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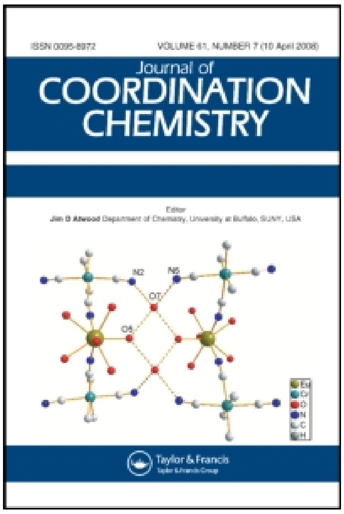

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Syntheses and structural characterization of inorganic-organic hybrid solids of diimidazolium hexachlorostannate complexes

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Syntheses and structural characterization of inorganic-organic hybrid solids of diimidazolium hexachlorostannate complexes

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Six organic-inorganic hybrid complexes of formula $[(H_2L)SnCl_6]$ prepared from imidazole derivatives (**1**, L1 = 1,4-*bis*(imidazolyl)butane; **2**, L2 = 1,1′-*bis*(imidazolyl)methane; **3**, L3 = *di*(2-benzimidazol-1-ylethyl)ether; **4**, L4 = 1,1′-*bis*(benzimidazolyl)methane; **5**, L5 = 2-(imidazol-1-yl)-1-phenylethanone; **6**, L6 = 7-imidazolyl-2,4-dimethyl-1,8-naphthyridine) and tin(II) chloride were characterized through X-ray diffraction analysis. The results reveal that **1–6** have 3D network structures built from hydrogen bonds between imidazolium cations, water molecules and $SnCl_6^{2-}$. The arrangement of the anions and cations in their solid state is dominated by the size, symmetry, and charge numbers of the imidazolium cations. The TGA studies show that the complexes are thermally stable.

Keywords: Tin; Imidazolium; Crystal structure; Thermal properties; Inorganic-organic hybrid

1. Introduction

The preparation of organic-inorganic hybrid materials with novel properties represents an important research field in solid-state chemistry [1, 2]. These materials are likely to exhibit diverse structures, improved properties, and functions unobserved in purely inorganic or organic phases, such as novel magnetic [3], electrical [4–6], and optical properties [7], providing many possibilities to construct attractive multifunctional materials.

Organic-inorganic hybrid compounds based on layers of anionic transition metal(II) halogen frameworks and organic ammonium cations such as 2D systems with $(RNH_3)_2M(II)X_4$ or $(NH_3RNH_3)M(II)X_4$ formula (M = Pb, Sn, Cu, etc.; X = I, Br, Cl; R = alkyl, phenyl, etc.) have been extensively studied in the field of low dimensional magnetism [8]. Structural transitions in hybrid solid materials containing long-chain alkylammonium cations were studied in order to better understand the biological lipid

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bilayers [9]. Most of the ammonium cations incorporated in these hybrid materials are either alkylammonium or single ring aromatic ammonium cations.

Metal halides such as SnX_2 (X = Cl, Br, and I) have been widely employed as semi-conducting components [10] in organic-inorganic hybrid semiconductors, and these materials have demonstrated potential applications in display and storage technologies because of their stable exciton, excellent film processability, and superior carrier mobility [11]. These hybrid tin-containing compounds have also been used as ferroelectric materials [12]. Recent reports focus mainly on introduction of protonated organic amine into metal halides [13]. Examples of bifunctional ammonium cations also bearing a hydrogen donor and/or acceptor part are scarce. Inorganic and organic salts containing octahedral $SnCl_6^{2-}$ and organic ammonium have been previously reported [14–17]. To explore the influence of the size and charge numbers of the cations on the structural variation, herein we report the synthesis and structures of hexachlorostannate complexes with mono and *bis*(imidazole) derivatives as mono or bifunctional organic ammonium cations.

2. Experimental

2.1. *Materials*

All reagents and solvents were used as received. **L1**–**L4** [18], **L5** [19], and **L6** [20] were prepared according to modified procedures.

2.2. *Physical measurements and analyses*

Elemental analysis was determined with a Perkin-Elmer 2400C instrument, and IR spectra were measured as KBr pellets using a Nicolet 5DX FX-IR spectrophotometer at the analysis center, Department of Chemistry, Zhejiang University. Thermogravimetric analyses (TGA) were studied by a Delta Series TA-SDT Q600 in a N_2 atmosphere between room temperature and 800°C (heating rate = $10^\circ C\,min^{-1}$) using Al crucibles.

