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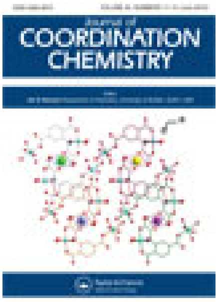

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Syntheses and structure characterization of four inorganic–organic hybrid solids based on N-containing aromatic Brønsted bases and chlorometallates

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Four organic–inorganic hybrid complexes ($[(HL1)_2SnCl_6]\cdot 2H_2O$ (**1**) (L1 = 2-methylquinoline), $[(HL2)_2(CdCl_4)]\cdot 2H_2O$ (**2**) (L2 = 5,7-dimethyl-1,8-naphthyridine-2-amine), $[(H_2L2)_2SnCl_6]\cdot 2(Cl)$ (**3**), and $[(H_2L3)SnCl_6]\cdot 2H_2O$ (**4**) (L3 = 3,6-bis(imidazol-1-yl)pyridazine)) derived from N-containing aromatic Brønsted bases and metal(II) chloride dihydrate (tin(II) chloride dihydrate and cadmium(II) chloride dihydrate) were prepared and characterized by IR, X-ray structure analysis, elemental analysis, and TG analysis. The aromatic rings of the cations in all of the compounds are essentially planar. X-ray diffraction analysis revealed that **2**–**4** have 3-D network structures built from hydrogen bonds between the cations and chlorometallates. Water molecules also play important roles in structure extension in **1**, **2**, and **4**. The arrangements of the anions and cations in their solid state are dominated by shape, size, and symmetry of the cations and the different structures of the chlorometallates as well as by hydrogen-bond interactions.

Keywords: Tin; Cadmium; Crystal structure; N-Containing aromatic Brønsted bases; Inorganic–organic hybrid

1. Introduction

Organic–inorganic hybrid materials represent new directions in solid-state chemistry [1, 2]. Organic–inorganic hybrids exhibit diverse structures, improved properties, and functions unobserved in purely inorganic or organic phases, such as magnetic [3], electrical [4–6], and optical properties [7]. Organic–inorganic hybrid materials may have applications in fuel cells [8], liquid crystal-material development [9], nonlinear optics [10], and drug delivery [11].

Organic–inorganic hybrid compounds based on layers of anionic transition metal(II) halogen frameworks and organic ammonium cations have been reported. For instance, 2-D systems, $(RNH_3)_2M(II)X_4$ or $(NH_3RNH_3)M(II)X_4$ (M = Pb, Sn, Cu, etc.; X = I, Br, Cl; R = alkyl, phenyl, etc.), have been studied in the field of low-dimensional magnetism [12]. Structural transitions in hybrids containing long-chain alkylammonium cations were studied to better understand biological lipid bilayers [13]. Most of the

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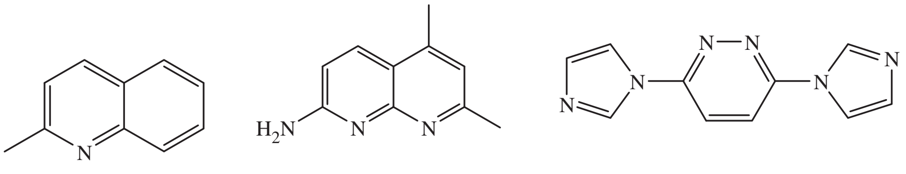

L1 L2 L3

Scheme 1. The N-containing aromatic Brønsted bases.

ammonium cations incorporated in hybrid materials were either alkylammonium or single-ring aromatic ammonium cations.

Metal halides such as SnX_2 ($X = Cl$, Br, and I) have been studied as semi-conducting components [14] in organic–inorganic hybrid semiconductors, demonstrating potential applications in display and storage technologies because of their stable exciton, excellent film processability, and superior carrier mobility [15]. Cd(II), being a d^{10} electron configuration, exhibits intriguing structural and photoluminescent properties [16]. Chlorocadmate(II) compounds represent a class of materials with unusual structures [17], where the ligands are chlorides and water, if present, giving rise to polymeric inorganic anions characterized by 1-D chains or 2-D layers. The presence of organic cations (commonly protonated amines) as spacers between the inorganic anions confers chemical flexibility on the compounds and enables the distances within the chains or the layers to be modulated. In these complexes, the frameworks of organoammonium cations and inorganic species are stabilized by hydrogen bonds and Coulombic attractions. The energetics of $N–H\cdots Cl–M$ hydrogen bonds and their possible role in supramolecular chemistry of inorganic–organic hybrid solids have been described in detail [18].

L1–L3 (L1 = 2-methylquinoline, L2 = 5,7-dimethyl-1,8-naphthyridine-2-amine and L3 = 3,6-bis(imidazol-1-yl)pyridazine) are Brønsted bases with one to four nitrogen atoms that can be protonated. When protonated the cations of L1–L3 are good donors for hydrogen bonds. The three bases all have aromatic units which may give aromatic stacking interactions. Thus carrying out the reaction between the N-containing aromatic bases and chlorometallates in acidic conditions may display different non-bonding interactions of these different functional groups. As an extension of our research of organic–inorganic hybrid complexes based on imidazole derivatives [19], herein we report the synthesis and structure of four chlorometallate complexes with N-containing aromatic Brønsted bases (scheme 1) as organic ammonium cations.

2. Experimental

2.1. *Materials*

L2 and L3 were prepared according to modified procedures [20, 21]. The other chemicals and solvents were of reagent grade and used as obtained from J & K Chemical Ltd.

2.2. *Physical measurements and analyses*

Elemental analyses (C, H, and N) were determined with a Perkin-Elmer 2400°C instrument, and infrared (IR) spectra were measured as KBr pellets using a Nicolet 5DX FX-IR spectrophotometer. Thermogravimetric analyses (TGA) were studied by a Delta Series TA-SDT Q600 in nitrogen between room temperature and 800°C (heating rate 10°C min^{-1}) using Al crucibles.

