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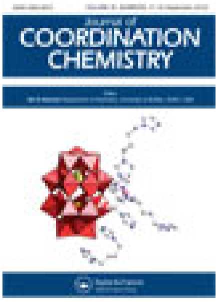

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Syntheses and molecular structures of four inorganic–organic hybrid compounds from N-containing aromatic bases and perchlorometallates of Zn, Cu, Sn, and Fe

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Four organic–inorganic crystals, $[(HL1)_2(ZnCl_4)]\cdot H_2O$ (**1**) (L1 = 2-methylquinoline), $[(HL1)_2(CuCl_4)]$ (**2**), $[(HL2)_2SnCl_6]$ (**3**) (L2 = 6-bromobenzo[d]thiazol-2-amine), and $[(HL3)FeCl_4]$ (**4**) (L3 = 5,7-dimethyl-1,8-naphthyridine-2-amine), derived from N-containing aromatic Brønsted bases and metal(II) chlorides (zinc(II) chloride, copper(II) chloride dihydrate, tin(II) chloride dihydrate, and iron(III) chloride hexahydrate) were prepared at room temperature and characterized by IR, X-ray structure analysis, elemental analysis, and TG analysis. The crystals are built up by perchlorometallates (Zn, Cu, Sn, and Fe) associated with organic cations through multiple non-covalent associations. X-ray diffraction analysis reveals that **1** and **2** have 3-D network structures built from hydrogen bonds between the cations and chlorometallates. Water molecules play an important role in structure extension in **1**. Anhydrous **3** and **4** produced from 2-aminoheterocyclic derivatives display 2-D sheet structures. Arrangements of anions and cations are dominated by shape and size of cations, and also by the different structures of the chlorometallates as well as non-bonding interactions in the crystal structures. Except for **1**, the other compounds are thermally stable below 240°C.

Keywords: Zinc; Copper; Tin; Iron; Crystal structure; N-Containing aromatic bases; Inorganic–organic hybrid

1. Introduction

Organic–inorganic hybrid materials are important in solid-state chemistry [1, 2] because of their magnetic [3], electrical [4–6], and optical properties [7]. Geometries of perhalometal anions MX_n^{2-} (M = metal, X = halogen) in the solid state depends on many factors, including electronic repulsion between halogens, crystal forces, and hydrogen bonds. Energetics of hydrogen-bonding involves protonated cation and halide anion of discrete MX_n^{2-} species, i.e., $N–H\cdots X–M$ and their possible role in supramolecular chemistry has been described [8].

Organic–inorganic compounds based on layers of anionic transition metal(II) halide frameworks and ammonium cations have attracted attention. For instance, 2-D systems with $(RNH_3)_2M(II)X_4$ or $(NH_3RNH_3)M(II)X_4$ formula (M = Pb, Sn, Cu, etc.; X = I,

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Br, Cl; R = alkyl, phenyl, etc.) have been studied in the field of low-dimensional magnetism [9]. Structural transitions in hybrids containing long-chain alkylammonium cations were studied in order to better understand the biological lipid bilayers [10]. Most ammonium cations incorporated in hybrid materials are either alkylammonium or single-ring aromatic ammonium cations.

L1–L3 (L1 = 2-methylquinoline, L2 = 6-bromobenzo[d]thiazol-2-amine, and L3 = 5,7-dimethyl-1,8-naphthyridine-2-amine) are aromatic Brønsted bases with one to three nitrogen atoms that can be protonated. Cations of L1–L3 are good hydrogen-bond donors. The three Brønsted bases have aromatic units which may give aromatic stacking interactions, thus reaction between N-containing aromatic Brønsted bases and chlorometallates in the acidic conditions may display different non-bonding ability of these different functional groups. As an extension of our research of organic–inorganic hybrid complexes based on imidazole derivatives [11], herein we report the syntheses and structures of four chlorometallates with aromatic bases (scheme 1) as the functional organic ammonium cations.

2. Experimental

2.1. *Materials*

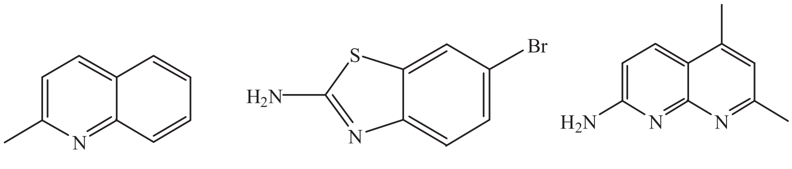
L3 was prepared according to the literature procedure [12]. The other chemicals and solvents were of reagent grade and used as obtained from J & K Chemical Ltd.

2.2. *Physical measurements and analyses*

Elemental analyses (CHNS) were determined with a Perkin-Elmer 2400C instrument, and 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 under N_2 between room temperature and 800°C (heating rate $10^{\circ}\mathrm{C\,min^{-1}}$) using Al crucibles.

2.3. *Preparation of the compounds*

2.3.1. Preparation of $[(HL1)_2(ZnCl_4)]\cdot H_2O$ (1). Zinc(II) chloride (13.7 mg, 0.10 mmol) dissolved in 1 mL of conc. hydrochloric acid and 2 mL of water was



L1 L2 L3

Scheme 1. The N-containing aromatic bases.

added to a methanol solution (2 mL) of 2-methylquinoline (L1) (28.6 mg, 0.20 mmol). After stirring for several minutes, the solution was filtered. The clear solution was allowed to stand at room temperature for several days to give colorless block crystals, which were collected and washed with water and ethanol. Yield: 45 mg, 87.62% (based on $ZnCl_2$). Anal. Calcd for $C_{20}H_{22}Cl_4N_2OZn$ (513.57) (%): C, 46.73; H, 4.28; N, 5.45. Found (%): C, 46.67; H, 4.23; N, 5.41. IR (KBr disc, cm^{-1}): 3664s, 3347s, 3246s, 1608m, 1518s, 1454m, 1362s, 1316w, 1196w, 1158w, 1097w, 1034w, 962w, 892w, 833w, 797w, 748w, 684w, 613w.