2.3. *Preparation of the compounds*

2.3.1. Preparation of $[(H_2L1)SnCl_6] \cdot H_2O$, (1). Tin(II) chloride dihydrate (47 mg, 0.20 mmol) dissolved in 1 mL of conc. hydrochloric acid, 3 mL of water, and 5 mL of methanol, was treated with **L1** (38 mg, 0.20 mmol). After stirring for several minutes, the solution was filtered. The clear solution stood at room temperature for several days to give colorless block crystals. Yield: 50 mg, 86%. Anal. Calcd for $C_{10}H_{18}Cl_6N_4OSn$ (541.67): C, 22.17; H, 3.35; N, 10.34%. Found: C, 22.07; H, 3.26; N, 10.28%. IR (KBr disc, cm^{-1}): 3546s, 3477m, 3240m, 3137s, 3063w, 2961w, 2866w, 1600m, 1573s, 1544s, 1465m, 1400m, 1403m, 1292m, 1276w, 1183w, 1140m, 1102m, 1081w, 1023m, 852m, 764s, 726w, 636m, 617w, 562m.

2.3.2. Preparation of [(H_2L2)$SnCl_6$], (2). The compound was prepared by the similar procedure as for **1** from tin(II) chloride dihydrate (47 mg, 0.20 mmol) and **L2** (14.8 mg, 0.10 mmol). Yield: 41 mg, 85.1%. Anal. Calcd for $C_7H_{10}Cl_6N_4Sn$ (481.58): C, 17.46; H, 2.09; N, 11.63%. Found: C, 17.38; H, 2.36; N, 11.54%. IR (KBr disc, cm^{-1}): 3296s, 3138m, 3065w, 3028w, 1620w, 1569m, 1538m, 1438m, 1397m, 1308s, 1271m, 1144m, 1083m, 1015m, 978m, 862w, 750s, 723m, 613m.

2.3.3. Preparation of [(H_2L3)$SnCl_6$] • $3H_2O$, (3). The compound was prepared by a similar procedure as for **1** from tin(II) chloride dihydrate (47 mg, 0.20 mmol) and **L3** (30.6 mg, 0.10 mmol). Yield: 57 mg, 82.1%. Anal. Calcd for $C_{18}H_{26}Cl_6N_4O_4Sn$ (693.82): C, 31.16; H, 3.78; N, 8.07%. Found: C, 31.57; H, 3.60; N, 8.15%. IR (KBr disc, cm^{-1}): 3511w, 3133w, 1613m, 1553s, 1499w, 1477s, 1448w, 1402w, 1376w, 1323m, 1284m, 1213m, 1122s, 1064m, 1010m, 923m, 857w, 756s, 702w, 624m, 582w, 470w, 422m.

2.3.4. Preparation of [(H_2L4)$SnCl_6$], (4). The compound was prepared by a similar procedure as for **1** from tin(II) chloride dihydrate (47 mg, 0.20 mmol) and **L4** (24.8 mg, 0.10 mmol). Yield: 50 mg, 86%. Anal. Calcd for $C_{15}H_{14}Cl_6N_4Sn$ (581.69): C, 30.97; H, 2.43; N, 9.63%. Found: C, 30.91; H, 2.32; N, 9.57%. IR (KBr disc, cm^{-1}): 3447w, 3279w, 3114w, 3060w, 1768w, 1614m, 1542m, 1496m, 1438s, 1398w, 1376w, 1342w, 1315w, 1259m, 1235w, 1207w, 1149w, 1129w, 1092w, 948w, 885w, 788w, 759s, 691m, 646m, 591m, 533w, 465w, 424m.

2.3.5. Preparation of [(HL5)$_2SnCl_6$], (5). The compound was prepared by a similar procedure as for **1** from tin(II) chloride dihydrate (23 mg, 0.10 mmol) and **L5** (18.6 mg, 0.10 mmol). Yield: 54 mg, 76.5%. Anal. Calcd for $C_{22}H_{22}Cl_6N_4O_2Sn$ (705.83): C, 37.43; H, 3.14; N, 7.94%. Found: C, 37.42; H, 3.11; N, 7.92%. IR (KBr disc, cm^{-1}): 3212w, 3143w, 1697s, 1597w, 1578w, 1543w, 1447m, 1400m, 1346m, 1316m, 1292w, 1229s, 1150w, 1104w, 1081m, 1020m, 984m, 816w, 763s, 691m, 644m, 620m, 572w.

2.3.6. Preparation of [(H_2L6)$SnCl_6$], (6). The compound was prepared by a similar procedure as for **1** from tin(II) chloride dihydrate (47 mg, 0.20 mmol) and **L6** (44.8 mg, 0.20 mmol). Yield: 90 mg, 80.1%. Anal. Calcd for $C_{13}H_{14}Cl_6N_4Sn$ (557.67): C, 27.99; H, 2.53; N, 10.04%. Found: C, 27.89; H, 2.48; N, 9.98%. IR (KBr disc, cm^{-1}): 3137s, 1615s, 1524s, 1403s, 1357s, 1329w, 1204w, 1162w, 1099w, 970w, 894w, 830w, 797w, 762w, 685w, 596w, 556w.

