Polyhedron 29 (2010) 317-327

Contents lists available at ScienceDirect

# Polyhedron



journal homepage: www.elsevier.com/locate/poly

# Synthesis, characterization and crystal structures of supramolecular complexes of copper(II)(2,2'-biimidazole) induced by inorganic counter anions

Qiong-Hua Jin<sup>a,\*</sup>, Li-Li Zhou<sup>a</sup>, Li-Jun Xu<sup>a</sup>, Yuan-Yuan Zhang<sup>a</sup>, Cun-Lin Zhang<sup>b</sup>, Xiao-Ming Lu<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Capital Normal University, Beijing 100048, PR China

<sup>b</sup> Beijing Key Laboratory for Terahertz Spectroscopy and Imaging, Key Laboratory of Terahertz Optoelectronics, Ministry of Education, Department of Physics, Capital Normal University, Beijing 100048, PR China

#### ARTICLE INFO

Article history: Available online 31 May 2009

Keywords: Supramolecular complexes Copper complexes Biimidazole Crystal structures

#### ABSTRACT

Four new complexes  $[Cu(H_2biim)_2(H_2O)](NO_3)_2$  (1),  $[Cu(H_2biim)_2](ClO_4)_2 \cdot 2DMSO$  (2),  $[Cu(H_2biim)_2]$  $[I_{0.36} \cdot (NO_3)_{0.64}]_2$  (3) and  $\{[Cu(H_2biim)_2(H_2O)](SiF_6)\} \cdot H_2O$  (4)  $(H_2biim = 2,2'-biimdazole, DMSO = dimethyl sulfoxide) have been synthesized and characterized by X-ray diffraction. The different inorganic anions <math>NO_3^-$ ,  $ClO_4^-$ ,  $[I_{0.36} \cdot (NO_3)_{0.64}]^-$  and  $SiF_6^{2-}$  in these complexes lead to different 3D structures. Among them, complex 3 has an interesting 3D porous structure with two  $[I_{0.36} \cdot (NO_3)_{0.64}]^-$  ions as guests in the cavity. Compound 4 was obtained by the reaction of  $Cu(BF_4)_2$  with  $H_2$ biim in water in glass bottle. The robust hydrogen bond of typeV  $R_2^{-1}(7)$  played a key role in the formation of  $SiF_6^{-2-}$  in complex 4.

© 2009 Elsevier Ltd. All rights reserved.

#### 1. Introduction

Supramolecular polymers have received much attention due to their structural diversities and potential applications as new materials. The assembly of supramolecular complexes depends on many factors such as the nature of the metal, ligand, counterion and solvent. The consideration and utilization of the coordination bonds of a transition metal ion, intermolecular hydrogen bonds and  $\pi$ - $\pi$ packing interactions also help to control the molecular arrangement [1-4]. 2,2'-Biimidazole(H<sub>2</sub>biim) is an excellent candidate for building a supramolecular structure involving directed hydrogen bonding interactions. H<sub>2</sub>biim exists in the reported compounds in multifold forms, such as (1) neutral ligand H<sub>2</sub>biim [3]; (2) anion ligand Hbiim<sup>-</sup> [5,6]; (3) biim<sup>2-</sup> [7]; (4) cation H<sub>3</sub>biim<sup>+</sup> [8] and (5) H<sub>4</sub>biim<sup>2+</sup> [9] (Scheme 1). The uncoordinated N–H groups in H<sub>2</sub>biim and its ions participate in various hydrogen bonds with counter anions or other acceptors. Hydrogen bond is regarded as robust power in the construction of supramolecular polymers. Hydrogen bond also provides useful information to understand the complicated process in biological systems [10].

Recently, the authors in [6] discuss the role of counter anions in crystal packing of Ag–H<sub>2</sub>biim complexes. A few Cu–H<sub>2</sub>biim complexes containing inorganic anions, such as  $[Cu(H_2biim)_2(H_2O)]$ -SO<sub>4</sub>·3H<sub>2</sub>O [3],  $[Cu(H_2biim)_2]Cl_2$  [11] and  $[Cu(H_2biim)_2]Br_2$  [12] have been reported, but the role of counter anions has not been studied fully. Here we report the synthesis and characterization of four new Cu(II)–H<sub>2</sub>biim complexes with inorganic counter ions,

\* Corresponding authors.

E-mail address: jinqh@mail.cnu.edu.cn (Q.-H. Jin).

[Cu(H<sub>2</sub>biim)<sub>2</sub>(H<sub>2</sub>O)](NO<sub>3</sub>)<sub>2</sub> (**1**), [Cu(H<sub>2</sub>biim)<sub>2</sub>] (ClO<sub>4</sub>)<sub>2</sub>·2DMSO (**2**), [Cu(H<sub>2</sub>biim)<sub>2</sub>] [I<sub>0.36</sub>·(NO<sub>3</sub>)<sub>0.64</sub>]<sub>2</sub> (**3**), {[Cu(H<sub>2</sub>biim)<sub>2</sub>(H<sub>2</sub>O)](SiF<sub>6</sub>)}·H<sub>2</sub>O (**4**). These four complexes have different 3D structures, due to the diverse type of robust hydrogen bonds, such as type I, II,V R<sub>2</sub><sup>1</sup>(7) and type III, IV R<sub>2</sub><sup>2</sup>(9), formed by different inorganic anions with H<sub>2</sub>biim and solvent molecules. Among them, complex **3** has an interesting 3D porous structure with two [I<sub>0.36</sub>·(NO<sub>3</sub>)<sub>0.64</sub>]<sup>-</sup> ions as guests in the cavity. Thanks to this special structure, it has the potential application as the supramolecular material. In complex **4**, the unexpected anion SiF<sub>6</sub><sup>2-</sup> was not directly coming from the starting materials, just like SiF<sub>6</sub><sup>2-</sup> in [Cd(H<sub>2</sub>biim)<sub>3</sub>]<sub>2</sub>SiF<sub>6</sub>(BF<sub>4</sub>)<sub>2</sub>· 6EtOH [13] and I<sub>2</sub>SO<sub>2</sub><sup>2-</sup> in [Pt(depe)<sub>2</sub>]I<sub>2</sub>SO<sub>2</sub> [14].

