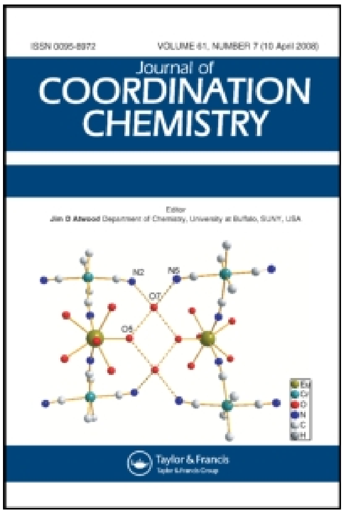

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Syntheses and structural characterization of inorganic-organic hybrid solids of bis-imidazolium chlorocadmate complexes

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Syntheses and structural characterization of inorganic–organic hybrid solids of bis-imidazolium chlorocadmate complexes

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Six organic–inorganic complexes derived from bis-imidazole derivatives ([$(H_2L1)(CdCl_3 \cdot H_2O)_2$] (**1**), L1 = 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole; [$(H_2L2)CdCl_4$] (**2**), L2 = 1,1′-bis(benzimidazolyl)methane; [$(H_2L3)CdCl_4$] (**3**), L3 = 1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole; [$(H_2L4)_4(CdCl_4)_4$] $\cdot$ $13H_2O$ (**4**), L4 = 1,5-bis(1-benzimidazolyl)-3-oxapentane; [$(H_2L5)CdCl_4$] (**5**), L5 = 1-(4-(1H-benzimidazol-1-yl)butyl)-1H-benzimidazole; [$(H_2L6)(Cd_2Cl_8)_{0.5}$] $\cdot$ H_2O (**6**), L6 = 3,6-bis(imidazol-1-yl)pyridazine), and cadmium(II) chloride dihydrate were prepared and characterized by IR, X-ray structure analysis, elemental analysis, and TG analysis. The imidazolyl moieties in all six compounds are essentially planar. X-ray diffraction analysis revealed that complexes **1–6** have 3-D network structures built from hydrogen bonds between imidazolium cations, chlorocadmate anions, and water. The arrangements of the anions and cations in their solid state are dominated not only by the size and symmetry of the imidazolium cations, but also by the different structure types of the chlorocadmate anions as well as the hydrogen-bonded interactions existing in the crystal structures. All of the complexes are thermally stable.

Keywords: Cadmium; Imidazolium; Crystal structure; Inorganic-organic hybrid

1. Introduction

Organic–inorganic hybrid materials represent new directions in solid-state chemistry [1, 2]. Organic–inorganic hybrids 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 possibilities to construct multifunctional materials.

Organic–inorganic hybrid compounds based on layers of anionic transition metal(II) halogen frameworks and organic 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, Br, Cl; R = alkyl, phenyl, etc.) have been extensively studied in the

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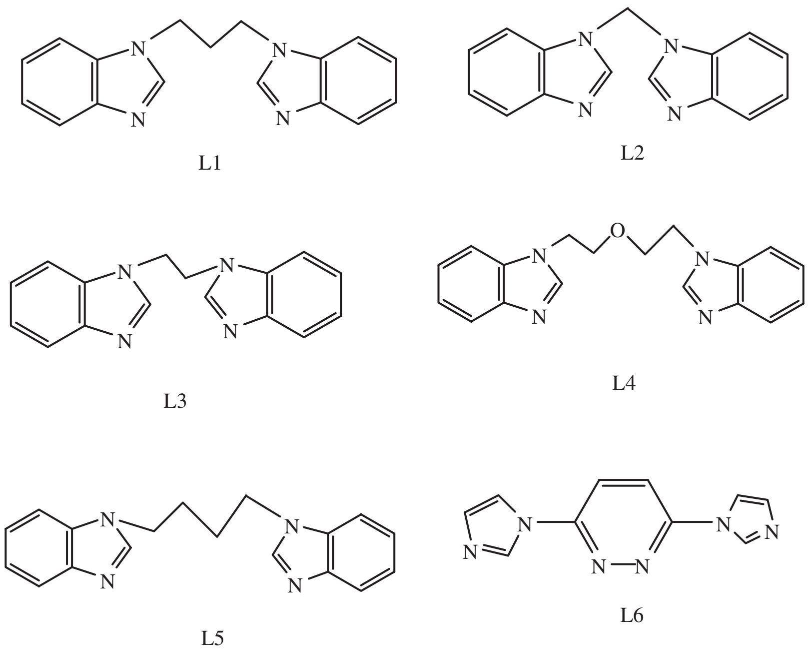
field of low-dimensional magnetism [8]. Structural transitions in hybrids containing long-chain alkylammonium cations were studied in order to better understand the biological lipid bilayers [9]. Most of the ammonium cations incorporated in hybrid materials are either alkylammonium or single ring aromatic ammonium cations.

Metal halides such as SnX_2 ($X = Cl$, Br, and I) have been widely studied as semiconducting components [10] in organic–inorganic hybrid semiconductors with potential applications in display and storage technologies because of their stable exciton, excellent film processability, and superior carrier mobility [11]. Cd(II) exhibits a variety of coordination numbers and geometries, depending on the crystal packing and on the ligands [12]. Chlorocadmate(II) compounds represent a class of materials with unusual structural archetypes, where the ligands are chloride and water, if present, that give 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. Hydrogen-bond interactions between the polar protonated amine groups of the organic cations and chloride of the inorganic anions contribute to the crystal packing.

Complexes based on metal salts of CdX_2 ($X = Cl$, SCN) and bifunctional ammonium cations have not been well-studied to date [13–17]. As an extension of our research of organic–inorganic hybrid complexes based on imidazole derivatives [18], herein we report the synthesis and structure of six chlorocadmate complexes with imidazole derivatives (scheme 1) as bifunctional organic ammonium cations.



Scheme 1. The bis-imidazoles used in this article.

2. Experimental

2.1. *Materials*

The chemicals and solvents used in this work are of analytical grade and available commercially and were used without purification. L1–L5 [19] and L6 [20] were prepared according to the modified literature procedures.

2.2. *Physical measurements and analyses*

Elemental analysis was determined with a Perkin-Elmer 2400C instrument and infrared (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 performed by a Delta Series TA-SDT Q600 in nitrogen 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 $[(H_2L1)(CdCl_3 \cdot H_2O)_2]$ (1). Cadmium(II) chloride dihydrate (23 mg, 0.10 mmol) dissolved in 1 mL of conc. hydrochloric acid and 5 mL of water was treated with L1 (28 mg, 0.10 mmol). After stirring for several minutes, the solution was filtered. The clear solution was stored at room temperature for several days to give colorless block crystals. Yield: 65 mg, 86.45%. Anal. Calcd for $C_{17}H_{22}Cd_2Cl_6N_4O_2$ (%): C, 27.13; H, 2.93; N, 7.45. Found (%): C, 27.11; H, 2.90; N, 7.39. IR (KBr disc, cm^{-1}): 3500s, 3360s, 3290s, 3120s, 3040s, 1760s, 1605s, 1580s, 1560s, 1500s, 1440s, 1380s, 1260m, 1240m, 1180m, 1140m, 1060m, 1010m, 970m, 930m, 870m, 760m, 620m, 580m.

2.3.2. Preparation of $[(H_2L2)CdCl_4]$ (2). Compound **2** was prepared by similar procedure as for **1** from cadmium(II) chloride dihydrate (23 mg, 0.10 mmol) and L2 (25 mg, 0.10 mmol) in 1 mL of conc. hydrochloric acid and 3 mL of water. The compound was isolated as colorless block crystals. Yield: 43 mg, 85.23%. Anal. Calcd for $C_{15}H_{14}CdCl_4N_4$ (%): C, 35.68; H, 2.77; N, 11.10. Found (%): C, 35.64; H, 2.72; N, 11.06. 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.

