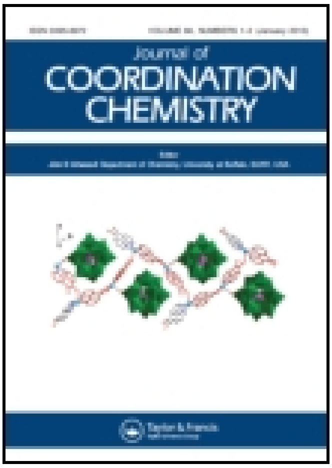
This article was downloaded by: [Institute Of Atmospheric Physics]
On: 09 December 2014, At: 15:27
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Click for updates

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Syntheses and structural characterization of six ionic salts based on bis(benzimidazole)/bis(imidazole) and perchlorometallates of Zn and Cu

Jianming Pan[a], Qing Wei[a], Jingxi Ju[a], Bin Liu[ab], Shouwen Jin[ab], Zhanghui Lin[b] & Daqi Wang[c]

[a] Zhejiang Province Key Laboratory of Noble Metal Catalytic Materials and Technology, Hangzhou, PR China

[b] Department of Biological and Environmental, Tianmu College ZheJiang A & F University, Zhuji, PR China

[c] Department of Chemistry, Liaocheng University, Liaocheng, PR China

Accepted author version posted online: 18 Sep 2014.Published online: 08 Oct 2014.

To cite this article: Jianming Pan, Qing Wei, Jingxi Ju, Bin Liu, Shouwen Jin, Zhanghui Lin & Daqi Wang (2014) Syntheses and structural characterization of six ionic salts based on bis(benzimidazole)/bis(imidazole) and perchlorometallates of Zn and Cu, Journal of Coordination Chemistry, 67:22, 3578-3597, DOI: 10.1080/00958972.2014.966701

To link to this article: http://dx.doi.org/10.1080/00958972.2014.966701

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

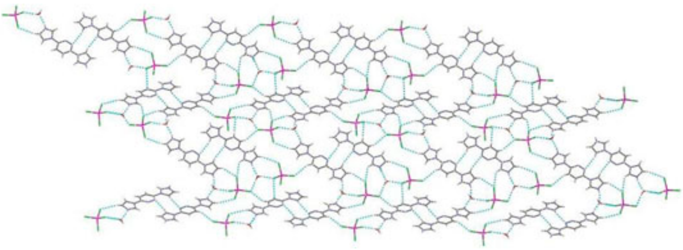
Journal of Coordination Chemistry, 2014
Vol. 67, No. 22, 3578–3597, http://dx.doi.org/10.1080/00958972.2014.966701

Syntheses and structural characterization of six ionic salts based on bis(benzimidazole)/bis(imidazole) and perchlorometallates of Zn and Cu

JIANMING PAN†, QING WEI†, JINGXI JU†, BIN LIU*†‡, SHOUWEN JIN*†‡,
ZHANGHUI LIN‡ and DAQI WANG§

†Zhejiang Province Key Laboratory of Noble Metal Catalytic Materials and Technology, Hangzhou, PR China
‡Department of Biological and Environmental, Tianmu College ZheJiang A & F University, Zhuji, PR China
§Department of Chemistry, Liaocheng University, Liaocheng, PR China

(*Received 10 December 2013; accepted 28 August 2014*)



Due to the weak interactions, the compound displays 3-D layer structure.

Six salts, ([$(H_2L1)(ZnCl_4)$] (**1**) (L1 = 1,1′-bis(benzimidazolyl)methane), [$(H_2L1)(CuCl_4)$]·H_2O (**2**), [$(H_2L2)(ZnCl_4)$] (**3**) (L2 = 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole), [($H_2L2)(CuCl_4)$] (**4**), [$(H_2L3)(CuCl_4)$]·H_2O (**5**) (L3 = 1- (4-(1H-benzimidazol-1-yl)butyl)-1H-benzimidazole), and [$(H_2L4)(ZnCl_4)$]·H_2O (**6**) (L4 = 3,6-bis(imidazol-1-yl)pyridazine)), derived from bis(benzimidazole)/bis(imidazole) and metal(II) chloride dihydrate (zinc(II) chloride and copper(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 planar. X-ray diffraction analysis revealed that all the complexes have 3-D layer network structures built from hydrogen bonds between the cations and chlorometallate anions. Water molecules also play an important role in structure extension in **2**, **5,** and **6**. The arrangements of the anions and cations in their solid state are dominated not only by size and symmetry of the cations, but also by the non-covalent interactions existing in the crystal structures.

Keywords: Zinc; Copper; Crystal structure; Bis(benzimidazole); Ionic salts

---

*Corresponding authors. Email: floatwood@163.com (B. Liu); jinsw@zafu.edu.cn (S. Jin)

1. Introduction

Ionic salts containing organic and inorganic components represent new directions in solid-state chemistry [1, 2]. Ionic salts from the organic cations and the inorganic anions are likely to 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]. Ionic salts may provide applications in various fields such as fuel cells [8], liquid crystal-material development [9], non-linear optics [10], and drug delivery [11].

Ionic salts based on layers of anionic transition metal(II) halogen frameworks and organic ammonium cations have attracted attention. For instance, 2-D systems with $(RNH_3)_2Cu(II)X_4$ or $(NH_3RNH_3)Cu(II)X_4$ (X = I, Br, Cl; R = alkyl, phenyl, etc.) have been extensively studied in low-dimensional magnetism [12]. Structural transitions in ionic salts containing long-chain alkylammonium cations were studied to better understand biological lipid bilayers [13]. Most ammonium cations incorporated in the ionic salts were either alkylammonium or single ring aromatic ammonium cations.

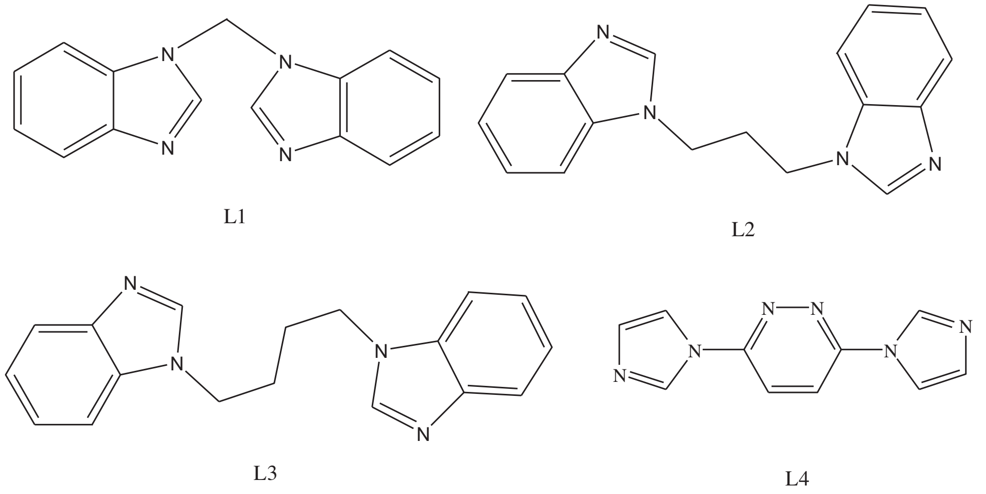
Metal halides such as SnX_2 (X = Cl, Br, and I) have been studied as semi-conducting components [14] in the field of semiconductors formed by ionic salts, which have demonstrated applications in display and storage technologies because of their stable exciton, excellent film processability, and superior carrier mobility [15]. Perchlorometallate compounds represent a class of materials with unusual structural archetypes [16], where the ligands are essentially chlorides and water molecules, 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. In these complexes, the frameworks of the organoammonium cations and their counter inorganic species are stabilized by hydrogen bonds and Coulombic attractions. The energetics of N–H···Cl–M (M = metal) hydrogen bonds and their possible role in supramolecular chemistry of ionic salts have been described [17].

Coordination compounds bearing imidazolyl groups have been widely explored [18]. However, ionic salts containing imidazolyl moieties have not been well studied [19]. L1–L4 are all Brønsted bases with more than two nitrogens that can be protonated. When protonated, the cations of L1–L4 are good donors in forming hydrogen bonds. In addition, the four Brønsted bases have aromatic units which may give aromatic stacking interactions, thus carrying out the reaction between the N-containing aromatic Brønsted bases and chlorometallates in acidic conditions and may display different non-bonding ability of these different functional groups. As an extension of our research of ionic salts based on imidazole derivatives [20], herein we report the synthesis and structure of six perchlorometallate complexes with bis(benzimidazole)/bis(imidazole) derivatives (scheme 1) as the functional organic ammonium cations.

2. Experimental

2.1. *Materials*

L1–L4 were prepared according to the procedures in the literature [21, 22]. The other chemicals and solvents were of reagent grade and used as obtained from J & K Chemical Ltd.



Scheme 1. The bis(benzimidazole)/bis(imidazole) used in this paper.

2.2. *Physical measurements and analyses*

Elemental analyses (CHN) 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 in a N_2 atmosphere between room temperature and 800 °C (heating rate 10 °C min^{-1}).

2.3. *Preparation of the compounds*

2.3.1. Preparation of [(H_2L1)($ZnCl_4$)], 1. Zinc(II) chloride (13.7 mg, 0.10 mM) dissolved in 1 mL of conc. hydrochloric acid and 2 mL of water was added to a methanol solution (2 mL) of 1,1′-bis(benzimidazolyl)methane (L1) (25.0 mg, 0.10 mM). 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: 37.0 mg, 80.9% (based on L1). Anal. Calcd for $C_{15}H_{14}Cl_4N_4Zn$ (457.47): C, 39.35; H, 3.06; N, 12.24%. Found: C, 39.27; H, 3.01; N, 12.17%. IR (KBr disk, cm^{-1}): 3452w, 3329w, 3141w, 3037w, 1761w, 1614m, 1559m, 1493m, 1444m, 1389w, 1345w, 1291w, 1257m, 1203w, 1158w, 1102w, 1059w, 999m, 948w, 893w, 849w, 791w, 756s, 691m, 648m, 619m.

