

# Formamidinium Salts of Low Valent Metal Halide Anions $\text{MX}_3^-$ ( $\text{M} = \text{Ge}, \text{Sn}$ ) and $\text{M}_2\text{X}_6^{2-}$ ( $\text{M} = \text{Ga}, \text{In}$ )

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 70<sup>th</sup> birthday*

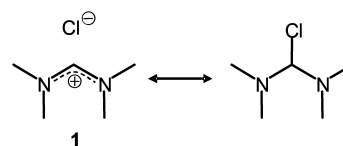
Tetramethylformamidinium trichlorogermanite,  $[\text{CH}(\text{NMe}_2)_2][\text{GeCl}_3]$ , tetramethylformamidinium trichlorostannite,  $[\text{CH}(\text{NMe}_2)_2][\text{SnCl}_3]$ , *bis*-(tetramethylformamidinium hexaiododigallate,  $[\text{CH}(\text{NMe}_2)_2]_2[\text{Ga}_2\text{I}_6]$  and *bis*-(tetramethylformamidinium hexachlorodiindate,  $[\text{CH}(\text{NMe}_2)_2]_2[\text{In}_2\text{Cl}_6]$  have been prepared by the reactions between tetramethylformamidinium chloride,  $[\text{CH}(\text{NMe}_2)_2]\text{Cl}$ , and the corresponding low valent halides  $\text{GeCl}_2$  (as dioxane adduct),  $\text{SnCl}_2$ , “GaI” and  $\text{InCl}$ . Their crystal structures have been determined by single crystal X-ray diffraction.  $[\text{CH}(\text{NMe}_2)_2][\text{GeCl}_3]$  aggregates in a centrosymmetric dimeric structure, in which two trigonal pyramidal  $\text{GeCl}_3$  units are connected together by two weak  $\text{Ge}\cdots\text{Cl}$  bonds and each Ge atom is bonded to one cation by a weak  $\text{Ge}\cdots\text{N}$  contact. Two sets of weak hydrogen bonds  $\text{C-H}\cdots\text{Cl}$  are observed with bond lengths of 2.87(2) Å and 2.85(2) Å. In  $[\text{CH}(\text{NMe}_2)_2][\text{SnCl}_3]$ , the  $\text{SnCl}_3^-$  units adopts a (3+3) coordination with three normal Sn-Cl bonds and three weak  $\text{Sn}\cdots\text{Cl}$  contacts.  $[\text{CH}(\text{NMe}_2)_2]_2[\text{Ga}_2\text{I}_6]$  and  $[\text{CH}(\text{NMe}_2)_2]_2[\text{In}_2\text{Cl}_6]$  contain metal-metal bonded anions with distorted staggered ethane-like conformations. The metal-metal bond lengths are 2.423(1) Å (Ga-Ga) and 2.719(1) Å (In-In). Their Raman spectra contain intense bands at 118.7  $\text{cm}^{-1}$  (Ga-Ga) and 174.7  $\text{cm}^{-1}$  (In-In) associated with metal-metal stretching modes.

**Key words:** Formamidinium Salts, Germanite, Stannite, Digallate, Diindate

## Introduction

Organometallic compounds with donor functions in geminal position relative to the metal atom are a synthetically highly useful class of compounds [1]. The original intention of this work was to find a synthetic pathway to aminals metallated at the central carbon atom, *i.e.* compounds with  $(\text{R}_2\text{N})_2\text{CHM}$  units. These compounds would have two geminal nitrogen donor functions relative to the metal atom. Such substances could constitute interesting molecules paralleling the phosphorous analogous metal diphosphinomethanides, which proved to have a highly diverse coordination chemistry [2].

It was reported that covalent Si-C bonds could be generated by the reaction of trichlorosilane with bis(dimethylamino)methane or from iminium salts in Benkeser type reactions employing the  $\text{HSiCl}_3/\text{NEt}_3$  reagent [3,4]. However, the reaction of  $[\text{Me}_2\text{NCH}_2]\text{Cl}$  with  $\text{SnCl}_2$  is reported to give a



product  $\text{Me}_2\text{NCH}_2\text{SnCl}_3$ , described as ionic compound  $[\text{Me}_2\text{NCH}_2][\text{SnCl}_3]$  [3]. It arose the question, whether it would be possible to react formamidinium chloride,  $[(\text{Me}_2\text{N})_2\text{CH}]\text{Cl}$  (**1**), with low valent metal halides of the group 13 and 14 elements to give compounds of the type  $(\text{R}_2\text{N})_2\text{CHMCl}_2$  ( $\text{M} = \text{Ga}, \text{In}$ ) and  $(\text{R}_2\text{N})_2\text{CHMCl}_3$  ( $\text{M} = \text{Ge}, \text{Sn}$ ). Formamidinium chloride is an ionic compound which can be described as the ionic, mesomeric form of covalently bonded bis(dimethylamino)chloromethane. The insertion reactions of low valent metal halide units could formally either occur into the covalent C-Cl bond or in an ionic mechanism with the formamidinium form of the reagent.

The ionic mechanism involves the well established addition of chloride anions to  $\text{GeCl}_2$  and  $\text{SnCl}_2$ , which lead to trichlorometallate(II) ions [5]. The resulting units  $\text{MCl}_3^-$  ( $\text{M} = \text{Ge}, \text{Sn}$ ) can act as soft donor ligands, *e.g.* for late transition metals and gold(I) [6]. It is also known, that salts of the  $\text{GeCl}_3^-$  anion can be applied as a nucleophilic reagents for the preparation of organometallic compounds  $\text{RGeCl}_3$  [7]. Gallium and indium(I) halides have also been used in insertion reactions into carbon-halogen bonds to form organogallium and indium compounds [8, 9].