2.3.3. Preparation of $[(H_2L3)CdCl_4]$ (3). Compound **3** was prepared by similar procedure as for **1** from cadmium(II) chloride dihydrate (23 mg, 0.10 mmol) and L3 (28 mg, 0.10 mmol) in 1.5 mL of conc. hydrochloric acid and 4 mL of water. The compound was isolated as colorless blocks. Yield: 43 mg, 82.93%. Anal. Calcd for $C_{16}H_{16}CdCl_4N_4$ (%): C, 37.03; H, 3.08; N, 10.80. Found (%): C, 37.01; H, 3.03; N, 10.76. IR (KBr disc, cm^{-1}): 3680s, 3320s, 3120s, 2980s, 1960m, 1860m, 1615m, 1540m, 1480m, 1460m, 1410m, 1360m, 1320m, 1280m, 1220m, 1190m, 1140m, 1100m, 1060m, 1020m, 920m, 860m, 740m, 610m, 580m, 440m.

2.3.4. Preparation of [$(H_2L4)_4(CdCl_4)_4$]•$13H_2O$ (4). Compound **4** was prepared by similar procedure as for **1** from cadmium(II) chloride dihydrate (23 mg, 0.10 mmol) and L4 (31 mg, 0.10 mmol) in 4 mL of conc. hydrochloric acid and 10 mL of water. The compound was isolated as colorless blocks. Yield: 50 mg, 80.50%. Elemental Anal. Calcd for $C_{72}H_{106}Cd_4Cl_{16}N_{16}O_{17}$ (%): C, 34.77; H, 4.27; N, 9.01. Found (%): C, 34.72; H, 4.24; N, 9.05. IR (KBr disc, cm^{-1}): 3440s, 3296m, 3120s, 3080s, 2940m, 2860m, 1960m, 1720m, 1680m, 1620m, 1550m, 1510m, 1450m, 1380m, 1340m, 1290m, 1210m, 1170m, 1100m, 1040m, 880m, 820m, 760m, 620m, 570m, 440m.

2.3.5. Preparation of [$(H_2L5)CdCl_4$] (5). Compound **5** was prepared by similar procedure as for **1** from cadmium(II) chloride dihydrate (23 mg, 0.10 mmol) and L5 (29 mg, 0.10 mmol) in 3 mL of conc. hydrochloric acid and 5 mL of water. The compound was isolated as colorless blocks. Yield: 42 mg, 76.84%. Anal. Calcd for $C_{18}H_{20}CdCl_4N_4$ (%): C, 39.52; H, 3.66; N, 10.25. Found (%): C, 39.50; H, 3.62; N, 10.21. IR (KBr disc, cm^{-1}): 3440s, 3290m, 3120s, 3040s, 2860s, 2360m, 1760m, 1620m, 1560m, 1450m, 1380m, 1330m, 1240m, 1120m, 1010m, 940m, 860m, 740m, 620m, 520m, 440m.

2.3.6. Preparation of [$(H_2L6)(Cd_2Cl_8)_{0.5}$]•H_2O (6). Compound **6** was prepared by similar procedure as for **1** from cadmium(II) chloride dihydrate (23 mg, 0.10 mmol) and L6 (21 mg, 0.10 mmol) in 5 mL of conc. hydrochloric acid and 8 mL of water. The compound was isolated as colorless blocks. Yield: 39 mg, 80.17%. Anal. Calcd for $C_{10}H_{12}CdCl_4N_6O$ (%): C, 24.67; H, 2.47; N, 17.27. Found (%): C, 24.66; H, 2.44; N, 17.25. IR (KBr disc, cm^{-1}): 3440m, 3340m, 3210s, 3140m, 3040m, 2920m, 2640m, 1880m, 1700m, 1620m, 1540m, 1520m, 1460m, 1420m, 1340m, 1240m, 1140m, 1070m, 1020m, 960m, 840m, 710m, 650m, 610m, 440m.

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 a Mo-Kα radiation ($\lambda = 0.71073$ Å) using an $\omega - 2\theta$ scan mode. Data collection and reduction were performed using *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 hydrogens were generated geometrically and included in structure factor calculations.

3. Results and discussion

3.1. *Preparation and general characterization*

Most organically templated halocadmiums reported previously were prepared by the conventional solution approach, thus **1–6** were prepared by the conventional solution method. Reactions of $CdCl_2 \cdot 2H_2O$ and the imidazolyl derivatives in acidic aqueous solutions afforded different imidazolium salts of chlorocadmates ($CdCl_3^-$, $CdCl_4^{2-}$,

$Cd_2Cl_8^{4-}$), respectively, with the same ratio of reactants (1 : 1). The reason may lie in the different solubilities of the corresponding ligands, which lead to different structures of the corresponding compounds. All of the compounds were isolated as colorless crystals in high yields. These compounds are not soluble in most common solvents. The ability of cadmium chloride complexes to act as hydrogen-bond acceptors has been noted in previous examples [16]. These metal-assisted hydrogen bonds typically have short CdCl···HN (or HO) distances in the range 2.01–2.82 Å and Cd–Cl···H angles in the range 80.63–136.15° with normal angles at hydrogen (e.g., $N–H\cdots Cl \geq 126°$).

IR spectra show strong vibrations 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 and C=N stretches of the imidazolyl or aromatic rings. The compositions of these compounds were determined by elemental analysis and their structures were fully characterized by X-ray diffraction analysis. Hydrogens connected to O or N were fixed from the difference electron density map, which also indirectly confirms protonation of the imidazole derivatives. The crystallographic data and refinement details are summarized in tables 1 and 2, selected bond distances and bond angles are listed in table 3, and some important hydrogen bonds are listed in table 4.

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

	1	**2**	**3**
Formula	$C_{17}H_{22}Cd_2Cl_6N_4O_2$	$C_{15}H_{14}CdCl_4N_4$	$C_{16}H_{16}CdCl_4N_4$
Formula weight	751.89	504.50	518.53
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*C2/c*	*Pbca*	*P2(1)/c*
Unit cell dimensions (Å, °)			
a	20.640(2)	15.0885(16)	16.4495(18)
B	7.6479(8)	14.9131(13)	15.9494(16)
c	15.4601(16)	16.7192(18)	7.3780(9)
α	90	90	90
β	97.7130(10)	90	93.7970(10)
γ	90	90	90
Volume (A^3), *Z*	2418.4(4), 4	3762.1(7), 8	1931.4(4), 4
Calculated density ($mg\,m^{-3}$)	2.065	1.781	1.783
Absorption coefficient (mm^{-1})	2.445	1.733	1.691
F(000)	1464	1984	1024
Crystal size (mm^3)	0.45 × 0.30 × 0.26	0.49 × 0.28 × 0.23	0.28 × 0.22 × 0.03
θ range (°)	1.99–25.02	2.27–25.02	1.24–25.02
Limiting indices	$-24 \leq h \leq 23$; $-8 \leq k \leq 9$; $-18 \leq l \leq 17$	$-17 \leq h \leq 16$; $-17 \leq k \leq 17$; $-19 \leq l \leq 13$	$-18 \leq h \leq 19$; $-18 \leq k \leq 18$; $-7 \leq l \leq 8$
Reflections collected	5779	15,923	9572
Independent reflection	2123 [*R*(int) = 0.0419]	3316 [*R*(int) = 0.0714]	3371 [*R*(int) = 0.1255]
Goodness-of-fit on F^2	1.090	1.157	1.077
Final *R* indices [$I > 2\sigma(I)$]	0.0238, 0.0576	0.0324, 0.0616	0.1467, 0.3474
R indices (all data)	0.0293, 0.0625	0.0631, 0.0796	0.1868, 0.3719
Largest difference peak and hole ($e\,Å^{-3}$)	0.638, −0.600	0.462, −0.591	2.820, −1.365