# 2. Experimental

#### 2.1. Materials and measurements

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses (C, H, N) were performed on a Vario EL analyzer. Infrared spectra were recorded on a Brucker EQUINOX 55 FT-IR spectrometer photometer as KBr pellets in the 4000–400 cm<sup>-1</sup>. Thermal analyses were formed on a Netzsch STA 449C instrument, with a heating rate of 10 °C/min in nitrogen.

# 2.2. Synthesis of complexes 1-4

## 2.2.1. [Cu(H<sub>2</sub>biim)<sub>2</sub>(H<sub>2</sub>O)](NO<sub>3</sub>)<sub>2</sub> (1)

A mixture of  $Cu(NO_3)_2 \cdot 3H_2O$  (0.2416 g, 1 mmol) and  $H_2biim$  (0.2680 g, 2 mmol) in water (30 ml) was refluxed for 3 h and a clear solution was obtained. The mixture was concentrated under



<sup>0277-5387/\$ -</sup> see front matter  $\odot$  2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2009.05.052



vacuum to a volume of 10 ml. The resulting solution was filtered and allowed to evaporate slowly at room temperature. After three days, dark green crystals were formed. *Anal.* Calc. for  $C_{12}H_{14}N_{10}O_7Cu$ : C, 30.50; H, 3.14; N, 29.71. Found: C, 30.38; H, 2.95; N, 29.54%. IR (KBr disc,  $\nu/cm^{-1}$ ): 3445m, 3122s, 2996s, 2760w, 2456w, 1764w, 1620w, 1525s, 1385s, 1324s, 1250w, 1179s, 1134s, 1095s, 1003m, 940w, 915w, 803m, 763s, 682s, 507w, 446w.

#### 2.2.2. [Cu(H<sub>2</sub>biim)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO (2)

A mixture of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.3705 g, 1 mmol) and H<sub>2</sub>biim (0.2680 g, 2 mmol) in EtOH (30 ml) was refluxed for 6 h and the green colored precipitated product was obtained. The precipitate was dissolved in solution of EtOH/DMSO with the volume ratio of 1:1 (10/10 ml). The resulting solution was filtered and allowed to evaporate in a refrigerator. After a week, green crystals were formed. *Anal.* Calc. for C<sub>16</sub>H<sub>24</sub>N<sub>8</sub>O<sub>10</sub>S<sub>2</sub>Cl<sub>2</sub>Cu: C, 28.05; H, 3.55; N, 16.40. Found: C, 27.95; H, 3.49; N, 3.49%. IR (KBr disc, *v*/cm<sup>-1</sup>): 3431m, 3123s, 2998s, 2761w, 1630w, 1527m, 1429m, 1324m, 1179s, 1120s, 1093s, 1019w, 999w, 947w, 854w, 764s, 682, 627s, 446w.

#### Table 1

Crystallographic data for complexes 1-4.

#### 2.2.3. $[Cu(H_2 biim)_2] [I_{0.36} \cdot (NO_3)_{0.64}]_2$ (3)

A mixture of Cu(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.3080 g, 1 mmol) and KI (0.1660 g, 1 mmol) in water (10 ml) was stirred for 30 min and H<sub>2</sub>biim (0.2680 g, 2 mmol) was added to the mixture which was refluxed for 1 h. The resulting solution was filtered and allowed to evaporate slowly at room temperature. After one week, dark green crystals were formed. *Anal.* Calc. for  $C_{12}H_{12}I_{0.72}N_{9.30}O_{3.84}Cu$ : C, 28.62; H, 2.38; N, 25.88 Found: 28.62; H, 2.41; N, 25.88%. IR (KBr disc,  $\nu/cm^{-1}$ ): 3128s, 1636w, 1528s, 1416s, 1385vs, 1339s, 1301s, 1178s, 1136s, 1099s, 1051m, 1004m, 939w, 870w, 821w, 770s, 714w, 685s, 507m, 445m.

#### 2.2.4. { $[Cu(H_2biim)_2(H_2O)](SiF_6)$ }· $H_2O$ (4)

Cu(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1186 g, 0.5 mmol) was dissolved in 30 ml of water and H<sub>2</sub>biim (0.1340 g, 1 mmol) was added to the resulting solution. The mixture was refluxed for 6 h and a clear solution was obtained. The mixture was concentrated under vacuum to a volume of 20 ml. The resulting solution was filtered and the filtrate was left in air to evaporate to form crystals of **4** after two months. The BF<sub>4</sub><sup>-</sup> ions reacted with the glass container and formed SiF<sub>6</sub><sup>2-</sup> species, which crystallized with the Cu compound as observed by X-ray analysis. *Anal.* Calc. for C<sub>12</sub>H<sub>16</sub>F<sub>6</sub>N<sub>8</sub>O<sub>2</sub>SiCu: C, 28.24; H, 3.14; N, 21.96. Found: C, 28.61; H, 3.26; N, 21.68%. IR (KBr disc;  $\nu/cm^{-1}$ ): 3494m, 3421m, 3278s, 3167m, 3148m, 1676w, 1634w, 1528s, 1429s, 1385m, 1324w, 1249w, 1178m, 1134m, 1115w, 1098s, 1002w, 850w, 832w, 751vs, 684s, 651w, 505w, 474s, 443m.