In this contribution we report about the products of these reactions, which are formamidinium salts of the anions  $[\text{GeCl}_3]^-$ ,  $[\text{SnCl}_3]^-$ ,  $[\text{Ga}_2\text{I}_6]^{2-}$  and  $[\text{In}_2\text{Cl}_6]^{2-}$  rather than the desired compounds with covalent metal carbon bonds. Their crystal structures and vibrational spectra are also reported.

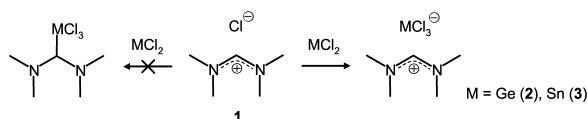
## Results and Discussion

### Reaction of $[(\text{Me}_2\text{N})_2\text{CH}]\text{Cl}$ with $\text{GeCl}_2$ , $\text{SnCl}_2$ , “GaI” and $\text{InCl}$

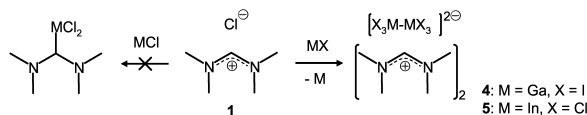
Tetramethylformamidinium chloride (**1**) was reacted with the dioxane adduct of germanium(II) chloride and with tin(II) chloride in THF. In these reactions the tetramethylformamidinium trichlorogermanite (**2**) and tetramethylformamidinium trichlorostannite (**3**) were formed, but not the covalently bonded isomers bis(dimethylamino)methyltrichlorogermane and -stannane, respectively. Both **2** and **3** can be isolated as colourless crystals after storage of the solutions at  $-25^\circ\text{C}$  overnight.

The products **2** and **3** were characterised by elemental analyses and by crystal structure determinations (see next sections). Measurement of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in  $\text{THF-d}^8$  solutions confirmed the presence of the tetramethylformamidinium ions.

During the reaction of **1** with “gallium(I) iodide”, prepared from elemental gallium and iodine [11], and indium(I) chloride the colour of the reactants ( $\text{GaI}$ ,  $\text{InCl}$ ) disappeared and the reaction mixture turned dark grey upon warming to ambient temperature. Heating the grey filtration residues led to melting and bright metal mirrors occurred on the walls of the glassware.



Scheme 1.



Scheme 2.

This means that metals were produced during redox reactions. The other products, which could be isolated, are the tetramethylformamidinium salts of hexaiododigallate(II) (**4**) and hexachlorodiindate(II) (**5**). They could be crystallized from the concentrated solution in  $\text{CH}_3\text{CN}$  at  $-25^\circ\text{C}$ .

Crystals of **4** are slightly yellowish, while **5** is a colourless compound. In the reaction with “GaI” some of the crystals which precipitated from more concentrated solutions of the reaction mixture were also lighter in colour so that we assume them to contain mixed halide species  $[\text{Cl}_x\text{I}_{3-x}\text{GaGaCl}_y\text{I}_{3-y}]^{2-}$ , which would be expected to balance stoichiometry. **4** and **5** were characterised by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy in  $\text{THF-d}^8$  solutions, by elemental analyses, by vibrational spectroscopy (see below) and crystal structure determination (see next sections).

### Crystal structures of **1**, **2** and **3**

For comparison with the crystal structures of **2** and **3**, we also determined the structure of  $[(\text{CH}(\text{NMe}_2)_2)\text{Cl}]$  (**1**), which is presented in Fig. 1. Selected bond lengths and angles of the formamidinium units of these compounds are listed in Table 1.

The crystal structure of **1** is an arrangement of ions, which in addition to coulombic forces are held together by at least six weak hydrogen bonds as depicted in Fig. 2. As these hydrogen bonds are long-range interactions, the acceptor can attract more than one hydrogen atom simultaneously [12]. It has already been demonstrated that bifurcated hydrogen bonds are common in  $\text{O-H}\cdots\text{O}$ ,  $\text{N-H}\cdots\text{O}$  structures and were also observed in  $\text{C-H}\cdots\text{O/N}$  patterns [13]. The strongest  $\text{C-H}\cdots\text{Cl}$  contact in **1** is only  $2.55(3) \text{ \AA}$  (HB3), which can be categorized as “weak-donor-strong-acceptor” hydrogen bond. The hydrogen bonds labelled HB2, HB4 and HB5 are characterized by slightly longer  $\text{H}\cdots\text{Cl}$  distances [ $2.79(3) \text{ \AA}$ ,  $2.55(3) \text{ \AA}$ ,  $2.79(3) \text{ \AA}$ , respectively], but all of them are still about  $0.2 \text{ \AA}$  shorter than the corresponding van der Waals distance at  $2.95 \text{ \AA}$  [14]. Two further weak hydrogen bonds [HB1  $2.86(2) \text{ \AA}$ , HB6  $2.87(3) \text{ \AA}$ ] have even longer  $\text{H}\cdots\text{Cl}$  distances compared with the four mentioned above.