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

	4	**5**	**6**
Formula	$C_{72}H_{106}Cd_4Cl_{16}N_{16}O_{17}$	$C_{18}H_{20}CdCl_4N_4$	$C_{10}H_{12}CdCl_4N_6O$
Formula weight	2484.53	546.58	486.46
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*P2(1)/c*	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	7.3050(5)	7.6760(10)	8.2280(10)
b	38.273(3)	7.8801(11)	10.4261(12)
c	18.5552(13)	17.8889(19)	11.2559(14)
α	90	83.9420(10)	110.814(2)
β	99.5090(10)	81.8400(10)	90.3600(10)
γ	90	88.071(2)	110.191(2)
Volume (A^3), Z	5116.4(6), 2	1064.9(2), 2	837.92(17), 2
Calculated density (mg m^{-3})	1.613	1.705	1.928
Absorption coefficient (mm^{-1})	1.303	1.538	1.949
$F(000)$	2500	544	476
Crystal size (mm^3)	0.41 × 0.23 × 0.16	0.18 × 0.16 × 0.05	0.41 × 0.40 × 0.28
θ range (°)	1.54–25.02	2.31–25.02	1.96–25.02
Limiting indices	$-8 \le h \le 8$; $-45 \le k \le 44$; $-11 \le l \le 22$	$-9 \le h \le 5$; $-8 \le k \le 9$; $-21 \le l \le 21$	$-9 \le h \le 9$; $-12 \le k \le 9$; $-10 \le l \le 13$
Reflections collected	26,248	5430	4380
Reflections independent	8961 [R(int) = 0.1032]	3689 [R(int) = 0.0479]	2910 [R(int) = 0.0184]
Goodness-of-fit on F^2	1.018	1.012	1.084
Final R indices [$I > 2\sigma(I)$]	0.1074, 0.2591	0.0633, 0.1911	0.0284, 0.0622
R indices (all data)	0.1863, 0.3201	0.0813, 0.2118	0.0368, 0.0670
Largest difference peak and hole (e Å^{-3})	2.071 and −1.444	1.479 and −1.064	0.383 and −0.576

3.2. *Structural descriptions*

3.2.1. Crystal structure of [(H_2L1)($CdCl_3 \cdot H_2O$)$_2$] (1). Compound **1** [H_2L1 · ($CdCl_3$ · H_2O)$_2$] (L1 = 1,3-bis(benzimidazolyl)propane) crystallizes in a monoclinic *C2/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 $CdCl_3^-$ anion, a half diprotonated L1 cation, and one coordinated water (figure 1). An important role of the coordinated water is to adjust the anionic charge from $[CdCl_4]^{2-}$ to $[CdCl_3(H_2O)]^-$ by replacing the Cl^-. L1 is doubly protonated and the cation with the NH^+ groups on the benzimidazole rings in **1** resembles 4,4′-H_2bipy cations [14].

The coordination geometry around Cd(II) is a distorted octahedron with Cl_5O binding. Each Cd atom is coordinated by five chlorides and one water, in which four chlorides occupy the basal plane, while one water and one chloride occupy axial positions. Protonated L1 displays *trans* configuration, in which the inversion center is located at C(9). The Cl^- take on two types of coordination, terminal Cl(3), μ_2-mode Cl(1) and Cl(2). Each bridged Cl^- plays a key role in forming the double-chain structure. The terminal Cl^- takes part in the hydrogen-bonding interactions with water from adjacent chains. The Cd–Cl bond distances range from 2.6089(8) to 2.6582(8) Å, in the range of reported results (2.5733–2.6672 and 2.518–2.678 Å) [14, 15]. The Cd–Cl(terminal) = 2.6160(8) Å are less than Cd–Cl(μ_2) = 2.6303(8)–2.6582(8), in agreement with the literature results [16]. The Cd–O_{water} bond length (2.328(2) Å) is comparable

Table 3. Selected bond lengths (Å) and angles (°) for **1–6**.