2.4. *X-ray crystallography*

Single-crystal X-ray diffraction data for **1**–**6** were collected at 298(2) K on a Siemens Smart/CCD area-detector diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) by using an ω-2θ scan mode. Data collection and reduction were performed using the SMART and *SAINT* software [21]. The structures were solved by direct methods, and non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F_2 using *SHELXTL* [22]. The hydrogen atoms were generated geometrically

Table 1. Data collection, structure solution, and refinement parameters for **1**–**3**.

	1	**2**	**3**
Formula	$C_{10}H_{18}Cl_6N_4OSn$	$C_7H_{10}Cl_6N_4Sn$	$C_{18}H_{26}Cl_6N_4O_4Sn$
Fw	541.67	481.58	693.82
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbca*	*P*2/*c*	$P\bar{1}$
a (Å)	12.382(15)	8.1289(10)	7.618(2)
b (Å)	14.389(18)	7.4336(9)	13.247(3)
c (Å)	22.66(3)	12.8216(15)	14.019(4)
α (°)			91.676(3)
β (°)	90	90.474(2)	96.435(2)
γ (°)			104.648(2)
V (A^3)	4038(9)	774.74(16)	1357.7(6)
Z	8	2	2
D_{Calcd} (Mg m^{-3})	1.782	2.064	1.697
Absorption coefficient (mm^{-1})	2.064	2.670	1.563
$F(000)$	2128	464	692
Crystal size (mm^3)	$0.28 \times 0.21 \times 0.15$	$0.21 \times 0.18 \times 0.15$	$0.25 \times 0.23 \times 0.20$
θ range (°)	1.80 – 25.01	2.51 – 25.01	1.46 – 25.00
Limiting indices	$-13 \le h \le 13$, $-16 \le k \le 17$, $-19 \le l \le 26$	$-9 \le h \le 8$, $-6 \le k \le 8$, $-14 \le l \le 15$	$-9 \le h \le 9$, $-14 \le k \le 15$, $-16 \le l \le 9$
Reflections collected	14165	3937	6835
Reflections independent (R_{int})	3324 (0.1065)	1365 (0.0174)	4655 (0.0207)
Goodness-of-fit on F^2	1.146	1.087	1.059
Final R indices [$I > 2\sigma I$]	0.0845, 0.2355	0.0164, 0.0406	0.0371, 0.0822
R indices (all data)	0.1290, 0.2555	0.0180, 0.0420	0.0689, 0.1012
Largest diff. peak and hole (e A^{-3})	1.072, −1.313	0.232, −0.461	0.844, −0.387

and included in structure factor calculations. Further details of the structural analysis are summarized in tables 1 and 2.

3. Results and discussion

3.1. *Synthesis and IR spectra*

Inorganic and organic salts containing $SnCl_6^{2-}$ and organic ammonium, previously reported [14–17], were prepared from Sn(IV) chloride. Reactions of $SnCl_2$ and the imidazolyl derivatives in acidic aqueous solution afford imidazolium salts of $SnCl_6^{2-}$ exclusively regardless of the ratio of the reactants. Imidazolium salts of $SnCl_4^{2-}$ were not obtained. Obviously Sn(II) was completely oxidized to Sn(IV) by air. All compounds were isolated as colorless crystals in high yields. These compounds are not soluble in almost all common solvents. IR spectra show strong stretches at 3296–3321 cm^{-1}, assignable to NH groups of the imidazolium cations. Bands at 1610 and 1450 cm^{-1} can be assigned to characteristic C=C, C=N stretching vibrations of the imidazolyl or aromatic rings.

The composition of these compounds $[(HL)_2(SnCl_6)]$ (L = imidazolyl derivatives) was determined by elemental analysis, and their structures were fully characterized by X-ray diffraction. The crystallographic data and refinement details are summarized in tables 1 and 2.

Table 2. Data collection, structure solution, and refinement parameters for **4**–**6**.

