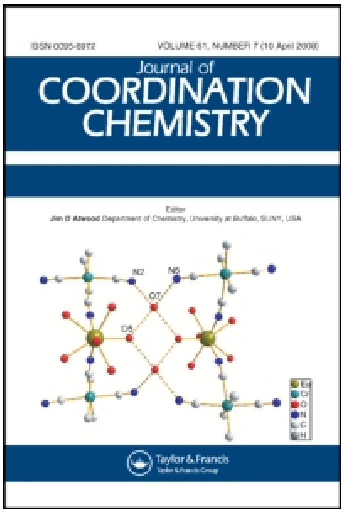

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Sun, Ya-Guang , Guo, Mei-Yan , Xiong, Gang , Ding, Fu , Wang, Lei , Jiang, Bing , Zhu, Ming-Chang , Gao, En-Jun and Verpoort, Francis(2010) 'Hydrothermal synthesis, structure, and photoluminescence of four complexes based on 1H-imidazole-4,5-dicarboxylate or 1H-imidazole-2-carboxylate ligands', Journal of Coordination Chemistry, 63: 24, 4188 — 4200, First published on: 15 November 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.532550

URL: http://dx.doi.org/10.1080/00958972.2010.532550

Journal of Coordination Chemistry
Vol. 63, No. 24, 20 December 2010, 4188–4200

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Hydrothermal synthesis, structure, and photoluminescence of four complexes based on 1H-imidazole-4,5-dicarboxylate or 1H-imidazole-2-carboxylate ligands

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(*Received 18 July 2010; in final form 22 September 2010*)

Four complexes, $[Ag_4(bipy)_2(Himdc)_2(H_2O)_2]_n$ (**1**), $[Ag(H_2imdc)]_n$ (**2**), $[K(H_3imdc)(H_2imdc)(H_2O)_2]_n$ (**3**), and $[Cu(Himc)_2]$ (**4**) ($H_3imdc = $ 1H-imidazole-4,5-dicarboxylic acid, $H_2imc = $ 1H-imidazole-2-carboxylic acid, and bipy = 4,4′-bipyridine), were hydrothermally synthesized and characterized by single-crystal X-ray diffraction analysis and elemental analysis. The obtained complexes exhibit different coordination structures; **1** contains a 2-D supramolecular layer based on two chains arraying uniformly in an ABAB manner. Compound **2** displays sawtooth-shaped 1-D chains extending to 2-D layers *via* hydrogen bond interactions. Compound **3** possesses a 3-D framework structure based on a 1-D chain *via* hydrogen bonding interactions. Compound **4** has a 3-D framework structure bearing a pcu-type topology. In addition, the photoluminescence for **1** has been investigated.

Keywords: Hydrothermal synthesis; Crystal structure; 1H-imidazole-4,5-dicarboxylic acid

1. Introduction

Recent progress in metal organic framework (MOF) chemistry has been the development of a class of MOFs known as zeolitic imidazole frameworks (ZIFs) [1], a new class of porous crystals with extended 3-D structures constructed from metal (M) ions bridged by imidazolates (Im). An important characteristic of those ZIFs is that the M–Im–M bridging angle is similar to the Si–O–Si angle (145°), consequently it should be possible to make new porous materials applicable in gas absorption or catalysis [2]. Yaghi and co-workers [2] developed a general synthetic procedure to generate porous crystalline ZIFs. They found that the molar ratio, the concentration of the metal ion and linker, and the temperature of the reaction are crucial to achieve monocrystalline materials of ZIFs [3]. Moreover, the rigidity and symmetry of the ligands also play key

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.532550

roles in obtaining ZIFs [4]. The rigid 4,5-imidazole dicarboxylic acid (H_3imdc), an excellent N, O-donor, has already proven to be very efficient for the generation of MOFs. As the 1H-imidazole-4,5-dicarboxylic acid (H_3imdc) has interesting characteristics, its mono-, di-, and tri-deprotonated anions (H_2imdc^-, $Himdc^{2-}$, and $imdc^{3-}$) can be generated by controlling the pH carefully, in which each individual nitrogen is a very strong *N*-ligating donor for a d-metal ion. Due to the electronic properties of carboxyl group oxygens, coordination to metal ions can occur in different modes [5].

In situ ligand synthesis is of growing interest as a new approach for the synthesis of coordination polymers. Although potential coordination sites were reduced and steric hindrance was transferred because of decarboxylation, a number of coordination polymers with intriguing structural motifs derived from *in situ* decarboxylation of ligands have been prepared [6]. In this article, we generate four new compounds, $[Ag_4(bipy)_2(Himdc)_2(H_2O)_2]_n$ (**1**), $[Ag(H_2imdc)]_n$ (**2**), $[K(H_3imdc)(H_2imdc)(H_2O)_2]_n$ (**3**), and $[Cu(Himc)_2]$ (**4**) (H_3imdc = 1H-imidazole-4,5-dicarboxylic acid, H_2imc = 1H-imidazole-2-carboxylic acid, and bipy = 4,4′-bipyridine). While **1** and **2** display 2-D layer structures, **3** exhibits a 3-D supramolecular framework structure, and **4** has a supramolecular framework structure containing a pcu-type topology. Luminescent properties of **1** have been investigated.