2.3. *Preparation of the compounds*

2.3.1. Preparation of 5,7-dimethyl-1,8-naphthyridine-2-amine (L2). 2,6-Diaminopyridine (21.8 g, 20.0 mmol), 2,4-pentanedione (21.0 g, 21.0 mmol), and powdered anhydrous $ZnCl_2$ (11.0 g, 80.0 mmol) were mixed, then refluxed with stirring for 10 h. The reaction mixture was added slowly with good stirring and ice bath cooling to 15 g of sodium hydroxide in 60 mL water. The brown solid was filtered after the solution cooled overnight at 5°C, then was washed twice with cold water and dried. The crude material was recrystallized from $CHCl_3$ to give light yellow needles. Yield: 11.8 g, 34.2%.

2.3.2. Preparation of 3,6-bis(imidazol-1-yl)pyridazine (L3). Imidazole (4.5 g, 66 mmol) was dissolved in anhydrous DMF (20 mL) and cooled to *ca* 5°C, then oil-free NaH (1.6 g, 66.6 mmol) was added portionwise. When all of the NaH was added, the solution was stirred for another 1 h to ensure complete reaction of NaH. Then 3,6-dichloropyridazine (4.5 g, 30 mmol) dissolved in 30 mL DMF was added. The reaction mixture was refluxed for 8 h, cooled to room temperature, and added to ice water. The resulting brown product was isolated by vacuum filtration and recrystallized from DMF to give prism crystals. Yield: 3.53 g, 56%.

2.3.3. Preparation of $[(HL1)_2(SnCl_6)]\cdot 2H_2O$ (1). Tin(II) chloride dihydrate (23.5 mg, 0.10 mmol) dissolved in 1 mL of conc. hydrochloric acid and 3 mL of water was treated with L1 (28.6 mg, 0.2 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: 40 mg, 60.99% (based on $SnCl_2\cdot 2H_2O$). Anal. Calcd for $C_{20}H_{24}Cl_6N_2O_2Sn$ (655.80) (%): C, 36.59; H, 3.66; N, 4.27. Found (%): C, 36.53; H, 3.58; N, 4.22. IR (KBr disc, cm^{-1}): 3566s, 3326s, 3224m, 3136s, 1609s, 1524s, 1448s, 1349s, 1322w, 1208w, 1162w, 1088w, 967m, 892w, 830w, 789w, 760w, 685w, 586w, 552w.

2.3.4. Preparation of $[(HL2)_2(CdCl_4)]\cdot 2H_2O$ (2). L2 (5,7-dimethyl-1,8-naphthyridine-2-amine, 34.8 mg, 0.2 mmol) dissolved in 3 mL of conc. hydrochloric acid and 5 mL of water was treated with cadmium(II) chloride dihydrate (46 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: 55 mg, 86.12% (based on L2). Anal. Calcd for $C_{20}H_{28}CdCl_4N_6O_2$ (638.68): C, 37.58; H, 4.38; N, 13.15. Found: C, 37.55; H, 4.36; N, 13.08. IR (KBr disc, cm^{-1}): 3520s, 3370s, 3280s, 3200s, 3120s, 3040s, 1612s, 1573s, 1528s, 1446s, 1357s, 1318w, 1212w, 1168w, 1110w, 970w, 894w, 835w, 780w, 720w, 682w, 610m.

2.3.5. Preparation of $[(H_2L2)_2SnCl_6]\cdot 2(Cl)$ (3). The compound was prepared by the similar procedure as for **2** from tin(II) chloride dihydrate (47 mg, 0.20 mmol) and 5,7-dimethyl-1,8-naphthyridine-2-amine (34.8 mg, 0.2 mmol) in 4 mL of conc. hydrochloric acid, and 3 mL of water. The compound was isolated as pale yellow block crystals. Yield: 67 mg, 89% (based on L2). Anal. Calcd for $C_{20}H_{26}Cl_8N_6Sn$ (752.76): C, 31.88; H, 3.45; N, 11.16. Found: C, 31.84; H, 3.41; N, 11.11. IR (KBr disc, cm^{-1}): 3321s, 3297s, 3137s, 2976m, 1615s, 1524s, 1451s, 1382 s, 1329w, 1204w, 1162w, 1099w, 974w, 898w, 829w, 797w, 764w, 686w, 606w.

2.3.6. Preparation of $[(H_2L3)SnCl_6]\cdot 2H_2O$ (4). The compound was prepared by similar procedure to that for **2** from tin(II) chloride dihydrate (23.5 mg, 0.10 mmol) and L3 (21 mg, 0.10 mmol) in 5 mL of conc. hydrochloric acid, and 8 mL of water. The compound was isolated as colorless block crystals. Yield: 39 mg, 67.05%. Anal. Calcd for $C_{10}H_{14}Cl_6N_6O_2Sn$ (581.66): C, 20.63; H, 2.41; N, 14.44. Found: C, 20.59; H, 2.36; N, 14.42. IR (KBr disc, cm^{-1}): 3508m, 3342m, 3208s, 3134m, 3046m, 2922m, 2634m, 1876m, 1696m, 1614m, 1538m, 1509m, 1452m, 1416m, 1334m, 1226m, 1136m, 1066m, 1015m, 956m, 834m, 708m, 645m, 602m.

2.4. *X-ray crystallography*

Single-crystal X-ray diffraction data for **1–4** 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 *SMART* and *SAINT* [22]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the *SHELXTL* package [23]. Hydrogen atoms were generated geometrically and included in structure factor calculations.

3. Results and discussion

3.1. *Preparation and general characterization*

Most organically templated halometallates reported previously were prepared by conventional solution approach, thus all of the title compounds were prepared by a solution method. The four compounds were prepared with the same ratio of the reactants (1 : 1) except **1** derived from L1. For the tin compounds, tin is +4 although the original material was $SnCl_2 \cdot 2H_2O$, similar to published results [19, 24]. Here the $SnCl_2$ may be oxidized by oxygen in the air. All of the compounds were isolated as colorless crystals in yields higher than 60%. These compounds are not soluble in almost all common solvents. The ability of metal chloride complexes to act as hydrogen-bond acceptors has been noted in our database work [19] and previous examples (see, e.g. [25]).