	4	**5**	**6**
Formula	$C_{15}H_{14}Cl_6N_4Sn$	$C_{22}H_{22}Cl_6N_4O_2Sn$	$C_{13}H_{14}Cl_6N_4Sn$
Fw	581.69	705.83	557.67
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbcm*	$P\bar{1}$	*C*c
a (Å)	7.827(2)	8.244(9)	16.563(5)
b (Å)	15.516(5)	12.169(14)	15.264(5)
c (Å)	16.441(5)	15.103(17)	7.818(3)
α (°)		77.537(14)	
β (°)	90	81.285(14)	102.767(4)
γ (°)		72.464(13)	
V (A^3)	1996.6(11)	1405(3)	1927.7(11)
Z	4	2	4
D_{Calcd} (Mg m^{-3})	1.935	1.669	1.922
Absorption coefficient (mm^{-1})	2.091	1.508	2.161
F(000)	1136	700	1088
Crystal size (mm^3)	$0.10 \times 0.09 \times 0.08$	$0.37 \times 0.23 \times 0.18$	$0.45 \times 0.12 \times 0.05$
θ range (°)	2.48 – 25.50	1.39 – 25.25	1.84 – 26.00
Limiting indices	$-9 \le h \le 9$, $-18 \le k \le 18$, $-19 \le l \le 19$	$-9 \le h \le 9$, $-14 \le k \le 14$, $-18 \le l \le 17$	$-20 \le h \le 20$, $-18 \le k \le 18$, $-9 \le l \le 9$
Reflections collected	14176	7239	7368
Reflections independent (R_{int})	1931 (0.0352)	4970 (0.0271)	3672 (0.0346)
Goodness-of-fit on F^2	1.211	1.000	1.044
Final R indices [$I > 2\sigma I$]	0.0626, 0.1331	0.0596, 0.1499	0.0579, 0.1259
R indices (all data)	0.0645, 0.1339	0.0962, 0.1798	0.0737, 0.1354
Largest diff. peak and hole (e A^{-3})	1.326, −1.676	2.655, −0.851	1.124, −0.976

3.2. *Structural description*

The imidazolium hexachlorostannate complexes **1**–**6** have the general formula [$(HL)_2(SnCl_6)$], and their structures consist of imidazolium and $SnCl_6^{2-}$, held together by hydrogen bonds. The anions are octahedral surrounded by six chlorides. The Sn–Cl bonds for **1**–**6** fall in the range 2.402(3)–2.483(3) Å and those involved in hydrogen bonding are at the upper range. These Sn–Cl distances are normal and consistent with those reported [15, 17]. The *cis*-Cl–Sn–Cl angles are close to 90° and *trans*-Cl–Sn–Cl angles are close to 180°.

Compound **1** [$(H_2L1)SnCl_6] \cdot H_2O$ (**L1** = 1,4-*bis*(imidazolyl)butane) crystallizes in an orthorhombic *P*bca space group, and there are eight formula units in the unit cell. X-ray diffraction analysis shows that the complex is composed of one $SnCl_6^{2-}$ anion, one diprotonated **L1** cation, and one water. **L1** is doubly protonated resembling 4,4′-H_2bipy cations in reported tin complexes [23]. The imidazolium cations and $SnCl_6^-$ are alternatively arranged. Extensive hydrogen bonds are observed between the cations, anions, and the lattice water molecules. One imidazolium forms hydrogen bonds with $SnCl_6^-$ with the $N \cdots Cl^i$ (i: $x - 1/2$, y, $-z + 1/2$) separation of 3.250(13) Å, and another links water molecule with $N \cdots O^i$ (i: $-x + 3/2$, $y - 1/2$, z) distance of 2.782(17) Å. The hydrogen bond parameters are summarized in table 3. In addition, water also participates in extensive hydrogen bonds with the chlorostannate and imidazolium cations. These hydrogen bonds link the cations, counter anions, and the lattice water molecules into a three-dimensional network structure. The 3D structure is shown in figure 1.

Table 3. Hydrogen-bond geometries for **1**–**6** (Å, °).[a]