2. Experimental

2.1. *Materials and equipment*

All chemicals purchased were of reagent grade and used without purification. Water used in the reactions was distilled prior to use. Elemental analyses (C, H, and N) were carried out with a Perkin Elmer 240 C elemental analyzer. IR spectra were recorded from 400 to 4000 cm^{-1} on a Nicolet 470 spectrophotometer using KBr pellets. The fluorescence spectrum was measured applying a Perkin Elmer LS55 fluorescence spectrophotometer. All syntheses were carried out in 23 mL Teflon-lined autoclaves under autogenous pressure. The reaction vessels were filled to 50% volume capacity.

2.2. *Syntheses of 1–4*

2.2.1. Synthesis of $[Ag_4(bipy)_2(Himdc)_2(H_2O)_2]_n$ (1). A mixture of H_3imdc (0.0624 g, 0.4 mmol), $AgNO_3$ (0.0340 g, 0.2 mmol), 4,4′-bipyridine (0.0312 g, 0.2 mmol), and water (10 mL) was placed in a 23 mL Teflon-lined stainless steel vessel and heated at 140°C for 3 days after which it was slowly cooled to room temperature. Colorless crystals were collected (65% yield based on $AgNO_3$). IR: 3365(br), 1660(s), 1609(s), 1483(s), 1458(m), 1370(s), 1306(s), 1331(m), 1232(s), 1191(m), 1061(m), 1073(m), 3846(s), and 789(s). Anal. Calcd for $C_{30}H_{24}Ag_4N_8O_{10}$: C, 33.12; H, 2.22; and N, 10.30. Found: C, 33.11; H, 2.19; and N, 10.26.

2.2.2. Synthesis of $[Ag(H_2imdc)]_n$ (2). A mixture of H_3imdc (0.0624 g, 0.4 mmol), $AgNO_3$ (0.0340 g, 0.2 mmol), and deionized water (10 mL) was sealed in a 23 mL Teflon-lined stainless steel vessel and heated at 140°C for 3 days under autogenous pressure after which it was cooled slowly to room temperature. Colorless crystals were collected (54% yield based on $AgNO_3$). IR: 3438(s), 1650(s), 1630(s), 1585(s), 1385(s), 1370(s), 1234(m), 1108(m), 815(s), and 772(s). Anal. Calcd for $C_5H_3AgN_2O_4$: C, 22.84; H, 1.15; and N, 10.65. Found: C, 22.65; H, 1.09; and N, 10.59.

2.2.3. Synthesis of [K(H_3imdc)(H_2imdc)(H_2O)$_2$]$_n$ (3). A mixture of H_3imdc (0.0624 g, 0.4 mmol), $AgNO_3$ (0.0340 g, 0.2 mmol), and KOH (0.0112 g, 0.2 mmol) in deionized water (10 mL) was placed in a 23 mL Teflon-lined stainless steel vessel and heated at 140°C for 3 days under autogenous conditions after which it was cooled slowly to room temperature. Colorless crystals were collected (43% yield based on KOH). IR: 3350(br), 1611(s), 1533(s), 1408(s), 1217(m), 1155(s), 1049(s), 955(s), 815(s), 723(m), and 650(m). Anal. Calcd for $C_{10}H_{11}KN_4O_{10}$: C, 31.09; H, 2.87; and N, 14.50. Found: C, 31.02; H, 2.83; and N, 14.47.

2.2.4. Synthesis of Cu(Himc)$_2$ (4). A mixture of H_3imdc (0.0624 g, 0.4 mmol), $CuCl_2 \cdot 2H_2O$ (0.0340 g, 0.2 mmol), and deionized water (10 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL) and heated at 140°C for 3 days under autogenous conditions after which it was cooled slowly to room temperature. Light blue crystals were collected (50% yield based on $CuCl_2 \cdot 2H_2O$). IR: 3330(m), 1601(m), 1521(s), 1412(s), 1145(s), 1212(m), 1132(s), 816(s), and 718(m). Anal. Calcd for $C_8H_6O_4N_4Cu$: C, 33.63; H, 2.12; and N, 19.61. Found: C, 33.58; H, 2.10; and N, 19.53.

2.3. *X-ray crystallographic study*

Crystallographic data were collected using a Bruker SMART Apex CCD diffractometer applying graphite-monochromated Mo-Kα radiation (0.710 73 Å) at 293 K in the ω–2θ scan mode. An empirical absorption correction was applied to the data using the *SADABS* program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL crystallographic software package [7]. All non-H atoms were refined anisotropically. Hydrogens were placed in calculated positions and refined using a riding mode. The crystallographic data, selected bond lengths, and angles for **1**–**4** are given in tables 1 and 2, respectively; hydrogen bond parameters are provided in table 3.

3. Results and discussion

3.1. *Descriptions of the structures*

3.1.1. [Ag_4(bipy)$_2$(Himdc)$_2$(H_2O)$_2$]$_n$ (1). X-ray diffraction analyses reveal that the structure of **1** contains four crystallographic independent Ag(I) ions, as shown in figure 1. They all possess a coordination number of three; Ag(1) connects with two nitrogens and one oxygen, N(1) and O_1 from Himdc^{2-} and N4A from 4,4′-bipyridine. Ag(2) also connects with two nitrogens, N(2) atom from Himdc^{2-} and N(3) from 4,4′-bipyridine and O(5) from a coordinated water. Ag(3) and Ag(4) have similar