2.3.2. Preparation of [$(HL1)_2(CuCl_4)$] (2). Copper(II) chloride dihydrate (17.5 mg, 0.10 mmol) dissolved in 1 mL of conc. hydrochloric acid and 3 mL of water was treated with L1 (28.6 mg, 0.20 mmol). After stirring for several minutes, the solution was filtered. The clear solution was allowed to stand at room temperature for several days to give yellow block crystals, which were collected and washed with water and ethanol. Yield: 40 mg, 81.02% (based on $CuCl_2 \cdot 2H_2O$). Anal. Calcd for $C_{20}H_{20}Cl_4CuN_2$ (493.72) (%): C, 48.61; H, 4.05; N, 5.67. Found (%): C, 48.58; H, 3.97; N, 5.62. IR (KBr disc, cm^{-1}): 3362s, 3274m, 3063s, 1609m, 1524s, 1448m, 1349s, 1322w, 1208w, 1162w, 1088w, 967 m, 889w, 830w, 789w, 760w, 685w, 628w.

2.3.3. Preparation of [(HL2)2Sncl6] (3). To an ethanol solution (8 mL) of 6-bromobenzo[d]thiazol-2-amine (22.9 mg, 0.1 mmol) was added tin(II) chloride dihydrate (23.5 mg, 0.10 mmol) in 4 mL of conc. hydrochloric acid and 3 mL of water. The compound was isolated as pale yellow block crystals, which were collected and washed with water and ethanol. Yield: 69 mg, 87.16% (based on $SnCl_2 \cdot 2H_2O$). Anal. Calcd for $C_{14}H_{12}Br_2Cl_6N_4S_2Sn$ (791.61) (%): C, 21.22; H, 1.51; N, 7.07; S, 8.08. Found (%): C, 21.18; H, 1.45; N, 6.99; S, 8.05. IR (KBr disc, cm^{-1}): 3351s, 3229s, 3148m, 3097s, 2987m, 1605m, 1524s, 1445m, 1382s, 1329w, 1275w, 1112w, 1069w, 974w, 918w, 863 m, 811 m, 797w, 764w, 686w, 606w.

2.3.4. Preparation of [$(HL3)FeCl_4$] (4). L3 (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 iron(III) chloride hexahydrate (54 mg, 0.20 mmol). After stirring for several minutes, the solution was filtered and the clear solution was allowed to stand at room temperature for several days to give red block crystals, which were collected and washed with water and ethanol. Yield: 55 mg, 73.95% (based on L3). Anal. Calcd for $C_{10}H_{12}Cl_4FeN_3$ (371.88) (%): C, 32.27; H, 3.23; N, 11.29. Found (%): C, 32.21; H, 3.18; N, 11.24. IR (KBr disc, cm^{-1}): 3387s, 3268s, 3123s, 3040s, 1612m, 1573s, 1528s, 1446m, 1357s, 1318w, 1212w, 1168w, 1110w, 970w, 894w, 835w, 780w, 720w, 682w, 610m.

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* software [13]. 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 *SHELXTL* package [14]. 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, as are all of the title compounds. Compounds **1** and **2** derived from L1 were prepared with the same 1 : 2 ratio of the reactants, while **3** and **4** were produced at a 1 : 1 ratio of the reactants. For the tin compound, tin has a valence number of +4 although $SnCl_2{\cdot}2H_2O$ was starting material, similar to the published results [11, 15]. Here, $SnCl_2$ may be oxidized by oxygen in air. The compounds were isolated as colorless crystals in yields higher than 70%. These compounds are not soluble in common solvents, including water and alcohols. The ability of metal chloride complexes to act as hydrogen-bond acceptors has been noted in our database work [11] and previous examples [16].

IR spectra show strong vibrations at 3120–3387 cm^{-1}, assignable to NH and NH_2 of the cations. Bands at 1610 and 1450 cm^{-1} can be assigned to characteristic C=C and C=N stretches of pyridyl, naphthyridinyl, thiazolyl, or aromatic rings. Compositions of these compounds were determined by elemental analysis (CHNS), and their structures were fully characterized by X-ray diffraction. Hydrogen atoms connected to O or N were placed in calculated positions, indirectly confirming protonation of the N-containing bases. Crystallographic data and refinement details are summarized in table 1, selected bond distances and angles listed in table 2, and some important hydrogen bonds in table 3.

3.2. *Thermal properties*

For **1**, the first weight loss of 3.38% (Calcd 3.50%) corresponds to loss of the free water from 71.6 to 78.5°C; the second weight loss of 56.01% (Calcd 56.07%) from 259.6 to 302.2°C results from loss of both $(HL1)^+$ cations. TGA studies show that **2** is stable below 300°C; weight loss of 58.22% (Calcd 58.33%) corresponds to loss of two $(HL1)^{2+}$ at 249.8–294.6°C. For **3**, decomposition of $(HL2)^+$ begins at 341.2°C and ends at 368.6°C (Obsd 28.89%, Calcd 29.05%). TGA studies show that **4** is stable below 300°C with weight loss of 46.68% (Calcd 46.79%) corresponding to loss of one $(HL3)^+$ at 342.5–368.8°C. Cations in **1** and **2** are removed at similar temperatures, as do cations of **3** and **4**; decomposition temperatures of cations in **1** and **2** are lower than the corresponding decomposition temperatures of **3** and **4**. This phenomenon may be explained by the cations in **1** and **2** having similar hydrogen bonds, as do the cations in **3** and **4**, but cations in **3** and **4** are involved in more hydrogen bonds than that of cations in **1** and **2** (table 3).