D–H$\cdots$A	d(D–H)	d(H$\cdots$A)	d(D$\cdots$A)	∠(DHA)
1				
N(2)–H(2)$\cdots$O(1)#1	0.86	1.98	2.782(17)	154.3
N(4)–H(4)$\cdots$Cl(1)#2	0.86	2.43	3.250(13)	159.5
O(1)–H(11)$\cdots$Cl(1)#3	0.85	2.74	3.507(12)	150.5
O(1)–H(11)$\cdots$Cl(5)#3	0.85	2.88	3.468(14)	127.9
O(1)–H(11)$\cdots$Cl(6)#3	0.85	2.98	3.543(11)	125.9
O(1)–H(12)$\cdots$Cl(3)	0.85	2.82	3.259(12)	113.6
2				
N(2)–H(2)$\cdots$Cl(3)#2	0.86	2.670	3.337(18)	135.31
N(2)–H(2)$\cdots$Cl(3)#3	0.860	2.785	3.408(19)	130.64
3				
O(4)–H(26)$\cdots$Cl(4)#2	0.85	2.97	3.607(5)	133.7
O(4)–H(26)$\cdots$Cl(5)	0.85	2.97	3.714(5)	148.1
O(4)–H(26)$\cdots$Cl(6)	0.85	2.81	3.421(5)	130.1
O(4)–H(25)$\cdots$O(2)#3	0.85	1.95	2.781(7)	164.0
O(3)–H(24)$\cdots$Cl(4)#4	0.85	2.56	3.338(5)	152.1
O(3)–H(23)$\cdots$Cl(6)#5	0.85	2.56	3.396(6)	169.3
O(2)–H(22)$\cdots$Cl(3)#1	0.85	2.98	3.432(5)	115.5
O(2)–H(22)$\cdots$Cl(2)	0.85	2.51	3.343(5)	166.6
O(2)–H(21)$\cdots$O(3)	0.85	2.02	2.721(6)	139.7
N(4)–H(4)$\cdots$O(2)#6	0.86	2.06	2.859(7)	155.4
N(2)–H(2)$\cdots$O(4)	0.86	1.83	2.689(6)	175.4
4				
N(2)–H(2)$\cdots$Cl(3)#4	0.86	2.46	3.186(10)	142.4
N(2)–H(2)$\cdots$Cl(1)#3	0.86	3.04	3.655(12)	130.3
5				
N(2)–H(2)$\cdots$Cl(6)#1	0.86	2.41	3.251(8)	164.3
N(4)–H(4)$\cdots$Cl(3)#3	0.86	2.42	3.264(9)	166.9
6				
N(2)–H(20)$\cdots$Cl(1)#1	0.86	2.60	3.453(11)	174.3

[a] Symmetry codes for **1**: #1: $-x+3/2$, $y-1/2$, z; #2: $x-1/2$, y, $-z+1/2$; #3: $-x+3/2$, $y+1/2$, z; symmetry codes for **2**: #2: $-x+1$, y, $-z+1/2$; #3: $x+1$, $-y+1$, $z-1/2$; symmetry codes for **3**: #1: $-x+1$, $-y+1$, $-z$; #2: $-x+1$, $-y$, $-z+1$. #3: $-x+2$, $-y+1$, $-z+1$; #4: $x+1$, $y+1$, z; #5: $-x+1$, $-y+1$, $-z+1$; #6: x, y, $z+1$; symmetry codes for **4**: #3: $-x+1$, $y+1/2$, $-z+1/2$, #4: x, y, $z-1$; symmetry codes for **5**: #1: $-x$, $-y+1$, $-z+1$, #3: $-x+2$, $-y+1$, $-z$; symmetry codes for **6**: #1: $x+1/2$, $-y+1/2$, $z+1/2$.

Complex **2** was prepared by reacting 1,1′-*bis*(imidazolyl)methane (**L2**) with two equivalents of tin(II) chloride dihydrate in methanol and water mixed solvent. No water was involved in the lattice as determined by elemental analysis. Complex **2** crystallizes in the monoclinic space group *P*2/c with two formula units in the unit cell, and the asymmetric unit consists of a half diimidazolium cation and a half $SnCl_6^{2-}$ anion. The full structure is generated by the inversion center at Sn and C4 atom. The organic dications form a layered lamellar through Π–Π stacking. The organic layers and the anions are alternatively arranged and linked through $N(2)–H(2)\cdots Cl(3)^{i}$ (i: $-x+1$, y, $-z+1/2$) and $N(2)–H(2)\cdots Cl(3)^{ii}$ (ii: $x+1$, $-y+1$, $z-1/2$) hydrogen bonds. The diimidazolium and the Sn are held together *via* hydrogen bonds and weak π–π interactions to form a three-dimensional structure, shown in figure 2. Obviously, the layered structure with ABAB stacking sequence is stabilized by hydrogen bonds and weak π–π stacking forces.

Similar to **2**, complex **3** of the formula $[(H_2L3)SnCl_6]\cdot 3H_2O$ (**L3** = di(2-benzimidazol-1-ylethyl)ether) was prepared by reacting **L3** with two equivalents of tin(II) chloride dihydrate in methanol and water. Complex **3** crystallizes in the monoclinic space group $P\bar{1}$ with two formula units in the unit cell. The asymmetric unit consists of two