IR spectra show strong vibrations at 3208–3370 cm^{-1}, assignable to NH and NH_2 of the cations. The bands for lattice water molecules are at 3508–3566 cm^{-1}. Bands at 1610 and 1450 cm^{-1} can be assigned to C=C and C=N stretches of the pyridyl, naphthyridinyl, imidazolyl or aromatic rings. Compositions were determined by elemental analysis (C, H, and N), and their structures were fully characterized by X-ray diffraction analysis. Hydrogen atoms connected to O or N were placed in calculated positions, which also indirectly confirms protonation of the N-containing bases. For compounds with L2 and L3, the least basic nitrogen atoms are not protonated. The crystallographic data and refinement details are summarized in table 1 and selected bond distances and angles are listed in table 2; some important hydrogen bonds are listed in table 3.

3.2. *Thermal properties*

The TGA studies show that water in **1** are removed between 72.2°C and 76.6°C (Observ. 5.34%, Calcd 5.49%). There is a sharp weight loss from 249.4°C to 278.2°C for decomposition of the two cations (Observ. 43.81%, Calcd 43.92%). For **2**, the first weight loss of 5.59% (Calcd 5.64%) corresponds to loss of water at 68.1–71.9°C; the second weight loss of 54.42% (Calcd 54.48%) at 298–336°C results from loss of both $(HL2)^+$. TGA studies show that **3** is stable below 300°C, with weight loss of 46.41% (Calcd 46.49%) corresponding to loss of two $(H_2L2)^{2+}$ at 354–384°C. For **4**, the free water molecules are released from 71.4 to 76.6°C (Observ. 6.12%, Calcd 6.19%) and decomposition of $(H_2L3)^{2+}$ begins at 338°C and ends at 362°C (Observ. 36.66%, Calcd 36.79%).

3.3. *Structural descriptions*

3.3.1. Crystal structure of $[(HL1)_2SnCl_6]\cdot 2H_2O$ (1). Complex **1** was prepared by reacting 2 mol of 2-methylquinoline (L1) with 1 mol of tin(II) chloride dihydrate in water in the presence of hydrochloric acid. Two water molecules are involved in the lattice as determined by elemental analysis. Different from its unsolvated compound which crystallizes in the monoclinic space group *C*2/*c* with unit cell content of four formula units [26], **1** crystallizes in the monoclinic space group *P*2(1)/*c* with unit cell content of two formula units. The asymmetric unit of **1** consists of one 2-methylquinolium cation, a half of $SnCl_6^{2-}$, and one free water molecule (figure 1). The geometry of the cyclic component HL1 is generally similar to that of the parent in the corresponding unsolvated compound [26]. Tin is coordinated in a distorted octahedron, with two groups of three chlorides related by inversion symmetry. The Sn–Cl bonds were 2.4177(13)–2.4403(12) Å. The Cl–Sn–Cl angles between neighboring chlorides deviate slightly from 90° and Cl–Sn–Cl angles are exactly 180° between two *trans* chlorides as required by symmetry. These geometric parameters are similar to previously published results [19].

The $SnCl_6^{2-}$ were connected by free water molecules through O–H···Cl hydrogen bonds with O–Cl distances of 3.277(4)–3.409(3) Å to form a 1-D chain running along the *a*-axis. In the anion chain adjacent Sn–Sn separation is 7.438 Å. Here water molecules as donors form three O–H···Cl hydrogen bonds in tridentate bridge fashion,

Table 1. Data collection, structure solution, and refinement parameters for **1–4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{20}H_{24}Cl_6N_2O_2Sn$	$C_{20}H_{28}CdCl_4N_6O_2$	$C_{20}H_{26}Cl_8N_6Sn$	$C_{10}H_{14}Cl_6N_6O_2Sn$
Formula weight	655.80	638.68	752.76	581.66
Temperature (K)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$	$C2/c$	$C2/c$
Unit cell dimensions (Å, °)				
a	7.4379(7)	7.3323(9)	13.3070(14)	16.1076(15)
b	12.8947(12)	21.712(2)	14.4831(16)	11.3239(9)
c	13.9471(14)	17.1314(14)	15.0479(18)	11.0733(8)
α	90	90	90	90
β	103.602(2)	100.532(2)	99.5570(10)	94.1200(10)
γ	90	90	90	90
Volume (Å^3), Z	1300.1(2), 2	2681.4(5), 4	2859.9(6), 4	2014.6(3), 4
Calculated density (Mg m^{-3})	1.675	1.582	1.748	1.918
Absorption coefficient (mm^{-1})	1.619	1.241	1.664	2.082
$F(000)$	652	1288	1496	1136
Crystal size (mm^3)	0.47 × 0.30 × 0.16	0.40 × 0.30 × 0.29	0.41 × 0.33 × 0.21	0.37 × 0.33 × 0.16
θ range for data collection (°)	2.18–25.02	1.53–25.02	2.09–25.02	2.20–25.01
Limiting indices	$-7 \leq h \leq 8$; $-15 \leq k \leq 12$; $-16 \leq l \leq 16$	$-8 \leq h \leq 8$; $-21 \leq k\ 25$; $-20 \leq l \leq 18$	$-14 \leq h \leq 15$; $-17 \leq k \leq 13$; $-15 \leq l \leq 17$	$-19 \leq h \leq 14$;$-12 \leq k \leq 13$; $-11 \leq l \leq 13$
Reflections collected	6359	13372	7289	4962
Independent reflection	2288 [(R_{int}) = 0.0565]	4732 [(R_{int}) = 0.0410]	2519 [(R_{int}) = 0.0276]	1782 [(Rint) = 0.0396]
Goodness-of-fit on F^2	1.082	1.033	1.097	1.079
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0441$, $wR_2 = 0.1204$	$R_1 = 0.0396$, $wR_2 = 0.0730$	$R_1 = 0.0257$, $wR_2 = 0.0552$	$R_1 = 0.0262$, $wR_2 = 0.0627$
R indices (all data)	$R_1 = 0.0557$, $wR_2 = 0.1365$	$R_1 = 0.0759$, $wR_2 = 0.0890$	$R_1 = 0.0367$, $wR_2 = 0.0621$	$R_1 = 0.0346$, $wR_2 = 0.0689$
Largest difference peak and hole (e A^{-3})	1.712 and −1.009	0.546 and −0.491	0.619 and −0.482	0.656 and −0.604