Table 1. Crystal data and structure refinement for **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{30}H_{24}Ag_4N_8O_{10}$	$C_5H_3AgN_2O_4$	$C_{10}H_{11}KN_4O_{10}$	$C_8H_6CuN_4O_4$
Formula weight	1088.05	262.96	386.33	285.72
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2(1)/c$	$P2(1)/c$	Pnnm	$P\bar{1}$
Unit cell dimensions (Å, °)				
a	13.954(3)	11.696(2)	14.895(3)	3.6339(15)
b	17.734(4)	7.6918(15)	14.884(3)	6.518(3)
c	13.428(3)	7.0963(14)	6.5362(13)	9.712(4)
α	90	90	90	78.761(7)
β	110.03(3)	90.81(3)	90	87.462(7)
γ	90	90	90	82.022(7)
Volume (Å^3), Z	3121.8(11), 4	638.3(2), 4	1449.1(5), 4	223.41(17), 1
$F(000)$	2112	504	792	143
θ range for data collection (°)	1.55–27.51	3.17–25.00	1.93–27.51	3.22–25.00
Limiting indices	$-17 \le h \le 18$ $-23 \le k \le 23$ $-13 \le l \le 17$	$-13 \le h \le 11$ $-9 \le k \le 9$ $-8 \le l \le 8$	$-19 \le h \le 11$ $-19 \le k \le 19$ $-8 \le l \le 8$	$-4 \le h \le 4$ $-7 \le k \le 7$ $-11 \le l \le 11$
Reflections collected	21,755	3792	9935	1317
Independent reflections	[R(int) = 0.0303] 7159	[R(int) = 0.0224] 1126	[R(int) = 0.0296] 1816	[R(int) = 0.0249] 791
Completeness (%)	99.6	99.8	99.7	99.90
Goodness-of-fit on F^2	1.003	1.026	1.161	1.116
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0247$, $wR_2 = 0.0574$	$R_1 = 0.0245$, $wR_2 = 0.0591$	$R_1 = 0.0325$, $wR_2 = 0.0928$	$R_1 = 0.0360$, $wR_2 = 0.0915$
R indices (all data)	$R_1 = 0.0311$, $wR_2 = 0.0595$	$R_1 = 0.0262$, $wR_2 = 0.0598$	$R_1 = 0.0364$, $wR_2 = 0.0949$	$R_1 = 0.0382$, $wR_2 = 0.0925$

coordination to Ag(2) and Ag(1) ions. As a result, Ag(1), Ag(3) and Ag(2), Ag(4) are bridged, respectively, by Himdc^{2-} and 4,4′-bipyridine, and form two 1-D infinite chains along the b axis. The two chains array uniformly in an ABAB manner along the c-axis *via* hydrogen bond interactions (∠O5–H5B···O6 is 165°, O5–O6 is 2.8064 Å, ∠O10–H10B···O4 is 168°, O10–O4 is 2.8499 Å) and π–π stacking interactions (the centroid distances are 3.4480 and 3.5638 Å) resulting in a 2-D network (figure 2).

3.1.2. [Ag(H_2imdc)]$_n$ (2).

An ORTEP view of **2** reveals that there is one Ag ion and one 1H-imidazole-4,5-dicarboxylate (figure 3). This compound has been described in detail by Zhao and his co-workers [8]. Although we adopt 140°C as reaction temperature rather than 120°C, we found out that the structure of **2** is similar to Zhao's structure by comparison of the single-crystal X-ray diffraction analysis. From this, it follows that for **2** the reaction temperature is not so restricted to obtain **2**.

3.1.3. [K(H_3imdc)(H_2imdc)(H_2O)$_2$]$_n$ (3).

In order to obtain different framework structures, variation of the pH was carried out. Here the pH was modified from 2 to 5.8 – 6.3 *via* the addition of KOH. To our surprise, Ag(I) did not participate in coordination and unexpectedly **3** was obtained. X-ray single crystal structural analysis discloses that there is one K$^+$ and four ligands. The K$^+$ is eight coordinate *via* four oxygens (O4, O5, O4A, O5A) from four ligands and the remaining four coordination

Table 2. Selected bond distances (Å) and angles (°).