Compound	1	2	3	4		5	
	[CH(NMe <sub>2</sub> ) <sub>2</sub> ] Cl	[CH(NMe <sub>2</sub> ) <sub>2</sub> ] [GeCl <sub>3</sub> ] <sup>−</sup>	[CH(NMe <sub>2</sub> ) <sub>2</sub> ] [SnCl <sub>3</sub> ]	[CH(NMe <sub>2</sub> ) <sub>2</sub> ]	[Ga <sub>2</sub> I <sub>6</sub> ]	[CH(NMe <sub>2</sub> ) <sub>2</sub> ]	[In <sub>2</sub> Cl <sub>6</sub> ]
C1–N1	1.325(3)	1.303(3)	1.302(3)	1.323(7)	1.306(8)	1.301(4)	1.309(4)
C1–N2	1.321(3)	1.318(3)	1.303(3)	1.302(7)	1.307(8)	1.316(4)	1.310(4)
C2–N1	1.476(3)	1.459(3)	1.475(3)	1.446(9)	1.476(8)	1.474(4)	1.459(4)
C3–N1	1.471(3)	1.459(3)	1.465(4)	1.461(8)	1.471(8)	1.468(4)	1.462(4)
C4–N2	1.480(3)	1.462(3)	1.462(3)	1.450(8)	1.467(8)	1.462(5)	1.462(5)
C5–N2	1.480(3)	1.466(3)	1.457(3)	1.469(7)	1.484(8)	1.468(5)	1.460(5)
N1–C1–N2	128.6(2)	128.6(2)	130.9(2)	131.0(5)	130.5(6)	130.7(3)	131.0(3)
C2–N1–C1	118.3(2)	118.3(2)	118.1(2)	119.0(6)	118.2(6)	118.3(3)	118.6(3)
C3–N1–C1	126.9(2)	126.4(2)	127.0(2)	125.5(6)	126.5(5)	127.6(3)	127.2(2)
C2–N1–C3	114.7(2)	115.3(2)	114.9(2)	115.5(6)	115.3(5)	113.6(3)	114.2(3)
C4–N2–C1	117.9(2)	118.8(2)	118.2(2)	118.2(5)	118.3(5)	118.5(3)	118.2(3)
C5–N2–C1	126.5(2)	125.4(2)	127.0(2)	127.6(5)	127.5(6)	126.7(3)	127.2(2)
C4–N2–C5	115.5(2)	114.9(2)	114.4(2)	114.2(5)	114.0(5)	114.8(3)	114.3(3)

Table 1. Selected bond lengths and angles for the [CH(NMe<sub>2</sub>)<sub>2</sub>]<sup>+</sup> cations in compounds **1** to **5** [Å, °].

Table 2. Hydrogen bonding geometry in **1** [Å, °].

	C–H...Cl	<i>d</i> (C–H)	<i>d</i> (H...Cl)	<i>d</i> (C...Cl)	∠(C–H...Cl)
HB1	C5'–H5'A...Cl	0.98(2)	2.86(2)	3.790(1)	159(1)
HB2	C3'–H3'A...Cl	0.96(3)	2.79(3)	3.587(1)	142(1)
HB3	C1''–H1''...Cl	0.98(3)	2.55(3)	3.506(1)	168(1)
HB4	C4'''–H4'''B...Cl	0.99(3)	2.79(3)	3.721(1)	158(1)
HB5	C4''''–H4''''A...Cl	1.02(3)	2.73(3)	3.719(1)	165(1)
HB6	C5–H5B...Cl	0.96(3)	2.87(3)	3.782(1)	160(1)

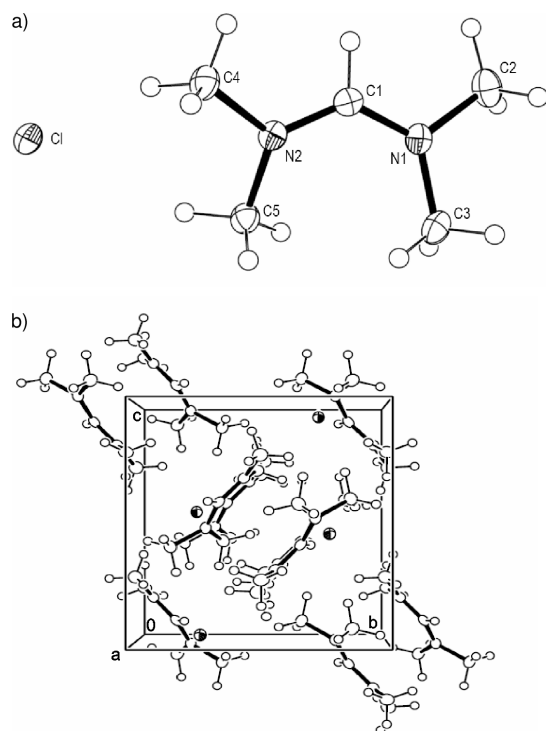


Fig. 1. Crystal structure of **1**. a: ORTEP drawing with 50% probability ellipsoids. b: The cell contents projected on (100).

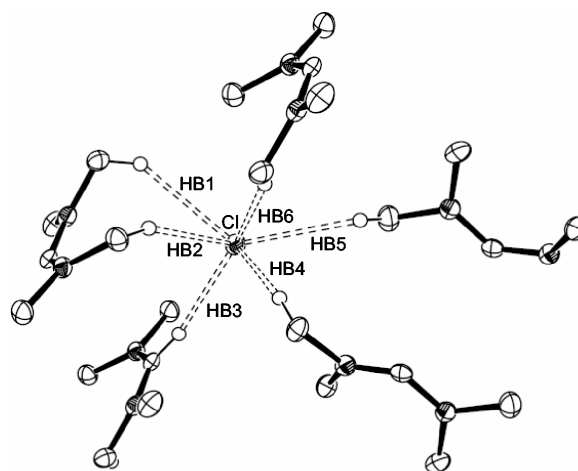
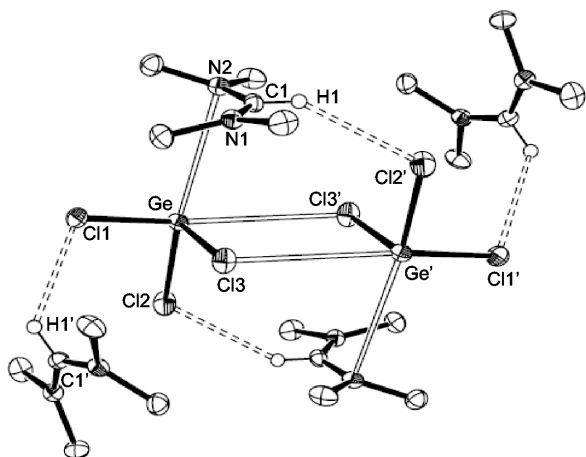


Fig. 2. The hydrogen bonding network about the chloride ion in **1**. ORTEP drawing with 50% probability ellipsoids. Weak hydrogen bonds are abbreviated as HB.