2.3.2. Preparation of [(H_2L1)($CuCl_4$)]·H_2O, 2. Copper(II) chloride dihydrate (17.5 mg, 0.10 mM) dissolved in 1 mL of conc. hydrochloric acid and 3 mL of water was added to a methanol solution (2 mL) of 1,1′-bis(benzimidazolyl)methane (L1) (25.0 mg, 0.10 mM). After stirring for several minutes, the solution was filtered. The clear solution stood at room temperature for several days to give yellow block crystals, which were collected and washed with water and ethanol. Yield: 35.0 mg, 73.9% (based on L1). Anal. Calcd for $C_{15}H_{16}Cl_4CuN_4O$ (473.66): C, 38.00; H, 3.38; N, 11.82%. Found: C, 37.91; H, 3.31; N, 11.75%. IR (KBr disk, cm^{-1}): 3594w, 3445m, 3371m, 3270w, 3119w, 3058w, 1755w, 1620m, 1542m, 1488m, 1441m, 1386w, 1347w, 1315w, 1268m, 1235w, 1184w, 1140w, 1082w, 1033m, 966w, 885w, 827w, 777m, 691m, 644m, 611m.

2.3.3. Preparation of [(H_2L2)($ZnCl_4$)], 3. Zinc(II) chloride (13.7 mg, 0.10 mM) dissolved in 1 mL of conc. hydrochloric acid and 2 mL of water was added to a methanol solution (4 mL) of 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole (L2) (28.0 mg, 0.10 mM). 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: 39.0 mg, 80.3% (based on L2). Anal. Calcd for $C_{17}H_{18}Cl_4N_4Zn$ (485.52): C, 42.02; H, 3.71; N, 11.53%. Found: C, 41.96; H, 3.65; N, 11.48%. IR (KBr disk, cm^{-1}): 3450m, 3360m, 3279m, 3132m, 3044m, 1746m, 1609m, 1563m, 1506m, 1447m, 1385m, 1328m, 1267m, 1199m, 1140m, 1084m, 1041m, 979m, 923m, 874m, 827m, 760m, 690m, 656m, 608m.

2.3.4. Preparation of [(H_2L2)($CuCl_4$)], 4. Copper(II) chloride dihydrate (17.5 mg, 0.10 mM) dissolved in 1 mL of conc. hydrochloric acid and 3 mL of water was added to a methanol solution (4 mL) of 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole (L2) (28.0 mg, 0.10 mM). After stirring for several minutes, the solution was filtered. The clear solution stood at room temperature for several days to give yellow block crystals, which were collected and washed with water and ethanol. Yield: 37.0 mg, 76.5% (based on L2). Anal. Calcd for $C_{17}H_{18}Cl_4CuN_4$ (483.69): C, 42.18; H, 3.72; N, 11.58%. Found: C, 42.11; H, 3.66; N, 11.53%. IR (KBr disk, cm^{-1}): 3437w, 3333w, 3279w, 3120m, 3058m, 1750m, 1599m, 1542m, 1495m, 1436m, 1378m, 1266m, 1204m, 1165m, 1101m, 1042m, 997m, 934m, 880m, 824m, 756m, 695m, 665m, 625m.

2.3.5. Preparation of [(H_2L3)($CuCl_4$)]·H_2O, 5. Copper(II) chloride dihydrate (17.5 mg, 0.10 mM) dissolved in 1 mL of conc. hydrochloric acid and 3 mL of water was added to a methanol solution (6 mL) of 1-(4-(1H-benzimidazol-1-yl)butyl)-1H-benzimidazole (L3) (29.0 mg, 0.10 mM). After stirring for several minutes, the solution was filtered. The clear solution stood at room temperature for several days to give yellow block crystals, which were collected and washed with water and ethanol. Yield: 41.0 mg, 79.5% (based on L3). Anal. Calcd for $C_{18}H_{22}Cl_4CuN_4O$ (515.74): C, 41.88; H, 4.27; N, 10.86%. Found: C, 41.82; H, 4.25; N, 10.79%. IR (KBr disk, cm^{-1}): 3690w, 3449w, 3374m, 3149m, 3053m, 2943m, 2876m, 2363m, 1751m, 1624m, 1577m, 1511m, 1453m, 1398m, 1335m, 1287m, 1224m, 1162m, 1081m, 1022m, 964m, 899m, 846m, 776m, 712m, 653m, 603m.

2.3.6. Preparation of [(H_2L4)($ZnCl_4$)]·H_2O, 6. Zinc(II) chloride (13.7 mg, 0.10 mM) dissolved in 1 mL of conc. hydrochloric acid and 2 mL of water was added to L4 (21.0 mg, 0.10 mM) in 5 mL of conc. hydrochloric acid and 8 mL of water. 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: 34.0 mg, 77.4% (based on L4). Anal. Calcd for $C_{10}H_{12}Cl_4N_6OZn$ (439.43): C, 27.31; H, 2.73; N, 19.12%. Found: C, 27.26; H, 2.69; N, 19.08%. IR (KBr disk, cm^{-1}): 3641w, 3428m, 3362m, 3155m, 3066m, 2965m, 2658m, 1873m, 1692m, 1629m, 1567m, 1514m, 1453m, 1396m, 1334m, 1267m, 1205m, 1155m, 1087m, 1022m, 956m, 877m, 803m, 719m, 666m, 613m.

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 MoKα radiation ($\lambda = 0.71073$ Å) by using a ω-2θ scan mode. Data collection and reduction were performed using *SMART* and *SAINT* [23]. 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 [24]. The hydrogens 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 the conventional solution approach, thus all of the compounds were prepared by the solution method. The six compounds were prepared with the same ratio of the reactants (1 : 1). All of the compounds were isolated as colorless crystals in yields of 73.9–80.9%. The ability of metal chloride complexes to act as hydrogen bond acceptors has been noted in our database work [20] and previous examples (see for example Ref. [25]).

IR spectra show stretches at 3452–3329 cm^{-1}, assignable to NH groups of the cations. The bands for the lattice water molecules are at 3594–3690 cm^{-1}. The bands at 1610 and 1450 cm^{-1} can be assigned to C=C and C=N stretches of the imidazolyl, pyridazine or aromatic rings. The compositions of these compounds were determined by elemental analysis (CHN) and their structures were fully characterized by X-ray diffraction analysis. For the compounds with L1–L4, it is the N at the imidazole unit that has been protonated. The crystallographic data and refinement details are summarized in tables 1 and 2, and selected bond distances and angles are listed in table 3; some important hydrogen bonds are listed in table 4.

3.2. *Thermal properties*

TGA studies showed that **1** is stable below 300 °C with decomposition of $(H_2L1)^{2+}$ at 323.6–375.24 °C (Observ. 54.58%, Calcd 54.65%). The TGA curve showed that the water molecules in **2** are removed between 95.4 and 98.9 °C (Observ. 3.72%, Calcd 3.80%). There is a weight loss at 315.5–363.1 °C from decomposition of $(H_2L1)^{2+}$ (Observ. 52.69%, Calcd 52.78%). For **3**, the weight loss of 57.60% (Calcd 57.67%) corresponds to loss of $(H_2L2)^{2+}$ from 337.8 to 382.0 °C. For **4**, decomposition of $(H_2L2)^{2+}$ begins at 343.7 °C and ends at 387.2 °C (Observ. 57.82%, Calcd 57.89%). For **5**, the first weight loss of 3.44% was attributed to loss of one water at 88.3–95.4 °C (Calcd 3.39%); the second weight loss at 329.1–368.8 °C was due to loss of $(H_2L3)^{2+}$ (Observ. 56.93%, Calcd 57.00%). For **6**, the water was removed between 93.3 and 97.4 °C (Observ. 4.01%, Calcd 4.10%) and loss of $(H_2L4)^{2+}$ occurs at 326.8–392.5 °C.

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

	1	**2**	**3**
Formula	$C_{15}H_{14}Cl_4N_4Zn$	$C_{15}H_{16}Cl_4CuN_4O$	$C_{17}H_{18}Cl_4N_4Zn$
Fw	457.47	473.66	485.52
T (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*P2(1)/n*	*P-1*	*P2(1)/n*
a (Å)	9.5141(11)	7.8770(6)	10.8968(8)
b (Å)	14.0289(14)	9.7006(8)	10.3796(7)
c (Å)	13.7290(12)	13.5967(11)	17.9032(13)
α (°)	90	82.385(2)	90
β (°)	95.2830(10)	75.1680(10)	104.3080(10)
γ (°)	90	73.9600(10)	90
V (A^3)	1824.7(3)	963.09(13)	1962.1(2)
Z	4	2	4
D_{Calcd} Mg m^{-3}	1.665	1.633	1.644
Absorption coefficient, mm^{-1}	1.936	1.700	1.806
F (0 0 0)	920	478	984
Crystal size, mm^3	0.50 × 0.46 × 0.43	0.42 × 0.20 × 0.12	0.40 × 0.37 × 0.36
θ range, °	2.59–25.01	2.60–25.02	2.29–25.02
Limiting indices	$-11 \le h \le 9$ $-16 \le k \le 16$ $-15 \le l \le 16$	$-9 \le h \le 9$ $-10 \le k \le 11$ $-11 \le l \le 16$	$-12 \le h \le 12$ $-8 \le k \le 12$ $-14 \le l \le 21$
Reflections collected	8934	4846	8766
Reflections independent (R int)	3216 (0.0408)	3350 (0.0219)	3449 (0.0291)
Goodness-of-fit on F^2	1.031	1.022	1.025
Final R indices [$I > 2\sigma I$]	0.0318, 0.0750	0.0345, 0.0821	0.0326, 0.0799
R indices (all data)	0.0456, 0.0835	0.0497, 0.0922	0.0431, 0.0876
Largest diff. peak/hole (e A^{-3})	0.370/−0.564	0.606/−0.428	0.608/−0.491

3.3. *Structural descriptions*

3.3.1. Crystal structure of [(H_2L1)($ZnCl_4$)], 1. Complex **1** was prepared by reacting equimolar 1,1′-bis(benzimidazolyl)methane (L1) and zinc(II) chloride in water in the presence of hydrochloric acid. There were no water molecules involved in the lattice as determined by elemental analysis. Figure 1 shows the molecular structure of **1**, which crystallizes in the monoclinic space group *P2(1)/n* with unit cell content of four formula units; the asymmetric unit consists of one dibenzimidazolium dication and one $ZnCl_4^{2-}$. The exobidentate L1 is doubly protonated and the cation with the NH^+ groups on the benzimidazole rings in **1** resembles 4,4′-H_2bipy cations from the exobidentate 4,4′-bipy [26].