1			
Cd(1)–O(1)	2.328(2)	Cd(1)–Cl(3)	2.6160(8)
Cd(1)–Cl(2)	2.6303(8)	Cd(1)–Cl(1)	2.6582(8)
O(1)–Cd(1)–Cl(2)#1	90.77(6)	O(1)–Cd(1)–Cl(3)	176.06(6)
Cl(2)#1–Cd(1)–Cl(3)	92.28(3)	O(1)–Cd(1)–Cl(1)#1	86.71(7)
Cl(2)#1–Cd(1)–Cl(1)#1	86.33(3)	Cl(3)–Cd(1)–Cl(1)#1	90.99(3)
O(1)–Cd(1)–Cl(2)	83.96(6)	Cl(2)#1–Cd(1)–Cl(2)	174.079(16)
Cl(3)–Cd(1)–Cl(2)	93.11(3)	Cl(1)#1–Cd(1)–Cl(2)	96.03(3)
O(1)–Cd(1)–Cl(1)	88.40(7)	Cl(2)#1–Cd(1)–Cl(1)	91.94(3)
Cl(3)–Cd(1)–Cl(1)	93.99(3)	Cl(1)#1–Cd(1)–Cl(1)	174.789(10)
Cl(2)–Cd(1)–Cl(1)	85.24(3)	Cd(1)#2–Cl(1)–Cd(1)	92.97(2)
Cd(1)#2–Cl(2)–Cd(1)	94.00(2)		
2			
Cd(1)–Cl(3)	2.4210(13)	Cd(1)–Cl(2)	2.4264(12)
Cd(1)–Cl(4)	2.4497(12)	Cd(1)–Cl(1)	2.5042(13)
Cl(3)–Cd(1)–Cl(2)	123.35(5)	Cl(3)–Cd(1)–Cl(4)	110.00(5)
Cl(2)–Cd(1)–Cl(4)	106.54(4)	Cl(3)–Cd(1)–Cl(1)	106.94(5)
Cl(2)–Cd(1)–Cl(1)	102.44(4)	Cl(4)–Cd(1)–Cl(1)	106.23(5)
3			
Cd(1)–Cl(4)	2.419(7)	Cd(1)–Cl(2)	2.439(6)
Cd(1)–Cl(3)	2.456(7)	Cd(1)–Cl(1)	2.483(5)
Cl(4)–Cd(1)–Cl(2)	118.6(3)	Cl(4)–Cd(1)–Cl(3)	109.6(3)
Cl(2)–Cd(1)–Cl(3)	110.8(2)	Cl(4)–Cd(1)–Cl(1)	109.6(2)
Cl(2)–Cd(1)–Cl(1)	101.40(18)	Cl(3)–Cd(1)–Cl(1)	105.9(2)
4			
Cd(1)–Cl(4)	2.35(4)	Cd(1)–Cl(3)	2.39(3)
Cd(1)–Cl(2)	2.40(3)	Cd(1)–Cl(1)	2.406(4)
Cd(1)–Cl(2′)	2.46(3)	Cd(1)–Cl(3′)	2.50(2)
Cd(1)–Cl(4′)	2.60(4)	Cd(2)–Cl(5′)	2.22(14)
Cd(2)–Cl(8)	2.415(10)	Cd(2)–Cl(6)	2.423(7)
Cd(2)–Cl(5)	2.43(2)	Cd(2)–Cl(7)	2.469(9)
Cd(2)–Cl(6′)	2.53(5)	Cd(2)–Cl(8′)	2.56(4)
Cd(2)–Cl(7′)	2.60(6)	Cl(4)–Cd(1)–Cl(3)	102.0(16)
Cl(4)–Cd(1)–Cl(2)	115.7(14)	Cl(3)–Cd(1)–Cl(2)	108.8(11)
Cl(4)–Cd(1)–Cl(1)	101.9(12)	Cl(3)–Cd(1)–Cl(1)	120.2(19)
Cl(2)–Cd(1)–Cl(1)	108.5(9)	Cl(4)–Cd(1)–Cl(2′)	105(3)
Cl(3)–Cd(1)–Cl(2′)	117(2)	Cl(2)–Cd(1)–Cl(2′)	11(2)
Cl(1)–Cd(1)–Cl(2′)	108.2(7)	Cl(4)–Cd(1)–Cl(3′)	115.9(12)
Cl(3)–Cd(1)–Cl(3′)	16.1(9)	Cl(2)–Cd(1)–Cl(3′)	106.9(9)
Cl(1)–Cd(1)–Cl(3′)	107.4(14)	Cl(2′)–Cd(1)–Cl(3′)	117(2)
Cl(4)–Cd(1)–Cl(4′)	7.4(11)	Cl(3)–Cd(1)–Cl(4′)	96.7(16)
Cl(2)–Cd(1)–Cl(4′)	113.4(12)	Cl(1)–Cd(1)–Cl(4′)	109.1(10)
Cl(2′)–Cd(1)–Cl(4′)	104(2)	Cl(8)–Cd(2)–Cl(6)	109.6(7)
Cl(8)–Cd(2)–Cl(5)	117.4(10)	Cl(6)–Cd(2)–Cl(5)	108.1(6)
Cl(8)–Cd(2)–Cl(7)	107.7(4)	Cl(6)–Cd(2)–Cl(7)	109.9(4)
Cl(5)–Cd(2)–Cl(7)	103.9(6)		
5			
Cd(1)–Cl(3)	2.427(2)	Cd(1)–Cl(2)	2.427(2)
Cd(1)–Cl(1)	2.472(2)	Cd(1)–Cl(4)	2.476(2)
Cl(3)–Cd(1)–Cl(2)	115.26(9)	Cl(3)–Cd(1)–Cl(1)	105.39(9)
Cl(2)–Cd(1)–Cl(1)	110.01(8)	Cl(3)–Cd(1)–Cl(4)	109.23(9)
Cl(2)–Cd(1)–Cl(4)	107.41(8)	Cl(1)–Cd(1)–Cl(4)	109.45(8)
6			
Cd(1)–Cl(2)	2.4733(10)	Cd(1)–Cl(4)	2.4768(9)
Cd(1)–Cl(1)	2.5429(9)	Cd(1)–Cl(3)	2.6445(9)
Cd(1)–Cl(1)#1	2.7355(9)	Cl(1)–Cd(1)#1	2.7355(9)
Cl(2)–Cd(1)–Cl(4)	123.39(3)	Cl(2)–Cd(1)–Cl(1)	110.80(3)
Cl(4)–Cd(1)–Cl(1)	125.72(3)	Cl(2)–Cd(1)–Cl(3)	93.66(3)
Cl(4)–Cd(1)–Cl(3)	90.62(3)	Cl(1)–Cd(1)–Cl(3)	88.85(3)
Cl(2)–Cd(1)–Cl(1)#1	95.46(3)	Cl(4)–Cd(1)–Cl(1)#1	90.19(3)
Cl(1)–Cd(1)–Cl(1)#1	81.38(3)	Cl(3)–Cd(1)–Cl(1)#1	168.50(3)
Cd(1)–Cl(1)–Cd(1)#1	98.62(3)		

Symmetry transformations used to generate equivalent atoms for **1**: #1 $-x+3/2$, $y-1/2$, $-z+3/2$; #2 $-x+3/2$, $y+1/2$, $-z+3/2$. Symmetry codes for **6**: #1 $-x+1$, $-y+2$, $-z+1$.

Table 4. Hydrogen-bond geometries for **1–6**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (°)
1				
N(2)–H(2)···Cl(3)#4	0.86	2.35	3.151(3)	154.9
O(1)–H(1C)···Cl(3)#2	0.85	2.36	3.208(3)	178.2
O(1)–H(1D)···Cl(3)#5	0.85	2.38	3.232(2)	178.0
2				
N(4)–H(4)···Cl(1)#1	0.86	2.41	3.149(4)	144.1
N(2)–H(2)···Cl(1)#2	0.86	2.29	3.083(4)	152.5
3				
N(4)–H(4)···Cl(1)#3	0.86	2.49	3.187(18)	139.1
N(2)–H(2)···Cl(1)#4	0.86	2.77	3.360(17)	126.9
N(2)–H(2)···Cl(2)#4	0.86	2.55	3.268(16)	141.6
4				
O(7)–H(7D)···Cl(2)#1	0.85	2.48	3.30(5)	163.6
O(7)–H(7D)···Cl(2′)#1	0.85	2.09	2.93(9)	170.4
O(7)–H(7C)···O(3)#2	0.85	1.78	2.61(4)	165.2
O(6)–H(6E)···Cl(4)#3	0.85	2.25	3.08(5)	167.7
O(6)–H(6E)···Cl(4′)#3	0.85	2.07	2.91(4)	176.6
O(6)–H(6D)···Cl(2′)#4	0.85	2.31	3.15(7)	166.9
O(6)–H(6D)···Cl(2)#4	0.85	2.01	2.86(5)	175.2
O(5)–H(5D)···Cl(7)	0.85	2.18	2.97(3)	156.0
O(5)–H(5C)···Cl(6)#5	0.85	2.05	2.90(3)	174.6
O(4)–H(4E)···O(1)#6	0.85	2.01	2.84(4)	166.4
O(4)–H(4D)···Cl(4′)#3	0.85	2.32	3.15(5)	163.3
O(3)–H(3D)···O(5)#2	0.85	1.76	2.58(3)	160.8
O(3)–H(3C)···O(2)#7	0.85	2.01	2.76(3)	145.3
O(2)–H(2D)···O(7)#8	0.85	1.84	2.51(5)	134.5
O(2)–H(2C)···O(6)	0.85	1.77	2.58(4)	160.4
O(1)–H(1D)···Cl(8)#2	0.85	2.75	3.53(3)	153.0
O(1)–H(1C)···Cl(7)#2	0.85	2.82	3.60(3)	154.3
O(1)–H(1C)···Cl(7′)#2	0.85	2.04	2.79(11)	147.0
N(8)–H(8)···O(4)	0.86	1.91	2.73(3)	159.3
N(6)–H(6)···O(2)	0.86	1.82	2.68(3)	171.0
N(4)–H(4)···O(3)	0.86	1.79	2.650(19)	174.5
N(2)–H(2)···O(1)	0.86	1.92	2.77(2)	170.4
5				
N(2)–H(2)···Cl(1)#1	0.86	2.43	3.164(7)	144.0
6				
O(1)–H(1D)···Cl(3)#2	0.85	2.56	3.343(3)	153.9
O(1)–H(1C)···Cl(2)#2	0.85	2.53	3.315(3)	153.7
N(6)–H(6)···O(1)#3	0.86	1.83	2.683(4)	173.9
N(4)–H(4)···Cl(3)#4	0.86	2.35	3.157(3)	157.1

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

with our previously reported results [23], but longer than the corresponding distance in $[Cd(A)(H_2O)_2]_n$ [A = adipate dianion] [24]. Compound **1** contains $CdCl_2$ dihalide-bridged chains extending along the *b*-axis, similar to $[CdBr_2(Him)_2]_n$ (Him = imidazole) containing $CdBr_2$ dihalide-bridged chains [25]. The Cd···Cd separation is 3.832 Å within the chains and 7.860 Å between adjacent chains.