Compound **2** crystallizes as a centrosymmetric dimer and contains three regular Ge–Cl bonds with a mean length of 2.298 Å (see Table 3). The Cl–Ge–Cl angles fall over a range between 95.0(1)° and 96.3(1)°. These geometry parameters agree well with corresponding values in other studies of the analogous compounds [5a, 15]. The Ge atoms in **2** are (3+2)-coordinated (Fig. 3). The fourth contact at the Ge atom is a Ge...Cl secondary bond with a length of 3.723(1) Å, reasonably less than the van der Waals distance of 3.90 Å [ $r_{VDW}$  (Ge) = 2.15 Å [16]]. Furthermore, a weak N...Ge contact [3.565(1) Å] is found to establish a direct connection between cation and anion in the crystal of **2**. Such a contact has not been reported before for [GeCl<sub>3</sub>]<sup>−</sup> salts with other nitrogen containing cations. This coordination

Table 3. Selected bond lengths and angles about the Ge(II) atom in **2** [ $\text{\AA}$ ,  $^\circ$ ].

Ge-Cl1	2.315(1)	Ge-Cl2	2.298(1)
Ge-Cl3	2.282(1)	Ge-Cl3'	3.723(1)
Ge-N2	3.565(1)		
Cl1-Ge-Cl2	95.8(1)	Cl1-Ge-Cl3	95.0(1)
Cl2-Ge-Cl3	96.3(1)	Cl1-Ge-Cl3'	164.3(1)
Cl2-Ge-Cl3'	95.9(1)	Cl3-Ge-Cl3'	73.4(1)
N2-Ge-Cl1	90.7(1)	N2-Ge-Cl2	173.6(1)
N2-Ge-Cl3	82.8(1)	N2-Ge-Cl4	77.7(1)

Fig. 3. The dimeric molecular structure of **2**, ORTEP drawing with 50% probability ellipsoids. Empty bonds represent Ge-Cl and Ge-N secondary contacts, dashed line for hydrogen bond. Hydrogen atoms at methyl groups are omitted for clarity.

mode is different from (3+3)-coordinated polymeric pseudo-octahedral structures encountered frequently in the cases of trichlorogermanite salts of inorganic or small organic cations (with less than four carbon atoms), such as  $\text{Cs}[\text{GeCl}_3]$  [17],  $\text{Rb}[\text{GeCl}_3]$  [15a],  $[\text{MeNH}_3][\text{GeCl}_3]$  [18],  $[\text{Me}_4\text{N}][\text{GeCl}_3]$  [5a],  $[\text{PrPH}_3][\text{GeCl}_3]$  [15b] and  $[\text{Me}_3\text{PH}][\text{GeCl}_3]$  [15c]. In the situation of the large cation trichlorogermanite(II) compounds, such as  $[\text{PhNEt}_3][\text{GeCl}_3]$  [15d],  $[\text{PPh}_4][\text{GeCl}_3]$  [6] and  $[\text{Bu}_3\text{PCl}][\text{GeCl}_3]$  [15e], “free”  $[\text{GeCl}_3]$  units are present.

There are two further contacts in **2**, which can be classified as weak hydrogen bonds of the  $\text{C-H}\cdots\text{Cl}$  type with lengths of 2.87(2)  $\text{\AA}$  and 2.85(2)  $\text{\AA}$  (Table 4). These values fit quite well in the range of weak hydrogen bond lengths reported,  $\text{C-H}\cdots\text{Cl-Ge}$  2.81(5)–2.84(5)  $\text{\AA}$  [15c],  $\text{C-H}\cdots\text{Cl-Sn}$  2.78–2.90  $\text{\AA}$  [19].

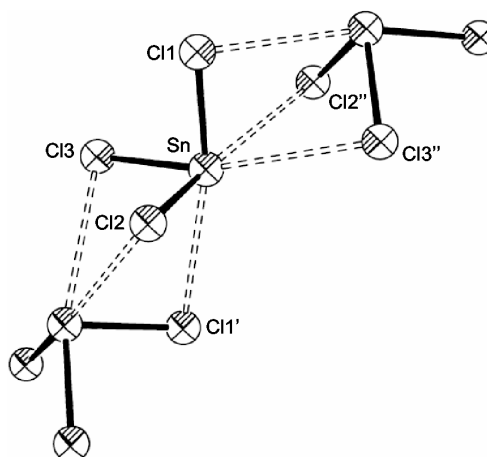
In the crystals of **3**, the  $[\text{SnCl}_3]^-$  anions form trigonal pyramidal units (Fig. 4) with three short Sn-Cl bonds [2.505(1), 2.506(1), 2.538(1)  $\text{\AA}$ ] (Table 5).

Table 4. Hydrogen bonding geometry in **2** [ $\text{\AA}$ ,  $^\circ$ ].

$\text{C-H}\cdots\text{Cl}$	$d(\text{C-H})$	$d(\text{H}\cdots\text{Cl})$	$d(\text{C}\cdots\text{Cl})$	$\langle\langle\text{C}\cdots\text{H}\cdots\text{Cl}\rangle\rangle$
$\text{Cl1-H1}\cdots\text{Cl2}^*$	0.93(2)	2.87(2)	3.684(1)	148(1)
$\text{Cl1'-H1'}\cdots\text{Cl1}$	0.93(2)	2.85(2)	3.458(1)	124(1)

Table 5. Selected bond lengths and angles of the  $\text{SnCl}_3$  unit in **3** [ $\text{\AA}$ ,  $^\circ$ ].