#### 2.3. Crystal structure determination and refinement

Crystals of **1–4** suitable for single-crystal X-ray diffraction were mounted on a Bruker SMART diffractometer equipped with a CCD area detector with graphite monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). All data were corrected by the semi-empirical method using the sadABS program. The program sAINT [15] was used for integration of the diffraction profiles.

Complex	1	2	3	4
Formula	C <sub>12</sub> H <sub>14</sub> N <sub>10</sub> O <sub>7</sub> Cu	C <sub>16</sub> H <sub>24</sub> N <sub>8</sub> O <sub>10</sub> S <sub>2</sub> Cl <sub>2</sub>	C <sub>12</sub> H <sub>12</sub> I <sub>0.72</sub> N <sub>9.30</sub> O <sub>3.84</sub> C	C12H16N8O2SiF6Cu
Mr	473.87	Cu	u	509.96
Temperature (K)	273(2)	686.99	502.86	298(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	Сс	P1	P2(1)/c	P2(1)/c
Crystal size (mm)	$0.12\times0.10\times0.06$	$0.42\times0.39\times0.17$	$0.43 \times 0.32 \times 0.18$	$0.23\times0.20\times0.12$
a (Å)	19.6043(18)	7.1160(10)	13.7856(13)	10.5177(11)
b (Å)	6.8193(6)	10.2731(13)	6.8603(8)	9.6204(9)
c (Å)	14.2812(13)	10.3289(15)	18.7785(19)	17.971(2)
α (°)	90	113.464(2)	90	90
β(°)	113.5410(10)	97.1830(10)	107.286(2)	95.1750(10)
γ (°)	90	91.5360(10)	90	90
V (Å <sup>3</sup> )	1750.3(3)	684.77(16)	1695.7(3)	1811.0(3)
Ζ	4	1	4	4
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.798	1.666	1.970	1.870
θ Range (°)	25.04	25.00	25.01	25.01
F(0 0 0)	964	351	988	1028
Data/restraint/parameters	1551/1/141	2372/0/208	26.41	3194/0/272
Reflections collected	4407	3569	8110	8825
Independent reflections	1551	2372	2995	3194
Goodness-of-fit on $F^2$	1.125	1.078	1.044	1.072
R <sub>int</sub>	0.0191	0.0118	0.0376	0.0263
$R_1[I > 2\sigma(I)]$	0.0264	0.0334	0.0323	0.0275
$wR_2[I > 2\sigma(I)]$	0.0655	0.0876	0.0765	0.0611
R <sub>1</sub> (all data)	0.0294	0.0419	0.0462	0.0409
wR <sub>2</sub> (all data)	0.0670	0.0960	0.0833	0.0684
Residuals (e Å <sup>-3</sup> )	0.257, -0.321	0.416, -0.351	0.489, -0.367	0.263, -0.281

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

Complex 1					
Cu(1)-N(3) Cu(1)-N(1)#1 N(3)-Cu(1)-N(1) N(3)#1-Cu(1)-N(1)#1 N(3)#1-Cu(1)-O(4)	1.9994(17) 2.0306(18) 82.23(7) 82.23(7) 90.76(6)	$\begin{array}{c} Cu(1)-N(3)\#1\\ Cu(1)-O(4)\\ N(3)\#1-Cu(1)-N(1)\\ N(1)-Cu(1)-N(1)\#1\\ N(1)-Cu(1)-O(4) \end{array}$	1.9994(17) 2.207(3) 97.39(7) 151.05(11) 104.47(6)	$\begin{array}{c} Cu(1)-N(1)\\ N(3)-Cu(1)-N(3)\#1\\ N(3)-Cu(1)-N(1)\#1\\ N(3)-Cu(1)-O(4)\\ N(1)\#1-Cu(1)-O(4) \end{array}$	2.0306(18) 178.49(11) 97.39(7) 90.76(6) 104.47(6)
Complex <b>2</b> Cu(1)–N(1) N(3)–Cu(1)–N(1)#1 Cl(1)–O(1)	2.021(2) 82.23(9) 1.410(3)	Cu(1)-N(3) N(3)#1-Cu(1)-N(3) O(3')-Cl(1)-O(2)	2.018(2) 80.00(9) 52.6(15)	N(3)-Cu(1)-N(1) N(1)#1-Cu(1)-N(1) O(3')-Cl(1)-O(2')	97.77(9) 180.00(11) 114(2)
Complex <b>3</b> Cu(1)-N(1) Cu(1)-N(5) N(7)-Cu(1)-N(3) N(3)-Cu(1)-N(5)	2.000(3) 2.012(3) 178.01(13) 97.89(12)	Cu(1)-N(7) N(1)-Cu(1)-N(7) N(1)-Cu(1)-N(5)	2.004(3) 98.56(12) 166.17(13)	Cu(1)-N(3) N(1)-Cu(1)-N(3) N(7)-Cu(1)-N(5)	2.006(3) 82.14(11) 81.88(12)
Complex <b>4</b> Cu(1)–N(5) Cu(1)–N(1) N(5)–Cu(1)–N(3) N(7)–Cu(1)–N(1) N(7)–Cu(1)–O(1)	2.012(2) 2.028(2) 97.13(8) 97.32(8) 95.49(7)	Cu(1)-N(7) Cu(1)-O(1) N(7)-Cu(1)-N(3) N(3)-Cu(1)-N(1) N(3)-Cu(1)-O(1)	2.023(2) 2.2304(18) 167.78(8) 81.53(8) 96.73(8)	Cu(1)-N(3) N(5)-Cu(1)-N(7) N(5)-Cu(1)-N(1) N(5)-Cu(1)O(1) N(1)-Cu(1)-O(1)	$\begin{array}{c} 2.025(2) \\ 81.66(8) \\ 169.03(9) \\ 94.87(8) \\ 96.10(8) \end{array}$