Compound **1**			
Ag(1)–N(1)	2.132(2)	Ag(1)–N(4)#1	2.142(2)
Ag(4)–N(7)	2.153(2)	Ag(2)–N(3)	2.186(2)
Ag(2)–O(5)	2.517(2)	Ag(3)–N(5)	2.135(2)
Ag(3)–N(8)#1	2.170(2)	Ag(4)–N(6)	2.123(2)
N(1)–Ag(1)–N(4)#1	170.77(7)	N(2)–Ag(2)–N(3)	159.18(8)
N(2)–Ag(2)–O(5)	114.16(7)	N(3)–Ag(2)–O(5)	86.56(7)
N(5)–Ag(3)–N(8)#1	171.39(7)	N(6)–Ag(4)–N(7)	167.24(9)
Ag(2)–O(5)–H(5A)	115(2)	Ag(2)–O(5)–H(5B)	103(2)
C(5)–N(1)–Ag(1)	133.42(17)	C(2)–N(1)–Ag(1)	120.36(15)
C(13)–N(4)–Ag(1)#2	119.69(18)	C(14)–N(4)–Ag(1)#2	122.64(17)
C(20)–N(5)–Ag(3)	130.15(17)	C(17)–N(5)–Ag(3)	124.70(16)
C(20)–N(6)–Ag(4)	136.76(17)	C(18)–N(6)–Ag(4)	118.09(16)
Compound **2**			
Ag(1)–N(1)#1	2.163(3)	Ag(1)–O(1)	2.178(3)
Ag(1)–O(1)#1	2.697(3)	Ag(1)–Ag(1)#2	3.6019(9)
N(1)#1–Ag(1)–O(1)	169.85(11)	N(1)#1–Ag(1)–O(1)#1	69.01(10)
O(1)–Ag(1)–O(1)#1	112.58(5)	N(1)#1–Ag(1)–Ag(1)#2	121.87(8)
O(1)–Ag(1)–Ag(1)#2	64.06(8)	O(1)#1–Ag(1)–Ag(1)#2	139.19(6)
C(1)–O(1)–Ag(1)	115.3(2)	C(1)–O(1)–Ag(1)#3	109.1(2)
Ag(1)–O(1)–Ag(1)#3	134.85(12)	C(3)–N(1)–Ag(1)#3	133.4(3)
C(2)–N(1)–Ag(1)#3	121.1(2)		
Compound **3**			
K(1)–O(9)	2.7311(14)	K(1)–O(10)	2.7316(14)
K(1)–O(4)	2.8230(14)	K(1)–O(5)	2.8237(14)
K(1)–K(1)#2	3.2278(12)	K(1)–K(1)#1	3.3084(12)
O(4)–K(1)#2	2.8231(14)	O(5)–K(1)#2	2.8237(14)
O(9)–K(1)#1	2.7311(14)	O(10)–K(1)#1	2.7316(14)
O(9)–K(1)–O(9)#1	105.44(5)	O(9)–K(1)–O(10)	68.47(5)
O(9)#1–K(1)–O(10)	68.49(5)	O(9)–K(1)–O(10)#1	68.49(5)
O(10)–K(1)–O(10)#1	105.46(5)	O(9)#1–K(1)–O(4)	130.64(5)
O(10)–K(1)–O(4)	76.63(3)	O(4)–K(1)–O(4)#2	110.27(4)
O(9)#1–K(1)–O(4)#2	92.37(4)	O(10)–K(1)–O(4)#2	157.46(5)
Compound **4**			
Cu(1)–N(1)	1.936(3)	Cu(1)–O(1)	1.963(2)
N(1)–Cu(1)–N(1)#1	180.00(10)	N(1)–Cu(1)–O(1)	83.54(11)
N(1)#1–Cu(1)–O(1)	96.46(11)	N(1)#1–Cu(1)–O(1)#1	83.54(11)
C(3)–N(1)–Cu(1)	111.5(2)	O(1)–Cu(1)–O(1)#1	180.000(1)
C(1)–O(1)–Cu(1)	114.9(2)	C(2)–N(1)–Cu(1)	142.6(2)

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

sites are occupied by four oxygens from four coordinating waters (O9, O10, O9A, O10A) completing a square-antiprismatic geometry, as shown in figure 4. The four ligands which are in the same plane all adopt a μ_2-O coordination mode to bridge two K ions and give a K_2O_4 cage unit. Four waters in the same plane also are μ_2-O linking the K_2O_4 units to form a 1-D chain. The 1-D chain looks like a string of lanterns (figure 5). A 3-D supramolecular framework is constructed through abundant hydrogen bond interactions between ligands and waters (O9–H9B $\cdots$ O7 is 3.2312 Å, O9–H9B $\cdots$ O8 is 2.8403 Å, O10–H10A $\cdots$ O7 is 2.8719 Å, O10–H10B $\cdots$ O1 is 2.8363 Å, O10 $\cdots$ H10B–O2 is 3.2319 Å, ∠O9–H9B $\cdots$ O7 is 140°, ∠O9–H9B $\cdots$ O8 is 163°, ∠O10–H10A $\cdots$ O7 is 171°, ∠O10–H10B $\cdots$ O1 is 168°, ∠O10 $\cdots$ H10B–O2 is 135°), as shown in figure 6.

Table 3. Selected H-bond lengths (Å) and angles (°) for **1**–**4**.

Donor–H···Acceptor	D–H	H···A	D···A	D–H···A
Compound **1**				
O(5)–H(5B)···O(6) (i)	0.86	1.97	2.8064	165
O(10)–H(10B)···O(4) (ii)	0.87	2.00	2.8499	168
Compound **2**				
N2···H2–O4 (i)	0.86	2.02	2.7454	142
C3···H3–O3 (ii)	0.93	2.31	3.1512	150
Compound **3**				
N(1)–H(1)···N(1) (i)	0.86	1.86	2.7213(5)	178
N(2)–H(2)···O(5) (ii)	0.86	2.03	2.8891(6)	178
N(2)–H(2)···O(6) (ii)	0.86	2.44	2.9482(6)	119
O(2)–H(2A)···O(3)	0.86	1.57	2.4226(5)	173
N(3)–H(3)···O(3)	0.86	2.43	2.9474(6)	119
N(3)–H(3)···O(4)	0.86	2.03	2.8896(6)	178
N(4)–H(4)···N(4) (ii)	0.86	1.86	2.7201(5)	178
O(7)–H(7A)···O(6)	0.86	1.56	2.4200(5)	172
Compound **4**				
N(2)–H(2A)···O(2) (i)	0.86	1.96	2.7799	158
C(2)–H(2B)···O(1) (i)	0.93	2.47	3.1281	128
C(4)–H(4)···O(2) (ii)	0.93	2.42	3.2728	152

Translation of ARU-code to equivalent position code: for **1**: (i) x, $1/2-y$, $1/2+z$, (ii) x, $1/2-y$, $-1/2+z$; for **2**: (i) $1-x$, $-1/2+y$, $1/2-z$, (ii) x, $-1+y$, z; for **3**: (i) $-x$, $1-y$, z, (ii) $1-x$, $-y$, z; for **4**: (i) $1+x$, $-1+y$, z, (ii) $-x$, $1-y$, $-z$.