The cation adopted the *trans* conformation. The Zn–Cl bonds were 2.2442(9)–2.3186(8) Å. The Cl–Zn–Cl angles between two neighboring chlorides deviate somewhat from 109° [Cl(4)–Zn(1)–Cl(3), 119.93(4)°; Cl(4)–Zn(1)–Cl(2), 109.09(3)°; Cl(3)–Zn(1)–Cl(2), 107.81(3)°; Cl(4)–Zn(1)–Cl(1), 107.50(3)°; Cl(3)–Zn(1)–Cl(1), 101.23(3)°; Cl(2)–Zn(1)–Cl(1), 110.97(3)°], indicating that the Zn is in a distorted tetrahedral environment with 115.45(3)° average of the two large Cl–Zn–Cl angles. These values are in agreement with those previously reported [27]. The rms deviations of the rings with N1 and N2, and N3 and N4 are 0.0090(2) Å and 0.0133(3) Å, respectively; both rings intersect at an angle of 67.9° with each other.

At one NH of the dication there was bonded an anion through the N–H···Cl (N(4)–H(4)···Cl(1)#1, 3.105(3) Å, 171(4)°, #1 $-x + 1$, $-y + 1$, $-z + 1$) hydrogen bond arising from one NH of the dication to form a heteroadduct. The heteroadducts were linked by the bifurcated

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

	4	**5**	**6**
Formula	$C_{17}H_{18}Cl_4CuN_4$	$C_{18}H_{22}Cl_4CuN_4O$	$C_{10}H_{12}Cl_4N_6OZn$
Fw	483.69	515.74	439.43
T (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P-1*	*P2(1)/c*	*P2(1)/n*
a (Å)	8.1056(5)	15.9007(15)	8.5998(7)
b (Å)	9.2330(7)	17.2757(19)	17.6007(17)
c (Å)	14.6138(14)	7.9542(8)	11.0997(11)
α (°)	99.7460(10)	90	90
β (°)	91.2810(10)	89.9840(10)	94.4480(10)
γ (°)	111.764(2)	90	90
V (A^3)	996.73(14)	2185.0(4)	1675.0(3)
Z	2	4	4
D_{Calcd} Mg m^{-3}	1.612	1.568	1.743
Absorption coefficient, mm^{-1}	1.641	1.505	2.112
F (0 0 0)	490	1052	880
Crystal size, mm^3	0.40 × 0.36 × 0.23	0.40 × 0.36 × 0.23	0.44 × 0.29 × 0.10
θ range (°)	2.42–25.02	2.68–25.02	2.64–25.02
Limiting indices	$-9 \leq h \leq 9$ $-9 \leq k \leq 10$ $-14 \leq l \leq 17$	$-18 \leq h \leq 11$ $-20 \leq k \leq 19$ $-9 \leq l \leq 9$	$-9 \leq h \leq 10$ $-20 \leq k \leq 15$ $-13 \leq l \leq 13$
Reflections collected	5006	10,780	8160
Reflections independent (*R* int)	3464 (0.0220)	3838 (0.0452)	2943 (0.0727)
Goodness-of-fit on F^2	1.061	1.079	1.027
Final *R* indices [$I > 2\sigma I$]	0.0344, 0.0776	0.0395, 0.0830	0.0391, 0.0905
R indices (all data)	0.0498, 0.0870	0.0818, 0.1076	0.0620, 0.1062
Largest diff. peak/hole (e A^{-3})	0.324/−0.416	0.405/−0.352	0.448/−0.743

N–H···Cl hydrogen bonds arising from the other NH of the dication and Cl^- with N–Cl distances of 3.334(2)–3.570(3) Å to form a 1-D chain. The chains were joined by the CH–Cl associations between the phenyl CH of the cation and Cl^- with C–Cl distances of 3.537(3)–3.742(3) Å to form a 2-D sheet extending at the direction that made a dihedral angle of ca. 60° with the *bc* plane (figure 2). Two neighboring sheets were held together by CH–Cl associations between the N–CH–N of the cation and Cl(2) anion with C–Cl distances of 3.417(2)–3.498(2) Å, CH–Cl association between the same Cl that has CH–Cl associations with the N–CH–N of the cation and the phenyl CH of the cation with C–Cl distance of 3.755(4) Å, CH_2–Cl association between the CH_2 spacer and the same Cl with C–Cl distance of 3.688(3) Å, and π–π stacking interactions between the benzimidazole rings with Cg–Cg distance of 3.354(2) Å to form a 2-D double sheet structure. Cl(2) anion functioned as a quadruple acceptor in forming the non-covalent associations. To the best of our knowledge, this is the first case, one Cl^- was involved in forming quadruple non-classical hydrogen bonds. Herein the two sheets in the double sheet were joined by the same face of the two sheets, and both sheets were slipped some distances from each other along its extending direction. The double sheets were further stacked along the direction that was perpendicular with its extending direction by the intersheet $Cl^-\pi$ association arising from the imidazole moiety with Cl–Cg separation of 3.433(1) Å to form a 3-D layer network structure.

Table 3. Selected bond lengths [Å] and angles [°] for **1–6**.

1			
Zn(1)–Cl(4)	2.2442(9)	Zn(1)–Cl(3)	2.2594(8)
Zn(1)–Cl(2)	2.2792(8)	Zn(1)–Cl(1)	2.3186(8)
Cl(4)–Zn(1)–Cl(3)	119.93(4)	Cl(4)–Zn(1)–Cl(2)	109.09(3)
Cl(3)–Zn(1)–Cl(2)	107.81(3)	Cl(4)–Zn(1)–Cl(1)	107.50(3)
Cl(3)–Zn(1)–Cl(1)	101.23(3)	Cl(2)–Zn(1)–Cl(1)	110.97(3)
2			
Cu(1)–Cl(4)	2.2348(9)	Cu(1)–Cl(2)	2.2439(9)
Cu(1)–Cl(3)	2.2589(9)	Cu(1)–Cl(1)	2.2638(9)
Cl(4)–Cu(1)–Cl(2)	97.89(4)	Cl(4)–Cu(1)–Cl(3)	101.18(4)
Cl(2)–Cu(1)–Cl(3)	131.02(4)	Cl(4)–Cu(1)–Cl(1)	135.61(4)
Cl(2)–Cu(1)–Cl(1)	99.41(3)	Cl(3)–Cu(1)–Cl(1)	97.55(4)
3			
Zn(1)–Cl(1)	2.2481(8)	Zn(1)–Cl(2)	2.2733(8)
Zn(1)–Cl(3)	2.2767(9)	Zn(1)–Cl(4)	2.3128(8)
Cl(1)–Zn(1)–Cl(2)	112.78(3)	Cl(1)–Zn(1)–Cl(3)	112.05(3)
Cl(2)–Zn(1)–Cl(3)	108.51(3)	Cl(1)–Zn(1)–Cl(4)	108.15(3)
Cl(2)–Zn(1)–Cl(4)	110.64(3)	Cl(3)–Zn(1)–Cl(4)	104.40(4)
4			
Cu(1)–Cl(4)	2.2142(10)	Cu(1)–Cl(3)	2.2397(9)
Cu(1)–Cl(2)	2.2748(9)	Cu(1)–Cl(1)	2.2753(10)
Cl(4)–Cu(1)–Cl(3)	138.06(4)	Cl(4)–Cu(1)–Cl(2)	98.38(4)
Cl(3)–Cu(1)–Cl(2)	97.70(4)	Cl(4)–Cu(1)–Cl(1)	98.99(4)
Cl(3)–Cu(1)–Cl(1)	98.80(4)	Cl(2)–Cu(1)–Cl(1)	131.39(4)
5			
Cu(1)–Cl(3)	2.2067(13)	Cu(1)–Cl(4)	2.2434(12)
Cu(1)–Cl(1)	2.2504(10)	Cu(1)–Cl(2)	2.2757(12)
Cl(3)–Cu(1)–Cl(4)	99.15(5)	Cl(3)–Cu(1)–Cl(1)	95.69(4)
Cl(4)–Cu(1)–Cl(1)	141.88(5)	Cl(3)–Cu(1)–Cl(2)	139.68(6)
Cl(4)–Cu(1)–Cl(2)	96.75(5)	Cl(1)–Cu(1)–Cl(2)	94.14(4)
6			
Zn(1)–Cl(3)	2.2437(11)	Zn(1)–Cl(4)	2.2491(11)
Zn(1)–Cl(2)	2.2706(11)	Zn(1)–Cl(1)	2.2757(10)
Cl(3)–Zn(1)–Cl(4)	111.75(4)	Cl(3)–Zn(1)–Cl(2)	109.54(5)
Cl(4)–Zn(1)–Cl(2)	110.56(4)	Cl(3)–Zn(1)–Cl(1)	110.64(4)
Cl(4)–Zn(1)–Cl(1)	106.67(4)	Cl(2)–Zn(1)–Cl(1)	107.56(4)

3.3.2. Crystal structure of [(H_2L1)($CuCl_4$)]·H_2O, 2. Compound **2** crystallizes in a triclinic *P-1* space group and there are two formula units in its cell. X-ray diffraction analysis shows that the complex is composed of one diprotonated L1 cation, one $[CuCl_4]^{2-}$, and one free water (figure 3).