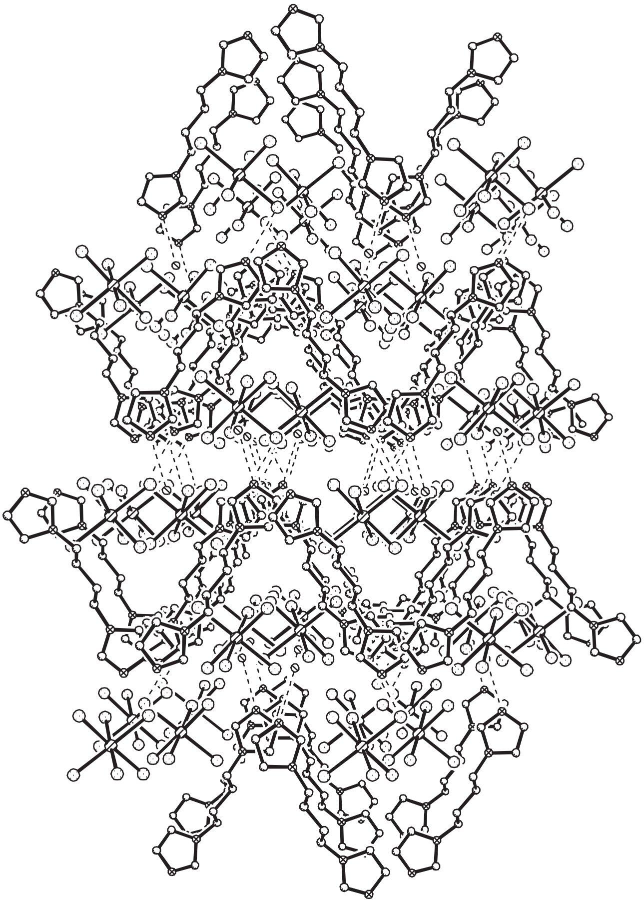

Figure 1. Packing diagram of **1** showing the three-dimensional network.

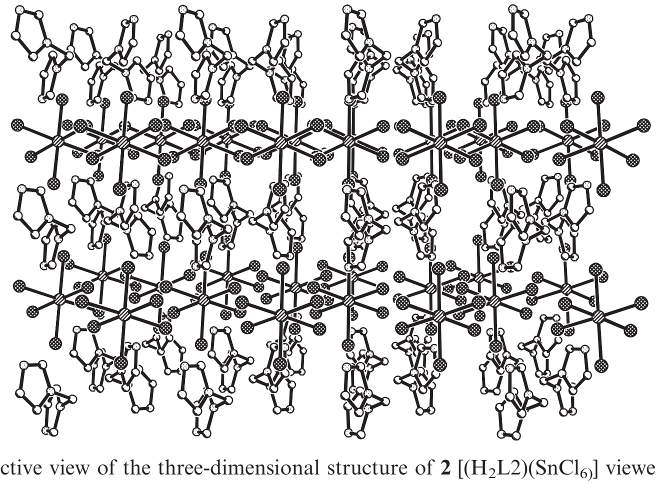

Figure 2. Perspective view of the three-dimensional structure of **2** [$(H_2L2)(SnCl_6)$] viewed down the *a* axis.

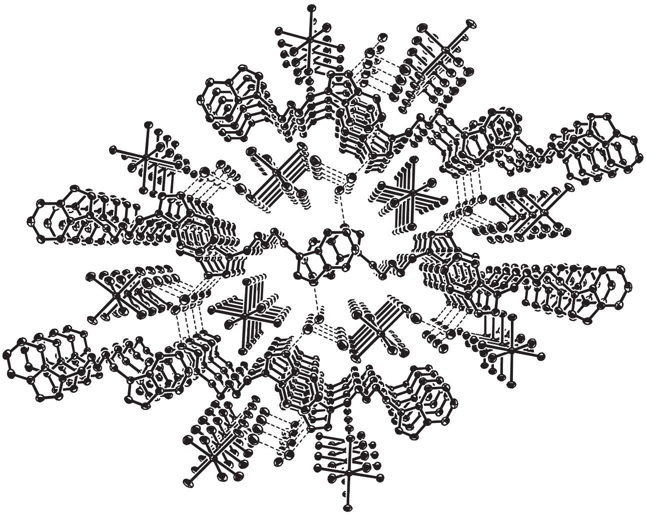

Figure 3. Packing diagram showing the arrangement of the anions and the channel structure of **3** $[(H_2L3)SnCl_6] \cdot 3H_2O$ viewed down the *a*-axis.

independent Sn(VI) atoms, both with an occupation factor of 0.5. In addition to two half $SnCl_6^{2-}$ and one diimidazolium cation, there are three water molecules in the crystal lattice. As a consequence of extensive hydrogen bonds involving imidazolium, water, and $SnCl_6^{2-}$, and the π–π interaction between the benzimidazolium cations and waters, the three components are linked into a three-dimensional framework structure. Two **L3** and water molecules form 26-membered rings and the stacking results in formation of channels along the *a*-axis. The $SnCl_6^{2-}$ anions fill in the channels as shown in figure 3. The anions interact with the channel wall through hydrogen bonds. The four shortest contacts are 3.343(5), 3.396(6), 3.338(5), and 3.432(5) Å for O2 ··· Cl2, O3 ··· Cl6, O3 ··· Cl4, and O2 ··· Cl3, respectively (symmetry codes: i: #1 $-x+1$, $-y+1$, $-z+1$; ii: 4 $x+1$, $y+1$, z; iii: $-x+1$, $-y+1$, $-z$).