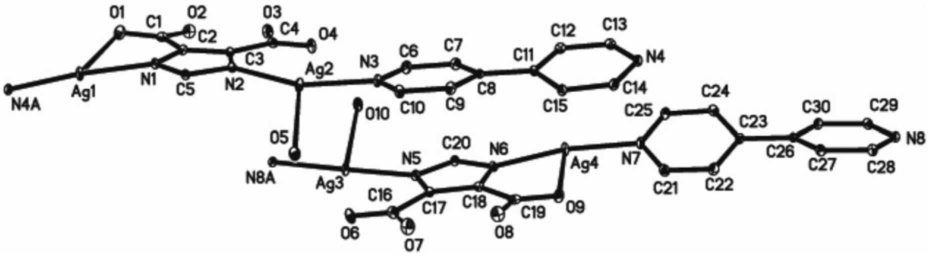

Figure 1. Coordination environment of Ag ions in **1** drawn at 30% probability level. All hydrogens are omitted for clarity.

3.1.4. Cu(Himc)$_2$ (4). Compound **4** is a mononuclear structure, as shown in figure 7. In the presence of Cu^{2+}, *in situ* decarboxylation of 1H-imidazole-4,5-dicarboxylate transforms it into 1H-imidazole-2-carboxylate under hydrothermal conditions [9]. The Cu(II) is four-coordinate by two carboxylate oxygens and two imidazole nitrogens from two Himc$^-$ ligands. Bond lengths of Cu1–N1 and Cu1–O1 are 1.936(3) and 1.963(2) Å, respectively. The angles of N1A–Cu1···N1 and O1A–Cu1···O1 are 180.0° and the angles of N1–Cu1···O1 and N1A–Cu1···O1 are 83.54(11)° and 96.46(11)°, respectively, revealing that Cu(II) is located in a rectangle geometry. The two imidazole rings are non-coplanar, but parallel and the distance between the two imidazole ring planes is 0.269 Å. On the other hand, C–H···O (∠C2–H2···O1 is 128°, C2–O1 is 3.1238 Å, ∠C4–H4···O2 is 152°, C4–O2 is 3.2694 Å) and N–H···O (∠N2–H2A···O2 is 158°,

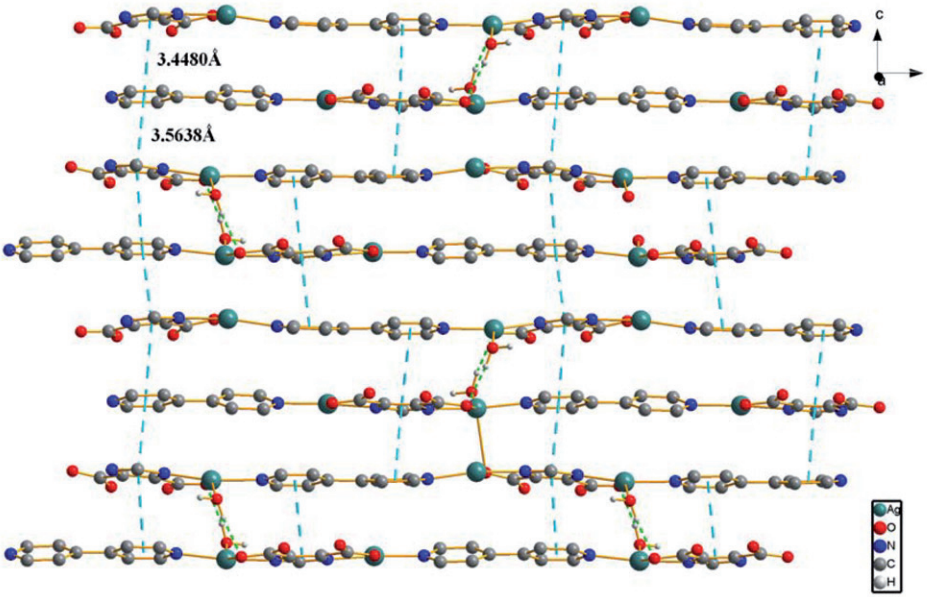

Figure 2. The 2-D network of **1** *via* hydrogen bond interactions and face-to-face π–π stacking interactions.

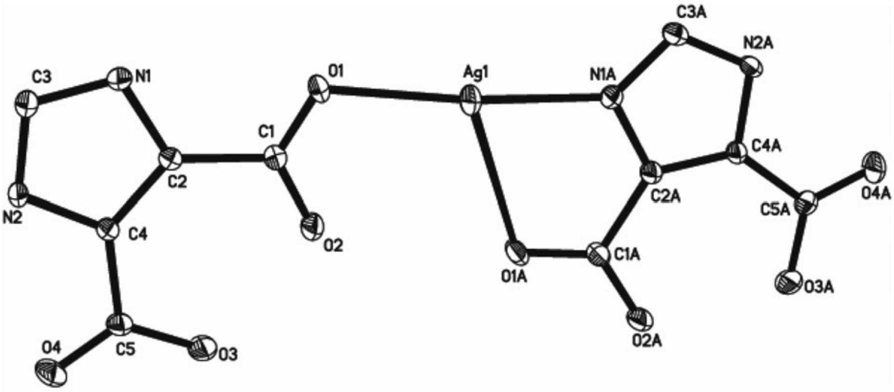

Figure 3. Coordination environment of Ag ions in **2** drawn at 30% probability level. All hydrogens are omitted for clarity.