The geometry of the HL1 is generally very similar to that in **1**. The coordination geometry around Cu(II) was a distorted tetrahedron with Cl_4 binding set. The Cu–Cl bond distances are 2.2348(9)–2.2638(9) Å, normal and consistent with similar compounds in which the Cu is tetrahedral [28]. The rms deviations of the rings with N1 and N2, and N3 and N4 are 0.0062(2) Å and 0.0078(2) Å, respectively, both rings incline at an angle of 67.1 (1)° with each other.

Different from **1**, the dication adopted the *cis* conformation. At every dication there was bonded a $[CuCl_4]^{2-}$ through N–H···Cl hydrogen bond between one NH(N(4)–H(4)) of the dication and the Cl(Cl(1)) anion with N–Cl distance of 3.130(3) Å, and a water molecule

Table 4. Hydrogen-bond geometries for **1**–**6** (Å, °).

D–H···A	d(D···A) **[Å]**
1	
N(4)–H(4)···Cl(1)#1	3.105(3)
N(2)–H(2)···Cl(3)#2	3.570(3)
N(2)–H(2)···Cl(1)#2	3.334(2)
2	
O(1)–H(1F)···Cl(2)#1	3.224(3)
O(1)–H(1E)···Cl(3)	3.315(3)
N(4)–H(4)···Cl(1)#2	3.130(3)
N(2)–H(2)···O(1)#3	2.687(4)
3	
N(4)–H(4)···Cl(3)#1	3.220(3)
N(2)–H(2)···Cl(4)#2	3.389(3)
N(2)–H(2)···Cl(4)#3	3.252(3)
4	
N(4)–H(4)···Cl(1)#1	3.451(3)
N(4)–H(4)···Cl(1)#2	3.277(3)
N(2)–H(2)···Cl(2)#3	3.144(3)
5	
O(1)–H(1F)···Cl(1)#3	3.447(4)
O(1)–H(1E)···Cl(4)	3.241(4)
N(4)–H(4)···Cl(2)#4	3.341(4)
N(4)–H(4)···Cl(1)#4	3.207(4)
N(2)–H(2)···Cl(2)#5	3.113(4)
6	
O(1)–H(1D)···Cl(1)#1	3.200(3)
O(1)–H(1C)···Cl(4)	3.112(3)
N(6)–H(6)···O(1)#2	2.801(5)
N(4)–H(4)···O(1)#3	2.763(4)

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

via the N–H···O hydrogen bond between the other NH unit of the cation and water with N–O distance of 2.687(4) Å to form a tricomponent adduct. The tricomponent adducts were linked by the O–H···Cl hydrogen bond between water and Cl(2) anion with O–Cl distance of 3.224(3) Å to form 1-D chain running along the *c* axis. The Cu–Cu distance along the chain was 13.859(3) Å, while the interchain Cu–Cu separation was 9.701(2) Å. The chains were combined by the interchain CH–Cl association between the phenyl CH(C(7)–H(7)) of the cation and Cl(2) anion with C–Cl distance of 3.811(1) Å to form a 2-D grid sheet structure extending at the direction that made a dihedral angle of ca. 60° with the *bc* plane (figure 4). Two adjacent sheets were joined by intersheet Cl–π associations between Cl$^-$ and the aromatic ring of the cation with Cl–Cg distances of 3.338(2)–3.449(2) Å and

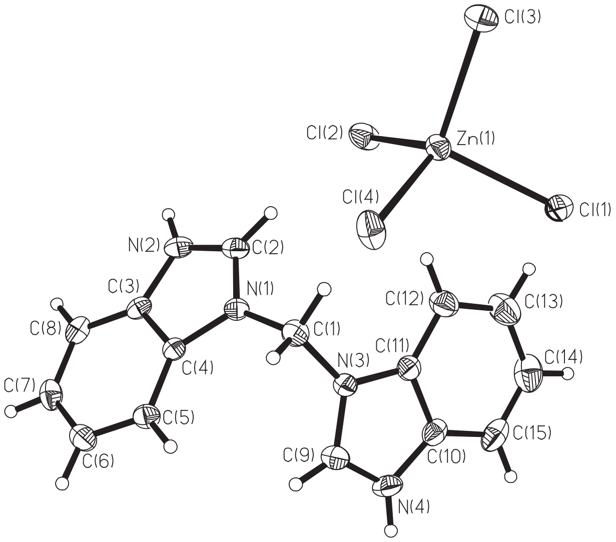


Figure 1. Molecular structure of **1** showing the atomic numbering scheme at 30% thermal ellipsoid probability level.

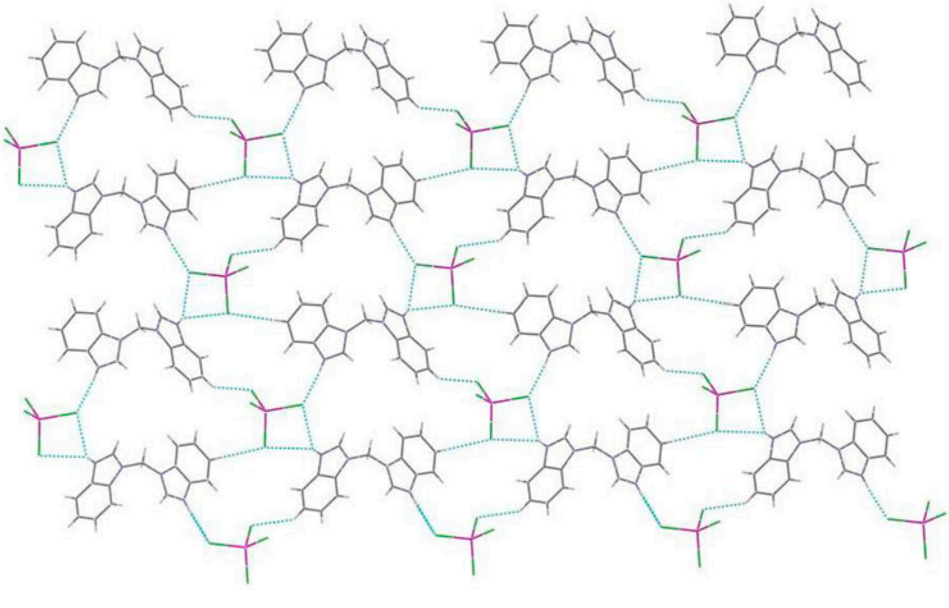


Figure 2. 2-D sheet structure of **1** extending in the direction that made a dihedral angle of ca. 60° with the *bc* plane.

O–H···Cl hydrogen bond between water and Cl^- with O–Cl distance of 3.315(3) Å to form a 2-D double sheet. The 2-D double sheets were further stacked along the direction that was perpendicular with its extending direction by the CH–Cl associations with C–Cl

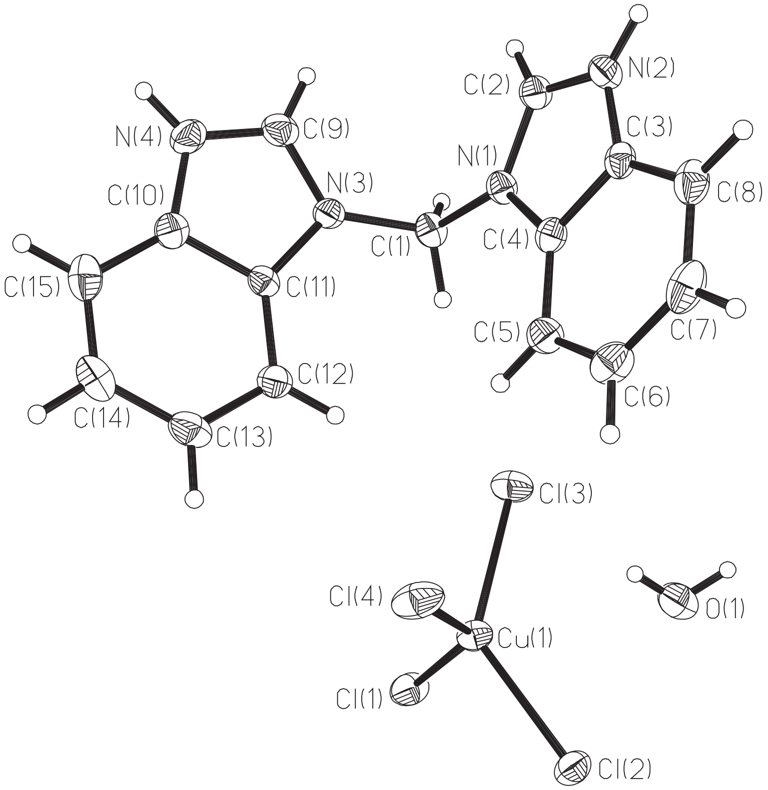


Figure 3. Molecular structure of **2** showing the atomic numbering scheme at 30% ellipsoid probability level.