All structures were solved by direct methods using the SHELXS program of the SHELXTL-97 package and refined with SHELXL [16]. Metal atom centers were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier

syntheses. The final refinements were performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on  $F^2$ . All the hydrogen atoms were first found in difference electron density maps, and then placed in the

#### Table 3

Hydrogen bonding interactions (Å) and angles (°) for complexes 1-4.

D-H	d(D-H)	$d(H \cdot \cdot \cdot A)$	∠DHA	$d(D{\cdots}A)$	А	Symmetry
Complex <b>1</b>						
N(2) - H(7)	0.860	2.03	147.1	2.788(3)	O(3)#2	[-x + 1, y, -z + 3/2]
N(2)-H(7)	0.860	2.64	127.8	3.2354(18)	O(4)#3	[x, -y + 1, z - 1/2]
N(4)-H(8)	0.860	2.06	146.0	2.816(3)	O(3)#2	[-x+1, -y+2, -z+1]
N(4) - H(8)	0.860	2.52	124.7	3.096(3)	O(2)#4	[-x+3/2, y+1/2, -z+3/2]
O(4) - H(4)	0.8499(11)	1.926(6)	170(3)	2.767(2)	O(1)#5	[-x+1, y+1, -z+3/2]
O(4) - H(4)	0.8499(11)	2.55(3)	126(3)	3.126(2)	O(3)#5	
O(4)-H(4)	0.8499(11)	2.600(15)	153(3)	3.381(2)	N(9)#5	
Complex <b>2</b>						
N2-H2	0.860	2.356	129.86	2.981	01	[x, y, z-1]
N2-H2	0.860	2.410	142.55	3.137	05	[-x + 1, -y + 1, -z]
Complex 3						
N2-H2	0.860	2.189	139.04	2.894	05 b	[-x, -y + 1, -z + 1]
N2-H2	0.860	2.857	154.11	3.650	12 a	[-x, -y + 1, -z + 1]
N4-H4	0.860	2.020	173.98	2.876	06 b	[-x, -y + 1, -z + 1]
N4-H4	0.860	2.437	129.62	3.058	05 b	[-x, -y + 1, -z + 1]
N4-H4	0.860	2.630	156.86	3.437	12 a	[-x, -y + 1, -z + 1]
N4-H4	0.860	2.630	156.86	3.437	N10 b	[-x, -y + 1, -z + 1]
N6-H6	0.860	2.255	147.25	3.015	01 b	[-x + 1, y + 1/2, -z + 3/2]
N6-H6	0.860	2.615	112.53	3.050	04 b	[-x + 1, y + 1/2, -z + 3/2]
N6-H6	0.860	2.834	155.77	3.635	I1 a	[-x + 1, y + 1/2, -z + 3/2]
N8-H8	0.860	2.179	153.64	2.974	O3_b	[-x+1, y+1/2, -z+3/2]
N8-H8	0.860	2.447	142.45	3.173	01_b	[-x+1, y+1/2, -z+3/2]
N8-H8	0.860	2.657	162.23	3.486	N9_b	[-x+1, y+1/2, -z+3/2]
N8-H8	0.860	2.657	162.23	3.486	I1_a	[-x + 1, y + 1/2, -z + 3/2]
Complex <b>4</b>						
N2-H2	0.860	2.047	144.68	2.793	F2	[-x+1, -y+1, -z+1]
N2-H2	0.860	2.167	147.03	2.926	F3	[-x+1, -y+1, -z+1]
N4-H4	0.860	1.996	145.37	2.747	F2	[-x+1, -y+1, -z+1]
N4-H4	0.860	2.462	128.67	3.074	02	[x, -y + 3/2, z + 1/2]
N6-H6	0.860	2.108	135.69	2.789	F6	
N6-H6	0.860	2.335	122.22	2.887	F5	[-x+2, y+1/2, -z+1/2]
N8-H8	0.860	2.193	130.77	2.831	F6	
N8-H8	0.860	2.305	143.56	3.040	01	[-x+2, -y+1, -z+1]
01-H1A	0.850	1.905	172.45	2.749	F3	[x, -y + 3/2, z + 1/2]
01-H1B	0.850	2.030	172.62	2.875	02	[-x+1, -y+1, -z+1]
02-H2A	0.850	1.988	173.68	2.834	F1	[x - 1, y, z]
02-H2A	0.850	2.519	114.39	2.972	F6	[x - 1, y, z]
O2-H2B	0.850	2.132	145.06	2.870	F5	[-x + 1, y + 1/2, -z + 1/2]
O2-H2B	0.850	2.348	133.04	2.993	F2	[-x+1, y+1/2, -z+1/2]

calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. Further crystallographic data and experimental details for the structural analyses of all complexes are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations and the hydrogen bonds for complexes **1–4** are summarized in Tables 2 and 3, respectively.