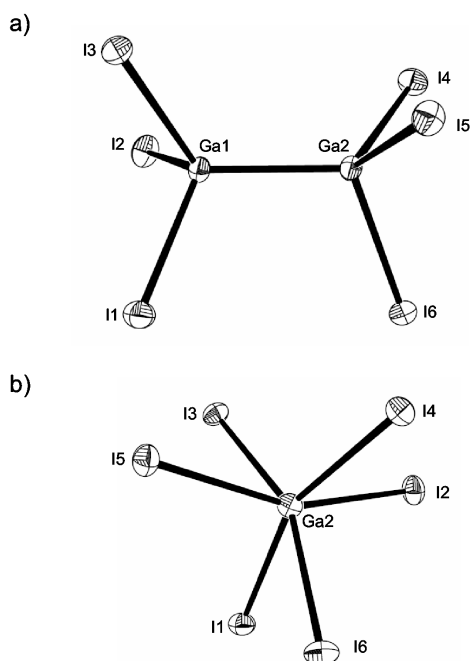
Sn-Cl1	2.506(1)	Sn-Cl2	2.505(1)
Sn-Cl3	2.538(1)	Sn-Cl1'	3.465(1)
Sn-Cl2''	3.495(1)	Sn-Cl3''	3.591(1)
Cl1-Sn-Cl2	91.4(1)	Cl1-Sn-Cl3	92.7(1)
Cl2-Sn-Cl3	93.6(1)	Cl1'-Sn-Cl2''	112.5(1)
Cl1'-Sn-Cl3''	112.0(1)	Cl2''-Sn-Cl3''	62.5(1)

Fig. 4. The polymeric chain structure of **3**, ORTEP drawing with 50% probability ellipsoids.

In addition three long intermolecular  $\text{Sn}\cdots\text{Cl}$  contacts [3.465(1), 3.495(1), 3.591(1)  $\text{\AA}$ ] are observed. These values are less than the sum of the van der Waals radii (3.92  $\text{\AA}$  [14]). This six-fold coordination of the Sn atoms was already observed for cesium trichlorostannite  $\text{Cs}[\text{SnX}_3]$  ( $\text{M} = \text{Cl}, \text{Br}, \text{I}$ ) [20], or trichlorostannite(II) salts of small organic cations, *e.g.*  $[\text{MeNH}_3][\text{SnX}_3]$  [21]. Usually the analogous compounds with larger cations have (3+2)-coordinated  $\text{Sn}^{\text{II}}$  centers, such as  $[\text{tBuNH}_3][\text{SnCl}_3]$  [21c],  $[\text{Pr}_4\text{N}][\text{SnI}_3]$  [22], (2-thienylmethyl)ammonium trichlorostannite [23], or (3+1) coordination types as in  $[\text{C}_5\text{Me}_5\text{Ge}][\text{SnCl}_3]$  [24] and sometimes they even comprise “free”  $[\text{SnCl}_3]^-$  units in  $[\text{PPh}_4][\text{SnCl}_3]$  [19]. The environment of  $\text{Sn}^{\text{II}}$  is best described as distorted  $\text{Cl}_6$  octahedron with two very different opposite triangular faces and thus forms a one-dimensional polymeric chain separated by the cations. The mean Sn-Cl length (2.516  $\text{\AA}$ ) and Cl-Sn-Cl angles (92.6 $^\circ$ )

Table 6. Selected bond lengths and angles of  $M_2X_6^{2-}$  ( $M = Ga, In$ ) units in compounds **4** and **5**.

Compound	<b>4</b> [CH(NMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> [Ga <sub>2</sub> I <sub>6</sub> ]	<b>5</b> [CH(NMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> [In <sub>2</sub> Cl <sub>6</sub> ]
M1–M2	2.423(1)	2.719(1)
M1–X1	2.604(1)	2.411(1)
M1–X2	2.605(1)	2.402(1)
M1–X3	2.594(1)	2.397(1)
M2–X4	2.572(2)	2.418(1)
M2–X5	2.594(1)	2.409(1)
M2–X6	2.610(1)	2.412(1)
X1–M1–M2	110.1(1)	115.2(1)
X2–M1–M2	114.3(1)	115.4(1)
X3–M1–M2	116.1(1)	115.4(1)
X1–M1–X2	106.9(1)	103.2(1)
X1–M1–X3	105.6(1)	101.3(1)
X2–M1–X3	102.9(1)	104.5(1)
M1–M2–X4	116.9(1)	118.2(1)
M1–M2–X5	113.0(1)	113.0(1)
M1–M2–X6	109.1(1)	117.3(1)
X4–M2–X5	104.7(1)	103.5(1)
X4–M2–X6	105.2(1)	98.6(1)
X5–M2–X6	107.4(1)	104.1(1)

Fig. 5. The structure of  $Ga_2I_6^{2-}$  unit in **4**, ORTEP drawing with 50% probability ellipsoids. (a: side view; b: axial direction).

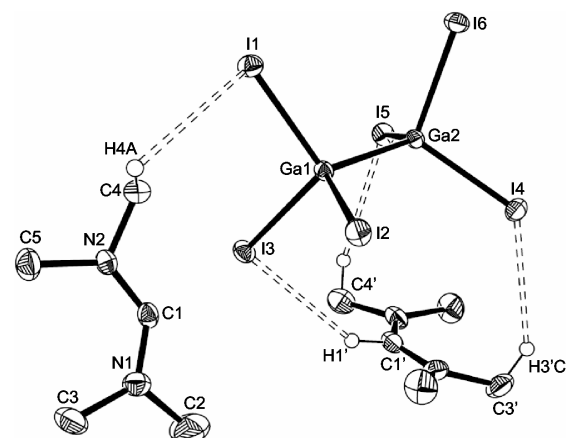
can be compared with the (3+2) coordinated species (2.530 Å, 91.7° and 2.526 Å, 89.9°) for two sets of  $[SnCl_3]^-$  groups in (2-thienylmethyl)ammonium trichlorostannite [22].

