

Ionic Liquids Based on Hexachloridometalate(V) Anions (Sb, Nb and Ta) and Nitrile-functionalized Pyridinium Cations

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Single crystals of 1-(cyanoethyl)-3-methyl-pyridin-1-ium hexachloridoantimonate(V) (**1**), 1-(cyanomethyl)-3-methyl-pyridin-1-ium hexachloridoniobate(V) (**2**), 1-(cyanomethyl)-3-methyl-pyridin-1-ium hexachloridotantalate(V) (**3**), 1-(cyanopropyl)-3-methyl-pyridin-1-ium hexachloridoniobate(V) (**4**), and 1-(cyanopropyl)-3-methyl-pyridin-1-ium hexachloridotantalate(V) (**5**) have been synthesized and characterized by X-ray diffraction. Compounds **1–3** crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$, and compounds **4** and **5** in the monoclinic space group $C2/c$ with $Z = 8$. FT-Raman spectra have been recorded and interpreted, especially with respect to the anions $[MCl_6]^-$. In addition, NMR spectra, a study of the melting behavior and elemental analyses complete the characterization.

Key words: Ionic Liquids, $[SbCl_6]^-$, $[NbCl_6]^-$, $[TaCl_6]^-$, Crystal Structure, Raman Spectroscopy

Introduction

Ionic liquids (ILs) is a commonly accepted term for low-melting molten salts. Usually, they are synthesized by combining bulky organic cations such as 1-alkyl-3-methyl-imidazolium or 1-alkyl-3/4-methyl-pyridinium with a wide variety of anions, mostly inorganic ones [1–4]. ILs have found widespread applications in organic and organometallic synthesis, catalysis [5–10], photovoltaic devices, electrochemical processes, for example as electrolytes for metal deposition, in polymerizations [11–13], and as solvents for analytical and physical reactions [14–16]. In the past few years, several functionalized ILs have been prepared and characterized [17, 18]. In particular, the nitrile-functionalized ILs, which were first reported by Dyson *et al.* [19], have received much attention due to their applications as media and ligands for catalytic reactions and as electrolytes for lithium batteries [20–24].

Only a few chloridometalate(V) ILs are known, and crystal structure determinations of such compounds have been rare. The title compounds belong to the growing group of potentially applicable ILs. Com-

monly, $SbCl_5$ and $NbCl_5$ act as chloride ion acceptors giving salt-like complex compounds with octahedral $[MCl_6]^-$ units ($M = Nb$ and Sb) [25–28]. The potential use of $[NbCl_6]^-$ -containing ILs concerns the electrochemical preparation of Nb compounds in different oxidation states as well as of Nb metal. Furthermore, hexachlorido-antimonates(V) with large organic cations as *e. g.* tetramethylphosphonium, piperidinium and dipropylammonium exhibit interesting ferroic (ferroelastic) properties [29–31].

Very often tantalum pentachloride is the starting material in modern tantalum chemistry. Today, tantalum's main use is in tantalum capacitors for electronic equipment [32]. Tantalum pentachloride also behaves as a strong chloride ion acceptor (Lewis acid) yielding $[TaCl_6]^-$ -containing compounds in basic and neutral chloride mixtures [33, 34]. $[TaCl_6]^-$ -containing compounds with large organic cations having low melting temperatures might be exhibiting potential application as electrolytes for the electrochemical deposition of tantalum [35].

This contribution is a continuation of the structural characterization of antimony, niobium and tantalum chloride compounds formed with and in chloride ion-

containing IL systems [25–28], with the intention to determine the crystal structure and the vibrational fundamentals of the new hexachloridometalates(V).

Results and Discussion

The synthesis route to the title compounds is depicted in Scheme 1. The pyridinium chlorides, $[(\text{CH}_2)_n\text{CNmpy}]\text{Cl}$ ($n = 1, 2$ and 3) are prepared in high yield from 3-methyl-pyridine and the appropriate chloroalkynitrile $\text{Cl}(\text{CH}_2)_n\text{CN}$ according to Dyson [19]. The addition of one equivalent of $[(\text{CH}_2)_n\text{CNmpy}]\text{Cl}$ ($n = 1, 2$ and 3) as a chloride donor to one equivalent of $M\text{Cl}_5$ ($M = \text{Sb, Nb}$ and Ta) in acetonitrile under reflux conditions results in crystalline products, the hexachloridometalate(V) complexes $[(\text{CH}_2)_n\text{CNmpy}][M\text{Cl}_6]$ (**1–5**) ($n = 1, 2, 3$ and $M = \text{Sb, Nb}$ and Ta) (Scheme 1).

Single crystals of products **1–5** could be obtained and their crystal structures determined by X-ray diffraction. The crystallographic data and details are given in Table 1. The structures of **1–5** are built up by discrete 1-cyanoalkyl-3-methyl-pyridinium cations and octahedral hexachloridometalate(V) anions.