Chains along the *b*-axis were further connected through O–H···Cl hydrogen bonds between coordinated water and terminal chlorides to form a 2-D ionic grid structure when viewed from the *a*-axis. In the ionic grids the chains were perpendicular to

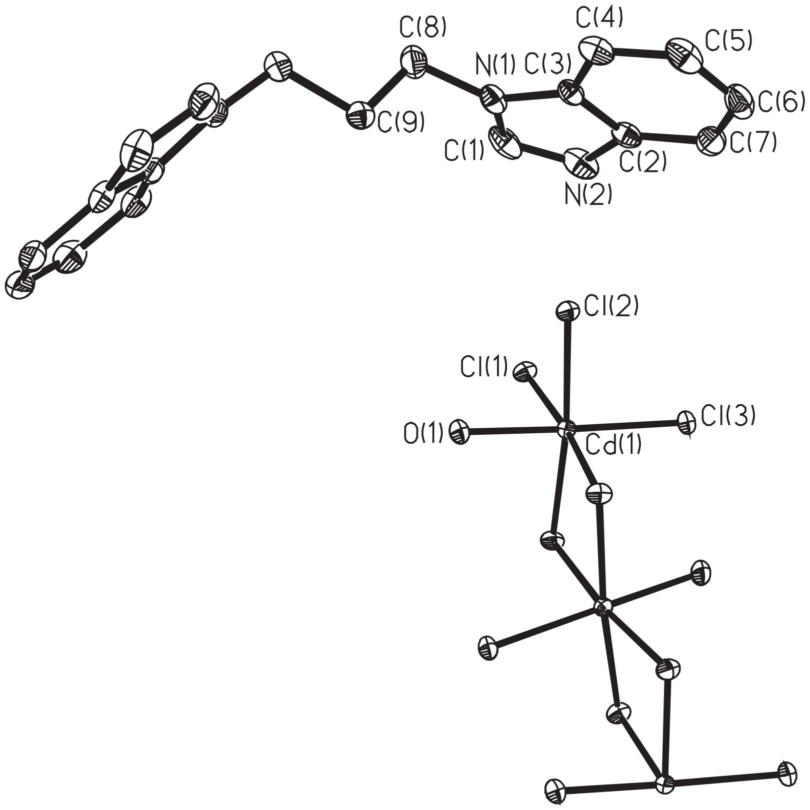


Figure 1. Molecular structure of **1** showing the atomic numbering scheme (30% ellipsoid probability).

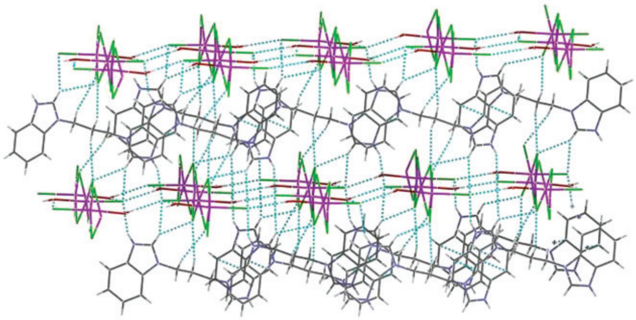


Figure 2. Packing diagram of **1** showing the 3-D ABAB network structure viewed down the *b*-axis.

the grids. The cations also formed a 2-D grid structure through π–π interactions between the parallel benzene rings, in which the separation between the aryl rings is 3.351 Å. Both benzimidazolium groups participate in N–H···Cl hydrogen bond interaction with $(CdCl_3 \cdot H_2O)_2$ anions, in which the N···Cl separation is 3.151(3) Å. The cationic grids and the ionic grids stacked alternatively and were connected through N–H···Cl and C–H···Cl hydrogen bonds (with C–Cl distance of 3.468 and 3.508 Å, respectively) to form a 3-D ABAB network structure, shown in figure 2.

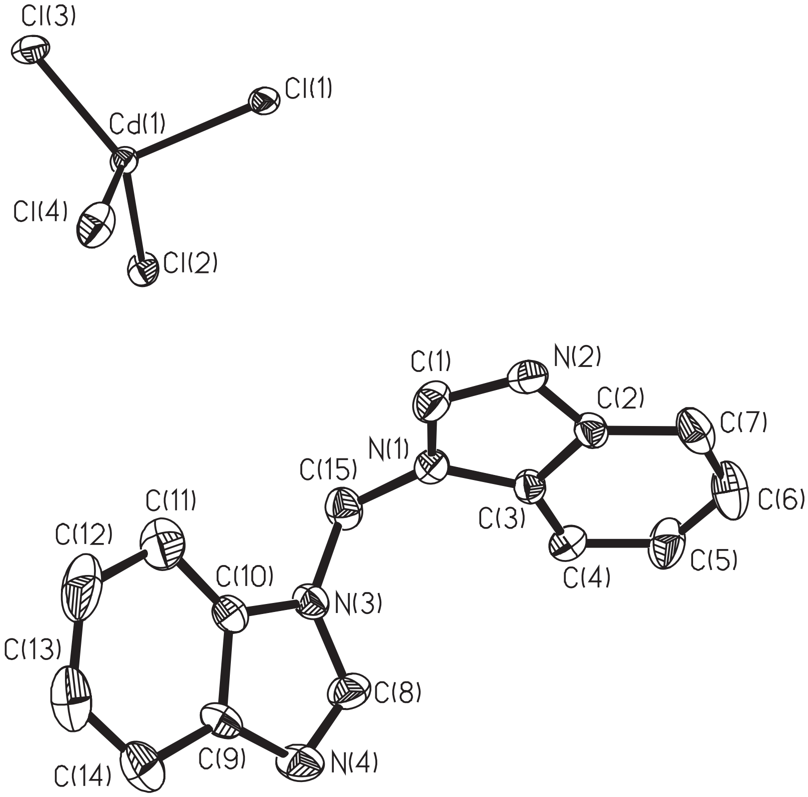


Figure 3. Molecular structure of **2** showing the atomic numbering scheme (30% thermal ellipsoid probability).

3.2.2. Crystal structure of [(H_2L2)($CdCl_4$)] (2). Complex **2** was prepared by reaction of 1,1′-bis(benzimidazolyl)methane (L2) with one equivalent of cadmium(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. Figure 3 shows the molecular structure of **2**, which crystallizes in the orthorhombic space group *Pbca* with unit cell content of eight formula units; the asymmetric unit consists of one dibenzimidazolium cation and one $CdCl_4^{2-}$ anion.

The full structure is generated by inversion center at Cd and C(15). The Cd–Cl bonds were in the range of 2.4210(13)–2.5042(13) Å. The Cl–Cd–Cl angles between two neighboring chlorides deviate from 109° [Cl(3)–Cd(1)–Cl(2) 123.35(5)°; Cl(3)–Cd(1)–Cl(4) 110.00(5)°; Cl(2)–Cd(1)–Cl(4) 106.54(4)°; Cl(3)–Cd(1)–Cl(1) 106.94(5)°; Cl(2)–Cd(1)–Cl(1) 102.44(4)°; Cl(4)–Cd(1)–Cl(1) 106.23(5)°], indicating that Cd is in a distorted tetrahedral environment with 116.17° average of the two large Cl–Cd–Cl angles.