Although **4** was prepared analogously to **2** by reacting 1,1′-*bis*(benzimidazolyl)-methane (**L4**) with two equivalents of tin(II) chloride dihydrate in methanol and water, only $[(H_2L4)SnCl_6]$ was obtained in high yield. X-ray diffraction analysis shows the asymmetric unit of the compound has one imidazolium dication and one $SnCl_6^{2-}$. The $SnCl_6^{2-}$ anions contact *via* weak Cl ··· Cl interactions forming the three-dimensional network structure. Eight neighboring $SnCl_6^{2-}$ constitute a cuboid with the Sn atoms at the corners of the cuboid and the lengths of the three edges (Sn···Sn contacts) are 7.827, 7.927, and 8.273 Å. The void is occupied by imidazolium cations. $SnCl_6^{2-}$ interacts with neighboring imidazolium through hydrogen bonds, as shown in figure 4. The shortest separation between the imidazolium and chloride is 3.186 Å. The alternate arrangement of $SnCl_6^{2-}$ and imidazolium cations generates a layered structure.

Reactions of tin(II) chloride dihydrate and 2-(imidazol-1-yl)-1-phenylethanone (**L5**) in the presence of hydrochloric acid gives $[(HL5)_2SnCl_6]$ in high yield as colorless crystals. X-ray structure determination showed the asymmetric unit contains two half $SnCl_6^{2-}$ and two imidazolium cations. The full structure is generated by the inversion center (0, 0.5, 0.5) and (0, 1, 0) at two Sn atoms. In the crystal lattice, the weak

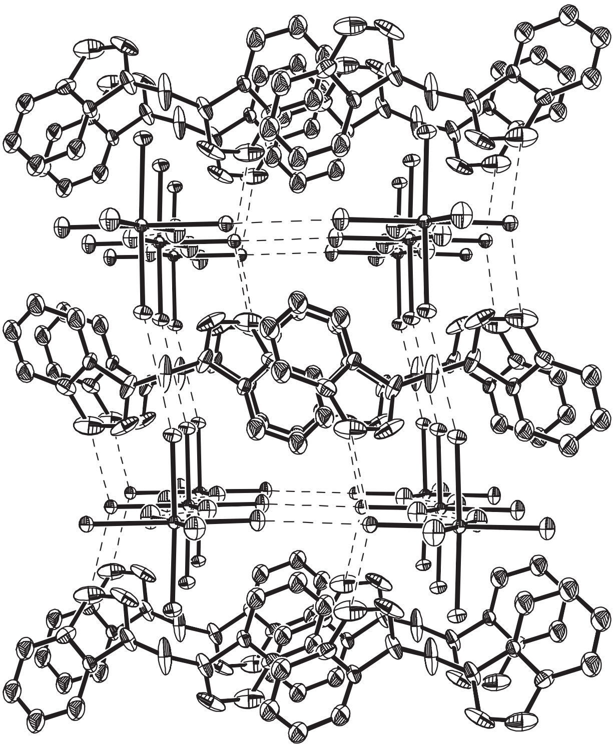

Figure 4. Perspective view of the three-dimensional structure of **4** showing the 3D network viewed down the *a*-axis.

intermolecular interaction between neighboring 2-(imidazolium-1-yl)-1-phenylethanone ions was also observed due to the existence of the enolic form. This is reflected by a short C18–C19 bond of 1.430(14) Å, which is significantly shorter than normal single C–C bonds. The organic cations and inorganic anions are linked by hydrogen bonds between NH^+ and Cl^- [N(2)–H(2) $\cdots$ Cl(6)#1 = 3.252(8) Å, symmetry codes: #1: $-x$, $-y+1$, $-z+1$]. Through these hydrogen bonds, the cations and anions are held together to form zigzag organic-inorganic chains, as depicted in figure 5. All these interactions gave a 3-D structure.

Complex $[(H_2L6)SnCl_6]$ **6** was prepared by reacting 7-imidazolyl-2,4-dimethyl-1,8-naphthyridine (**L6**) with tin(II) chloride dihydrate in methanol and water. The compound was isolated in 80.1% yield. The compound crystallizes in a monoclinic space group *C*c with unit content of four formula units. Two nitrogen atoms at the imidazole and naphthyridine rings were protonated to yield the dication. The organic cations formed a lamellar structure through aromatic π–π stacking interactions, while the $SnCl_6^{2-}$ anions connected the imidazolium cations through weak hydrogen bonds between Cl and NH or aromatic C–H groups. The shortest hydrogen bond was Cl $\cdots$ H–N3 with a Cl $\cdots$ N3 distance of 3.453 Å. The $SnCl_6^{2-}$ anions and the organic layers are alternatively arranged to form the inorganic-organic hybrid material. The hydrogen bonds hold the organic and inorganic layers together. The layered structure is shown in figure 6.