$[(\text{CH}_2)_2\text{CNmpy}][\text{SbCl}_6]$ (**1**) crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with two formula units per unit cell, consisting of alternating layers of $[(\text{CH}_2)_2\text{CNmpy}]^+$ cations and octahedral $[\text{SbCl}_6]^-$ anions with O_h symmetry (Fig. 1).

The pyridinium ring is completely planar, and the bond lengths are very close to those observed in other 1-alkyl-3-methyl-pyridinium salts [1, 2, 25–28, 36]. In the cationic units the $-\text{CH}_2-\text{C}\equiv\text{N}$ moiety is almost linear with a C–N distance of 1.145(1) Å, which is close to the literature values [19].

The quasi-octahedral anionic unit has *cis*-Cl–Sb–Cl angles all within 1.99° of 90°, and *trans*-Cl–Sb–Cl angles of 177.7(1) and 178.6(1)° in the equatorial posi-

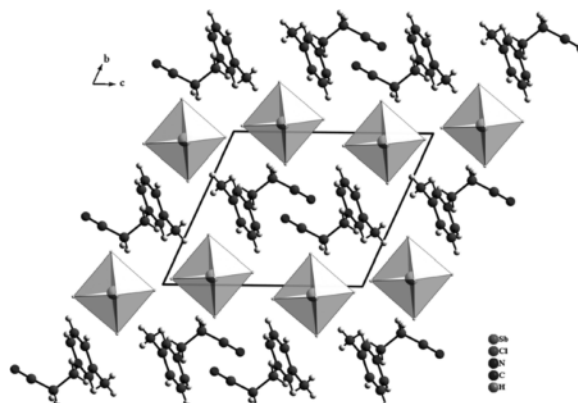
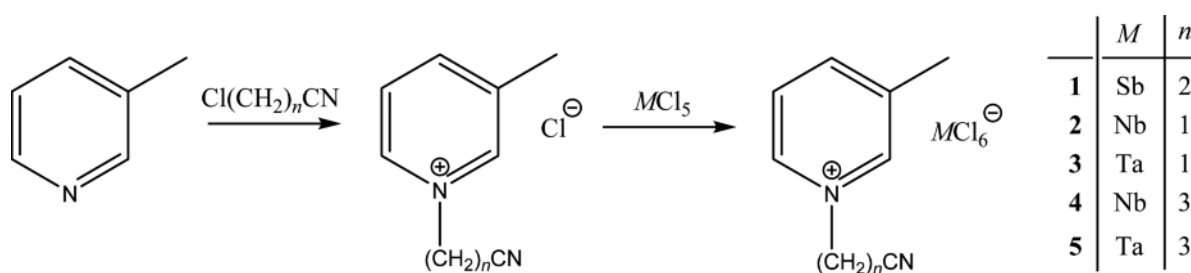


Fig. 1. Projection of the crystal structure of $[(\text{CH}_2)_2\text{CNmpy}][\text{SbCl}_6]$ (**1**) along the crystallographic a axis.

tions, and 178.8(1)° in the axial positions. The Sb–Cl bond lengths range from 2.351(2) to 2.391(2) Å (Table 2). These values compare well with those of reported hexachloridoantimonate(V) salts [25–28]. The contacts between anions and cations [3.658(1) and 3.728(1) Å] exist as weak C–H⋯Cl interactions involving neighbouring $[(\text{CH}_2)_2\text{CNmpy}]^+$ cations and $[\text{SbCl}_6]^-$ anions (Fig. 2).

$[\text{CH}_2\text{CNmpy}][\text{NbCl}_6]$ (**2**) and $[\text{CH}_2\text{CNmpy}][\text{TaCl}_6]$ (**3**) crystallize isotypically in the triclinic space group $P\bar{1}$ (no. 2) with two formula units per unit cell. Similar to compound **1**, the structures consist of alternate layers of $[\text{CH}_2\text{CNmpy}]^+$ cations and octahedral $[M\text{Cl}_6]^-$ anions ($M = \text{Nb}$ and Ta) (Fig. 3).

Similar to compound **1**, the $-\text{CH}_2-\text{C}\equiv\text{N}$ moiety in the cationic unit is almost linear with a C–N distance of 1.121(3) Å in **2** and 1.145(1) Å in **3**, which are close to the literature values [19]. The closest contact between cations (2.325(1) Å for **2** and 2.371(1) for **3**) exist as C–H⋯N interactions involving pyridinium-bound hydrogen atoms.



Scheme 1. Synthesis of the nitrile-functionalized pyridinium chlorides and hexachloridometalate(V) salts **1–5**.