# 3. Results and discussion

# 3.1. Synthesis of the complexes

The synthesis reactions of preparing complexes 1-4 are summarized in Scheme 2. To obtain the four compounds, it was important to take into account the ratio of starting materials, the nature of the solvent and the counter anions. The reaction of CuNO<sub>3</sub> with 2 equiv. of H<sub>2</sub>biim in water gave rise to complex 1. Complex 2 could be prepared by the reaction of CuClO<sub>4</sub> with 2 equiv. of H<sub>2</sub>biim in EtOH, its crystals were obtained by recrystallization from the









IV  $R_2^2(9)$ 

Scheme 3.

 $V R_2^{1}(7)$ 

mixed solvent DMSO and EtOH. When CuNO<sub>3</sub> and KI were used in the presence of 2 equiv. of H<sub>2</sub>biim in water, compound **3** was isolated. When Cu(BF<sub>4</sub>)<sub>2</sub> was treated with 2 equiv. of H<sub>2</sub>biim in water, interestingly, compound **4** including unexpected anion SiF<sub>6</sub><sup>2-</sup> was obtained after two months of evaporation. We agree with the literature [13] that the anion SiF<sub>6</sub><sup>2-</sup> was generated by the reaction of BF<sub>4</sub><sup>-</sup> with the glass container. The long time of crystals growing was also important for all BF<sub>4</sub><sup>-</sup> to be changed to SiF<sub>6</sub><sup>2-</sup>, while BF<sub>4</sub><sup>-</sup> and SiF<sub>6</sub><sup>2-</sup> coexist in [Cd(H<sub>2</sub>biim)<sub>3</sub>]<sub>2</sub>- SiF<sub>6</sub>(BF<sub>4</sub>)<sub>2</sub>. 6EtOH.

#### 3.2. Crystal structures of the complexes

#### 3.2.1. $[Cu(H_2biim)_2(H_2O)](NO_3)_2(1)$

The crystal structure of complex **1** indicates that the unit cell consists of one  $[Cu(H_2biim)_2(H_2O)]^{2+}$  cation and two  $NO_3^-$  anions. The structure of the cation  $[Cu(H_2biim)_2(H_2O)]^{2+}$  in **1** is similar to that in  $[Cu(H_2biim)_2(H_2O)]SO_4$ ·3H<sub>2</sub>O [3] and **4** (Fig 4a). The coordination environment around Cu<sup>II</sup> can be described as a distorted square pyramidal geometry. Four nitrogen atoms of two chelating



Fig. 1a. 1D zigzag chains of 1 along a-axis.

H<sub>2</sub>biim ligands form the basal plane of the pyramidal, and the metal deviates from this plane by 0.267 Å. These two H<sub>2</sub>biim molecules are not coplanar with the dihedral angle of 29.16°, and the two imidazole rings are close to coplanarity with the dihedral angle of 7.63°. In the cation species, the Cu–N bond distances [Cu1-N3 = 1.9994(17) Å, Cu1-N1 = 2.0306(18) Å] are shorter than the Cu–O distance [2.207(3) Å], which agree with the bond lengths of Cu–N and Cu–O in  $[Cu(H_2biim)_2(H_2O)]SO_4 \cdot 3H_2O[3]$ , respectively.

The molecules [Cu(H<sub>2</sub>biim)<sub>2</sub>(H<sub>2</sub>O)](NO<sub>3</sub>)<sub>2</sub> form infinite 1D zigzag chains along the *a*-axis through hydrogen bonds involving the N-H groups of H<sub>2</sub>biim ligands, water molecules and all the NO<sub>3</sub><sup>-</sup> anions. Each nitrate anion forms robust hydrogen bond of type I  $R_2^{1}(7)$  (Scheme 3) (N···O = 2.788(3) and 2.816(3)Å, N-H···O = 146.0° and 147.1°) with each H<sub>2</sub>biim ligand. Each nitrate anion further accepts a hydrogen bond from a coordinated water molecule, with a short  $04 \cdots 01$  separation of 2.767(2)Å and  $O4-H4\cdots O1$  segment close to linearity  $(170(3)^\circ)$ . Two adjacent [Cu(H<sub>2</sub>biim)<sub>2</sub>(H<sub>2</sub>O)](NO<sub>3</sub>)<sub>2</sub> units are further connected to each other via the hydrogen bonds of O4-H4...O1 resulting in a 1D zigzag chains along the *a*-axis (Fig. 1a). A similar pattern is found locally in the complex  $[Zn(H_2biim)_2(H_2O)](NO_3)_2$  [3] The extensive hydrogen bonds and  $\pi$ - $\pi$  interactions between the infinite chains are responsible for the supramolecular open framework structure of **1** along the crystallographic *b*-axis, as depicted in Fig. 1b.