Table 2. Selected bond lengths (Å) and angles (°) for **1–4**.

1			
Sn(1)–Cl(3)	2.4177(13)	Sn(1)–Cl(1)	2.4395(12)
Sn(1)–Cl(2)	2.4403(12)	Cl(3)–Sn(1)–Cl(1)	89.84(5)
Cl(3)#1–Sn(1)–Cl(1)	90.16(5)	Cl(3)–Sn(1)–Cl(1)#1	90.16(5)
Cl(3)–Sn(1)–Cl(2)	89.51(4)	Cl(3)#1–Sn(1)–Cl(2)	90.49(4)
Cl(1)–Sn(1)–Cl(2)	90.00(4)	Cl(1)#1–Sn(1)–Cl(2)	90.00(4)
Cl(3)–Sn(1)–Cl(2)#1	90.49(4)	Cl(3)#1–Sn(1)–Cl(2)#1	89.51(4)
Cl(1)#1–Sn(1)–Cl(2)#1	90.00(4)		
2			
Cd(1)–Cl(3)	2.4396(13)	Cd(1)–Cl(2)	2.4423(13)
Cd(1)–Cl(4)	2.4450(13)	Cd(1)–Cl(1)	2.4531(13)
Cl(3)–Cd(1)–Cl(2)	107.48(5)	Cl(3)–Cd(1)–Cl(4)	111.67(5)
Cl(2)–Cd(1)–Cl(4)	114.40(6)	Cl(3)–Cd(1)–Cl(1)	107.49(5)
Cl(2)–Cd(1)–Cl(1)	107.33(5)	Cl(4)–Cd(1)–Cl(1)	108.17(5)
3			
Sn(1)–Cl(3)	2.4196(9)	Sn(1)–Cl(1)	2.4247(8)
Sn(1)–Cl(2)	2.4426(8)	Cl(3)#1–Sn(1)–Cl(3)	93.71(5)
Cl(3)#1–Sn(1)–Cl(1)	89.47(3)	Cl(3)–Sn(1)–Cl(1)	91.04(3)
Cl(1)–Sn(1)–Cl(1)#1	179.25(5)	Cl(3)#1–Sn(1)–Cl(2)	175.95(3)
Cl(3)–Sn(1)–Cl(2)	89.79(3)	Cl(1)–Sn(1)–Cl(2)	88.44(3)
Cl(1)–Sn(1)–Cl(2)#1	91.02(3)	Cl(2)–Sn(1)–Cl(2)#1	86.78(4)
4			
Sn(1)–Cl(3)	2.4195(9)	Sn(1)–Cl(2)#1	2.4256(9)
Sn(1)–Cl(1)	2.4568(8)	N(1)–C(1)	1.318(4)
N(1)–N(1)#2	1.338(6)	N(2)–C(3)	1.344(4)
N(2)–C(5)	1.386(5)	N(2)–C(1)	1.429(4)
N(3)–C(3)	1.303(5)	N(3)–C(4)	1.377(5)
Cl(3)–Sn(1)–Cl(2)#1	89.17(3)	Cl(3)–Sn(1)–Cl(2)	90.83(3)
Cl(3)–Sn(1)–Cl(1)#1	90.49(3)	Cl(2)–Sn(1)–Cl(1)#1	89.92(3)
Cl(3)–Sn(1)–Cl(1)	89.51(3)	Cl(2)–Sn(1)–Cl(1)	90.08(3)

Symmetry transformations used to generate equivalent atoms for **1**: #1: $-x+1$, $-y+1$, $-z+2$; for **3**: #1: $-x$, y, $-z+1/2$; for **4**: #1: $-x+1/2$, $-y+3/2$, $-z$; #2: $-x$, y, $-z+3/2$.

i.e., one hydrogen forms two hydrogen bonds in bifurcate fashion with two Cl^- coming from the same anion, while another hydrogen forms only one hydrogen bond with Cl^- of the other adjacent $SnCl_6^{2-}$. Two water molecules and two $SnCl_6^{2-}$ form a 12-membered ring through the O–H···Cl contacts; in this case the corresponding anions and the water molecules in the 12-membered ring are related by inversion symmetry with the inversion centre lying at the midpoint of the two oxygen atoms of the two water molecules. The cations bond to water in the anion chain through N–H···O hydrogen bonds between NH^+ and water with N–O distance of 2.731(5) Å, smaller than the sum of the van der Waals contact [27]. Two cations bonded to the same 12-membered ring are also inversionally arranged; cations at the same side of the same anion chain were parallel, while those cations at different sides of the anion chain were antiparallely arranged. In the structure of **1** there are two independent parallel chains without interactions between the two chains (figure 2). The second chain is located above the first chain when viewed from the *c*-axis, but the second chain slipped *ca* half of the length of the *b*-axis from the first chain along the *b*-axis. Cations on the same side of the same chain were parallel. The cations in these two chains are not parallel to each other, forming an angle (*ca* 60°) with each other.

Table 3. Hydrogen-bond geometries for **1–4** (Å, °).