The dications and the anions connected alternatively through N–H···Cl hydrogen bonds to form 1-D zigzag chains (figure 4), in which the Cl^- acts as bifurcate hydrogen-bond acceptor for NH^+. In the chains there also exist C–H···Cl bonds between CH on benzene ring and the chloride with C–Cl distance of 3.731 Å. Adjacent chains were further connected through C–H···Cl hydrogen bonds (two kinds of C–H···Cl hydrogen

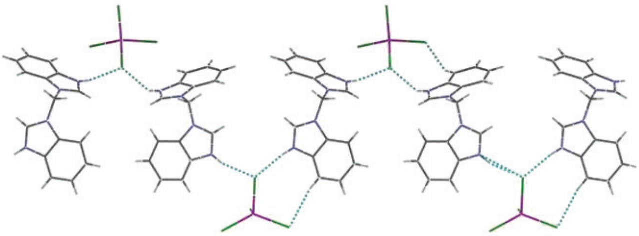


Figure 4. 1-D zigzag chain structure of [(H_2L2)($CdCl_4$)] viewed from the *b*-axis.

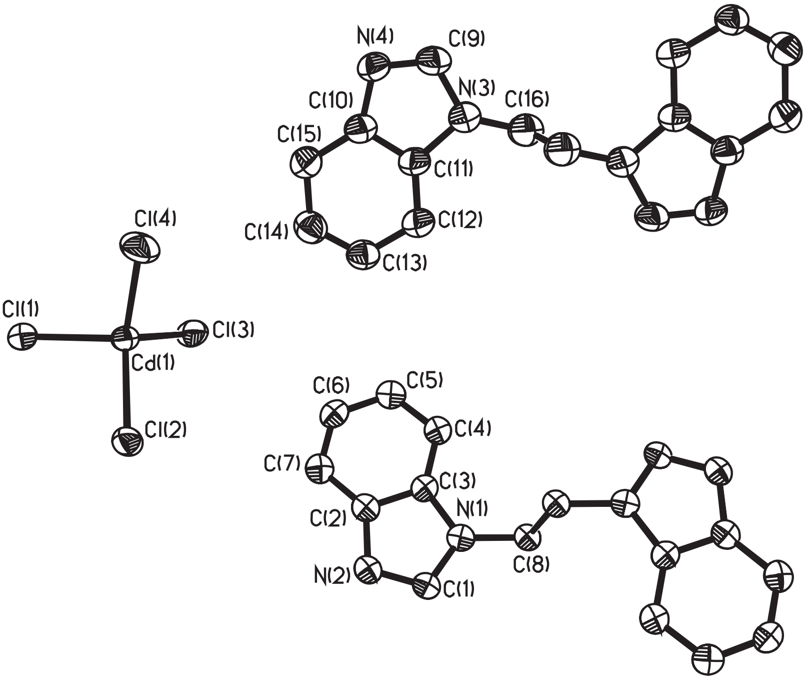


Figure 5. Molecular structure of **3** showing the atomic numbering scheme at 30% ellipsoid probability.

bonds exist between chloride and N–CH–N with C–Cl distance of 3.485 Å, and between chloride and CH on the benzene ring with C–Cl distance of 3.654 Å) to form a 3-D network structure.

3.2.3. Crystal structure of [(H_2L3)($CdCl_4$)] (3). Similarly to **2**, compound **3** was prepared by the reaction of L3 with one equivalent of cadmium(II) chloride dihydrate in acidic aqueous solution. Complex **3** crystallizes in the monoclinic space group *P2(1)/c* with unit cell content of four formula units. Figure 5 shows the molecular structure of the cation and anion. The asymmetric unit consists of one Cd(II) and one bis-benzimidazolium cation. The cations $(H_2L3)^{2+}$ are divided into two crystallographically independent groups. Within $(H_2L3)^{2+}$, the benzimidazole rings are almost planar (with mean deviation from the plane of 0.0098 Å) as expected. The cadmium is surrounded by

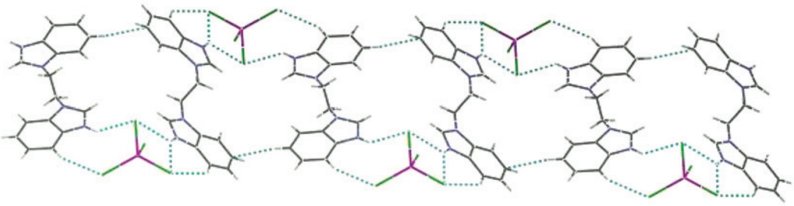


Figure 6. 1-D grid structure of **3** formed through N–H···Cl, CH-π interactions viewed down the *c*-axis.

four chlorides to display a slightly distorted tetrahedron which has a much smaller mean *trans* angle than the highly distorted anion of CuX_4^{2-} [26]. The Cd–Cl bond distances are in a narrow range of 2.419(7)–2.483(5) Å, which fit well with four-coordinate Cd. The dihedral angle between two benzimidazole planes from the same $(H_2L3)^{2+}$ is 0°, showing that the two benzimidazole planes are parallel, while the dihedral angle between two benzimidazole planes from two distinct $(H_2L3)^{2+}$ is 38.2°. Two cations and one anion form a 19-membered ring through N–H···Cl and CH-π interactions between two benzene rings. As acceptor, Cl(1) forms hydrogen bonds with NH^+ in bifurcate mode of which the N–Cl distances range from 3.187(18) to 3.360(17) Å. The N–Cl distances are in the range of reported results, but the N–H···Cl angles are much smaller than the literature results [26].

Adjacent 19-membered rings were connected by N–H···Cl hydrogen bonds, C–H···Cl hydrogen bonds (C–Cl distance is 3.543 Å), and CH-π interaction to form 1-D grids as shown in figure 6. The Cd–Cd separation in the same edge of the grid is 16.449 Å, while the Cd–Cd distances between two parallel edges of the grid are 16.208 and 15.769 Å. The grids stack along the *b*-axis through C–H···Cl interactions between adjacent grids to form a 3-D lamellar layer network. However, the stacking does not result in the formation of channels along the *b*-axis because the anions of the second grids are located in the center of the 19-membered rings of the first grids. The anions interact with the grids through hydrogen bonds of C–H···Cl formed between Cl^- and CH of benzene and 2-CH of the imidazole ring, of which the distances between C and Cl are 3.676 and 3.581 Å, respectively.

3.2.4. Crystal structure of $[(H_2L4)_4(CdCl_4)_4]\cdot 13H_2O$ (4). Complex **4** crystallizes in the monoclinic space group *P2(1)*/c with two formula units in the unit cell. The crystal structure of the title compound, as shown in figure 7, consists of two crystallographically independent anionic units of $CdCl_4^{2-}$ and two crystallographically independent cationic units whose formula is $(H_2L4)^{2+}$, both having an occupation factor of 1. The two L4 cations adopt a *cis* configuration with the planes of the two benzimidazole rings in the same ligand inclined by 30.9° and 30.3°, respectively. Dihedral angles between two benzimidazole planes from two distinct $(H_2L4)^{2+}$ are 2.6°, 2.9°, 27.3°, and 32.7°, respectively. In addition to two $CdCl_4^{2-}$ and two dibenzimidazolium cations, there are 13 free water molecules in the crystal lattice. In the anionic units Cd adopts distorted tetrahedral coordination. Similar to other complexes discussed above, all four coordination sites are provided by chlorides. Cl2 to Cl8 are all disordered over two positions. The Cd–Cl bond lengths ranged from 2.35(4) to 2.469(9) Å, in the range of reported tetrahedrally coordinated $CdCl_4^{2-}$ anions. In the whole molecule, N–H···Cl