## 3.2.2. [Cu(H<sub>2</sub>biim)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO (**2**)

The asymmetric unit of complex **2** consists of one  $[Cu(H_2biim)_2]^{2+}$  cation, two  $ClO_4^{-}$  anions, and two DMSO molecules. The structure

of  $[Cu(H_2biim)_2]^{2+}$  in **2** is similar to that in **3** (Fig. 3a). The metal center allows the formation of a distorted square-planar with four nitrogen atoms of two chelating H<sub>2</sub>biim ligands. The Cu–N bond distances [Cu-N1 = 2.021(2) and Cu-N3 = 2.018(2) Å] are similar to those in the compound of  $[Cu(H_2biim)_2]Cl_2$  [10][Cu-N11 = 2.010(2), Cu-N31 = 2.036(2) Å]. These distances are observed for H<sub>2</sub>biim–Cu complexes retrieved from the CSD [17]. The bite angle  $[N(3)#1-Cu(1)-N(3) = 80.00(9)^{\circ}]$  generated by the chelating H<sub>2</sub>biim is in the range registered in the CSD so far (N-Cu-N: 78.6–81.4°).

Packing is controlled to a great extent by the ability of coordinated H<sub>2</sub>biim to form hydrogen bonds with counter ions and solvent molecules. As shown in Fig. 2a, where all anions ClO<sub>4</sub>are omitted for clarity, the packing of the units  $[Cu(H_2biim)_2]^{2+}$  is an infinite step-like chain along *b*-axis. Two DMSO molecules and two ClO<sub>4</sub><sup>-</sup> anions are located at two sides of the cation, the hydrogen bonds are formed between the N-H donors of H<sub>2</sub>biim and the oxygen atoms from DMSO or ClO<sub>4</sub><sup>-</sup>. The uncoordinated perchlorate oxygen O1 acts as an acceptor for one of the N-H groups of a H<sub>2</sub>biim ligand with N2···O1 distance 2.981 Å and N2-H2···O1 angle 129.86°. The other connection involves the oxygen of DMSO molecule with both the N-H groups  $(N2 \cdot \cdot \cdot O5 = 3.137 N2 - 1.137 N2)$ H2···O5 = 142.55°, N4···O5 = 2.757, N4−H4···O5 = 154.16°). There are two weak contacts which further stabilize the complex, one is Cu···S (DMSO) (3.448 Å), the other is Cu···O(SiF<sub>6</sub><sup>2-</sup>ClO<sub>4</sub><sup>-</sup>) (2.700 Å). These chains are further assembled into a 3D framework by mutilple hydrogen bonds, weak interactions and  $\pi$ - $\pi$  interactions between H<sub>2</sub>biim ligands (Fig. 2b).



Fig. 1b. Supramolecular framework structure of 1 along b-axis.

3.2.3.  $[Cu(H_2biim)_2] [I_{0.36} (NO_3)_{0.64}]_2$  (**3**)

Complex **3** consists of one  $[Cu(H_2bim)_2]^{2+}$  cation and two  $[I_{0.36} \cdot (NO_3)_{0.64}]^-$  anions (Fig. 3a). The Cu–N bond distances

[Cu(1)-N(1) = 2.000(3), Cu(1)-N(7) = 2.004(3), Cu(1)-N(3) = 2.006(3)and Cu(1)-N(5) = 2.012(3) Å] are similar to those in complex **2**. The bite angle  $[N(7)-Cu(1)-N(5) = 81.88(12)^{\circ}]$  generated by the



**Fig. 2a.** Step-like chain of  $[Cu(H_2biim)_2]$  (ClO<sub>4</sub>)<sub>2</sub>·2DMSO unit along the *b*-axis. All ClO<sub>4</sub><sup>-</sup> were omitted for clarity.



**Fig. 2b.** Packing along *b*-axis. All O atoms in ClO<sub>4</sub><sup>-</sup> were disordered.



Fig. 3a. ORTEP drawing of  $[Cu(H_2biim)_2] [I_{0.36} \cdot (NO_3)_{0.64}]_2$  (3).

chelating of the H<sub>2</sub>biim is found in the upper limit of the range registered in the CSD so far (N–Cu–N: 78.6–81.4°) [17]. In  $[I_{0.36} \cdot (NO_3)_{0.64}]^-$ ,  $I^-$  ion and N atom locate in the same position (occupied 36% by  $I^-$  and 64% by  $NO_3^-$ ), which can be seen from the fact that  $N(H_2 biim) \cdots N(NO_3^-)$  and  $N(H_2 biim) \cdots I$  have the same distances, and  $I^-$  ion does not connect with any O atoms of  $NO_3^-$ .

Each building unit  $[Cu(H_2biim)_2]^{2+}$  in complex **3** links with O atoms, N atoms and I<sup>-</sup> anions of  $[I_{0.36}(NO_3)_{0.64}]^-$  via charge-



Fig. 3b. 1D zigzag chains of 3 along a-axis.

assisted hydrogen bonds N-H···I, N-H···N, N-H···O as well as two types of weak interactions O···Cu (2.772 Å) and I···Cu (3.190 Å) to form a zigzag chain along *a*-axis (Fig 3b). Four types of robust hydrogen bond synthons, namely type I, II R<sub>2</sub><sup>1</sup>(7), type III, IV R<sub>2</sub><sup>2</sup>(9) (Scheme 3) are found in complex **3**. The type II R<sub>2</sub><sup>1</sup>(7) synthon is formed by the the I<sup>-</sup> ion with N-H groups of H<sub>2</sub>biim, and the type IV R<sub>2</sub><sup>2</sup>(9) synthon might be formed through the induction of the type II R<sub>2</sub><sup>1</sup>(7) synthon. To our knowledge, the hydrogen bond of type IV R<sub>2</sub><sup>2</sup>(9) has not been reported before. The adjacent chains are interlinked by multiple hydrogen bonds and  $\pi$ - $\pi$  interactions between H<sub>2</sub>biim ligands to form the 3D porous framework along *b*-axis (Fig. 3c). Each cavity is of the scale  $4.2 \times 13.2$  Å with two clathrate [I<sub>0.36</sub>·(NO<sub>3</sub>)<sub>0.64</sub>]<sup>-</sup> inside. This interesting structure makes the complex possess potential application as the supramolecular material.