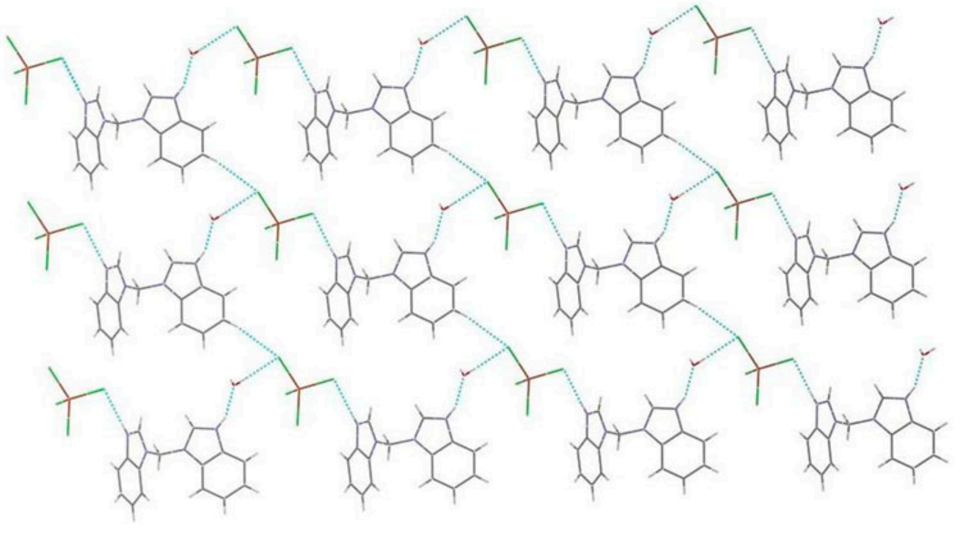


Figure 4. 2-D grid sheet structure of **2** extending in the direction that made a dihedral angle of ca. 60° with the *bc* plane.

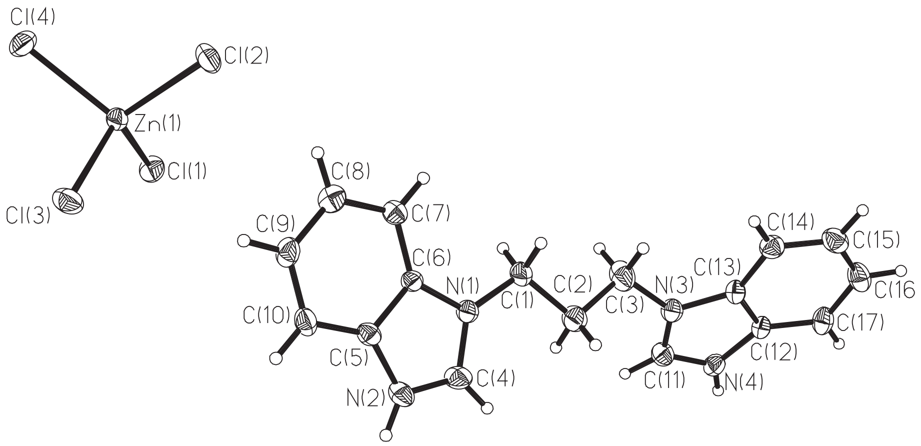


Figure 5. Molecular structure of **3** showing the atomic numbering scheme at 30% thermal ellipsoid probability level.

distances of 3.556(3)–3.659(3) Å and CH_2–Cl associations between the CH_2 spacer and Cl^- with C–Cl distances of 3.490(2)–3.775(2) Å to form a 3-D layer network structure. In this case, the neighboring double sheets were slipped some distances from each other along its extending directions.

3.3.3. Crystal structure of [(H_2L2)($ZnCl_4$)], 3. Similar to **1**, **3** was prepared by reacting 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole (L2) with 1 equivalent of zinc(II) chloride in water in the presence of hydrochloric acid. There were no water molecules involved in the lattice as determined by elemental analysis. Complex **3** crystallizes in the monoclinic space group *P2(1)/n* with unit cell content of four formula units and the asymmetric unit consists of one H_2L2 dication and one $ZnCl_4$ (figure 5).

The Zn–Cl bonds were 2.2481(8)–2.3128(8) Å, similar to the values in **1**. The bond distances Zn(1)–Cl(2) (2.2733(8) Å) and Zn(1)–Cl(3) (2.2767(9) Å) are almost equal to each other. The bond length Zn(1)–Cl(4) (2.3128(8) Å) is longer than the other Zn–Cl bonds, probably because Cl(4) forms more hydrogen bonds than the other chlorides (table 4). The Cl–Zn–Cl angles between each of the two neighboring chlorides are close to 109°, (Cl(1)–Zn(1)–Cl(2), 112.78(3)°; Cl(1)–Zn(1)–Cl(3), 112.05(3)°; Cl(2)–Zn(1)–Cl(3), 108.51(3)°; Cl (1)–Zn(1)–Cl(4), 108.15(3)°; Cl(2)–Zn(1)–Cl(4), 110.64(3)°; Cl(3)–Zn(1)–Cl(4), 104.40 (4)°), indicating the Zn ion is in a slightly distorted tetrahedral environment.

The rms deviations of the rings with N1 and N2, and N3 and N4 are 0.0135(1) and 0.0043(1) Å, respectively, both rings intersect at an angle of 45.8° with each other. The ring with N1 and N2 made an angle of 4.4(1)° with the plane defined by C1, C2, and C3. The ring with N3 and N4 made an angle of 49.3(2)° with the plane defined by C1, C2, and C3.

One anion was attached to the cation via the N–H···Cl hydrogen bond between the NH (N(4)–H(4)) cation and Cl(3) anion with N–Cl distance of 3.220(3) Å, CH–Cl association arising from the phenyl CH(N(17)–H(17)) of the cation and the Cl(2) of the anion with C–Cl distance of 3.536(2) Å to form a bicomponent adduct. The bicomponent adducts were linked by CH–Cl association with C–Cl distance of 3.679(3) Å to form a 1-D chain running

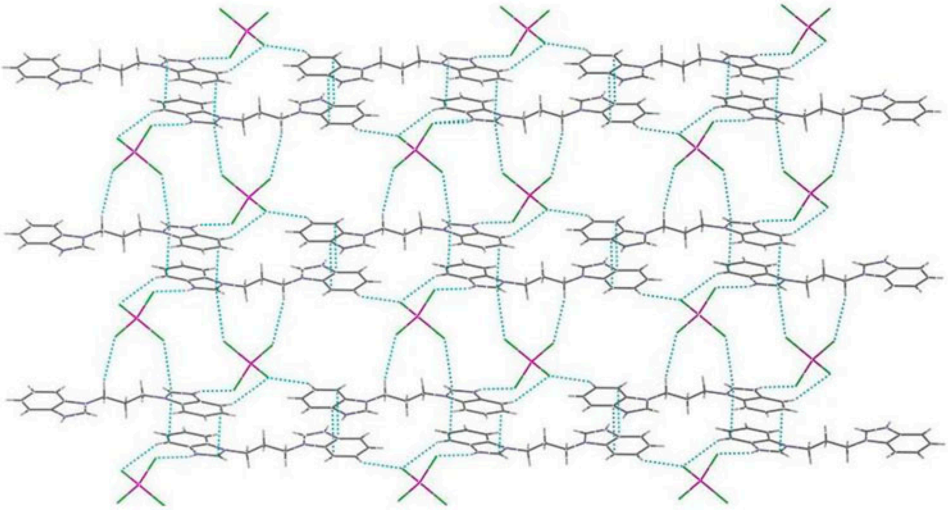


Figure 6. Packing diagram of **3** showing 2-D sheet extending parallel to the *bc* plane.

along the *c* axis. Two chains were joined by π–π associations between the aromatic rings of the cations with Cg–Cg separations of 3.359(2)–3.376(2) Å to form a 1-D double chain. The double chains were combined by the interchain Cl–π association between Cl^- and the aromatic ring of the cation with Cl–Cg distance of 3.263(1) Å, and CH_2–Cl association between the CH_2 unit at the spacer and Cl^- with C–Cl distance of 3.873(2) Å to form a 2-D sheet extending parallel to the *bc* plane (figure 6). The 2-D sheets were further stacked along the *a* axis through CH–Cl, CH_2–Cl, and CH_2–π interactions to form the 3-D layer network structure. In this case, the neighboring sheet layers were slipped some distances from each other along its extending direction.

3.3.4. Crystal structure of [(H_2L2)($CuCl_4$)], 4. Similar to **2**, **4** was prepared by reacting 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole (L2) with 1 equivalent of copper(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. Complex **4** crystallizes in the triclinic space group *P-1* with unit cell content of two formula units and the asymmetric unit consists of one H_2L2 dication and one $CuCl_4^{2-}$ (figure 7). L2 is doubly protonated and the cation with the NH^+ groups on the benzimidazole rings in **4** resembles the cations of **1–3**. Protonated L2 displays *cis* configuration, in which the symmetry center is located at C(2).

Cu–Cl bonds were 2.2142(10)–2.2753(10) Å, in the range of reported results (2.2347(9)–2.2497(8) Å) [28]. The Cl–Cu–Cl angles between two neighboring chlorides deviate significantly from 109°, (Cl(4)–Cu(1)–Cl(3), 138.06(4)°; Cl(4)–Cu(1)–Cl(2), 98.38(4)°; Cl(3)–Cu(1)–Cl(2) 97.70(4)°; Cl(4)–Cu(1)–Cl(1), 98.99(4)°; Cl(3)–Cu(1)–Cl(1), 98.80(4)°; Cl(2)–Cu(1)–Cl(1), 131.39(4)°), indicating the Cu ion is in a distorted tetrahedral environment. The rms deviations of the rings with N1 and N2, and N3 and N4 are 0.0103(1) Å and 0.0087(1) Å, respectively, both rings intersect at an angle of 70.5(2)° with each other. The ring with N1 and N2 made an angle of ca. 70.8(2)° with the plane defined by C1, C2, and C3. The ring with N3 and N4 made an angle of ca. 77.3(1)° with the plane defined by C1, C2, and C3.