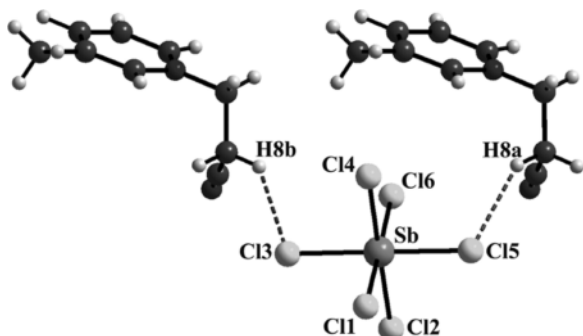


Fig. 2. Interactions between cations and anions in the crystal structure of **1**.

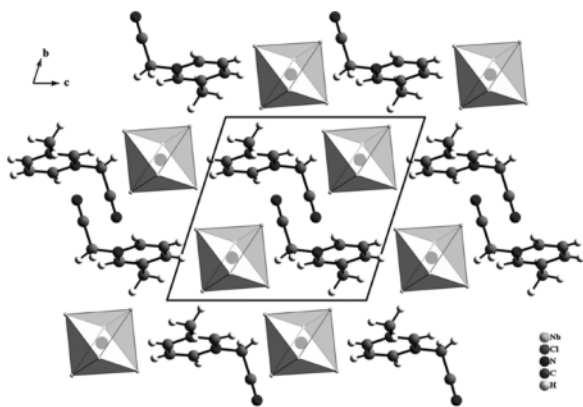


Fig. 3. Projection of the crystal structure of $[(\text{CH}_2\text{CNmpy})][\text{NbCl}_6]$ (**2**) along the *a* axis.

In **2** and **3** the anions have nearly an octahedral symmetry (O_h) with *cis*-Cl–Nb–Cl angles all within 1.0° of 90° , and *trans*-Cl–Nb–Cl angles of $178.0(1)$ and $178.8(1)^\circ$ in the equatorial positions, and $179.5(1)^\circ$ in the axial positions for compound **2** and *cis*-Cl–Ta–Cl angles all within 0.92° of 90° , and *trans*-Cl–Ta–Cl angles of $178.1(1)$ and $179.0(1)^\circ$ in the equatorial positions, and $179.4(1)^\circ$ in the axial positions for compound **3**. The Nb–Cl bond lengths range from $2.337(1)$ to $2.372(1)$ Å, and the Ta–Cl bond lengths from $2.335(2)$ to $2.375(2)$ Å (Table 2). These values agree very well with those observed in other hexachloridoniobate and hexachloridotantate(V) salts [25–28]. The contacts between anions and cations (from $3.673(1)$ to $3.750(1)$ in **1** and $3.703(1)$ to $3.761(1)$ in **2**) exist as weak C–H \cdots Cl interactions involving $[(\text{CH}_2\text{CNmpy})]^+$ cations and $[\text{MCl}_6]^-$ anions ($M = \text{Nb}$ and Ta) [37] (Fig. 4).

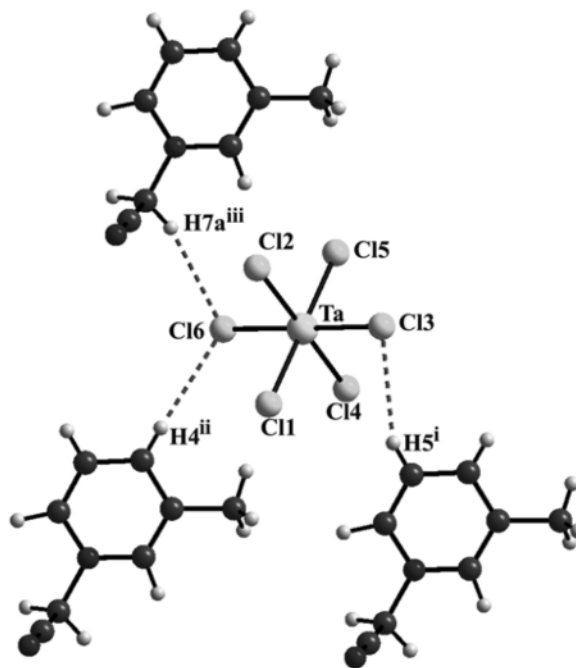


Fig. 4. Interaction between cations and anions in the crystal structure of **3**.

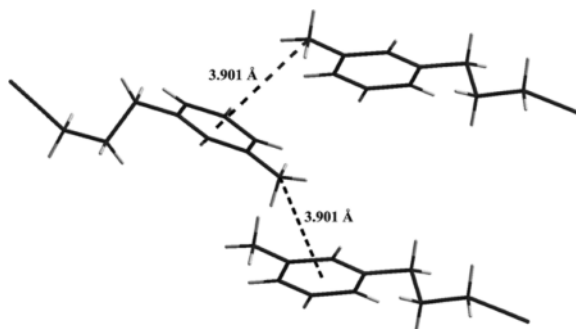


Fig. 5. C–H \cdots π interactions between cations in the crystal structure of **4**.