D–H···A	*d*(D···A)
1	
O(1)–H(1D)···Cl(2)#2	3.375(3)
O(1)–H(1D)···Cl(3)#3	3.277(4)
O(1)–H(1C)···Cl(1)#4	3.409(3)
N(1)–H(1)···O(1)#5	2.731(5)
2	
O(2)–H(2D)···Cl(2)#1	3.274(4)
O(2)–H(2C)···Cl(1)#2	3.213(4)
O(1)–H(1D)···Cl(4)#3	3.209(4)
O(1)–H(1C)···Cl(3)#4	3.290(4)
N(6)–H(6B)···Cl(1)#5	3.415(4)
N(6)–H(6A)···N(1)#6	3.166(5)
N(5)–H(5)···O(1)	2.789(5)
N(3)–H(3B)···O(1)#7	3.098(6)
N(3)–H(3B)···Cl(3)#8	3.359(5)
N(3)–H(3A)···N(4)#7	3.244(6)
N(2)–H(2)···O(2)	2.835(5)
3	
N(3)–H(3B)···Cl(4)#2	3.287(3)
N(3)–H(3 A)···Cl(2)	3.373(3)
N(2)–H(2)···Cl(4)#3	2.963(3)
N(1)–H(1)···Cl(4)#3	3.174(2)
4	
O(1)–H(1D)···Cl(3)#3	3.392(3)
O(1)–H(1C)···N(1)#4	2.995(4)
N(3)–H(3)···O(1)#5	2.851(4)

Symmetry codes for **1**: #2: $x+1, -y+3/2, z-1/2$; #3: $-x+2, y+1/2, -z+3/2$; #4: $-x+1, y+1/2, -z+3/2$; #5: $x-1, y, z$; for **2**: #1: $-x, y-1/2, -z+1/2$; #2: $-x+1, y-1/2, -z+1/2$; #3: $x, -y+3/2, z+1/2$; #4: $x+1, -y+3/2, z+1/2$; #5: $-x+1, -y+1, -z+1$; #6: $x, -y+1/2, z+1/2$; #7: $x, -y+1/2, z-1/2$; #8: $x+1, y-1$, z; for **3**: #2: $-x+1/2, -y+1/2, -z$; #3: $-x+1/2, y+1/2, -z+1/2$; for **4**: #3: $-x+1/2, y-1/2, -z+1/2$; #4: $x, y-1, z$; #5: $x, -y+1, z-1/2$.

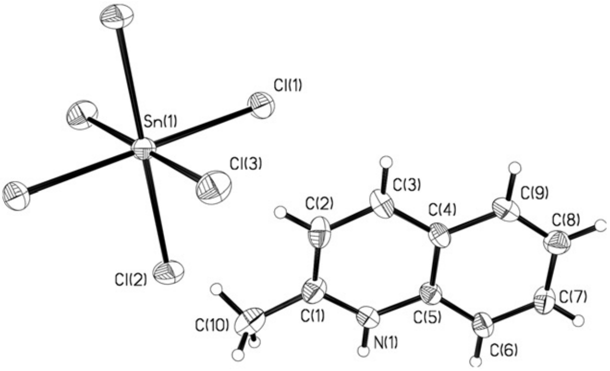

Figure 1. Molecular structure of **1** showing the atomic-numbering scheme at 30% thermal ellipsoid probability level.

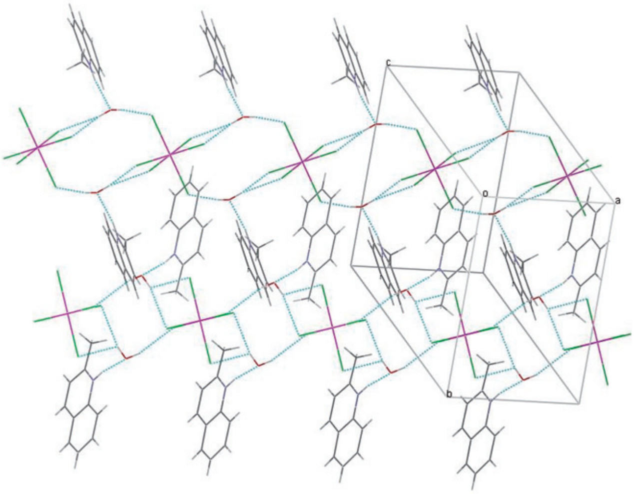

Figure 2. Two independent parallel chains running along the *a*-axis.

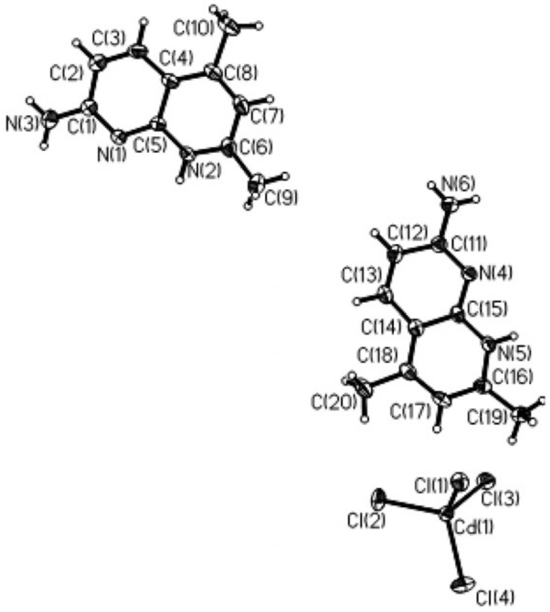

Figure 3. Molecular structure of **2** showing the atomic-numbering scheme at 30% ellipsoid probability level.