## 3.2.4. { $[Cu(H_2biim)_2(H_2O)]$ SiF<sub>6</sub>}·H<sub>2</sub>O (**4**)

Complex **4** consists of a  $[Cu(H_2biim)_2(H_2O)]^{2+}$  cation, a SiF<sub>6</sub><sup>2-</sup> anion and one lattice-water molecule (Fig. 4a). The coordination environment of Cu<sup>II</sup> ion in **4** is very similar to that of complex **1**. The Cu<sup>II</sup> ion is displaced from the  $[Cu(H_2biim)_2]^{2+}$  plane by 0.204 Å. The dihedral angle of the two chelating H<sub>2</sub>biim ligands is 12.29°, while the two imidazole rings are close to coplanarity with the dihedral angle of 2.61°. The Cu–N bond distances are in the range of 2.012(2)–2.028(2) Å. Unlike the SiF<sub>6</sub><sup>2-</sup> in  $[Cd(H_2biim)_3]_2SiF_6(BF_4)_2$ ·6EtOH [13], where all the six Si–F bond distances are equal, the anion SiF<sub>6</sub><sup>2-</sup> in **4** has different Si–F distances which are in the range of 1.6621(18)–1.7087(17) Å.

Each building block  $[Cu(H_2biim)_2(H_2O)]^{2+}$  is connected to two  $SiF_6^{2-}$  anions and each  $SiF_6^{2-}$  is connected with two  $[Cu(H_2biim)_2]$  $(H_2O)$ ]<sup>2+</sup> cations via hydrogen bonds of type V R<sub>2</sub><sup>-1</sup>(7) and O1-H1A···F3 to form a step-like infinite chain along c-axis (Fig. 4b). In the chain, all the aqua ligands are arranged in the same direction (either above or below the  $[Cu(H_2biim)_2]^{2+}$  plane). The chains are further assembled in a head-to-head or a tail-to-tail fashion by N8-H8...01 hydrogen bonds which are constructed by the coordinated water and the N–H group of H<sub>2</sub>biim. The SiF<sub>6</sub><sup>2–</sup> anions are also connected with lattice water molecules through hydrogen bonds O2-H2A···F1, O2-H2B···F5 and O2-H2B···F2. The hydrogen bonds formed by  $SiF_6^{2-}$  with other acceptors in **4** are different from those in [Cd(H<sub>2</sub>biim)<sub>3</sub>]<sub>2</sub>SiF<sub>6</sub>(BF<sub>4</sub>)<sub>2</sub>·6EtOH [11]. The coordinated water molecule in  $[Cu(H_2biim)_2(H_2O)]^{2+}$  is connected with lattice water through hydrogen bond O1-H1B...O2. The cation  $[Cu(H_2biim)_2(H_2O)]^{2+}$ , the anion  $SiF_6^{2-}$  and lattice water are connected by multiple hydrogen bonds as well as  $\pi$ - $\pi$  interactions between H<sub>2</sub>biim and H<sub>2</sub>biim to form a 3D framework (Fig. 4c).

#### 3.3. Discussion of the structures and the strange change of anions

In complexes **1–4**, all the inorganic counter anions NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>,  $[I_{0.36} (NO_3)_{0.64}]^-$  and SiF<sub>6</sub><sup>2-</sup> are uncoordinated. Different anions induce the cation building blocks to form different 3D structures because of their different charge, size and ability of forming hydrogen bond with other acceptors. In **1**, NO<sub>3</sub><sup>-</sup> induces the molecule to form an infinite line along the *a*-axis and then further form a 3D framework. In **2**, ClO<sub>4</sub><sup>-</sup> and DMSO induce the molecule to form an infinite step-like chain along *b*-axis, and further form a 3D structure. The anions NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> are directly coming from the starting materials Cu(NO<sub>3</sub>)<sub>2</sub> and Cu(ClO<sub>4</sub>)<sub>2</sub>. For **3** and **4**,  $[I_{0.36} (NO_3)_{0.64}]^-$  and SiF<sub>6</sub><sup>2-</sup> are obtained by unusual change of inorganic anions, which will be discussed in the following.

In **3**, the existence of unexpected  $[I_{0.36} \cdot (NO_3)_{0.64}]^-$  might be attributed to robust hydrogen bonds of type I–IV and the weak interaction I···Cu, which is similar to the weak interaction Br···Cu in  $[Cu(H_2biim)_2]$  Br<sub>2</sub> [12] and the weak interaction I···S in [Pt (depe)<sub>2</sub>] I<sub>2</sub>SO<sub>2</sub> [14].  $[I_{0.36} \cdot (NO_3)_{0.64}]^-$  helps compound **3** to form



**Fig. 3c.** Hydrogen-bonded porous structure of **3** along *b*-axis with two  $[I_{0.36} (NO_3)_{0.64}]^-$  as guest in the cavity.