$[(\text{CH}_2)_3\text{CNmpy}][\text{NbCl}_6]$ (**4**) and $[(\text{CH}_2)_3\text{Nmpy}][\text{TaCl}_6]$ (**5**) crystallize isotypically in the monoclinic space group $C2/c$ (no. 15) with eight formula units per unit cell. The cations and anions are packed *via* significant C–H \cdots π interactions as well as weak interionic C–H \cdots Cl hydrogen bonds. Two $[(\text{CH}_2)_3\text{CNmpy}]$ cations in compounds **4** and **5** are linked to each other by C–H \cdots π interactions between one methyl carbon (C12) and the pyridinium ring of another cation (Fig. 5).

The distances between methyl carbon atoms and the center of the pyridinium rings are estimated to be

Table 1. Crystal data and numbers pertinent to data collection and structure refinement of compounds 1–5.

	1	2	3	4	5
Formula	C ₉ H ₁₁ Cl ₆ N ₂ Sb	C ₈ H ₆ Cl ₆ N ₂ Nb	C ₈ H ₆ Cl ₆ N ₂ Ta	C ₁₀ H ₁₃ Cl ₆ N ₂ Nb	C ₁₀ H ₁₃ Cl ₆ N ₂ Ta
<i>M_r</i> , g mol ⁻¹	481.65	438.78	526.82	466.83	554.87
Crystal size, mm ³	0.28 × 0.26 × 0.25	0.22 × 0.21 × 0.20	0.20 × 0.19 × 0.16	0.25 × 0.20 × 0.18	0.23 × 0.20 × 0.15
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	8.116(3)	8.225(1)	8.202(1)	24.377(3)	24.367(4)
<i>b</i> , Å	10.224(3)	9.893(2)	9.907(1)	6.9948(5)	7.0131(6)
<i>c</i> , Å	11.568(3)	10.227(2)	10.265(1)	20.244(2)	20.266(3)
α , deg	65.84(2)	70.81(1)	71.04(1)	90	90
β , deg	86.53(2)	79.20(1)	79.25(1)	92.34(1)	92.38(1)
γ , deg	72.49(2)	79.19(1)	79.54(1)	90	90
<i>V</i> , Å ³	833.0(4)	764.9(2)	768.4(2)	3449.0(6)	3460.2(8)
<i>Z</i>	2	2	2	8	8
<i>d</i> _{calc.} , g cm ⁻³	1.92	1.91	2.28	1.80	2.13
μ (MoK α), mm ⁻¹	2.6	1.8	8.2	1.6	7.3
<i>F</i> (000), e	464	428	492	1840	2096
<i>T</i> , K	223(2)	223(2)	223(2)	223(2)	223(2)
2 θ range, deg	1.00–26.02	0.94–25.03	1.00–25.023	1.00–25.03	1.00–25.03
<i>hkl</i> ranges	$\pm 10, \pm 12, \pm 14$	$\pm 9, -11 \rightarrow 10, \pm 11$	$\pm 9, \pm 11, \pm 12$	$\pm 28, -8 \rightarrow 7, -22 \rightarrow 24$	$\pm 28, -8 \rightarrow 7, \pm 24$
Ref. measured/unique	15 803/3236	7574/2539	15 908/2680	26 977/3045	27 687/3061
<i>R</i> _{int}	0.0921	0.0583	0.0935	0.0684	0.1415
Param. refined	208	191	187	226	226
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]/ <i>R</i> ₁ (all data) ^{a,b}	0.0400/0.0577	0.0377/0.0434	0.0446/0.0468	0.0297/0.0371	0.0480/0.0639
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]/ <i>wR</i> ₂ (all data) ^{a,b}	0.0890/0.0954	0.0916/0.0949	0.0803/0.1021	0.0676/0.0701	0.0998/0.1051
GoF (<i>F</i> ²) ^c	1.034	1.104	1.062	1.149	1.110
$\Delta\rho_{\text{min}}$ (max/min), e Å ⁻³	0.86/−0.88	1.03/−1.07	3.17/−3.09	0.38/−0.57	1.25/−2.58

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$, $w = [\sigma^2(F_o^2) / \sum w(F_o^2)]^{1/2}$; ^c $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

Table 2. Interatomic distances (Å) and angles (deg) for the $[MCl_6]^-$ anions ($M = Sb, Nb$ and Ta) in compounds **1–5** with estimated standard deviations in parentheses.