3.3.2. Crystal structure of $[(HL2)_2(CdCl_4)]\cdot 2H_2O$ (2).

Compound **2**, $[(HL2)_2(CdCl_4)]\cdot 2H_2O$, crystallizes in a monoclinic *P*2(1)/*c* space group, and there are four formula units in its unit cell. X-ray diffraction analysis shows the complex composed of two monoprotonated L2 cations, one $[CdCl_4]^{2-}$ and two free water molecules (figure 3). In **2**, the ring N adjacent to the methyl is protonated and the cation with the NH^+ on the naphthyridine rings in **2** resembles 2-amino-4,6-dimethylpyridinium cations [28]. Similar to the organic salt 2,2′-dimethyl-7,7′(methylenediimino)di-1,8-naphthyridin-1-ium bis(perchlorate) [29], the less basic ring N has been protonated.

The coordination geometry around Cd(II) is a distorted tetrahedron with four chlorides. The Cd–Cl bond distances range from 2.4396(13) Å to 2.4531(13) Å, consistent with other similar compounds in which the cadmium has tetrahedral coordination [25]. Different from the coordination compound containing 2-amino-5,7-dimethyl-1,8-naphthyridine [30], the $N_{ring}CN_{ring}$ angles (N(1)–C(5)–N(2) and N(4)–C(15)–N(5) in **2** are both 116.4(4)°), are larger than the corresponding angles (112.7(3) and 112.6(3)°) in bis(2-amino-5,7-dimethyl-1,8-naphthyridine) dinitratocadmium. Thus we deduce that bidentate chelating coordination to cadmium led to a larger contraction (the $N_{ring}CN_{ring}$ angle should be *ca* 120° if there are no bonding interactions with the two ring nitrogen atoms) in the $N_{ring}CN_{ring}$ angle of the coordination compound containing 2-amino-5,7-dimethyl-1,8-naphthyridine [30] compared with the hydrogen-bonding interactions in **2**. Coordinate bonds are stronger than hydrogen bonds in this case.

Two monoprotonated naphthyridine cations were connected through weak complementary hydrogen bonds, N–H···N, to form dimers, the anions $[CdCl_4]^{2-}$ bond to the dimers through N–H···Cl hydrogen bonds between the amine and chlorides with N···Cl separation of 3.359(5) Å. The dimers in the same plane were connected through 5–CH_3···Cl interaction in which the C–Cl distance is 3.756 Å to form a 2-D sheet structure when viewed down the *a*-axis. In the 2-D sheet there were also CH–Cl interactions between CH of the cation and $[CdCl_4]^{2-}$ with C–Cl distance of 3.553 Å. The 2-D sheets were further linked through water molecules in which water acts as bis hydrogen-bond donor to form hydrogen bonds with two $[CdCl_4]^{2-}$ anions in a 3-D layer structure (figure 4). The two free water molecules each form three hydrogen bonds, each

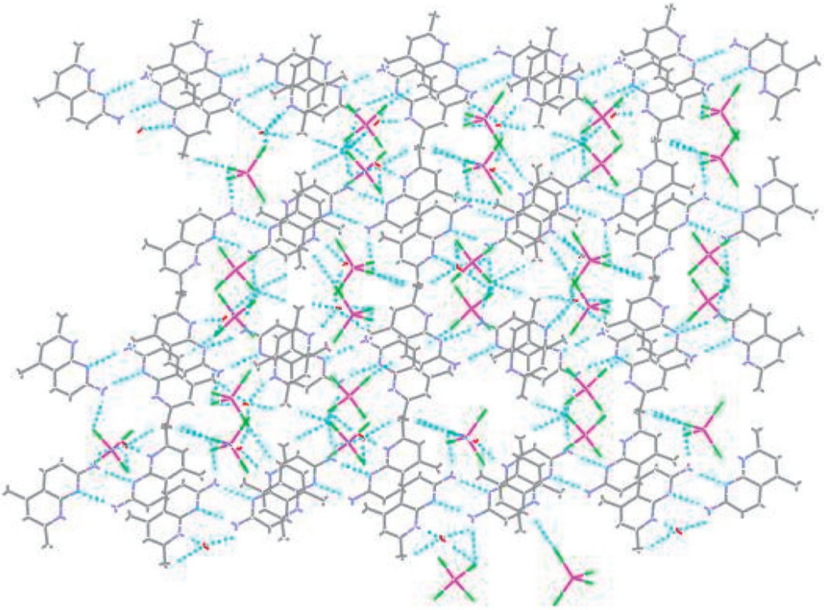

Figure 4. Packing diagram of **2** showing the 3-D layer structure.

hydrogen forms a O–H···Cl hydrogen bond with the anion, and each oxygen forms a N–H···O hydrogen bond with the NH^+ group with N–O distances ranging from 2.789(5) to 2.835(5) Å.

The N(5)–O(1) distance is 2.789(5) Å, which is considerably less than the sum of the van der Waals radii for N and O (3.07 Å) [27], so in the solid state, there are strong charge-assisted hydrogen bonds formed between the naphthyridinium NH^+ and water. In the other N–H···O hydrogen bond between water and NH_2 (N(3)–H(3B)···O(1)#7, symmetry code #7: x, $-y+1/2$, $z-1/2$), the N(3)–O(1) distance is 3.098(6) Å, comparable to the sum of the van der Waals radii, indicating a neutral hydrogen bond [27].

3.3.3. Crystal structure of $[(H_2L2)_2SnCl_6]\cdot 2(Cl)$ (3). Complex **3** was prepared by reacting 5,7-dimethyl-1,8-naphthyridine-2-amine (L2) with 1 equivalent of tin(II) chloride dihydrate in water in the presence of hydrochloric acid. There were no water molecules involved in the lattice as determined by elemental analysis. Different from **2**, both nitrogen atoms on the naphthyridine ring were protonated to form dications, the first case where two ring nitrogen atoms of naphthyridine have been protonated. Complex **3** crystallizes in the monoclinic space group $C2/c$ with unit cell content of four formula units; the asymmetric unit consists of one naphthyridinium dication, a half of $SnCl_6^{2-}$, and one free chloride (figure 5).