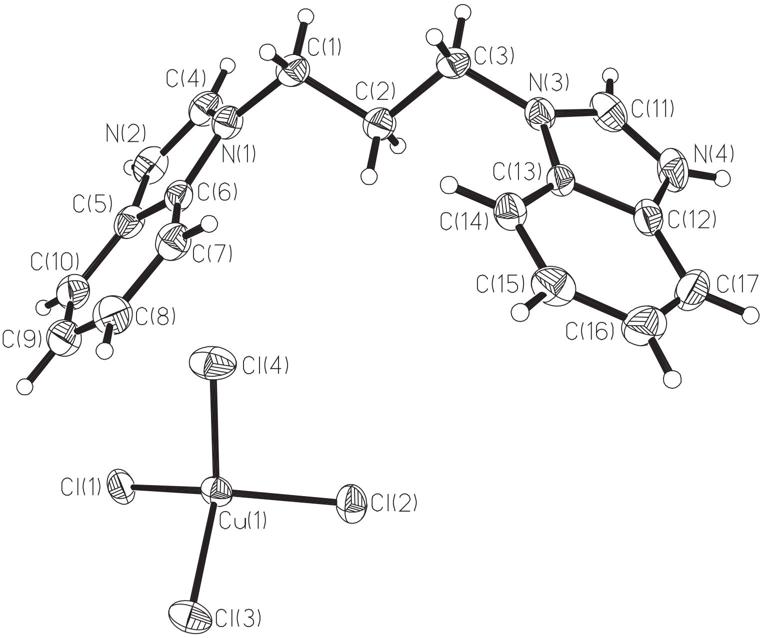


Figure 7. Molecular structure of **4** showing the atomic numbering scheme at 30% ellipsoid probability level.

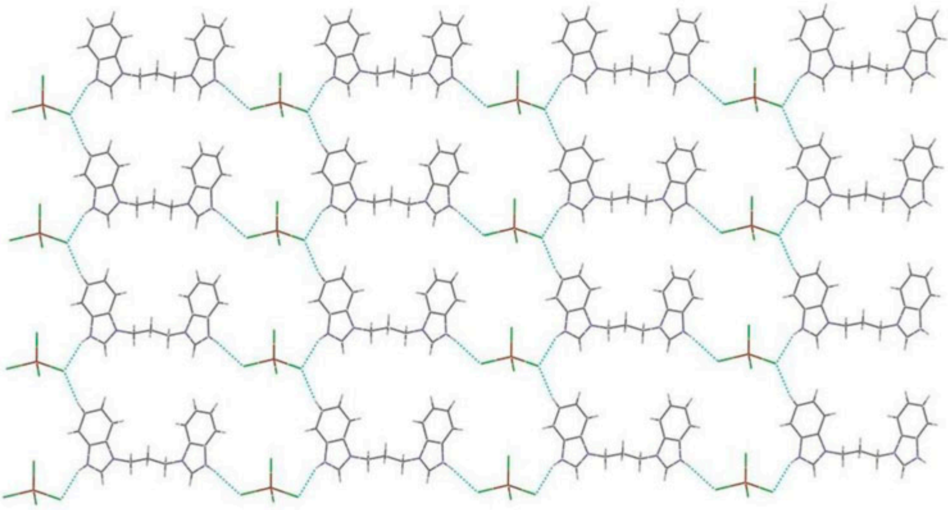


Figure 8. 2-D grid sheet structure of **4** extending along the direction that made an angle of ca. 60° with the bc plane.

The cation and anion were linked alternatively by N–H···Cl hydrogen bonds with N–Cl distances of 3.144(3)–3.451(3) Å to form the 1-D chain. The 1-D chains were joined by interchain CH–Cl association between the aromatic CH of the cation and Cl^- with C–Cl separation of 3.563(2) Å to form a 2-D grid sheet structure extending along the direction that made an angle of ca. 60° with the *bc* plane (figure 8). Two 2-D grid sheets were held together by intersheet CH_2–Cl interactions with C–Cl distances of 3.500(2)–3.862(2) Å, CH_2-π association between the CH_2 spacer and the aromatic ring of the cation with C–Cg distance of 3.471(3) Å, and π–π stacking interaction between the aromatic rings of the cations with Cg–Cg distance of 3.370(1) Å to form a 2-D double sheet. The two sheets in the double sheet were connected with the opposite faces of both sheets. The 2-D double sheets further stack along the direction that was perpendicular with its extending direction via the intersheet Cl–π association between Cl^- and the phenyl ring of the cation with Cl–Cg distance of 3.405(2) Å and CH–π association between the phenyl CH of the cation and the aromatic ring of the cation with C–Cg distance of 3.649(2) Å to form a 3-D layer network structure.

3.3.5. Crystal structure of [(H_2L3)($CuCl_4$)]·H_2O, 5. Although complex **5** was prepared analogously to **4** by reaction of 1-(4-(1H-benzimidazol-1-yl)butyl)-1H-benzimidazole (L3), with one equivalent of copper(II) chloride dihydrate in water in the presence of conc. hydrochloric acid, only [(H_2L3)($CuCl_4$)]·H_2O was obtained in high yield. X-ray structure determination revealed that the asymmetric unit contains one $CuCl_4^{2-}$, two halves of imidazolium, and one water. The structure is depicted in figure 9. The Cu ion is surrounded

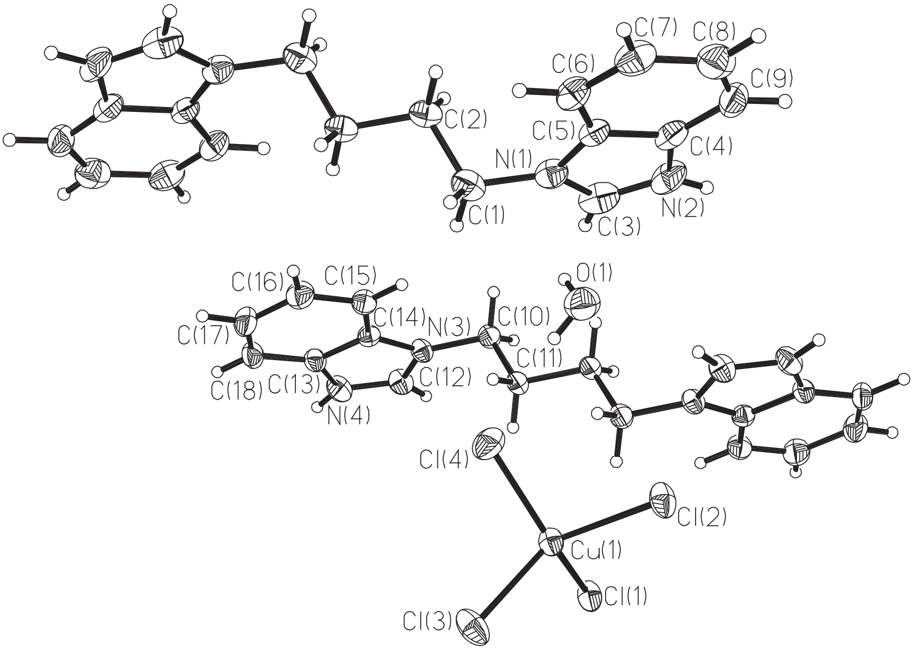


Figure 9. Molecular structure of **5** showing the atomic numbering scheme at 30% ellipsoid probability level.

by four chlorides in distorted tetrahedral geometry. The Cu–Cl bond distances are 2.2067 (13)–2.2757(12) Å.

At every NH group of one dication there was bonded an anion via the N–H···Cl hydrogen bonds between the NH group and two different Cl^- in the anion with N–Cl distances of 3.207(4)–3.341(4) Å, CH–Cl association between the N–CH–N of the cation and Cl^- with N–Cl distance of 3.443(2) Å, and a water molecule via the CH–O association between the N–CH–N of the cation and the water molecule with C–O distance of 3.305(3) Å, producing a five-component adduct. In this case, the NH and the CH groups at N–CH–N functioned as bifurcate donors. The five-component adducts associated with another dication via the N–H···Cl hydrogen bond (N(2)–H(2)···Cl(2)#5, 3.113(4) Å, 161(4)°, #5 x, $-y + 1/2$, $z - 1/2$) and CH–O association between the N–CH–N of the cation and the water molecule with C–O distance of 3.169(2) Å to form a six-component aggregate. The six-component aggregates were linked by the N–H···Cl hydrogen bond with N–Cl distance of 3.113(4) Å, and CH–O association between the N–CH–N of the cation and the water molecule with C–O distance of 3.169(2) Å to form a 1-D chain. The 1-D chains were linked by the CH–Cl association arising from the aromatic CH of the cation with C–Cl distance of 3.829(4) Å to form a 2-D sheet extending along the direction that made an angle of ca.

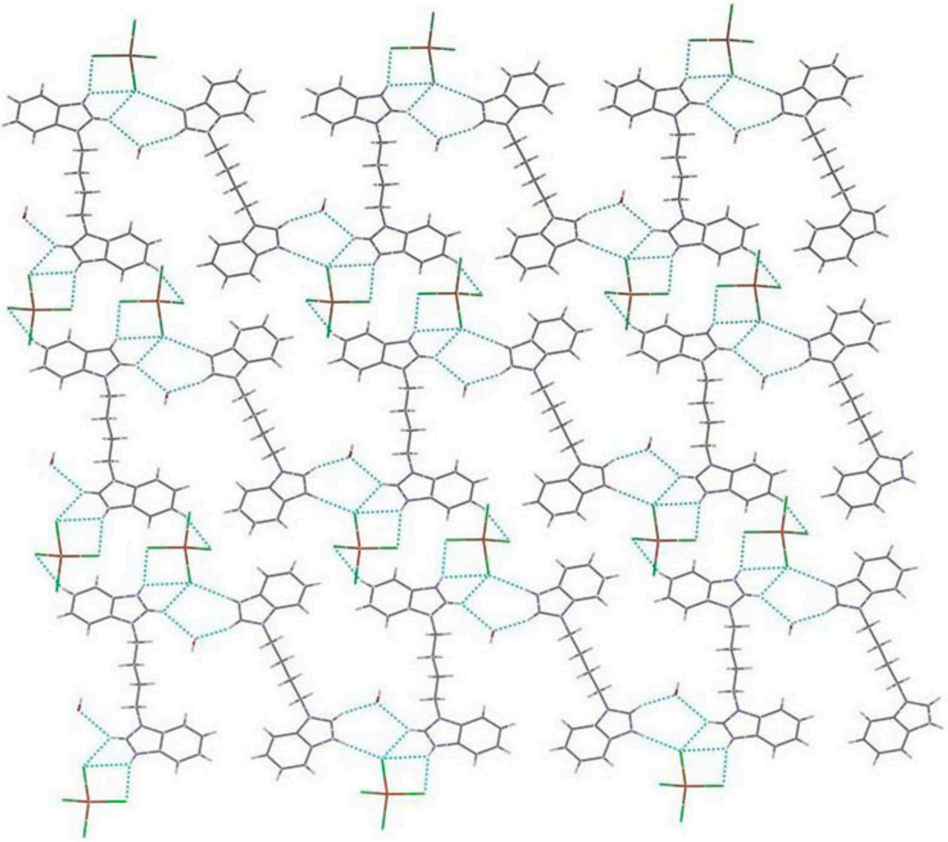


Figure 10. 2-D sheet structure of **5** extending along the direction that made an angle of ca. 60° with the *ab* plane.