Compound 1			
Sb–Cl(1)	2.351(2)	Cl(1)–Sb–Cl(2)	90.7(1)
Sb–Cl(2)	2.360(2)	Cl(1)–Sb–Cl(3)	177.7(1)
Sb–Cl(3)	2.363(2)	Cl(1)–Sb–Cl(6)	178.6(1)
Sb–Cl(4)	2.367(2)	Cl(3)–Sb–Cl(4)	90.0(1)
Sb–Cl(5)	2.370(2)	Cl(2)–Sb–Cl(6)	92.0(1)
Sb–Cl(6)	2.391(2)	Cl(2)–Sb–Cl(5)	178.8(1)
Compound 2			
Nb–Cl(1)	2.337(1)	Cl(1)–Nb–Cl(2)	90.6(1)
Nb–Cl(2)	2.341(1)	Cl(1)–Nb–Cl(3)	90.6(1)
Nb–Cl(3)	2.345(1)	Cl(2)–Nb–Cl(3)	91.0(1)
Nb–Cl(4)	2.347(1)	Cl(2)–Nb–Cl(4)	178.0(1)
Nb–Cl(5)	2.352(1)	Cl(1)–Nb–Cl(5)	179.5(1)
Nb–Cl(6)	2.372(1)	Cl(3)–Nb–Cl(6)	178.8(1)
Compound 3			
Ta–Cl(1)	2.335(2)	Cl(1)–Ta–Cl(2)	90.8(1)
Ta–Cl(2)	2.345(2)	Cl(2)–Ta–Cl(3)	90.7(1)
Ta–Cl(3)	2.349(2)	Cl(3)–Ta–Cl(4)	90.9(1)
Ta–Cl(4)	2.350(2)	Cl(2)–Ta–Cl(4)	178.1(1)
Ta–Cl(5)	2.351(2)	Cl(1)–Ta–Cl(5)	179.4(1)
Ta–Cl(6)	2.375(2)	Cl(3)–Ta–Cl(3)	179.0(1)
Compound 4			
Nb(1)–Cl(1), Cl(1) ⁱ	2.351(1)	Cl(1)–Nb(1)–Cl(1) ⁱ	89.8(1)
Nb(1)–Cl(2), Cl(2) ⁱ	2.352(1)	Cl(1)–Nb(1)–Cl(3)	177.3(1)
Nb(1)–Cl(3), Cl(3) ⁱ	2.356(1)	Cl(2)–Nb(1)–Cl(2) ⁱ	179.4(1)
Nb(2)–Cl(4), Cl(4) ⁱⁱ	2.343(1)	Cl(4)–Nb(2)–Cl(4) ⁱⁱ	180.0
Nb(2)–Cl(5), Cl(5) ⁱⁱ	2.348(1)	Cl(4)–Nb(2)–Cl(6)	90.2(1)
Nb(2)–Cl(6), Cl(6) ⁱ	2.361(8)	Cl(5)–Nb(2)–Cl(5) ⁱⁱ	180.0
Compound 5			
Ta(1)–Cl(1), Cl(1) ⁱ	2.345(2)	Cl(1)–Ta(1)–Cl(1) ⁱ	179.5(1)
Ta(1)–Cl(2), Cl(2) ⁱ	2.351(2)	Cl(1)–Ta(1)–Cl(2)	88.5(1)
Ta(1)–Cl(3), Cl(3) ⁱ	2.355(2)	Cl(2)–Ta(1)–Cl(3)	177.6(1)
Ta(2)–Cl(4), Cl(4) ⁱⁱ	2.341(3)	Cl(4)–Ta(2)–Cl(4) ⁱⁱ	180.0
Ta(2)–Cl(5), Cl(5) ⁱⁱ	2.349(3)	Cl(4)–Ta(2)–Cl(6)	90.3(1)
Ta(2)–Cl(6), Cl(6) ⁱ	2.358(2)	Cl(5)–Ta(2)–Cl(5) ⁱⁱ	180.0

ⁱ $-x, y, -z + 0.5$; ⁱⁱ $-x - 0.5, -y + 1.5, -z + 1$.

3.901 Å for **4** and 3.899 Å for **5**, which agree very well with the value expected for benzene...methane interactions [38].

The anionic units $[MCl_6]^-$ ($M = Nb$ and Ta) in **4** and **5** have the same octahedral structure as the anionic units in **1–3** (Table 2). Two weak C–H...Cl hydrogen bonds connect the $[(CH_2)_3CNmpy]^+$ and $[MCl_6]^-$ units ($M = Nb$ and Ta) forming layered structures. C–H...Cl distances of 3.719(1) and 3.877(1) Å are found

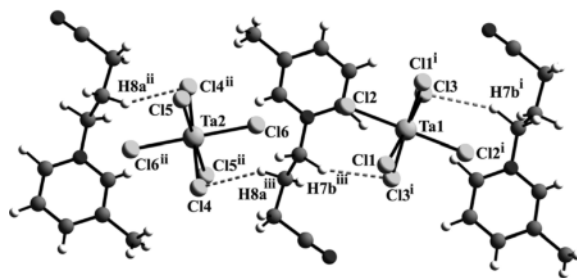


Fig. 6. C–H...Cl interactions between cations and anions in the crystal structure of **5**.

for compound **4**, and of 3.720(1) and 3.881(1) Å for compound **5** (Fig. 6).