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

	1	**2**	**3**	**4**
Empirical formula	$C_{20}H_{22}Cl_4N_2OZn$	$C_{20}H_{20}Cl_4CuN_2$	$C_{14}H_{12}Br_2Cl_6N_4S_2Sn$	$C_{10}H_{12}Cl_4FeN_3$
Formula weight	513.57	493.72	791.61	371.88
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	Orthorhombic
Space group	*P*2(1)/*c*	*C*2/*c*	*C*2/*c*	*Pnma*
Unit cell dimensions (Å, °)				
a	10.3084(9)	12.8076(11)	7.2140(6)	17.0875(19)
b	12.0929(11)	8.4850(7)	32.244(3)	7.0771(8)
c	18.3130(15)	19.401(2)	10.8891(9)	12.3695(15)
α	90	90	90	90
β	101.6880(10)	92.0400(10)	101.3510(10)	90
γ	90	90	90	90
Volume (Å^3), *Z*	2235.5(3), 4	2107.0(3), 4	2483.3(4), 4	1495.8(3), 4
Calculated density (Mg m^{-3})	1.526	1.556	2.117	1.651
Absorption coefficient (mm^{-1})	1.590	1.552	5.072	1.707
F(000)	1048	1004	1512	748
Crystal size (mm^3)	0.40 × 0.38 × 0.22	0.46 × 0.37 × 0.22	0.45 × 0.33 × 0.22	0.48 × 0.40 × 0.36
θ range (°)	2.63–25.02	2.88–25.01	2.53–25.01	2.90–25.02
Limiting indices	$-9 \le h \le 12$; $-14 \le k \le 14$; $-20 \le l \le 21$	$-15 \le h \le 7$; $-10 \le k \le 9$; $-23 \le l \le 22$	$-8 \le h \le 8$; $-38 \le k \le 27$; $-12 \le l \le 12$	$-15 \le h \le 20$; $-8 \le k \le 8$; $-14 \le l \le 14$
Reflections collected	10,984	5058	5991	7247
Reflections independent	3937 [*R*(int) = 0.0494)	1850 [*R*(int) = 0.0418]	2194 [*R*(int) = 0.0769]	1441 [*R*(int) = 0.0429]
Goodness-of-fit on F^2	1.039	1.068	1.083	1.138
Final *R* indices [$I > 2\sigma(I)$]	0.0410, 0.0880	0.0339, 0.0853	0.0496, 0.1119	0.0433, 0.1070
R indices (all data)	0.0730, 0.1095	0.0476, 0.0960	0.0813, 0.1269	0.0576, 0.1242
Largest difference peak/hole (e Å^{-3})	0.606 and −0.467	0.372 and −0.458	0.965 and −0.876	0.922 and −0.828

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

1			
Zn(1)–Cl(4)	2.2346(13)	Zn(1)–Cl(3)	2.2531(11)
Zn(1)–Cl(1)	2.2695(11)	Zn(1)–Cl(2)	2.2951(11)
N(1)–C(2)	1.323(5)	N(1)–C(6)	1.369(5)
N(2)–C(12)	1.323(5)	N(2)–C(16)	1.370(5)
Cl(4)–Zn(1)–Cl(3)	112.72(6)	Cl(4)–Zn(1)–Cl(1)	108.82(5)
Cl(3)–Zn(1)–Cl(1)	111.20(4)	Cl(4)–Zn(1)–Cl(2)	106.94(6)
Cl(3)–Zn(1)–Cl(2)	110.05(5)	Cl(1)–Zn(1)–Cl(2)	106.85(5)
C(2)–N(1)–C(6)	124.5(4)	C(12)–N(2)–C(16)	124.5(3)
2			
Cu(1)–Cl(2)	2.2347(9)	Cu(1)–Cl(1)	2.2497(8)
N(1)–C(2)	1.321(4)	N(1)–C(6)	1.373(4)
Cl(2)–Cu(1)–Cl(2)#1	140.26(6)	Cl(2)–Cu(1)–Cl(1)	97.78(3)
Cl(2)#1–Cu(1)–Cl(1)	98.84(3)	Cl(1)–Cu(1)–Cl(1)#1	129.66(5)
C(2)–N(1)–C(6)	124.5(3)		
3			
Sn(1)–Cl(2)	2.390(2)	Sn(1)–Cl(3)	2.4193(18)
Sn(1)–Cl(1)	2.469(2)	Br(1)–C(5)	1.878(8)
S(1)–C(1)	1.736(7)	S(1)–C(3)	1.747(8)
N(1)–C(1)	1.321(9)	N(1)–C(2)	1.414(9)
N(2)–C(1)	1.315(9)	Cl(2)–Sn(1)–Cl(2)#1	93.85(12)
Cl(2)–Sn(1)–Cl(3)#1	92.21(7)	Cl(2)–Sn(1)–Cl(3)	92.93(7)
Cl(3)#1–Sn(1)–Cl(3)	172.49(11)	Cl(2)–Sn(1)–Cl(1)	177.30(8)
Cl(2)#1–Sn(1)–Cl(1)	88.82(8)	Cl(3)#1–Sn(1)–Cl(1)	87.23(7)
Cl(3)–Sn(1)–Cl(1)	87.39(7)	Cl(1)–Sn(1)–Cl(1)#1	88.52(12)
C(1)–S(1)–C(3)	89.6(4)	C(1)–N(1)–C(2)	115.1(6)
N(2)–C(1)–N(1)	124.2(7)	N(2)–C(1)–S(1)	123.1(6)
N(1)–C(1)–S(1)	112.7(6)		
4			
Fe(1)–Cl(2)	2.1844(17)	Fe(1)–Cl(3)	2.1844(11)
Fe(1)–Cl(1)	2.1888(14)	N(1)–C(1)	1.333(6)
N(1)–C(5)	1.347(6)	N(2)–C(6)	1.335(6)
N(2)–C(5)	1.368(6)	N(3)–C(1)	1.341(7)
Cl(2)–Fe(1)–Cl(3)	110.98(5)	Cl(3)#1–Fe(1)–Cl(3)	105.29(7)
Cl(2)–Fe(1)–Cl(1)	106.80(6)	Cl(3)–Fe(1)–Cl(1)	111.44(4)
C(1)–N(1)–C(5)	115.9(4)	C(6)–N(2)–C(5)	123.5(4)
N(1)–C(1)–N(3)	117.1(4)	N(1)–C(5)–N(2)	114.9(4)

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

3.3. *Structural descriptions*

3.3.1. Crystal structure of [(HL1)$_2$(ZnCl$_4$)]•H$_2$O (1). Compound **1** 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 that the complex is composed of one $ZnCl_4^{2-}$, two monoprotonated L1, and one free water molecule (figure 1).

As expected the aromatic rings of the cations are almost planar with rms deviations of 0.0078 Å and 0.0123 Å for rings containing N1 and N2, respectively. The dihedral angle between the two quinoline planes is 42.3°, significantly smaller than the corresponding value in bis(2-methylquinolinium) bromide tetrabromoferrate (109.2°) [17].

