.05	0.75 × 0.30 × 0.03	0.70 × 0.30 × 0.05	0.43 × 0.13 × 0.04
T/°C	–100	–100	–100	–100	–100
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /a	P2 ₁ /a	P2 ₁ /a	P2 ₁ /a	P2 ₁ /a
a/Å	9.1715(7)	9.1894(2)	9.2091(3)	9.1865(5)	9.2100(3)
b/Å	9.8807(8)	9.9779(3)	10.1539(5)	10.1457(7)	10.1744(3)
c/Å	28.520(2)	28.5321(7)	28.5250(10)	28.4689(15)	28.4495(11)
β (°)	95.707(2)	96.0148(7)	96.2477(10)	96.1335(16)	96.1688(11)
V/Å ³	2571.7(3)	2601.74(12)	2651.47(18)	2638.2(3)	2650.46(15)
Z	4	4	4	4	4
ρ _c /g cm ⁻³	1.241	1.339	1.431	1.366	1.576
F(000)	1032	1104	1176	1136	1264
μ/mm ⁻¹	0.161	1.360	1.093	0.509	4.188
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Reflns collected/unique	22 634/5864	24 782/5884	25 221/6035	15 005/5954	11 776/3944
R ₁ (F _o) ^a	0.0465	0.0418	0.0262	0.0470	0.0349
wR ₂ (F _o ²) ^b	0.1059	0.0981	0.0656	0.1125	0.1100
R _{int}	0.0556	0.0452	0.0294	0.0536	0.0402

^a R₁ = Σ|F_o – |F_c||/Σ|F_o| for I > 2σ(I). ^b wR₂ = {Σ[w(F_o² – F_c²)]/Σ[w(F_o²)]}^{1/2} for I > 2σ(I).

5°/frame) at the fixed φ (30°) and χ (45°) angles and 32 ω scans (0–160°, 5°/frame) at the fixed φ (180°) and χ (45°) angles for C₁₈MImPF₆, C₁₈MImAsF₆ and C₁₈MImSbF₆ and 20 ω scans (130–190°, 3°/frame) at the fixed φ (30°) and χ (45°) angles and 54 ω scans (0–162°, 3°/frame) at the fixed φ (180°) and χ (45°) angles for C₁₈MImNbF₆ and C₁₈MImTaF₆. The exposure time was 300 s deg⁻¹. Integration, scaling and absorption corrections were performed using RAPID AUTO 2.40. The structure was solved using SIR-92²⁸ and refined by SHELXL-97²⁹ linked to Win-GX.³⁰ Anisotropic displacement factors were introduced for all atoms except for hydrogen. The crystallographic data and refinement results of C₁₈MImAF₆ are summarized in Table 3.

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