The Sn–Cl bonds were 2.4196(9)–2.4426(8) Å, in the range of reported results (2.402(3)–2.483(3) Å) [31]. The Sn(1)–Cl(3) (2.4196(9) Å) and Sn(1)–Cl(1) (2.4247(8) Å) bond distances are almost equal, while Sn(1)–Cl(2) (2.4426(8) Å) is longer than other Sn–Cl bonds, probably because Cl(2) forms more hydrogen bonds than the other chlorides.

The Cl–Sn–Cl angles between two neighboring chlorides are close to 90° (Cl(1)–Sn(1)–Cl(2) 88.44(3)°; Cl(3)–Sn(1)–Cl(1) 91.04(3)°; Cl(3)–Sn(1)–Cl(2) 89.79(3)°), indicating Sn is in a slightly distorted octahedral environment.

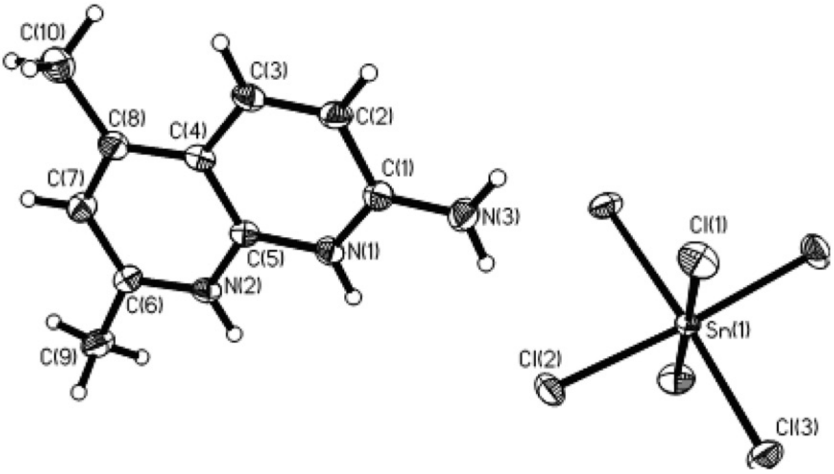

Figure 5. Molecular structure of **3** showing the atomic-numbering scheme at 30% thermal ellipsoid probability level.

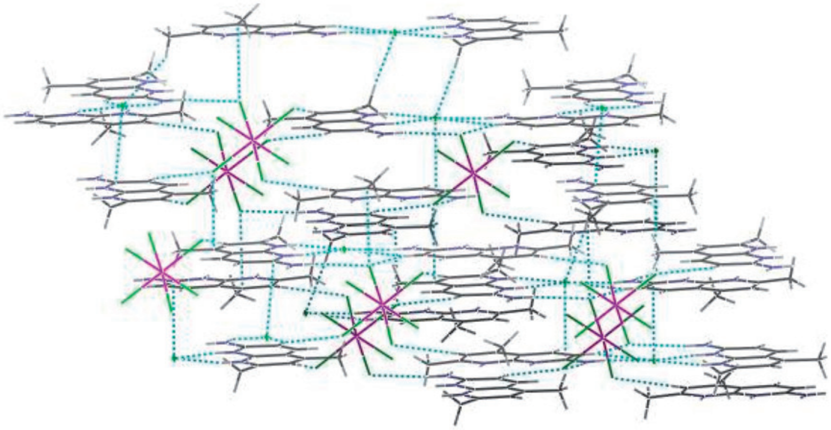

Figure 6. 3-D layer network formed *via* Cl–π, CH–Cl, and NH_{amine}–Cl interactions.

The naphthyridines were connected through the free Cl^- which formed hydrogen bonds simultaneously with amine of one naphthyridine and two NH^+ groups of the other naphthyridine to form a 1-D zigzag chain along the *c*-axis. In the chain there also exists CH–Cl interaction (with C–Cl distance of 3.577 Å) between free chloride and 6-CH of 1,8-naphthyridine. Adjacent chains were combined through CH–Cl (with C–Cl distance of 3.472 Å and 3.6 Å) and NH_{amine}–Cl hydrogen bonds to form a 2-D grid structure. The 2-D grids were further joined by Cl–π (with separation between the free Cl^- and the naphthyridine ring of 3.368 Å), CH–Cl (with C–Cl distance of 3.472 Å and 3.6 Å), and NH_{amine}–Cl (with N–Cl distance of 3.373 Å) to form a 3-D layer network, figure 6. Obviously, the 3-D structure is stabilized by these hydrogen bonds.

3.3.4. Crystal structure of $[(H_2L3)SnCl_6]\cdot 2H_2O$ (4). Complex **4** was also prepared by reacting 3,6-bis(imidazol-1-yl)pyridazine (L3) with tin(II) chloride dihydrate in water in the presence of conc. hydrochloric acid. The compound was isolated in high yield as colorless block crystals, crystallizing in a monoclinic space group $C2/c$ with unit cell of four formula units. The molecular structure is shown in figure 7. In the asymmetric unit of **4** there are half of the cations and the anion accompanied with one water molecule. Two nitrogen atoms of imidazole but no nitrogen atoms of pyridazine ring were protonated to yield the dication which conforms with literature results [32, 33]. In **4**, the tin is coordinated in a distorted octahedral geometry by six chlorides also.

Imidazole rings and pyridazine rings are both planar with largest deviation from the plane of 0.0091 Å. In the same cation the dihedral angle between the two imidazole rings is 65.1°, and the dihedral angle between the pyridazine and the imidazole rings is 32.6°, different from the literature values (70.8°, 45.9°, and 24.8°) [33]. All of the bond lengths are in the normal range, Sn–Cl are 2.4195(9) – 2.4568(8) Å. The *cis* Cl–Sn–Cl angles are close to 90° and the *trans* Cl–Sn–Cl angle is 180°, which fits well with the crystallographic symmetry of the compound.