The Zn–Cl bond lengths and Cl–Zn–Cl bond angles in $ZnCl_4^{2-}$ are not equal, but vary with the environment around Cl^-. In **1**, the Zn–Cl bond distances are

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

D–H···A	d(D···A) (Å)
1	
O(1)–H(1G)···Cl(3)#1	3.231(4)
O(1)–H(1F)···Cl(1)	3.330(3)
N(2)–H(2)···Cl(2)#2	3.170(3)
N(1)–H(1)···O(1)	2.731(4)
2	
N(1)–H(1)···Cl(1)#2	3.402(3)
N(1)–H(1)···Cl(2)#2	3.390(3)
3	
N(2)–H(2B)···Cl(1)#2	3.283(6)
N(2)–H(2A)···Cl(1)#3	3.280(6)
N(1)–H(1)···Cl(2)#4	3.362(6)
4	
N(3)–H(3B)···Cl(2)#2	3.541(5)
N(3)–H(3A)···Cl(1)	3.453(5)
N(2)–H(2)···Cl(3)	3.587(4)
N(2)–H(2)···Cl(3)#1	3.587(4)

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

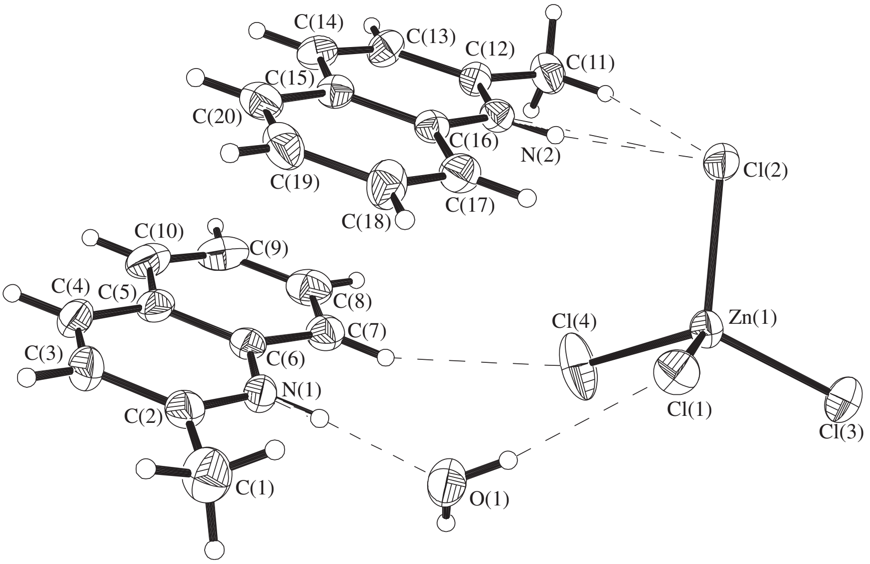


Figure 1. Molecular structure of 1 showing the atom-numbering scheme at 30% ellipsoid probability level.

2.2346(13)–2.2951(11) Å. Cl(4) does not accept hydrogen in forming classical hydrogen bond such as N–H···Cl and O–H···Cl, thus the Zn(1)–Cl(4) bond length is the shortest. The Cl–Zn–Cl bond angles range from 106.85(5) to 112.72(6)°, in agreement with those previously reported [18], clearly indicating that the coordination geometry of the Zn can

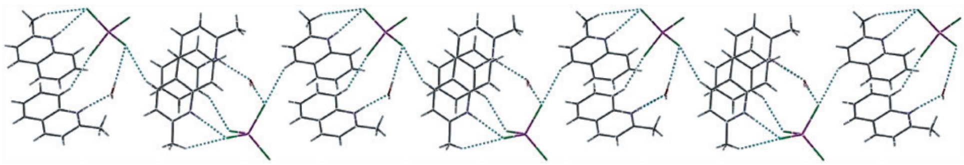


Figure 2. 1-D chain structure of **1** running parallel to the *c*-axis.

be regarded as being a slightly distorted tetrahedron [18]. The largest Cl–Zn–Cl bond angle (Cl(4)–Zn(1)–Cl(3), 112.72(6)°) is made by Cl(3) and Cl(4) with shorter Zn–Cl bonds. Angles around the protonated nitrogen atoms are similar to documented data [17].

One cation is bonded with water through N–HvO hydrogen bond, thus this cation has no N–HvCl contact with the anion (the water molecule blocks the donor position of the cation so that NH^+ have no classical hydrogen-bonding interaction with the anion). In another cation, an anion through N–H···Cl contact is bonded, and $CH_3\cdots Cl$ interaction also exists between 2-CH_3 of the cation and Cl of the anion with C···Cl distance of 3.791 Å. Herein, the two aromatic rings of the cations are parallel to each other, rotated 180° from each other. The two kinds of cations are joined via O–H···Cl contact arising from bonded water (donor) and the anion, and CH···Cl associations to form a tetra adduct. Such tetracomponent adducts are linked by the CH···Cl association between the 4-CH of the cation and Cl with C···Cl distance of 3.797 Å to form a 1-D chain running parallel to the *c*-axis (figure 2). In the chain, cations of neighboring tetracomponent adducts made an angle of 42.3° with each other, while cations at the first tetracomponent adduct were parallel to cations at the third tetracomponent adduct. The chains were further combined by CH···Cl interactions between the 7-CH of the cation and Cl belonging to two adjacent chains with C···Cl distance of 3.830 Å to form a 2-D sheet extending at the direction making an angle of *ca* 45° with the *ac*-plane (figure 3). Adjacent Zn–Zn separations in the same sheet are 8.160 and 15.890 Å, respectively, along the *b*-axis, while the closest Zn–Zn distance along the *c*-axis is 11.820 Å. Such sheets are further stacked perpendicular with its extending direction via CH···Cl interactions between the 6- and 7-CH of the cation and Cl with C···Cl distances of 3.742–3.830 Å and O–H···Cl association between the water molecule and the anion with O···Cl distance of 3.231(4) Å to form a 3-D network. An alternative reading of this structure is possible when we emphasize the relative arrangement of the anions and the cations, forming a 3-D ABAB (cation–anion–cation–anion) layer network structure when viewed from the *c*-axis.