Raman frequencies of the obtained solid salts **1–5** with their assignments are summarized in Table 3. The vibrational spectra can be divided in pyridinium stretchings (3100–2927 cm^{-1}), $C\equiv N$ stretching (2265–2253 cm^{-1}), pyridinium bendings (1600–540 cm^{-1}) and the $[MCl_6]^-$ relevant modes ($M = Sb, Nb$ and Ta) below 500 cm^{-1} (in the range of 500–100 cm^{-1}). The bands below around 100 cm^{-1} belong to lattice vibrations. The $[MCl_6]^-$ ions ($M = Sb, Nb$ and Ta) in compounds **1–5** show Raman spectra typical of octahedral symmetry (O_h) (Fig. 7). A vibrational analysis for such units results in [39]:

$$\Gamma_{\text{vib}}([MCl_6]^- / O_h) = A_{1g}(\text{RE}) + E_g(\text{RE}) + 2F_{1u}(\text{IR}) + F_{2g}(\text{RE}) + F_{2u}(\text{i. a.}),$$

with RE = Raman, IR = Infrared and i. a. = inactive, and with $A_{1g} + E_g + F_{1u}$ as stretchings and $F_{1u} + F_{2g}$ as bendings.

In detail, the very strong Raman modes at 332 cm^{-1} for **1**, 378 cm^{-1} for **2**, 367 cm^{-1} for **3**, 370 cm^{-1} for **4**, and 378 cm^{-1} for **5** can be assigned to ν_1/A_{1g} (Table 3). The weak to medium Raman bands at 289 cm^{-1} for **1**, 286 cm^{-1} for **2**, at 289 cm^{-1} for **3**, 285 cm^{-1} for **4**, and 278 cm^{-1} for **5** belong to the ν_1/E_g stretching and the strong bending modes at 171 cm^{-1} for **1**, 179 cm^{-1} for **2**, 177 cm^{-1} for **3**, 179 cm^{-1} for **4**, and 180 cm^{-1} for compound **5** belong to the bending ν_5/F_{2g} [25–28, 40, 41].

The melting points of the obtained salts **1–5** are summarized in Table 4. In the title compounds the size, the charge density and the symmetry of the cations have an important influence on the melting point. An increase of the alkyl chain from methyl to propyl decreases the melting point of the salts

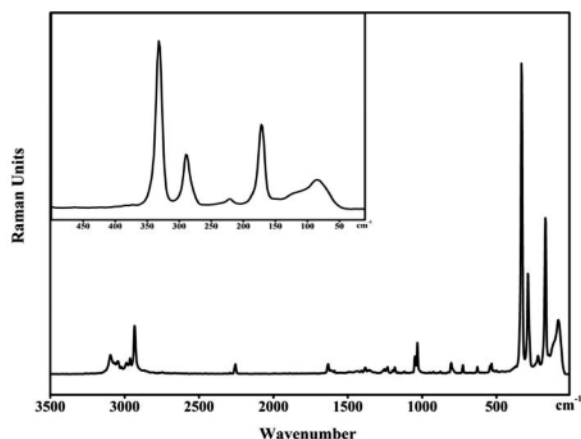


Fig. 7. FT-Raman spectrum ($\lambda_{\text{exc}} = 1064 \text{ nm}$) of $[(\text{CH}_2)_2\text{CNmpy}][\text{SbCl}_6]$ (**1**). Inset: $[\text{SbCl}_6]^-$ -relevant frequency region below 500 cm^{-1} (Raman intensity in arbitrary units).

Table 3. Raman frequencies (cm^{-1}) of crystalline **1–5** in the $[\text{MCl}_6]^-$ -relevant ($M = \text{Sb, Nb}$ and Ta) spectral region along with their estimated intensities and proposed assignments^a.

1	2	3	4	5	Assignment/ O_h mode description
332 vvs	378 vvs	367 vvs	370 vs	378 vs	$\nu_1/A_{1g} : \nu_s$
289 m-s	286 w	289 w-m	285 w-m	278 w	$\nu_2/E_g : \nu$
171 s	179 vs	177 vs	179 vs	180 s	$\nu_5/F_{2g} : \delta$
85 br	100 m	99 m	86 m, br		lattice vibration

^a Estimated intensities: s: strong, m: medium, w: weak, v: very, br: broad. ν : stretching, δ : bending.

Table 4. The melting points ($^\circ\text{C}$) of **1–5**.

Compound	M. p., $^\circ\text{C}$
$[\text{CH}_2\text{CNmpy}][\text{NbCl}_6]$ (2)	119.5
$[\text{CH}_2\text{CNmpy}][\text{TaCl}_6]$ (3)	127.8
$[(\text{CH}_2)_2\text{CNmpy}][\text{SbCl}_6]$ (1)	108.3
$[(\text{CH}_2)_3\text{CNmpy}][\text{NbCl}_6]$ (4)	90
$[(\text{CH}_2)_3\text{CNmpy}][\text{TaCl}_6]$ (5)	91

1–5 [3]. The $[\text{MCl}_6]^-$ anions ($M = \text{Sb, Nb}$ and Ta) in compounds **1–5** show nearly an octahedral symmetry (O_h). Since $[(\text{CH}_2)_3\text{CNmpy}][\text{NbCl}_6]$ (**4**) and $[(\text{CH}_2)_3\text{CNmpy}][\text{NbCl}_6]$ (**5**) are isotypically their melting points might be comparable. Unexpectedly the melting point of compound **3** is higher than that one **2**.