N2–O2 is 2.7799 Å) intermolecular hydrogen bond interactions bridge adjacent [Cu(Himc)$_2$] units to give (4,4) 2-D layers, depicted in figure 8(a). Furthermore, the face-to-face π–π stacking interactions between adjacent layers at 3.6339 Å generate a 3-D supramolecular architecture, exhibited in figure 9(a). After defining, [Cu(Himc)$_2$] units as a node, the hydrogen bond interactions and π–π stacking interactions as line, the 3-D supramolecular architecture can be simplified to a pcu-type topology (figure 9b). During our submission, this compound has been reported by Kondo *et al.* [10].

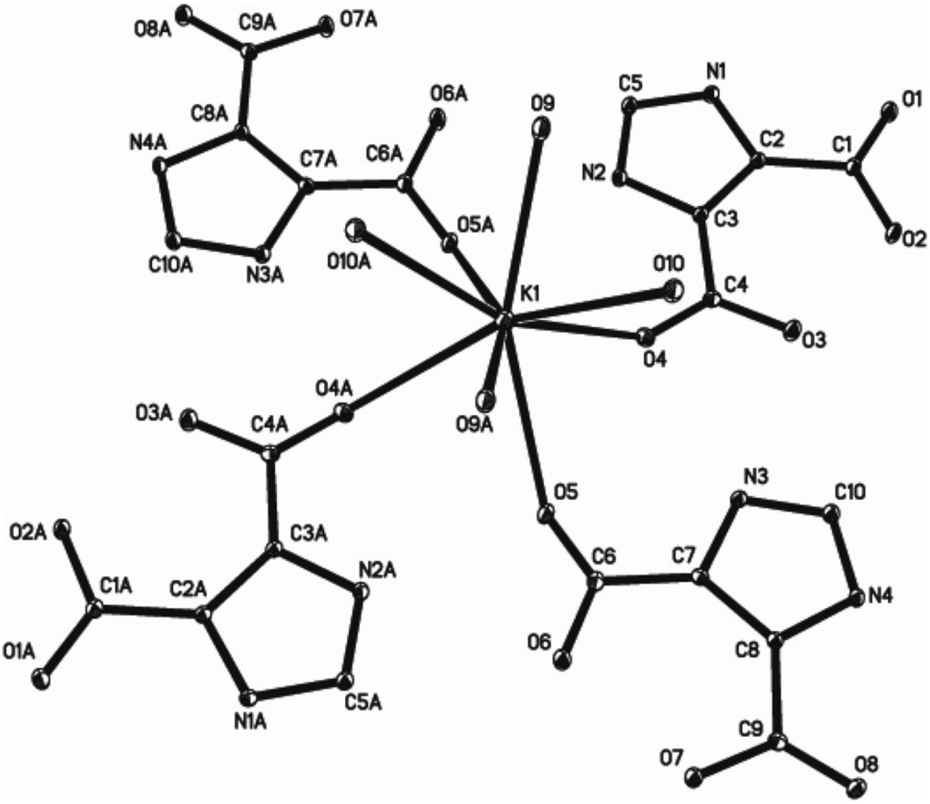

Figure 4. Coordination environment of K$^+$ in **3** drawn at 30% probability level. All hydrogens are omitted for clarity.

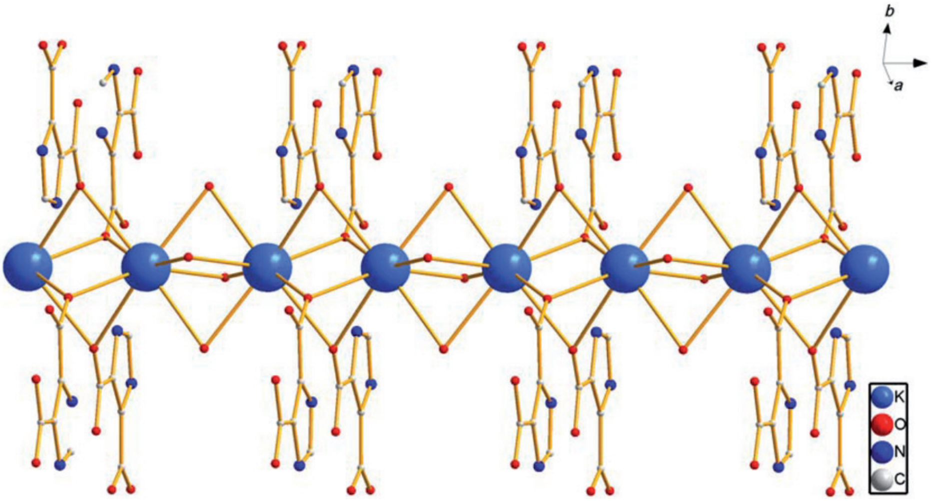

Figure 5. The 1-D chain structure in **3**. All hydrogens are omitted for clarity.