The cations and the anions are arranged alternately along the *a*-axis. The anions and cations are joined by six Cl–π interactions of which four arise from the pyridazine ring and Cl^- with Cl–Cg distance of 3.442–3.390 Å, the other two arise from the imidazole

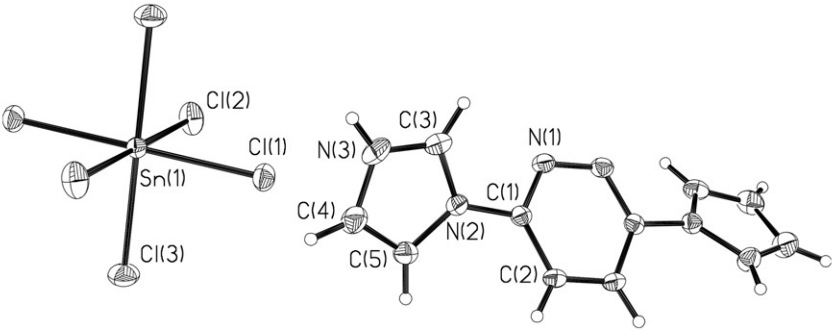

Figure 7. Molecular structure of **4** showing the atomic-numbering scheme at 30% ellipsoid probability level.

ring and Cl^- with Cl–Cg distance of 3.316 Å to form a 1-D chain along the *a*-axis. Here the Cl–π interactions of imidazole are somewhat stronger than that produced by pyridazine. In the chain, adjacent cations were antiparallel, and the third cation and the first cation were parallel to each other, as was the fourth cation and the second cation. In the same chain, the Sn–Sn distance is 9.440 Å; Sn–Sn distances between adjacent chains are 10.096 Å and 11.073 Å, respectively. Such 1-D parallel chains were held together by water molecules through one N–H$\cdots$O hydrogen bond between NH^+ and water with N–O distance of 2.851(4) Å, one O–H$\cdots$Cl interaction between the anion and water with O–Cl distance of 3.393 Å, and one CH–O interaction arising from N–CH–N of L3 and water with C–O distance of 3.100 Å to form a 2-D sheet extending along the *ac* plane (figure 8). Such sheets were further stacked along the *b*-axis through O–H$\cdots$N contacts between the pyridazine ring and water with O–N distance of 2.995 Å, and CH–Cl interactions between the cation and the anion with C–Cl distances of 3.624–3.737 Å. Under these interactions **4** displayed a 3-D network structure.

4. Conclusions

We synthesized four new inorganic–organic hybrid solids by solution reaction of $SnCl_2$/$CdCl_2$ with N-containing aromatic Brønsted bases in strongly acidic conditions. The Cd in **2** is tetrahedral, while Sn in **1**, **3**, and **4** are octahedral. For L2 and L3, the least basic nitrogen atoms are not protonated.

These compounds display two independent parallel chain structures, 3-D layer structure, and 3-D network structure with N–H$\cdots$Cl, N–H$\cdots$O, O–H$\cdots$N, and O–H$\cdots$Cl interactions as well as Coulombic interactions. Other than classical hydrogen-bonding interactions, secondary propagating interactions such as CH–Cl, Cl–π, and CH–O also play important roles in structure extension and stabilization. Cadmium chloride and $SnCl_2$ are effective hydrogen-bond acceptors, such that tetrachlorocadmate and hexachlorostannate may be exploited to prepare metal-containing hydrogen-bonded polymers composed of $[HL]_2^{2+}$ or $[H_2L]^{2+}$ salts of perchlorometallates. Choice of anions without hydrogen-bond donors and cations with strong hydrogen-bond donors is a successful strategy.

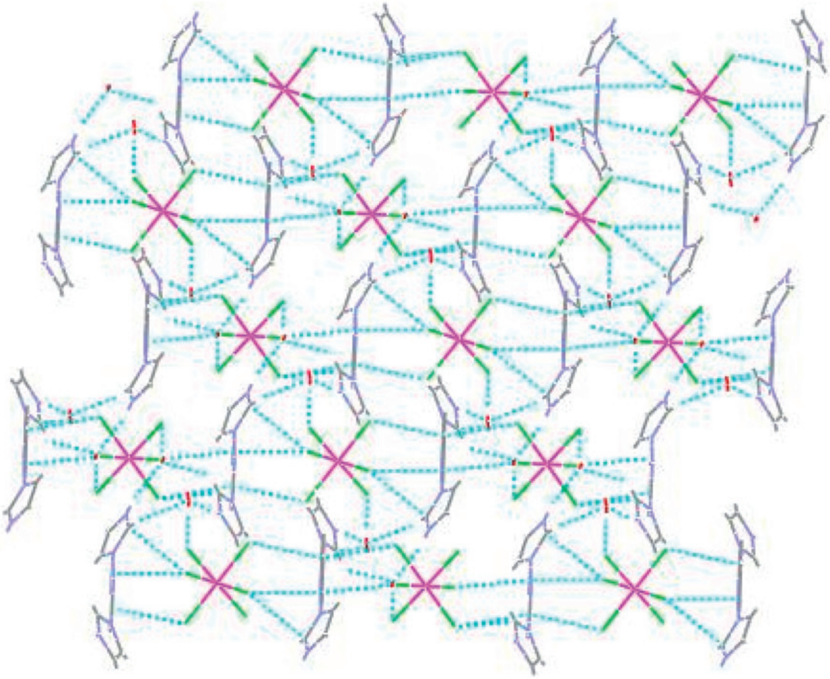

Figure 8. 2-D sheet structure of **4** formed through N–H···O, O–H···Cl, and CH–O interaction as viewed down the *b*-axis.

The structural motifs of these inorganic–organic hybrid complexes depend on the shape, size, and symmetry of the organic cations. Inorganic–organic hybrid compounds can be expected by variation of the organic cations. All of the compounds show high thermal stabilities.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 791896 for **1**, 739933 for **2**, 746313 for **3**, and 791895 for **4**. Copies of this information may be obtained free of charge *via* Fax: +44(1223)336-033 or E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk

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