3.3.2. Crystal structure of $[(HL1)_2(CuCl_4)]$ (2).

Complex **2** was prepared by reacting 2 mol of 2-methylquinoline (L1) with 1 mol of copper(II) chloride dihydrate in water in the presence of hydrochloric acid. There were no solvent or water molecules involved in the lattice as determined by elemental analysis. Complex **2** crystallizes in the monoclinic space group $C2/c$ with unit cell content of four formula units. Although having similar formulation with **1**, the asymmetric unit of **2** consists of only one 2-methylquinolium and a half of $CuCl_4^{2-}$ (figure 4). The geometry of the cyclic component HL1 is very

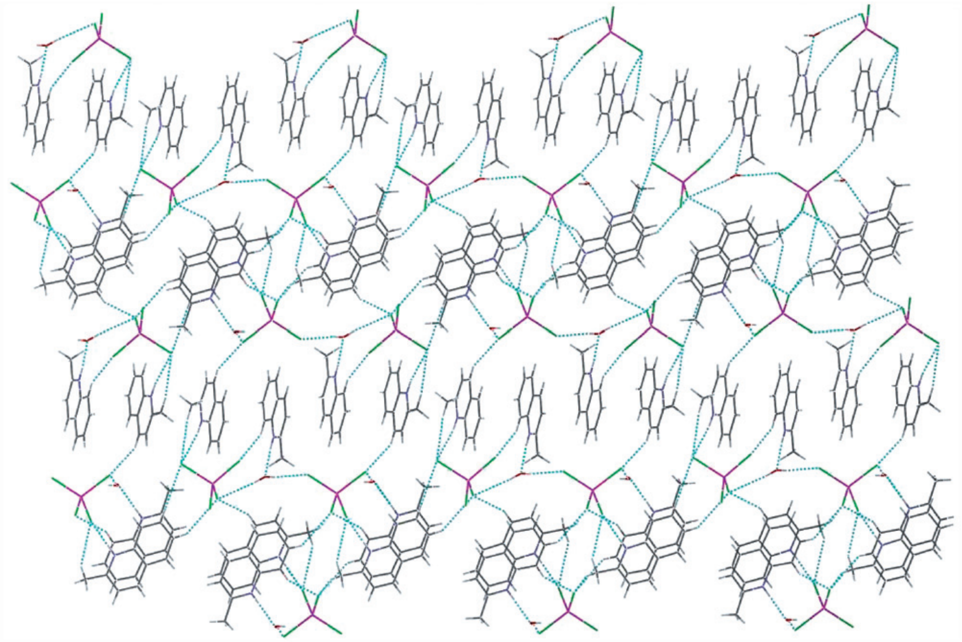


Figure 3. 2-D sheet formed *via* the interchain CH–Cl interactions, which is extending at the direction that made an angle of *ca* 45° with the *ac*-plane.

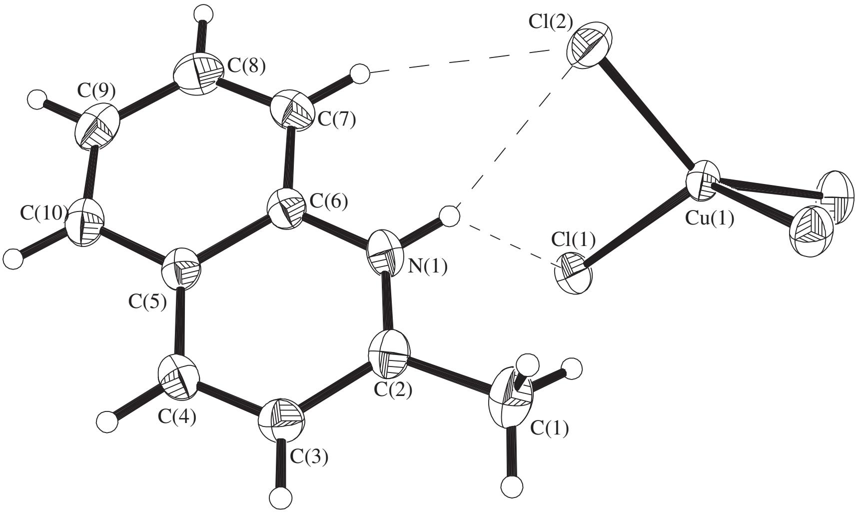


Figure 4. Molecular structure of **2** showing the atom-numbering scheme at 30% thermal ellipsoid probability level.

similar to that in **1**. Cu's are tetrahedrally surrounded by four chlorides to form $CuCl_4^{2-}$ with a 2-fold axis passing on the Cu. The Cu–Cl bonds were 2.2347(9)–2.2497(8) Å and Cl–Cu–Cl angles between neighboring chlorides deviate significantly from 90°, being 140.26(6)° and 129.66(5)°, respectively.