Table 7. Hydrogen bonding geometry in **4** [Å, °].

C–H...I	<i>d</i> (C–H)	<i>d</i> (H...I)	<i>d</i> (C...I)	∠(C–H...I)
C4–H4A...I1	0.98(4)	3.13(4)	3.707(1)	117(1)
C1'–H1'...I3	0.95(4)	3.14(4)	3.958(1)	145(1)
C4'–H4'B...I5	0.98(4)	3.13(4)	3.944(1)	142(1)
C3'–H3'C...I4	0.98(4)	3.09(4)	3.868(1)	138(1)

Table 8. Hydrogen bonding geometry in **5** [Å, °].

C–H...Cl	<i>d</i> (C–H)	<i>d</i> (H...Cl)	<i>d</i> (C...Cl)	∠(C–H...Cl)
C5'–H5'C...Cl4	1.01(4)	2.88(4)	3.885(1)	172(1)
C1–H1...Cl4	0.98(3)	2.75(4)	3.633(1)	151(1)
C1'–H1'...Cl3	0.98(3)	2.85(4)	3.499(1)	125(1)

Fig. 6. Crystal structure of **4**, ORTEP drawing with 50% probability ellipsoids. Weak contacts between H and I atoms are represented as dashed lines. Hydrogen atoms at methyl groups are omitted for clarity.

### Crystal structures of **4** and **5**

The crystal structures of **4** and **5** which show the cation-anion connectivity through hydrogen bridges are depicted in Figs 6 and 7. Geometry parameters concerning the formamidineum units are listed in Table 1, those for the  $M_2X_6^{2-}$  ions in Table 6 and data concerning the hydrogen bond networks are given in Tables 7 (**4**) and 8 (**5**).

The  $M_2X_6$  units in **4** and **5** adopt a distortedly staggered conformation (distorted  $D_{3d}$  symmetry) (see Fig. 5 for two views of the anion of **4**). The direct metal-metal bonds are 2.423(1) Å (Ga–Ga) in **4** and 2.719(1) Å (In–In) in **5**, respectively. These values are in good agreement with those of former studies: Ga–Ga 2.390(2) Å in  $[NMe_4]_2[Ga_2Cl_6]$  [25], 2.419(5) Å in  $[Pr_4N]_2[Ga_2Br_6]$  [26], 2.407–2.414 Å in  $[HNPh_3]_2[Ga_2X_6]$  ( $X = Cl, Br, I$ ) [27], In–In 2.67(1) Å in  $KInBr_3$  [28], 2.727(1) Å in  $[PPh_4]_2[In_2Cl_6]$  [29].

Table 9. Data from vibrational spectra of compounds **4** and **5** [ $\text{cm}^{-1}$ ].

<b>4</b>	<b>5</b>	assignment	description
188 m	324 s	$E_g$	$\nu(\text{M-X})$
84 m	112 s	$E_g$	$\delta(\text{MX}_3)$
76 s	82 m	$E_g$	$\text{MX}_3$ rocking
282 w	293 w	$A_{1g}$	$\nu(\text{M-X})$
119 vs	175 vs	$A_{1g}$	$\nu(\text{M-M})$
—	82 m	$A_{1g}$	$\delta(\text{MX}_3)$
199 vs	332 m, 284s <sup>a</sup>	$E_u$	$\nu(\text{M-X})$
155 s	292s	$A_{2u}$	$\nu(\text{M-X})$

<sup>a</sup> Fermi resonance from fundamental at  $308 \text{ cm}^{-1}$ .

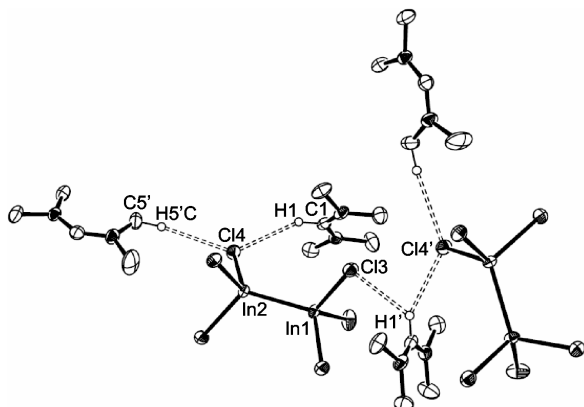


Fig. 7. The crystal structure of **5**, ORTEP drawing with 50% probability ellipsoids. Hydrogen bonds are represented as dashed lines. Hydrogen atoms at methyl groups are omitted for clarity.

In the structure of **5**, two cations are weakly connected to one chloride ion (Fig. 7),  $\text{C5}'\text{-H5}'\text{C}\cdots\text{Cl4}$   $2.83(1) \text{ \AA}$ ,  $\text{C1-H1}\cdots\text{Cl4}$   $2.75(1) \text{ \AA}$  (Table 8), while two of these units are in further contact through a hydrogen bridge  $\text{H1}'\cdots\text{Cl}$  [ $2.85(1) \text{ \AA}$ ], which is more than  $0.1 \text{ \AA}$  shorter than the van der Waals distance  $2.95 \text{ \AA}$ .