Conclusion

Five new ionic liquid salts, the 1-cyanoalkyl-3-methyl-pyridinium hexachloridometalates(V) **1–5**,

have been synthesized. The identity and purity of the compounds were confirmed by elemental analysis, NMR and Raman spectroscopy, and single-crystal X-ray diffraction. As expected, the complex $[\text{MCl}_6]^-$ units ($M = \text{Nb, Sb}$ and Ta) have an octahedral structure. All the compounds are soluble in CH_3CN and are sensitive to moisture.

Experimental Section

All manipulations and chemical reactions were carried out in a dry argon atmosphere using standard Schlenk, vacuum line and glove box techniques. Reagents were purchased from Sigma-Aldrich and were used without additional purification. CH_3CN was distilled and dried over P_4O_{10} . 1-Cyanoalkyl-3-methyl-pyridinium chlorides were prepared in high yield from 3-methyl-pyridine and the appropriate chloroalkylnitrile $\text{Cl}(\text{CH}_2)_n\text{CN}$ ($n = 1, 2$ and 3) according to Dyson [19].

The FT-Raman spectra of the title compounds **1–5** were recorded with a Raman module FRA 106 (Nd:YAG laser, 1064 nm) instrument attached to a Bruker IFS 66v interferometer. Respective samples were sealed under argon atmosphere in glass capillaries, and data were recorded at room temperature. The melting temperatures were determined on a Büchi 520 apparatus. NMR spectra were recorded on a Bruker Digital FT-NMR Avance 400 spectrometer at room temperature. Chemical shifts are reported in ppm relative to the ^1H residue of the deuterated solvent (DMSO).

1-(2-Cyanoethyl)-3-methyl-pyridinium hexachloridoantimonate(V), $[(\text{CH}_2)_2\text{CNmpy}][\text{SbCl}_6]$ (**1**)

$[(\text{CH}_2)_2\text{CNmpy}]\text{Cl}$ (182.5 mg, 1 mmol) was dissolved in dry acetonitrile (25 mL). SbCl_5 (299.1 mg, 1.0 mmol) was added, and the reaction mixture was stirred at room temperature for 8 h. The resulting solution was concentrated by partially removing the solvent under vacuum. After several days colorless block-shaped single crystals (342 mg) of compound **1** grew in the solution. Yield: 71%. M. p. 108.3 $^\circ\text{C}$. – ^1H NMR (400 MHz, DMSO, 25 $^\circ\text{C}$): $\delta = 9.20$ (1H, s, pyr-CH), 9.08 (1H, d, pyr-CH), 8.54 (1H, d, pyr-CH), 8.16 (1H, t, pyr-CH), 4.95 (2H, t, N- CH_2 - CH_2 -CN), 3.46 (2H, t, CN- CH_2 - CH_2) 2.50 (3H, s, CH_3) ppm. – Elemental analysis (%) for $\text{C}_9\text{H}_{11}\text{Cl}_6\text{N}_2\text{Sb}$ (481.52): calcd. C 22.44, H 2.30, N 5.82; found C 22.12, H 2.06, N 5.91. – Raman (intensity): 3096 w-m, 3039 w, 2963 w, 2933 m-s, 2255 w-m, 1633 w, 1410 w, 1344 w, 1248 w, 1049 m, 1032 m, 805 m, 727 w-m, 533 vw, 332 vvs, 389 m-s, 289 w-m, 221 vw, 171 vs, 85 br cm^{-1} .

1-(Cyanomethyl)-3-methyl-pyridinium hexachloridonioate(V), $[\text{CH}_2\text{CNmpy}][\text{NbCl}_6]$ (**2**)

Same procedure as that for **1**. Yield: 68%. M. p. 119.5 $^\circ\text{C}$. – ^1H NMR (400 MHz, DMSO, 25 $^\circ\text{C}$): $\delta = 9.23$ (1H, s, pyr-

CH), 9.15 (1H, d, pyr-CH), 8.60 (1H, d, pyr-CH), 8.19 (1H, t, pyr-CH), 6.14 (2H, s, N-CH₂-CN), 2.52 (3H, s, CH₃) ppm. – Elemental analysis (%) for C₈H₉Cl₆N₂Nb (438.78): calcd. C 21.90, H 2.07, N 6.38; found C 21.77, H 1.97, N 6.11. – Raman (intensity): 3096 w-m, 3044 w, 2988 w, 2950 m-s, 2939 m, 2265 w-m, 1589 w, 1416 w, 1340 w, 1253 w, 1206 w, 1033 m, 755 m, 534 vw, 378 vvs, 350 w, 286 w, 220 vw, 179 vs, 102 m cm⁻¹.