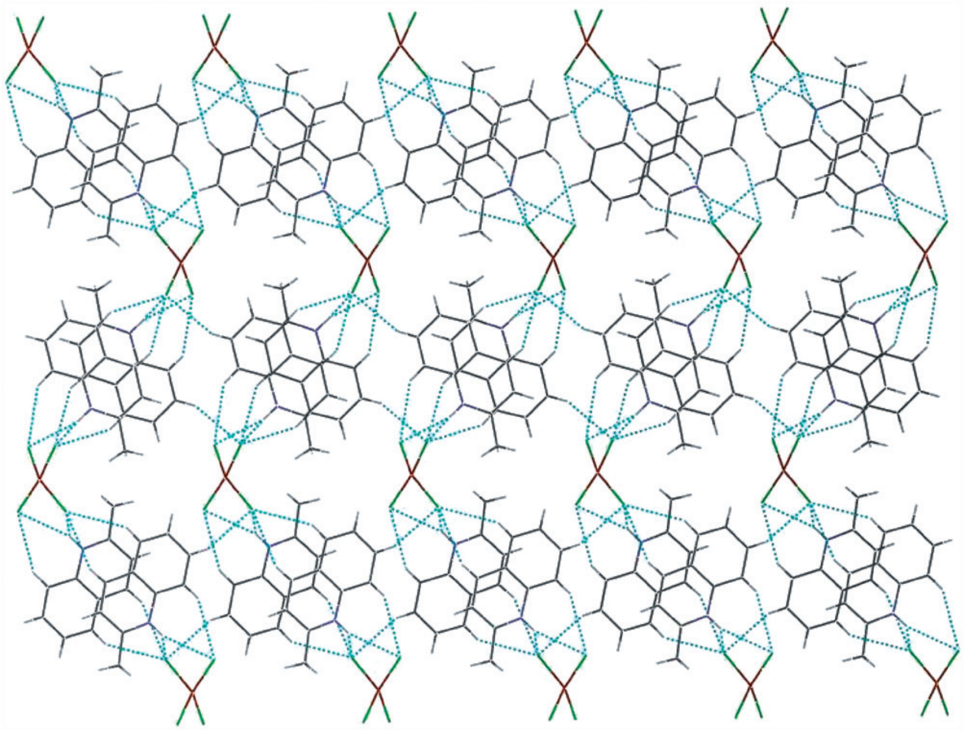


Figure 5. 2-D sheet structure of **2** extending parallel to the *bc*-plane.

At every anion there are two cations, bound through the bifurcated N–H···Cl interactions generated between NH^+ and two chlorides of the same anion with N···Cl distances of 3.390(3)–3.402(3) Å, and CH···Cl association between 8-CH of the cation and the other Cl^- with C···Cl distance of 3.663 Å. These non-bonding interactions of anion and cation generated a tricomponent adduct, with hydrogen-bonded ring motifs with graph sets of $R_2^1(6)$ and $R_2^1(4)$; two kinds of rings were fused together *via* the N–H···Cl association. For tetrahedral chlorides, the two cations bonded with the same anion are not in the same plane, located at above–below positions with partial overlap between the two cations. The tricomponent adducts were joined together by CH···Cl interactions between the 4- and 5-CH of the cation and Cl^- of the neighboring adduct with C···Cl distances of 3.593–3.686 Å to form a 2-D sheet extending parallel to the *bc*-plane (figure 5). Such sheets were further stacked along the *a*-axis by CH_3···Cl interactions with C···Cl distance of 3.769 Å to form a 3-D layer network. Adjacent sheets were slipped some distances from each other along the *b*- and *c*-axis directions.

3.3.3. Crystal structure of [$(HL2)_2SnCl_6$] (3). Complex **3** was prepared by reacting 6-bromobenzo[d]thiazol-2-amine (L2) with 1 equivalent of tin(II) chloride dihydrate in water/ethanol in the presence of hydrochloric acid. As shown in figure 6, only the nitrogen of the thiazole ring is protonated, not that of the amine. Thus, to ensure

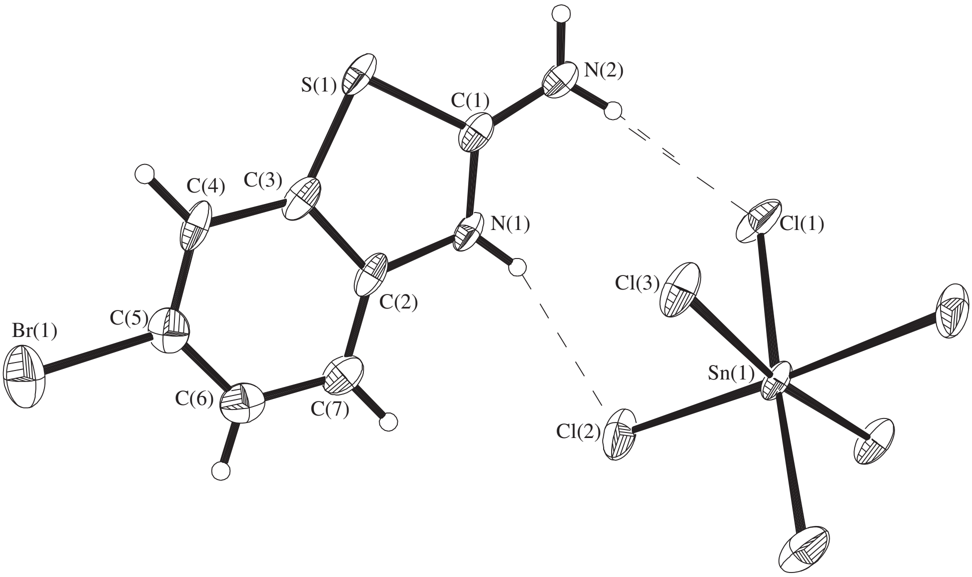


Figure 6. Molecular structure of **3** showing the atom-numbering scheme at 30% thermal ellipsoid probability level.

charge equilibrium, the structure associates each hexachlorostannate anion with two (2-aminobenzothiazolium) cations. Complex **3** crystallizes in the monoclinic space group *C*2/*c* with unit cell content of four formula units and the asymmetric unit consisting of one 6-bromobenzo[d]thiazolium-2-amine cation and a half of $SnCl_6^{2-}$.

Sn–Cl bonds were 2.390(2)–2.469(2) Å, in the range of reported values (2.402(3)–2.483(3) Å) [19]. Sn(1)–Cl(1) bond length (2.469(2) Å) is longer than the other Sn–Cl bonds, probably because Cl(1) forms more hydrogen bonds than other chlorides (table 3). The *cis* Cl–Sn–Cl angles ranged from 87.23(7) to 93.85(12)°, indicating Sn is in a slightly distorted octahedral environment. *Trans* Cl–Sn–Cl angles are close to 180°.

One anion and two cations produced a tricomponent adduct *via* bis(bidentate) N–H···Cl contacts with N···Cl distances of 3.280(6)–3.362(6) Å. The two cations were symmetry related to the symmetry center located at Sn. For the presence of the N–H···Cl contacts the cation and the anion generate a $R_2^2(8)$ ring. The tricomponent adducts were linked by N–H···Cl contacts between amino group and anion with N···Cl distance of 3.283(6) Å, CH···Cl, Cl···S interaction (between the Cl^- and the ring S with Cl···S separation of 3.409 Å), and S···S associations to form a 1-D wavechain running along the *c*-axis (figure 7). Herein the S···S distance is 3.577 Å, which is similar to the S···S distances (3.52–3.63 Å) in $(dpaH)_2[Hg(SCN)_4]$ (dpa = 2,2′-dipyridylamine) [20], yet it is less than the sum of the revised van der Waals radii of S (4.06 Å) [21].