There are also weak  $\text{H}\cdots\text{I}$  contacts in **6**. Each anion unit is “closely” connected to one cation by three hydrogen bonds,  $\text{C1}'\text{-H1}'\cdots\text{I3}$ ,  $\text{C4}'\text{-H4}'\text{B}\cdots\text{I5}$ ,  $\text{C3}'\text{-H3}'\text{C}\cdots\text{I4}$  (Fig. 8), and more “loosely” to another anion unit by the contact  $\text{C4-H4A}\cdots\text{I1}$  (Table 9).

#### Vibrational spectroscopy studies of **4** and **5**

The Raman spectra of **4** and **5** in the region below  $400 \text{ cm}^{-1}$  closely resemble those reported for  $[\text{Me}_4\text{N}][\text{Ga}_2\text{I}_6]$  [30],  $[\text{Ph}_3\text{PH}][\text{Ga}_2\text{I}_6]$  [31] and  $[\text{Bu}_4\text{N}][\text{In}_2\text{Cl}_6]$  [32]. The ethane-like staggered anion units have approximately  $D_{3d}$  symmetry. From the vibration representation for a  $D_{3d}$  ion, which is  $3A_{1g} + 3E_g + A_{1u} + 2A_{2u} + 3E_u$ , follows that there are

five infrared-active and six Raman-active vibrations. The  $A_{1g}$  and  $E_g$  modes are Raman-active, those of  $A_{2u}$  and  $E_u$  are infrared-active and the  $A_{1u}$  mode is the inactive torsional mode.

The assignment of the IR and Raman spectra of **4** and **5** follows the interpretation from the literature [30, 32] and is listed in Table 9. Only the lines assignable to the anion vibrations are listed there. The values are so close to those found in other salts of  $[\text{Ga}_2\text{I}_6]^{2-}$  [30, 31] and  $[\text{In}_2\text{Cl}_6]^{2-}$  [32] that they do not deserve a detailed discussion.

#### Experimental Section

**General remarks.** All reactions and manipulations were carried out under a dry nitrogen atmosphere with standard Schlenk and high vacuum techniques using standard double manifolds or a glove box operated under argon. Solvents were purified and dried by standard techniques immediately prior to use. All NMR data were collected on a Bruker AM 200 (operating at  $200 \text{ MHz}$  for  $^1\text{H}$  and  $75 \text{ MHz}$  for  $^{13}\text{C}$ ) FT-NMR spectrometer. Chemical shifts are quoted relative to TMS. A Bruker Apex X-ray diffractometer ( $\lambda = 0.71073 \text{ \AA}$ ) was used to collect the reflections for single crystal structure determination. Raman spectra were recorded on a Bruker FRA 106 (Nd: YAG-laser, wave length  $1064 \text{ nm}$ ). And IR spectra were measured with a Bruker IFS (103 V) using KBr pellets.  $[\text{CH}(\text{NMe}_2)_2]\text{Cl}$  was prepared by a literature method [33].

$[\text{CH}(\text{NMe}_2)_2][\text{GeCl}_3]$  (**2**). **1** ( $0.9 \text{ g}$ ,  $6.6 \text{ mmol}$ ) was mixed with  $\text{GeCl}_2\cdot\text{Dioxane}$  [34] ( $1.6 \text{ g}$ ,  $6.6 \text{ mmol}$ ) in a  $250 \text{ ml}$  flask in the glove box. The reaction vessel was cooled to  $-25 \text{ }^\circ\text{C}$  and  $100 \text{ ml}$  THF was added in one portion. The reaction mixture was warmed to ambient temperature and refluxed for  $60 \text{ min}$ , during which the suspension became clear. The solution was concentrated under vacuum and kept at  $-25 \text{ }^\circ\text{C}$  overnight. Well formed colourless crystals were obtained. Yield  $1.58 \text{ g}$  ( $86\%$ ), m.p.  $72 \text{ }^\circ\text{C}$ . Analysis for **2** ( $280.11 \text{ g mol}^{-1}$ ): calcd. C  $21.40$ , H  $4.60$ , N  $10.10$ ; found C  $20.96$ , H  $4.58$ , N  $9.81$ .  $^1\text{H}$  NMR ( $d_8\text{-THF}$ ):  $\delta = 3.30 / 3.39$  (s,  $12\text{H}$ ,  $\text{CH}_3$ ),  $7.80$  (s,  $1\text{H}$ , CH).  $^{13}\text{C}$  NMR ( $d_8\text{-THF}$ ):  $\delta = 41.1 / 47.9$  ( $\text{CH}_3$ ),  $158.4$  (NCN).

$[\text{CH}(\text{NMe}_2)_2][\text{SnCl}_3]$  (**3**). The same synthesis and work-up procedures as described for **2** were applied, with **1** ( $2.1 \text{ g}$ ,  $15.4 \text{ mmol}$ ) and  $\text{SnCl}_2$  ( $2.9 \text{ g}$ ,  $15.4 \text{ mmol}$ ). The only variation was the application of a prolonged reaction time at ambient temperature ( $10 \text{ h}$ ) after refluxing the reaction mixture for  $60 \text{ min}$ . Yield  $4.57 \text{ g}$  ( $88\%$ ), m.p.  $65 \text{ }^\circ\text{C}$ . Analysis for **3** ( $326.21 \text{ g mol}^{-1}$ ): calcd. C  $18.41$ , H  $4.02$ , N  $8.59$ ; found C  $18.24$ , H  $3.96$ , N  $8.48$ .  $^1\text{H}$  NMR ( $d_8\text{-THF}$ ):  $\delta = 3.37 / 3.45$  (s,  $12\text{H}$ ,  $\text{CH}_3$ ),  $7.96$  (s,  $1\text{H}$ , CH).  $^{13}\text{C}$  NMR ( $d_8\text{-THF}$ ):  $\delta = 41.5 / 48.5$  ( $\text{CH}_3$ ),  $159.4$  (NCN).