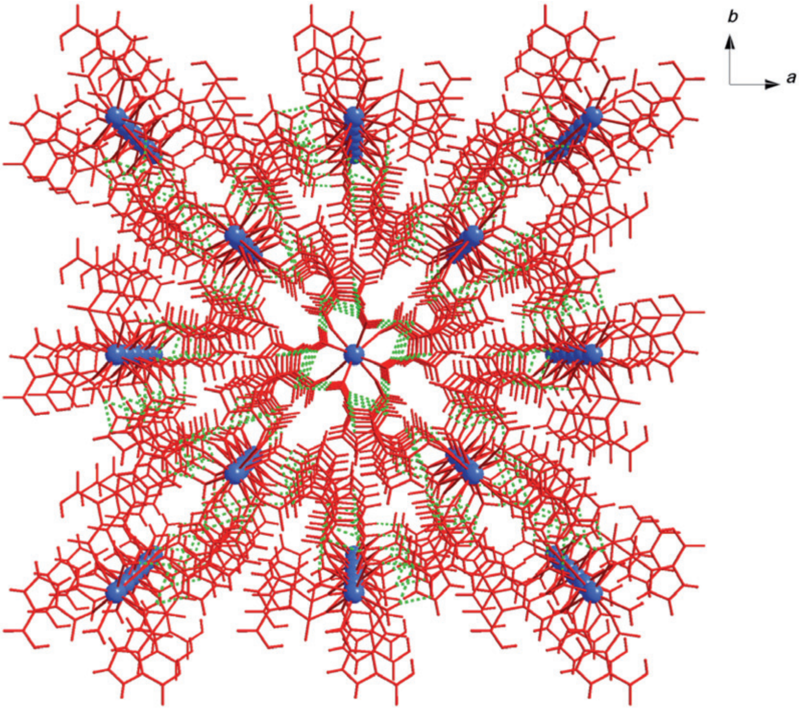

Figure 6. Perspective of the 3-D supramolecular structure of **3** generated *via* hydrogen bonds.

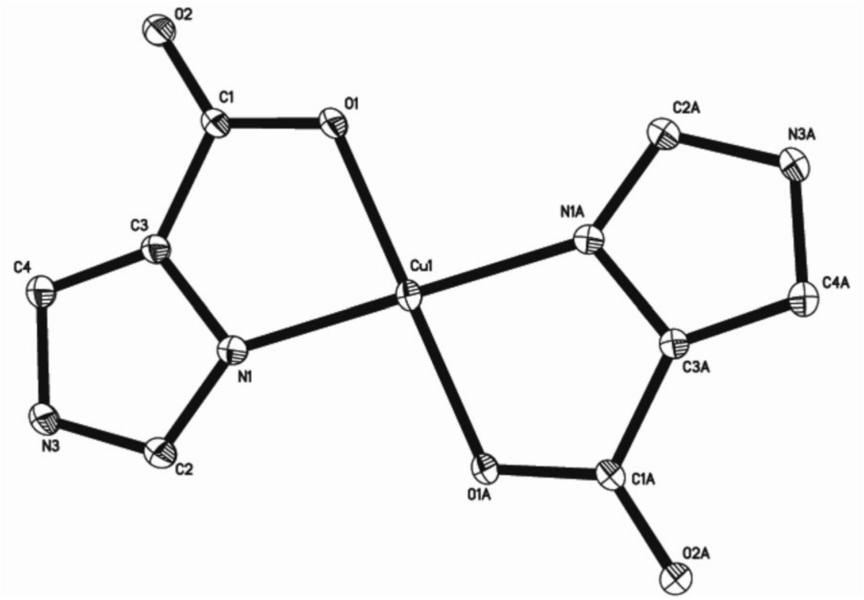

Figure 7. Coordination environment of Cu in **4** drawn at 30% probability level. All hydrogens are omitted for clarity.

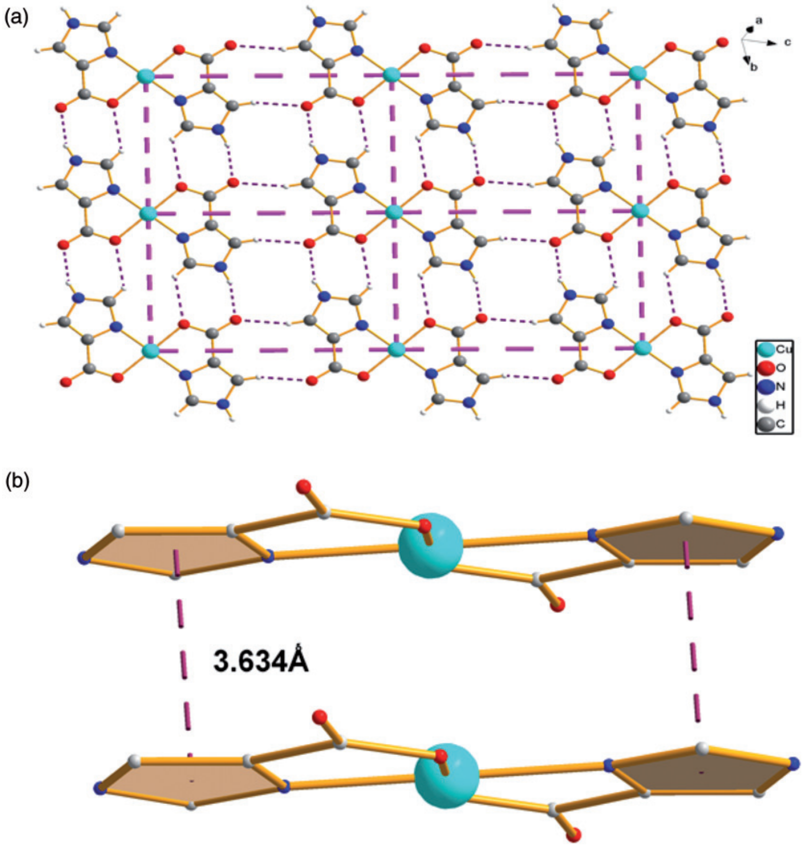

Figure 8. (a) The 2-D layer of **4** *via* intermolecular hydrogen bond interactions; (b) the interlayer face-to-face π–π stacking interactions.