The chains were further stacked along the *a*-axis via $\pi\cdots\pi$ interactions between aromatic rings of the cations with Cg···Cg distance of 3.375 Å to form 2-D sheets parallel to the *ac*-plane with the thickness of half the length of the *c*-axis (figure 8).

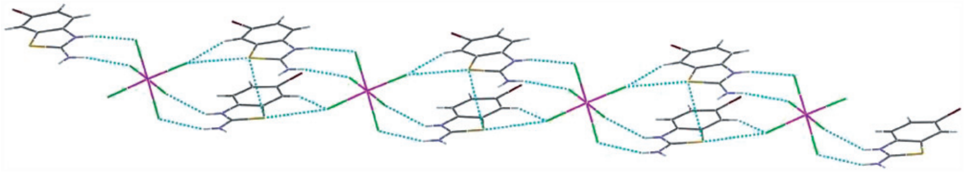


Figure 7. 1-D wavechain structure of **3** formed *via* N–H···Cl, CH···Cl, Cl···S, and S···S associations running along the *c*-axis.

3.3.4. Crystal structure of [(HL3)FeCl$_4$] (4). [(HL3)FeCl$_4$] (**4**) was also prepared by reacting L3 (5,7-dimethyl-1,8-naphthyridine-2-amine) with iron(III) chloride hexahydrate in water in the presence of conc. hydrochloric acid. The compound was isolated in high yield as red block crystals. The compound crystallizes in an orthorhombic space group *Pnma* with unit content of four formula units. The molecular structure is given in figure 9; in the asymmetric unit of **4** there are one cation and one anion.

In **4**, the ring N adjacent to the methyl group is protonated and the cation with the NH$^+$ on the naphthyridine rings in **4** resembles 2-amino-4,6-dimethylpyridinium cations [22], similar to the organic salt 2,2′-dimethyl-7,7′-(methylenediimino)di-1,8-naphthyridin-1-ium bis(perchlorate) [23]; here, it is also the less basic ring nitrogen that has been protonated.

Fe(III) is surrounded by four Cl$^-$ to form a tetrahedral Cl$_4$ binding set. The Fe–Cl bond distances range from 2.1844(11) to 2.1888(14) Å, almost equal to each other, indicating slight deviation from perfect tetrahedral environment around Fe. Different from 2-amino-5,7-dimethyl-1,8-naphthyridine [24], the N$_{\text{ring}}$CN$_{\text{ring}}$ angle in **4** (N(1)–C(5)–N(2), 114.9(4)°) is larger than the corresponding angles (112.7(3)° and 112.6(3)°) in bis(2-amino-5,7-dimethyl-1,8-naphthyridine) dinitratocadmium. We conclude that the bidentate chelating coordination to the metal ion led to a larger contraction (for the N$_{\text{ring}}$CN$_{\text{ring}}$ angle should be *ca* 120° if there are not any bonding interactions with the two ring nitrogen atoms) in the N$_{\text{ring}}$CN$_{\text{ring}}$ angle of bis(2-amino-5,7-dimethyl-1,8-naphthyridine) dinitratocadmium compared with the corresponding angle in **4**. In **4**, the major non-bonding contacts are hydrogen-bonding interactions. In bis(2-amino-5,7-dimethyl-1,8-naphthyridine) dinitratocadmium the coordinate bonds are stronger than hydrogen bonds.

One anion was bonded to one cation *via* three N–H···Cl interactions. Of the three N–H···Cl interactions one is between the amino group and Cl$^-$ with N···Cl distance of 3.453(5) Å and the other two are generated between NH$^+$ and two different Cl$^-$ from the same FeCl$_4^{2-}$ unit with N···Cl distance of 3.587(4) Å. The heteroadducts were linked by N–H···Cl association between the amino of one heteroadduct and the Cl anion of its neighboring heteroadduct with N···Cl distance of 3.541(5) Å, and CH···Cl association between the aromatic CH of the cation and Cl$^-$ with C···Cl distance of 3.580 Å to form a 1-D chain running parallel to the *ac*-plane (figure 10). The chains were combined by N–H···Cl association between the amino group of one chain and Cl$^-$ of its neighboring chain with N···Cl distance of 3.541(5) Å, and CH···Cl association between the aromatic CH of the cation and Cl$^-$ with C···Cl distance of 3.580 Å to form a 2-D sheet extending parallel to the *ac*-plane (figure 11).

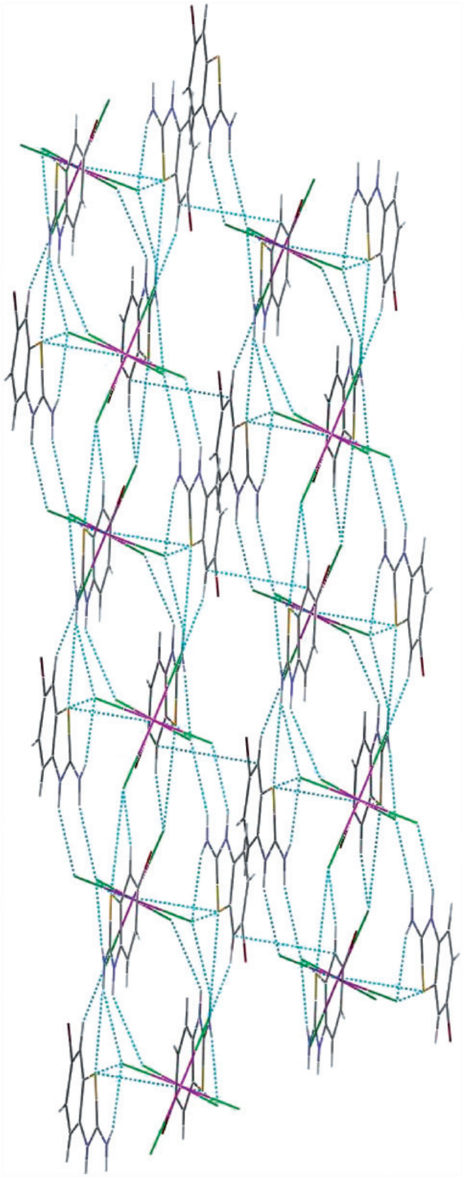


Figure 8. 2-D sheet structure of **3** formed *via* interchain π–π interactions extending parallel to the *ac*-plane.