Table 10. Crystal and refinement data for the solid state structure of compounds **1–5**.

Compounds	<b>1</b> [CH(NMe <sub>2</sub> ) <sub>2</sub> ]Cl	<b>2</b> [CH(NMe <sub>2</sub> ) <sub>2</sub> ] [GeCl <sub>3</sub> ]	<b>3</b> [CH(NMe <sub>2</sub> ) <sub>2</sub> ] [SnCl <sub>3</sub> ]	<b>4</b> [CH(NMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> [Ga <sub>2</sub> I <sub>6</sub> ]	<b>5</b> [CH(NMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> [In <sub>2</sub> Cl <sub>6</sub> ]
Cryst. system	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub>	<i>P</i> na2 <sub>1</sub>
<i>a</i> [Å]	8.748(3)	8.299(2)	8.324(2)	9.962(2)	22.970(11)
<i>b</i> [Å]	8.959(3)	13.737(3)	8.380(2)	9.910(2)	11.613(6)
<i>c</i> [Å]	9.709(3)	9.781(2)	16.134(5)	14.092(2)	8.935(5)
$\beta$ [°]	90.665(5)	90.765(4)	90	99.939(3)	90
<i>V</i> [Å <sup>3</sup> ]	760.9(4)	1098.8(4)	1125.5(6)	1370.3(4)	2383(2)
$\rho_{\text{calc}}$ [g cm <sup>−3</sup> ]	1.193	1.693	1.925	2.674	1.797
<i>Z</i>	4	4	4	2	4
$\mu$ [mm <sup>−1</sup> ]	0.412	3.465	2.932	8.726	2.608
Temp. [K]	123(2)	123(2)	153(2)	123(2)	123(2)
<i>T</i> <sub>min</sub> /max	0.8593/0.9878	0.1681/0.4901	0.4183/0.6513	0.4207/0.7216	0.6804/0.7116
2 $\theta_{\text{max}}$ [°]	55.06	60.08	60.08	60.00	59.94
Measd. refl.	4789	12302	13017	15886	26567
Unique refl.	1729	3204	3287	7814	6913
Observed refl.	1393	2827	3079	7397	6452
<i>R</i> <sub>int</sub>	0.0527	0.0439	0.0343	0.0308	0.0389
Parameters	125	152	152	207	303
<i>R</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]/ <i>wR</i> <sup>2</sup>	0.0527/0.1097	0.0340/0.0774	0.0213/0.0428	0.0316/0.0605	0.0249/0.0525
$\rho_{\text{H}}$ (min/max) [eÅ <sup>−3</sup> ]	−0.305/0.453	−1.164/0.899	−0.842/0.749	−0.761/0.865	−0.361/0.668
Flack param.			0.02(2)	0.04(2)	0.03(2)
CCDC-No.	244189	244187	244188	244186	244190

[CH(NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>[Ga<sub>2</sub>I<sub>6</sub>] (**4**). GaI [11] (1.0 g, 5.0 mmol) of was added to a stirred solution of **1** (0.69 g, 5.0 mmol) in 50 ml THF with the aid of a 'solid transfer container' at −78 °C. This salt addition was performed in small portions in order to minimize temperature fluctuations. The reaction mixture was stirred for 4 h at this temperature and allowed to warm up to ambient temperature overnight. The mixture was filtered through a cannula equipped with a glass wool filter and a clear solution was obtained. 5 ml of CH<sub>3</sub>CN was added to the yellowish heavy oil which resulted from removing all THF under vacuum from the solution. The vessel with the solution in CH<sub>3</sub>CN was immersed in a 1 l Dewar container filled with ethanol and was then allowed to cool down slowly to −25 °C. Well formed crystals were obtained in this way. m.p. 89 °C. Analysis for **4** (1103.21 g mol<sup>−1</sup>): calcd. C 18.17, H 4.01, N 8.57; found C 10.45, H 2.33, N 4.93. −<sup>1</sup>H NMR (d<sub>3</sub>-CD<sub>3</sub>CN):  $\delta$  = 3.19 / 3.28 (s, 24H, CH<sub>3</sub>), 7.50 (s, 2H, CH). −<sup>13</sup>C NMR (d<sub>3</sub>-CD<sub>3</sub>CN):  $\delta$  = 39.4 / 46.5 (CH<sub>3</sub>), 157.3 (NCN).

[CH(NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>[In<sub>2</sub>Cl<sub>6</sub>] (**5**). **1** (1.5 g, 10.9 mmol) was combined with InCl (1.68 g, 11.1 mmol) in a 100 ml flask in the glove box. The mixture was cooled to −78 °C and 50 ml THF was added. The work-up procedure was the same as described for **4**. Well formed colourless crystals were obtained. Yield 0.39 g (39%), m.p. 92 °C. Analysis for **5** (644.693 g mol<sup>−1</sup>): calcd. C 18.63, H 4.06,

N 8.69; found C 18.17, H 4.01, N 8.57. −<sup>1</sup>H NMR (d<sub>3</sub>-CD<sub>3</sub>CN):  $\delta$  = 3.19 / 3.28 (s, 24H, CH<sub>3</sub>), 7.49 (s, 2H, CH). −<sup>13</sup>C NMR (d<sub>3</sub>-CD<sub>3</sub>CN):  $\delta$  = 39.5 / 46.2 (CH<sub>3</sub>), 157.5 (NCN).

*Crystal structure analyses.* Single crystals of compounds **1–5** were mounted under inert perfluoropolyether at the tip of a glass fiber and were cooled in the cryostream of the diffractometer. Structure solutions were carried out using direct methods and the refinements of the structures were undertaken with the program SHELXTL 5.01 [35]. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms isotropically with a riding model. Further details of data collection and refinement are listed in Table 10. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications (see Table 1). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk].

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