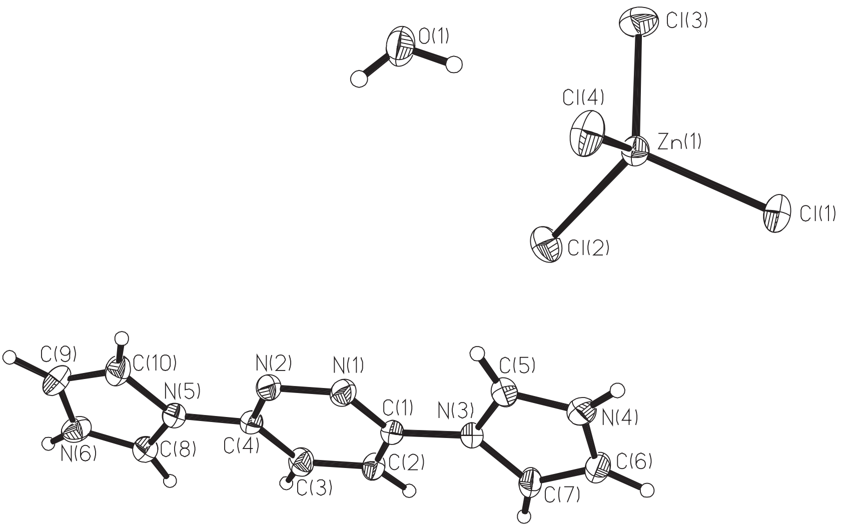


Figure 11. Molecular structure of **6** showing the atomic numbering scheme at 30% ellipsoid probability level.

60° with the *ab* plane (figure 10). The 2-D sheets were further stacked along the direction that was perpendicular with its extending direction via the intersheet O–H···Cl hydrogen bond between the water molecule and Cl^- with O–Cl separation of 3.241(4) Å, CH_2–Cl associations between the CH_2 spacer and Cl^- with C–Cl separations of 3.614(3)–3.810(3) Å, and CH_2–π association between the CH_2 spacer and the benzimidazole ring of the cation with C–Cg distance of 3.516(2) Å to form a 3-D layer network structure.

3.3.6. Crystal structure of $[(H_2L4)(ZnCl_4)]\cdot H_2O$, 6.

$[(H_2L4)(ZnCl_4)]\cdot H_2O$, **6**, was also prepared by reacting 3,6-bis(imidazol-1-yl)pyridazine (L4) with Zn(II) chloride in water in the presence of conc. hydrochloric acid. The compound was isolated in high yield as colorless block crystals. The compound crystallizes in a monoclinic space group *P2(1)/n* with unit content of four formula units. The molecular structure is given in figure 11. In the

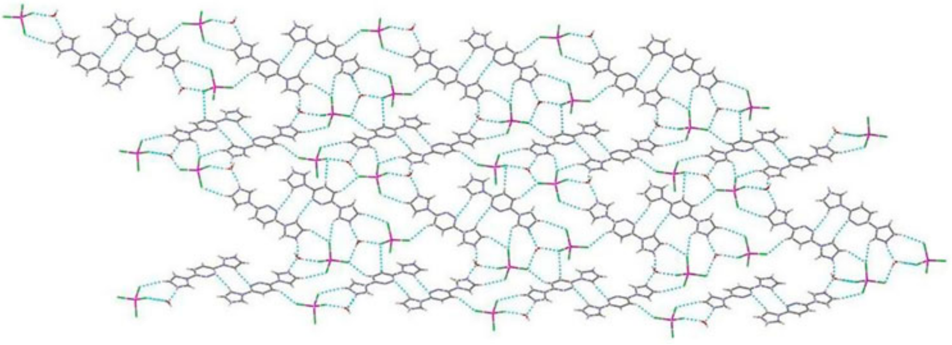


Figure 12. 2-D corrugated sheet structure of **6**.

asymmetric unit of **4** there are one cation and one anion, respectively, accompanied with one water. Two nitrogens at the imidazole ring but no nitrogen at the pyridazine ring were protonated to yield the dication which conforms with the literature results [29, 30]. In **6**, the Zn ion is coordinated in a distorted tetrahedral geometry by four chlorides also.

All of the bond lengths are in the normal range, Zn–Cl of 2.2437(11)–2.2757(10) Å. The Cl–Zn–Cl angles range from 106.67(4)° to 111.75(4)°, which fit well with the crystallographic symmetry of the compound. The rms deviation of the pyridazine ring is 0.0053(2) Å. The rms deviation of the imidazole ring with N3 and N4 is 0.0021(1) Å; this ring made a dihedral angle of 11.1° with the pyridazine ring. The rms deviation of the imidazole ring with N5 and N6 is 0.0024(2) Å and this ring intersected at an angle of 6.8(1)° with the pyridazine ring. In the same cation the dihedral angle between the two imidazole rings is 4.5(1)°, which is smaller than the previously reported results [30].

At every cation there was a water molecule via N–H···O hydrogen bond with N–O separation of 2.763(4) Å, and an anion via CH–Cl association arising from the imidazole 4-CH of the cation and Cl^- with C–Cl distance of 3.728(3) Å to form a tricomponent adduct. In the tricomponent adduct, the water associated with Cl^- via the O–H···Cl hydrogen bond with O–Cl separation of 3.112(3) Å. Two tricomponent adducts were joined by CH–N association between the 5-CH of the imidazole and the N at the pyridazine ring with C–N distance of 3.529(2) Å to form a six-component aggregate. The six-component aggregates were linked by CH–Cl association between the CH at the pyridazine moiety and Cl^- with C–Cl separation of 3.460(2) Å to form a 1-D chain. The 1-D chains were connected by interchain N–H···O hydrogen bond between the NH cation and water with N–O distance of 2.801(5) Å, CH–Cl associations between the same Cl^- and the 2-CH and 4-CH of the imidazole at two tricomponent adducts in the same six-component aggregate with C–Cl distances of 3.424(3)–3.646(3) Å and O–H···Cl hydrogen bond between the water molecule and Cl^- with O–Cl distance of 3.200(3) Å to form a 2-D corrugated sheet (figure 12). In the corrugated sheet the neighboring chains were almost perpendicular with each other, while the first chain was parallel to the third chain, as did the second chain and the fourth chain. The 2-D corrugated sheets were further stacked along the direction that was perpendicular with its extending direction via the CH–Cl associations from the CH unit at the imidazole group with C–Cl distances of 3.413(2)–3.683(2) Å, O–H···Cl hydrogen bond between the water molecule and Cl^- with O–Cl distance of 3.200(3) Å to form a 3-D layer network structure. Herein, the neighboring sheets were also slipped some distances from each other along its extending direction.

4. Conclusion

We synthesized six new ionic salts by solution reaction of $ZnCl_2$/$CuCl_2$ with bis(imidazole) derivatives in strong acidic conditions. The Zn and Cu ions in all the compounds are tetrahedrally coordinated by Cl^-. For the bis(imidazole) derivatives, the least basic nitrogens are not protonated.

These compounds display 3-D layer structures for the presence of N–H···Cl, N–H···O, O–H···O, and O–H···Cl hydrogen bonds as well as Coulombic interactions. In addition to classical hydrogen bonding interactions, secondary propagating interactions such as CH–N, CH–O, CH–Cl, CH_2–Cl, CH–π, CH_2–π, Cl–π, and π–π associations also play important roles in structure extension and stabilization. Based on the observation that the chlorometallates are effective hydrogen bond acceptors, we have shown that supramolecular synthons such as tetrachlorocuprate and tetrachlorozincate may be exploited to prepare metal-containing hydrogen-bonded polymers composed of $[H_2L]^{2+}$ salts of perchlorometallates. In the cases reported here, the choice of anions without hydrogen bond donor sites and cations with strong hydrogen bond donors is a successful strategy. All of the compounds show high thermal stabilities.

Supporting information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 894912 for **1**, 894874 for **2**, 894875 for **3**, 894911 for **4**, 894913 for **5**, and 900191 for **6**. Copies of this information may be obtained free of charge (Fax: +44(1223)336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Funding

This research was supported by Zhejiang Provincial Natural Science Foundation of China under [grant number LQ12B02001]; Zhejiang Province Key Laboratory of Noble Metal Catalytic Materials and Technology under [grant number 2013F10008] and Zhejiang Provincial Natural Science Foundation of China under [grant number LY14B010006] for the subsequent granted time of these foundations.

References

[1] (a) S.J. Zhang, G. Lanty, J.S. Lauret, E. Deleporte, P. Audebert, L. Galmiche. *Acta Mater.*, **57**, 3301 (2009); (b) C. Sanchez, B. Julián, P. Belleville, M. Popall. *J. Mater. Chem.*, **15**, 3559 (2005); (c) A.B. Descalzo, R. Martinez-Manez, F. Sancenón, K. Hoffmann, K. Rurack. *Angew. Chem. Int. Ed.*, **45**, 5924 (2006); (d) J.Y. Yuan, Y.Y. Xu, A.H.E. Müller. *Chem. Soc. Rev.*, **40**, 640 (2011).