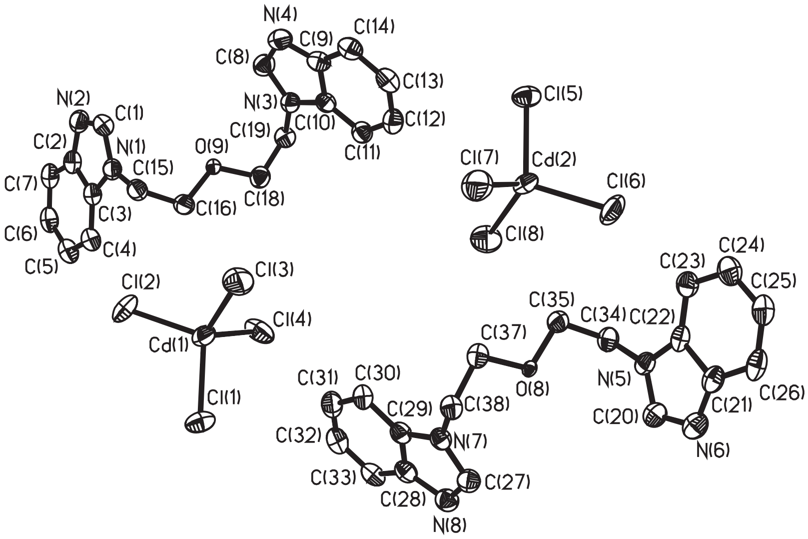


Figure 7. Molecular structure of **4** showing the atomic numbering scheme (30% ellipsoid probability).

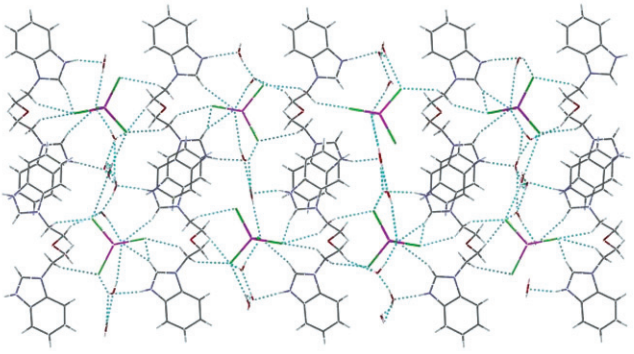


Figure 8. Perspective view of the 3-D ABAB layer structure viewed down the *a*-axis.

hydrogen bonds do not exist. The anions are connected by O–H···Cl hydrogen bonds to form a 1-D chain structure along the *a*-axis, adjacent chains were further connected by water along the *c*-axis to form a 2-D grid structure. Between adjacent chains, there exist water dimers, trimers, tetramers, and octamers, which are all hydrogen bonded to chlorides. The dications were bonded to the grids through N–H···O and CH···Cl hydrogen bonds, the whole molecule repeats this stack to form a 3-D ABAB layer structure, as shown in figure 8.

Obviously, the extensive hydrogen bonds between benzimidazolium cations, waters, and the anions played an important role in forming and stabilizing the 3-D framework structure. The anions interact with the water molecules through hydrogen bonds, in which the four shortest contacts are 3.08(5), 2.86(5), 2.97(3), and 2.90(3) Å for O6···Cl4#3, O2···Cl2#4, O5···Cl7, and O5···Cl6#5, respectively (symmetry codes: #3 $-x+1$, $-y+1$, $-z+1$; #4 $-x$, $-y+1$, $-z+1$; #5 $x-1$, y, z.).

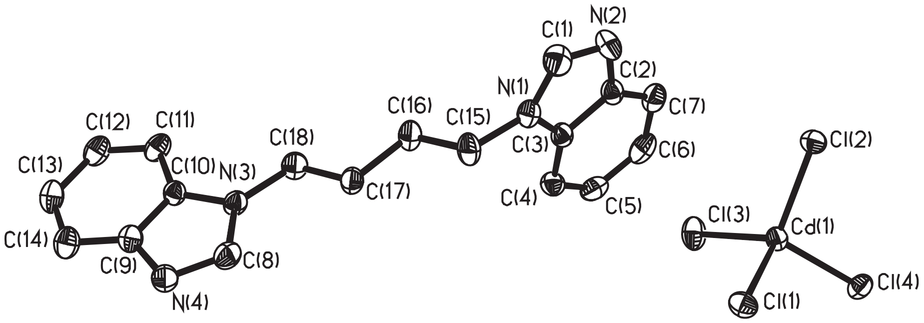


Figure 9. Molecular structure of **5** showing the atomic numbering scheme at 30% ellipsoid probability.

3.2.5. Crystal structure of [(H_2L5)$CdCl_4$] (5). Although complex **5** was prepared analogously to **4** by the reaction of 1-(4-(1H-benzimidazol-1-yl)butyl)-1H-benzimidazole (L5), with one equivalent of cadmium(II) chloride dihydrate in water in the presence of conc. hydrochloric acid, only [(H_2L5)$CdCl_4$] was obtained in high yield. X-ray structure determination revealed that the asymmetric unit contains one $CdCl_4^{2-}$ and one imidazolium. The structure is depicted in figure 9. The cadmium is surrounded by four chlorides in distorted tetrahedral geometry with a mean *trans* angle of 112.35°. The Cd–Cl bond distances fall into the narrow range of 2.427(2)–2.476(2) Å, which are normal and consistent with tetrahedral cadmium compounds [16]. Two chlorides of $CdCl_4^{2-}$ form two N–H···Cl hydrogen bonds with two adjacent cations. The two imidazole rings in the same cation were almost perpendicular (the dihedral angle between the two imidazole rings is 91.1°) with each other, different from the reported coordination compound of $\{[Zn(FcCOO)_2(L5)] \cdot 2H_2O\}_n$, in which the dihedral angle between the imidazole rings is 0.1° [27]. L5 is twisted with torsion angles of −172.6° and 175.52° for C17–C16–C15–N1 and N3–C18–C17–C16, respectively, also different from reported results (±58.70°) [28].

As expected, the benzimidazole rings are planar (the mean deviation from plane is 0.0063 Å) within $(H_2L5)^{2+}$. Two cations and two anions form a 24-membered ring through intermolecular N–H···Cl and C–H···Cl hydrogen bonds, with two benzimidazole rings of the same cation almost perpendicular to each other also, while the benzimidazole rings at diagonal positions in the 24-membered rings adopt antiparallel position. In the 24-membered rings the Cd–Cd distance is 10.05 Å, while the Cd–Cd separation between two adjacent 24-membered rings is 9.737 Å.

An alternative reading of this structure is possible when we emphasize the relative arrangement of the cations and the anions, i.e., the cations and the anions arrange alternatively along the *b*-axis through N–H···Cl and C–H···Cl (between 4-CH and chloride) hydrogen bonds to form a 1-D chain structure. Two adjacent chains are connected through C–H···Cl hydrogen bonds between N–CH–N and $CdCl_4^{2-}$ to form a 1-D grid structure as shown in figure 10. The grids were further connected through CH···Cl hydrogen bonds to form a 3-D lamellar network.

3.2.6. Crystal structure of [(H_2L6)$(Cd_2Cl_8)_{0.5}H_2O$] (6). Compound **6** was also prepared by the reaction of 3,6-bis(imidazol-1-yl)pyridazine (L6) with cadmium(II) chloride dihydrate in water in the presence of conc. hydrochloric acid. The compound

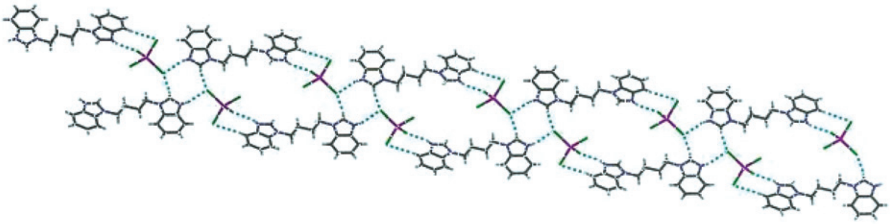


Figure 10. 1-D grid structure of **5** viewed along the *b*-axis.