1-(Cyanomethyl)-3-methyl-pyridinium hexachloridotantalate(V), [(CH₂CNmpy)][TaCl₆] (3)

Same procedure as that for **1**. Yield: 79%. M. p. 127.8 °C. – ¹H NMR (400 MHz, DMSO, 25 °C): δ = 9.25 (1H, s, pyr-CH), 9.17 (1H, d, pyr-CH), 8.60 (1H, d, pyr-CH), 8.17 (1H, t, pyr-CH), 6.16 (2H, s, N-CH₂-CN), 2.52 (3H, s, CH₃) ppm. – Elemental analysis (%) for C₈H₉Cl₆N₂Ta (526.20): calcd. C 18.24, H 1.72, N 5.32; found C 17.92, H 1.64, N 5.17. – Raman (intensity): 3094 w-m, 3042 w, 2986 w, 2949 m, 2931 m, 2264 w-m, 1599 w, 1416 w, 1344 w, 1250 w, 1033 m, 754 m, 534 vw, 367 vvs, 330 vw, 289 w-m, 219 vw, 177 vs, 110 m cm⁻¹.

1-(3-Cyanopropyl)-3-methyl-pyridinium hexochloridoniobate(V), [(CH₂)₃CNmpy][NbCl₆] (4)

Same procedure as that for **1**. Yield: 45.2%. M. p. 90 °C. – ¹H NMR (400 MHz, DMSO, 25 °C): δ = 9.12 (1H, s, pyr-CH), 9.02 (1H, d, pyr-CH), 8.48 (1H, d, pyr-CH), 8.09 (1H, t, pyr-CH), 4.69 (2H, t, N-CH₂-CH₂-), 2.70 (2H, t, -CH₂-CH₂) 2.49 (3H, s, CH₃), 2.30 (2H, m, -CH₂-CH₂-CH₂) ppm. – Elemental analysis (%) for C₁₀H₁₃Cl₆N₂Nb (488.61): calcd. C 25.73, H 2.81, N 6.00; found C 25.50, H 2.65, N 5.78. – Raman (intensity): 3090 w-m, 3040 w, 2957 w-m, 2927 m-s, 2253 w-m, 1627 vw, 1379 w, 1258 w, 1033 m-s, 802 w, 726 w-m, 544 w, 370 vs, 285 w-m, 221 w, 179 vs, 86 m, br cm⁻¹.

1-(3-Cyanopropyl)-3-methyl-pyridinium hexochloridotantalate(V), [(CH₂)₃CNmpy][TaCl₆] (5)

Same procedure as that for **1**. Yield: 56%. M. p. 91 °C. – ¹H NMR (400 MHz, DMSO, 25 °C): δ = 9.16 (1H, s, pyr-CH), 9.05 (1H, d, pyr-CH), 8.47 (1H, d, pyr-CH), 8.08 (1H, t,

pyr-CH), 4.70 (2H, t, N-CH₂-CH₂-), 2.69 (2H, t, -CH₂-CH₂) 2.49 (3H, s, CH₃), 2.32 (2H, m, -CH₂-CH₂-CH₂) ppm. – Elemental analysis (%) for C₁₀H₁₃Cl₆N₂Ta (555.86): calcd. C 21.65, H 2.36, N 5.05; found C 22.02, H 2.25, N 4.98. – Raman (intensity): 3095 w-m, 3044 w, 2960 w, 2929 m, 2254 w-m, 1611 vw, 1381 w, 1235 w, 10363 m, 805 w, 730 w, 550 w, 378 vs, 278 vw, 221 w, 180 vs cm⁻¹.

X-Ray structure determination

Because the title compounds are sensitive towards hydrolysis by moist air, the selection of crystals was performed in an argon-filled glove box. Crystals were transferred into glass capillaries which were sealed. All data were collected on a Stoe IPDS-II single-crystal X-ray diffractometer with graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å) at 223 K. Crystal structure solution by Direct Methods using SHELXS-97 [42] yielded in all cases the heavy atom positions. Subsequent least-squares refinements with SHELXL-97 [43] and difference Fourier analyses allowed the localization of the remaining atom positions. The H positions of [(CH₂)_nCNmpy]⁺ ($n = 1, 2$ and 3) were determined by a final difference Fourier synthesis. Crystal data and structure refinement parameters of the structures are summarized in Table 1. For the preparation of the structure drawings, the programs DIAMOND [44] and POV-RAY [45] were used.

CCDC 941286 for **1**, CCDC 941284 for **2**, CCDC 941285 for **3**, CCDC 941287 for **4**, and CCDC 941288 for compound **5** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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