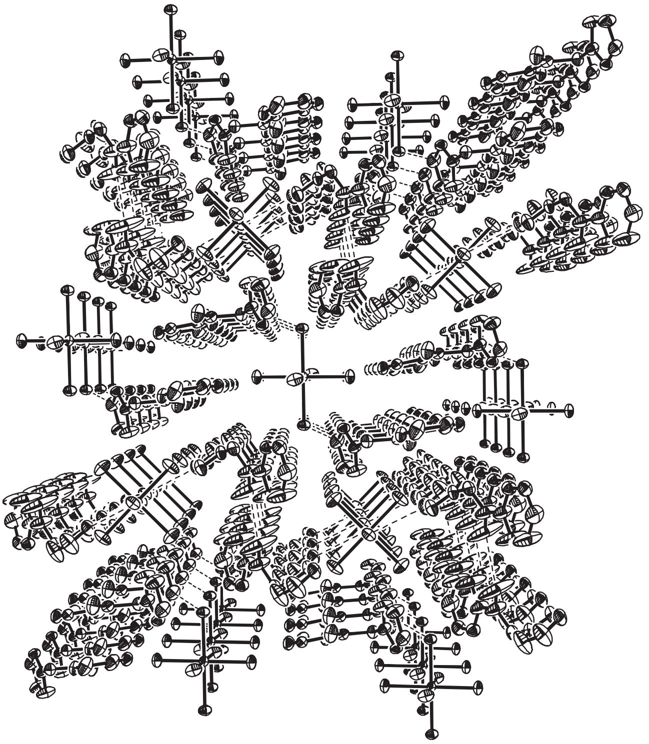

Figure 5. Packing diagram of **5** showing the arrangement of the anions and hydrogen bonds viewed down the *a* axis.

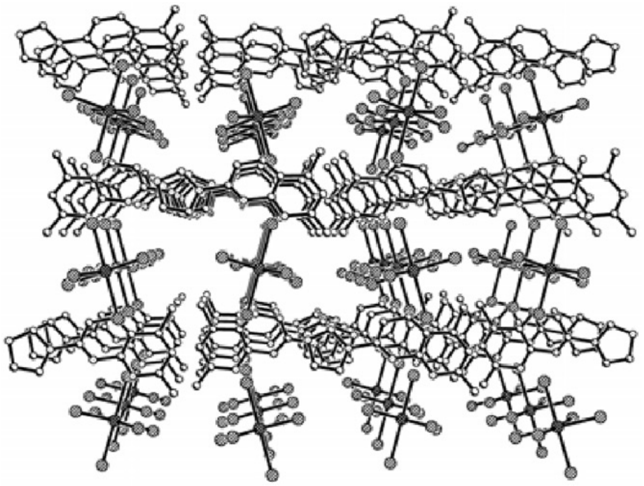

Figure 6. Packing diagram showing the three-dimensional layered structure of **6** and the hydrogen bonds between cations and anions.

3.3. *Thermal properties*

For **1**, the weight loss of 3.33% (Calcd 3.32%) corresponds to loss of one free water in the temperature range 83.3–95.9°C. The TGA studies showed that **2** is stable below 300°C. Its decomposition begins at 344°C, and there is a sharp weight loss in the temperature range 344–374°C. For **3**, the free water molecules were lost below 120°C, and weight loss of 43.98% (Calcd 44.44%) corresponds to loss of H_2L3 in the temperature range 367–406°C. TGA curve of **4** shows that the complex is stable below 200°C, and the weight loss of 54.97% in the temperature range 245–357°C results from loss of (H_2L4) (Calcd 55.18%). Complex **5** begins decomposition at 304°C, with one sharp weight loss (71.51%) in the temperature range 304–364°C, due to the collapse of the framework structure. For **6**, the weight loss of 39.43% in the temperature range 228–326°C corresponds to loss of H_2L6 (Calcd 40.53%).

4. Conclusion

We synthesized six new imidazolium hexachlorostannate compounds by a simple route. These compounds exhibit diverse three-dimensional structures, and are thermally stable. The structure motifs of these inorganic-organic hybrid complexes depend on the size, symmetry, and the charge number of the organic cations. Because the imidazole derivatives are easily prepared and the structures are easily tuned, inorganic-organic tin compounds with novel structures and functionalities can be obtained by variation of the organic cations.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 613226 for **1**, 613228 for **2**, 613230 for **3**, 613227 for **4**, 613225 for **5**, 613229 for **6**. Copies of this information may be obtained free of charge from +44(1223)336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk

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