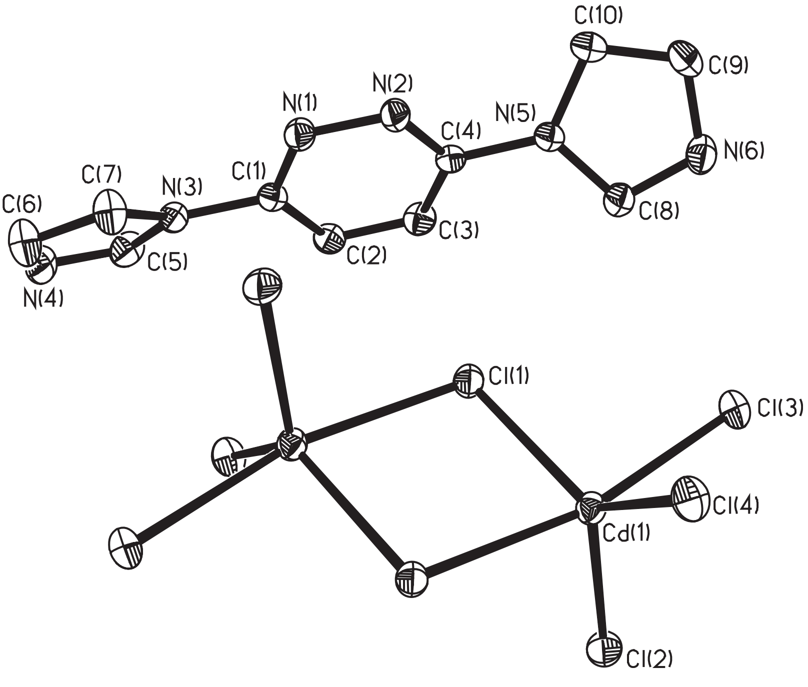


Figure 11. Molecular structure of **6** showing the atomic numbering scheme (thermal ellipsoids at 30% probability).

crystallizes in a triclinic space group $P\bar{1}$ with unit content of two formula units. The molecular structure is given in figure 11. Two nitrogens of imidazole, but not pyridazine, were protonated to yield the dication which conforms with the literature results [29]. In **6**, the cadmium is in a distorted tetragonal pyramidal geometry by five chlorides. The imidazole and pyridazine rings are both planar with largest deviation from plane of 0.0105 Å. In the same ligand the dihedral angle between the two imidazole rings is 70.8° and the angle between the pyridazine and the imidazole rings are 45.9° and 24.8°, different from literature values [29]. All bond lengths are in the normal range, Cd–Cl(1) (μ_2 coordination mode) is 2.5429(9) Å. The non-bridged Cd–Cl(terminal) bonds ranged from 2.4733(10) to 2.6445(9) Å with Cd–Cl(2) and Cd–Cl(4) bonds similar but shorter than Cd–Cl(3); Cl(3) formed more hydrogen bonds than Cl(2) and Cl(4).

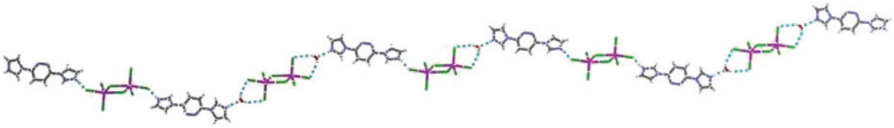


Figure 12. 1-D chain structure of **6** formed through classical hydrogen bonds between cations and anions.

The anions are dinuclear with Cd–Cd distance of 4.004 Å. The dinuclear cluster formed a parallelogram structure with inner angles of 98.62° and 81.38°, and with lengths of edges of 2.543 and 2.735 Å, respectively. The cations and anions connect alternatively through N–H···Cl, N–H···O, and O–H···Cl hydrogen bonds to form a 1-D chain structure (figure 12). The shortest hydrogen bond was N(6)–H(6)···O(1)#3 and the N(6)···O(1)#3 distance is 2.683(4) Å. There existed Cl-π and C–H···Cl interactions between adjacent chains, combining to form the 3-D network.

3.3. *Thermal properties*

For **1**, coordinated water was lost at 102.3–109.9°C. TGA studies showed that **2** is stable below 300°C with decomposition beginning at 344°C and a sharp weight loss at 344–384°C. For **3**, elimination of H_2L3^{2+} occurs at 367–416°C. For **4**, the 13 free waters were released from 72°C to 97.5°C and decomposition of $(H_2L4)^{2+}$ begins at 357°C and ends at 410°C. Complex **5** begins decomposition at 324°C, with one sharp weight loss at 324–364°C due to loss of $(H_2L5)^{2+}$. For **6**, water was removed below 90°C and loss of $(H_2L6)^{2+}$ occurs at 268–326°C.

4. Conclusions

In this article, we have successfully synthesized six new imidazolium chlorocadmate compounds by the solution reaction of $CdCl_2$ with bifunctional imidazole derivatives in strong acidic conditions. These compounds all display 3-D structures with N–H···Cl, N–H···O, O–H···Cl, and C–H···Cl interactions. Based on the observation that cadmium chloride complexes are effective hydrogen-bond acceptors, we have shown that supramolecular synthons such as chlorocadmates may be exploited to prepare hydrogen-bonded polymers of $[H_2L]^{2+}$ salts of perchlorocadmates. The cases reported here with anions without hydrogen-bond donor sites and cations with strong hydrogen-bond donors is a successful strategy.

Cadmium in the six compounds display tetrahedral, octahedral, and pentahedral coordination modes. The salts of **2**–**5** are isostructural, containing planar $(H_2L)^{2+}$ dications linked to slightly distorted tetrahedral $CdCl_4^{2-}$ (the mean *trans* angles range from 112.6 to 118.5°) through N–H···Cl or O–H···Cl hydrogen bonds. Cd–Cl bond distances obey the rules, dCd(tetra)–Cl: 2.419(7)–2.5042(13) Å < dCd(pent)–Cl(μ_2): 2.5429(9) Å < dCd(octa)–Cl(terminal): 2.6160(8) Å < dCd(octa)–Cl(μ_2): 2.6303(8)–2.6582(8) Å.

The structural motif of these inorganic–organic hybrid complexes depends on the size and symmetry of the organic cations. L1 and L4 with spacer length of odd numbers of atoms give **1** and **4** with 2-D grid structure, and each displays 3-D cation/anion/cation/anion layer structure. Compounds **2** and **6** consist of semi-flexible and rigid ligands, respectively, both forming a 1-D chain structure with the cations and anions arranged alternatively in the chain. The spacer lengths of L3 and L5 are even-numbered with two and four atoms, respectively, and the anions and cations of **3** and **5** form 19- and 24-membered rings, respectively, showing a 1-D grid structure with the grids further stacked to form 3-D lamellar layer networks. The anions functioned as electronic balancing ions and also play important roles in construction of the network. Because imidazole derivatives are easily prepared and the structures can be easily tuned, inorganic–organic hybrid cadmium compounds with novel structures and functionalities 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 Center, CCDC Nos. 746460 for **1**, 746461 for **2**, 746463 for **3**, 746464 for **4**, 746468 for **5**, 746462 for **6**. Copies of this information may be obtained free of charge *via* Fax: +44(1223)336-033, Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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