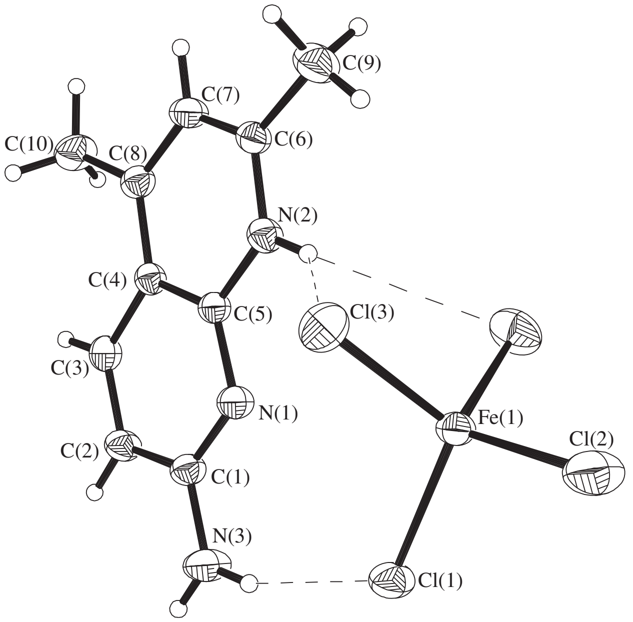


Figure 9. Molecular structure of **4** showing the atom-numbering scheme at 30% ellipsoid probability level.

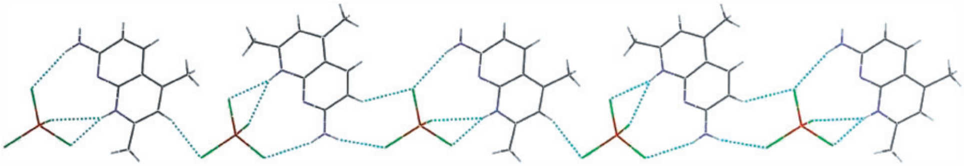


Figure 10. 1-D chain structure of **4** running parallel to the *ac*-plane.

4. Conclusions

Four new inorganic–organic hybrid solids were synthesized by solution reaction of $ZnCl_2$, $CuCl_2$, $SnCl_2$, and $FeCl_3$ with N-containing aromatic Brønsted bases in strong acidic conditions at room temperature. The crystals were characterized by X-ray structure analysis, EA, IR, and TG. The Zn, Cu, and Fe in **1**, **2**, and **4** display tetrahedral coordination with MCl_4^{2-}; Sn in **3** is octahedrally coordinated by Cl^- ions. For L2 and L3, the least basic nitrogen atoms have never been protonated.

The hybrid crystals are built by MCl_n^{2-} associated with $[HL]^+$. Multiple non-covalent associations maintain the structures of these compounds. The compounds display 3-D ABAB (cation–anion–cation–anion) layer network structure, 3-D layer structure, and 2-D sheet structure with N–H···Cl, N–H···O, and O–H···Cl interactions as well as Coulombic interactions. Secondary propagating interactions such as CH···Cl, CH_3···Cl, Cl···S, and S···S interactions also play important roles in structure stabilization. Chlorometallates are effective hydrogen-bond acceptors, and tetrachlorometallate and hexachlorometallate may be exploited to prepare hydrogen-bonded

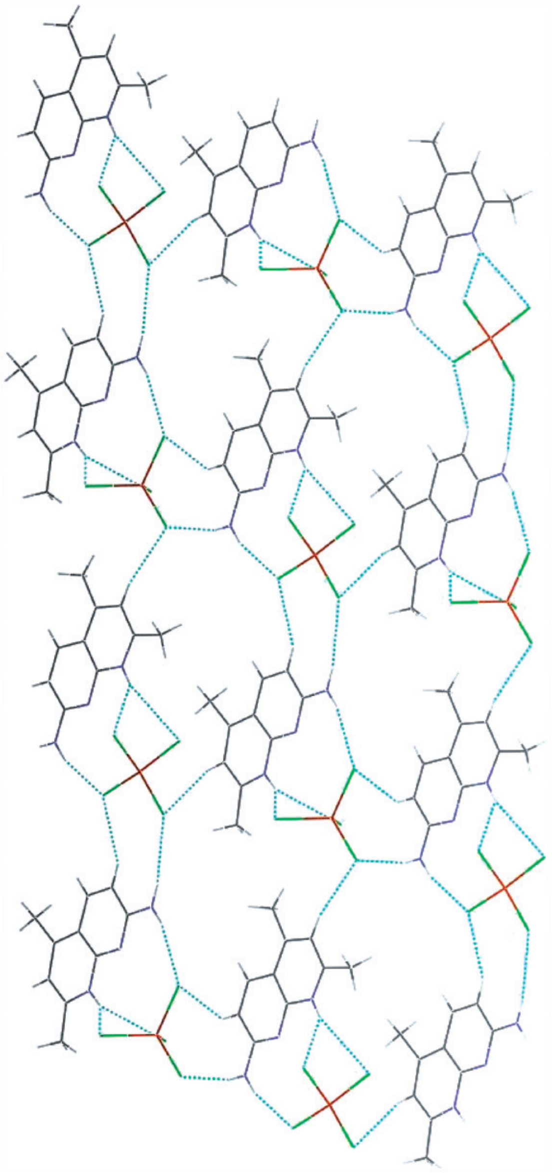


Figure 11. 2-D sheet structure of **4** formed through N–H···Cl, and CH–Cl interactions viewed down the *b*-axis.

polymers composed of $[HL]_2^{2+}$ or $[HL]^+$ salts of perchlorometallates. In the cases reported here, choice of anions without hydrogen-bond donor sites and cations with strong hydrogen-bond donors is a successful strategy.

The structure motifs of these inorganic–organic hybrid complexes depend on the shape and size of the organic cations. Inorganic–organic hybrid compounds with novel structures and functionalities can be expected by variation of the organic cations, and the perchlorometallates. All of the compounds show high thermal stabilities.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 850869 for **1**, 850870 for **2**, 851146 for **3**, and 850867 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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