[2] (a) L.M. Wu, X.T. Wu, L. Chen. *Coord. Chem. Rev.*, **253**, 2787 (2009); (b) V. Srivastava, K. Gaubert, M. Pucheault, M. Vaultier. *ChemCatChem.*, **1**, 94 (2009); (c) A. Dolbecq, E. Dumas, C.R. Mayer, P. Mialane. *Chem. Rev.*, **110**, 6009 (2010); (d) M. Vallet-Regí, M. Colilla, B. González. *Chem. Soc. Rev.*, **40**, 596 (2011).

[3] (a) S.N. Herringer, M.M. Turnbull, C.P. Landee, J.L. Wikaira. *J. Coord. Chem.*, **62**, 863 (2009); (b) D.J. Carnevale, C.P. Landee, M.M. Turnbull, M. Winn, F. Xiao. *J. Coord. Chem.*, **63**, 2223 (2010); (c) J.L. Wikaira, L. Li, R. Butcher, C.M. Fitchett, G.B. Jameson, C.P. Landee, S.G. Telfer, M.M. Turnbull. *J. Coord. Chem.*, **63**, 2949 (2010); (d) J. Qian, M.J. Xie, L. Feng, J.L. Tian, J. Shang, Y. Zhang, S.P. Yan. *J. Coord. Chem.*, **63**, 2239 (2010); (e) M.M. Turnbull, C.P. Landee, B.M. Wells. *Coord. Chem. Rev.*, **249**, 2567 (2005).

[4] (a) Y. Takahashi, R. Obara, K. Nakagawa, M. Nakano, J.Y. Tokita, T. Inabe. *Chem. Mater.*, **19**, 6312 (2007); (b) P. Gomez-Romero, M. Chojak, K. Cuentas-Gallegos, J.A. Asensio, P.J. Kulesza, N. Casan-Pastor, M. Lira-Cantu. *Electrochem. Commun.*, **5**, 149 (2003).

[5] I. Płowaś, P. Szklarz, R. Jakubas, G. Bator. *Mater. Res. Bull.*, **46**, 1177 (2011).

[6] E. Coronado, P. Day. *Chem. Rev.*, **104**, 5419 (2004).

[7] (a) H. Abid, A. Samet, T. Dammak, A. Mlayah, E.K. Hlil, Y. Abid. *J. Lumin.*, **131**, 1753 (2011); (b) Y.Y. Li, C.K. Lin, G.L. Zheng, Z.Y. Cheng, H. You, W.D. Wang, J. Lin. *Chem. Mater.*, **18**, 3463 (2006); (c) S. Walha, S. Yahyaoui, H. Naili, T. Mhiri, T. Bataille. *J. Coord. Chem.*, **63**, 1358 (2010).

[8] B.P. Tripathi, V.K. Shahi. *Prog. Polym. Sci.*, **36**, 945 (2011).

[9] A.S. Poulos, D. Constantin, P. Davidson, M. Impéror, B. Pansu, P. Panine, L. Nicole, C. Sanchez. *Langmuir*, **24**, 6285 (2008).

[10] P. Innocenzi, B. Lebeau. *J. Mater. Chem.*, **15**, 3821 (2005).

[11] (a) N. Wang, C. Wu, Y. Cheng, TXu Int. *J. Pharm.*, **408**, 39 (2011); (b) M. Catauro, D. Verardi, D. Melisi, F. Belotti, P. Mustarelli. *Appl. Biomater. Biomech.*, **8**, 42 (2010).

[12] (a) E. Wortham, A. Zorko, D. Arcon, A. Lappas. *Physica B*, **318**, 387 (2002); (b) C. Bellitto, P. Day. *J. Mater. Chem.*, **2**, 265 (1992); (c) R. Willet, H. Place, M. Middleton. *J. Am. Chem. Soc.*, **110**, 8639 (1988); (d) W. Depmeier. *Z. Kristallogr.*, **224**, 287 (2009); (e) M.Y. Wei, R.D. Willett, C.J. Gómez-García. *Inorg. Chem.*, **43**,

4534 (2004); (f) D.B. Mitzi. *Prog. Inorg. Chem.*, **48**, 1 (1999); (g) R.D. Willet. *Coord. Chem. Rev.*, **109**, 181 (1991); (h) R.D. Willet, H. Place, M. Middleton. *J. Am. Chem. Soc.*, **110**, 8639 (1998).

[13] (a) R. Kind, S. Pleko, H. Arend, R. Blinc, J. Seliger, B. Loar, J. Slak, A. Levstik, C. Filipi, G. Lahajnar, F. Milia, G. Chapuis, F. Milia, G. Chapuis. *J. Chem. Phys.*, **71**, 2118 (1979); (b) G.F. Needham, R.D. Willet, H.F. Frentzen. *J. Phys. Chem.*, **88**, 674 (1984).

[14] (a) Z.T. Xu, D.B. Mitzi. *Inorg. Chem.*, **42**, 6589 (2003); (b) J.L. Kuntson, J.D. Martin, D.B. Mitzi. *Inorg. Chem.*, **44**, 4699 (2005); (c) C. Aruta, F. Licci, A. Zappettini, F. Bolzoni, F. Rastelli, P. Ferro, T. Besagni. *Appl. Phys.*, **A81**, 963 (2005); (d) Z. Liu, G.Q. Shi, F.E. Chen, M.M. Ma. *Chin. J. Inorg. Chem.*, **19**, 1185 (2003).

[15] C.R. Kagan, D.B. Mitzi, C.D. Dimitrakopoulos. *Science*, **286**, 945 (1999).

[16] (a) C.E. Costin-Hogan, C.L. Chen, E. Hughes, A. Pickett, R. Valencia, N.P. Rath, A.M. Beatty. *CrystEngComm.*, **10**, 1910 (2008); (b) C.L. Chen, A.M. Beatty. *Chem. Commun.*, 76 (2007); (c) A. Thorn, R.D. Willet, B. Twamley. *Cryst. Growth Des.*, **6**, 1134 (2006); (d) A. Thorn, R.D. Willet, B. Twamley. *Inorg. Chem.*, **47**, 5775 (2008); (e) A. Thorn, R.D. Willet, B. Twamley. *Cryst. Growth Des.*, **5**, 673 (2005).

[17] L. Brammer, J.K. Swearingen, E.A. Bruton, P. Sherwood. *Proc. Natl. Acad. Sci. USA*, **99**, 4956 (2002).

[18] (a) C.M. Jin, L.Y. Wu, H. Lu, YXu Cryst. *Growth Des.*, **8**, 215 (2008); (b) C.M. Jin, H. Lu, L.Y. Wu, J. Huang. *Chem. Commun.*, 5039 (2006); (c) C.M. Jin, Z.F. Chen, T.Q. Sun, Y.J. Hu, S.L. Hu. *J. Mol. Struct.*, **889**, 186 (2008); (d) S.W. Jin, D.Q. Wang, Z.W. Zheng, J. Chen, C. Feng, X.H. Ye, Y.P. Zhou. *Z. Anorg. Allg. Chem.*, **636**, 1617 (2010); (e) C.M. Jin, Z. Zhu, M.X. Yao, X.G. Meng. *CrystEngComm*, **12**, 358 (2010); (f) G.H. Cui, J.R. Li, J.L. Tian, X.H. Bu, S.R. Batten. *Cryst. Growth Des.*, **5**, 1776 (2005); (g) J.F. Ma, J.F. Liu, Y. Xing, H.Q. Jia, Y.H. Lin. *J. Chem. Soc., Dalton Trans.*, 2403 (2000); (h) L. Ballester, I.P. Baxter, C.M. Duncan, D.M.L. Goodgame, D.A. Grachvogel, D.J. Williams. *Polyhedron*, **17**, 3613 (1998); (i) N. Masciocchi, C. Pettinari, E. Alberti, R. Pettinari, C. Di Nicola, A.F. Albisetti, A. Sironi. *Inorg. Chem.*, **46**, 10501 (2007).

[19] J. Yang, J.F. Ma, Y.Y. Liu, S.L. Li, G.L. Zheng. *Eur. J. Inorg. Chem.*, 2174 (2005).

[20] S.W. Jin, W.Z. Chen, H.Y. Qiu. *J. Coord. Chem.*, **8**, 1253 (2008).

[21] J.L. Lavandera, P. Cabildo, R.M. Claramunt. *J. Heterocycl. Chem.*, **25**, 771 (1988).

[22] M.J. Begley, P. Hubberstey, J. Stroud. *J. Chem. Soc., Dalton Trans.*, 4295 (1996).

[23] Bruker, *SMART and SAINT*. Bruker AXS, Madison, WI (2004).

[24] G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).

[25] J.H. Yu, X.M. Wang, L. Ye, Q. Hou, Q.F. Yang, J.Q. Xu. *CrystEngComm*, **11**, 1037 (2009).

[26] A.L. Gillon, A.G. Orpen, J. Starbuck, X.M. Wang, Y. Rodríguez-Martín, C. Ruiz-Pérez. *Chem. Commun.*, 2287 (1999).

[27] A. Hosseinian, A.R. Mahjoub. *Acta Cryst.*, **E65**, m1456 (2009).

[28] (a) S.W. Jin, D.Q. Wang. *J. Coord. Chem.*, **65**, 3188 (2012); (b) M.Y. Wei, R.D. Willett. *J. Chem. Cryst.*, **32**, 439 (2002); (c) R. Bhattacharya, S. Chanda, G. Bocelli, A. Cantoni, A. Ghosh. *J. Chem. Cryst.*, **34**, 393 (2004).

[29] M. Felloni, A.J. Blake, P. Hubberstey, C. Wilson, M. Schröder. *CrystEngComm*, **4**, 483 (2002).

[30] S.W. Jin, D.Q. Wang. *J. Coord. Chem.*, **63**, 3042 (2010).