3.2. *Photoluminescent property*

The photoluminescence spectrum of **1** in the solid state at room temperature is shown in figure 10. For **1**, under excitation at 300 nm the emission spectrum shows a broad band ranging from 400 to 500 nm having a maximum emission wavelength at 439 nm. From the photoluminescence spectrum, the photoluminescence of **1** may be due to an intra-ligand transition.

4. Conclusion

Four coordination compounds $[Ag_4(bipy)_2(Himdc)_2(H_2O)_2]_n$ (**1**), $[Ag(H_2imdc)]_n$ (**2**), $[K(H_3imdc)(H_2imdc)(H_2O)_2]_n$ (**3**), and $[Cu(Himc)_2]$ (**4**) have been synthesized applying 4,5-imidazoledicarboxylic acid under hydrothermal conditions. For **1,** two chains arrange in an ABAB manner *via* hydrogen bond interactions and π–π stacking

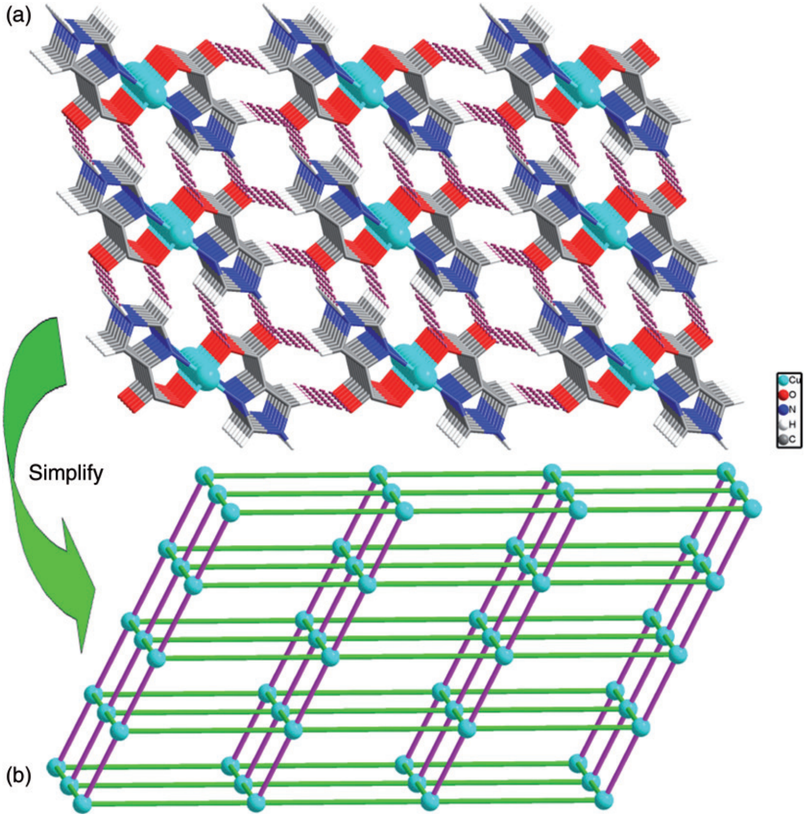

Figure 9. (a) The 3-D supramolecular structure for **4** *via* interlayer π–π stacking and hydrogen bond interactions; (b) the supramolecular structure with pcu-type topology after simplification.

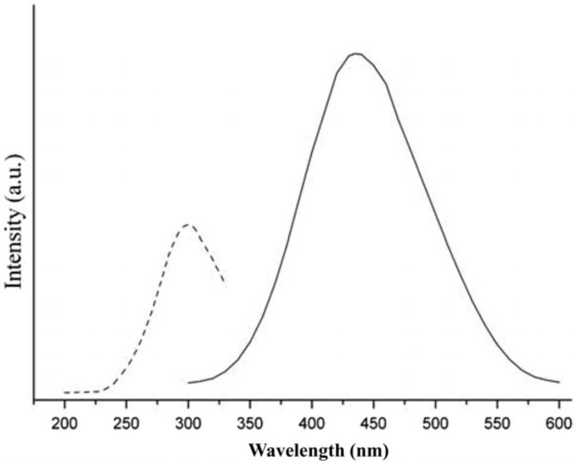

Figure 10. The solid-state photoluminescence spectra of **1** at room temperature (dotted line represents the excitation spectrum; sold line represents the emission spectrum).

interactions generating a 2-D network having a maximum emission wavelength at 439 nm. Compound **2** is not sensitive regarding preparation temperature. In **3**, K_2O_4 cage units are linked to form a 1-D chain which produces a 3-D supramolecular framework *via* hydrogen bond interactions. An *in-situ* decarboxylation occurs resulting in 1H-imidazole-2-carboxylate for **4**, which generated a 3-D supramolecular architecture consisting of a pcu-type topology. This study also demonstrates that variation of the synthesis conditions is critical for the generation of multidimensional frameworks with different structures. Further investigations on such interesting systems will be applied to other MOFs in our future work.

Supplementary material

CCDC no. 780605 (**1**), 780604 (**2**), 780606 (**3**), and 780607 (**4**) contain the supplementary crystallographic data. These data can be obtained *via* the Cambridge Crystallographic Data Centre (deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/deposit).

Acknowledgments

This project was sponsored by NSFC (21071100), SRF for ROCS, SEM., Liaoning BaiQianWan Talents Program, and the Doctor Foundation of Liaoning Province (No. 20071016).

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