Fig. 4a. ORTEP drawing of {[Cu(H<sub>2</sub>biim)<sub>2</sub>(H<sub>2</sub>O)] SiF<sub>6</sub>}·H<sub>2</sub>O (4).

an infinite chain along *a*-axis resulting in an interesting 3D porous structure. The porous structure does not appear in **1**,  $[Cu(H_2biim)_2]Cl_2$  and  $[Cu(H_2biim)_2]Br_2$ .

 $[Cu(H_2biim)_2]Cl_2$  and  $[Cu(H_2biim)_2]Br_2$ . In **4**, the appearance of SiF<sub>6</sub><sup>2-</sup> should be due to the robust hydrogen bonds of type V and hydrogen bond O-H(H<sub>2</sub>O)...F. The anion SiF<sub>6</sub><sup>2-</sup> can induce  $[Cu(H_2biim)_2(H_2O)]^{2+}$  to form a step-like infinite chain along *c*-axis resulting in a stable 3D structure. It was reported that hydrogen bonds between the F atom of  $BF_4^$ and the N–H group of H<sub>2</sub>biim with the unfavorable angle N–H…F (about 120°) cannot directly affect the crystal stability [13].

We suppose that the reaction mechanism of generating  $[I_{0,36}$ ·(NO<sub>3</sub>)<sub>0.64</sub>]<sup>-</sup> and SiF<sub>6</sub><sup>2-</sup> related to the fact that Cu(II) bonded-H<sub>2</sub>biim plays a role of catalyst and the catalyst property might be attribute to the hydrogen bonds.



Fig. 4b. Aquo ligands in the step-like chains of 4 in head-to-head and tail-to-tail arrangement along *c*-axis.

# 3.4. Thermal analysis

The thermal stability of 1, 3 and 4 was examined by thermal analysis (TGA). Because the CuClO<sub>4</sub> is an exploder, we cannot get the TGA data of complex 2. The TG experiments of the powder samples of 1 and 4 were carried out from 20 to 500 °C. The weight loss of  ${\sim}4.8\%$  for 1 and  ${\sim}9.11\%$  for 4 in the range of 37-185 °C corresponds to the loss of the coordinated water molecule of crystallization for 1 (3.8% calc.), the coordinated and lattice water molecule for 4 (7.06% calc.). The weight loss till 270 °C could be associated with the sublimation of the H<sub>2</sub>biim ligand (56.54% calc. for 1 and 53.28% calc. for 4). The residue species are  $CuNO_3$  for **1** and  $CuSiF_6$  for **4**, respectively. The thermal decomposition behavior of complex **3** is studied from 20 to 1000 °C. The weight loss at 274 °C corresponds to the loss of the H<sub>2</sub>biim ligand ( $\sim$ 53.28% calc.). The residue of Cu[I<sub>0.36</sub>·(NO<sub>3</sub>)<sub>0.64</sub>]<sub>2</sub> is decomposed at temperature of 567 °C (13.92% calc.) and the last residue is Cu<sub>2</sub>O.

#### 4. Conclusion

This paper confirms the important role of inorganic counter anions in Cu(II) chemistry, especially those which can form hydrogen bonds like NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>,  $[I_{0.36}\cdot(NO_3)_{0.64}]^-$  and SiF<sub>6</sub><sup>2-</sup>. Hydrogen bonds are believed to play a key role in the generation of unexpected anion SiF<sub>6</sub><sup>2-</sup> and  $[I_{0.36}\cdot(NO_3)_{0.64}]^-$ . The catalytic properties seem to be related to the formation of hydrogen bonds between the Cu-bonded H<sub>2</sub>biim with the inorganic anions and solvent, such as type I, II, V R<sub>2</sub><sup>1</sup>(7) and type III, IV R<sub>2</sub><sup>2</sup>(9) synthons. Our results may help people understand the action of copper enzymes such as the catalytic mechanism in biological systems and the design of new supramolecular materials.

#### Supplementary data

CCDC 702994, 707792, 713515 and 711330 contain the supplementary crystallographic data for compounds **1–4**. These data can



Fig. 4c. 3D framework of 4 along *b*-axis.

be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

#### Acknowledgements

This work has been supported by the National Science Foundation of China (Grant No. 20871085), the Committee of Education of Beijing Foundation of China (Grant No. KM200610028006), the Project sponsored by SRF for ROCS and SEM, the subsidy of Beijing Personnel Bureau, National Keystone Basic Research Program (973 Program) under Grant Nos. 2007CB310408, 2006CB302901, State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences.

# References

 A.K. Ghosh, A.D. Jana, D. Ghoshal, G. Mostafa, N. Ray Chaudhuri, Cryst. Growth Des. 6 (2006) 701.

- [2] Y.R. Zhong, M.L. Cao, H.J. Mo, B.H. Ye, Cryst. Growth Des. 8 (2008) 2282.
- [3] R.L. Sang, L. Xu, Polyhedron 25 (2006) 2167.
- [4] D. Ghoshal, A.K. Ghosh, T.K. Maji, T.-H. Lu, E. Zangrando, G. Mostafa, N. Ray Chaudhuri, Cryst. Growth Des. 5 (2005) 941.
- [5] S. Derossi, H. Adams, M.D. Ward, Dalton Trans. (2007) 33.
- [6] A. Mayboroda, P. Comba, H. Pritzkow, G. Rheinwald, H. Lang, G.v. Koten, Eur. J. Inorg. Chem. (2003) 1703.
- [7] R.L. Sang, L. Xu, Eur. J. Inorg. Chem. (2006) 1260.
- [8] Y.M. Fu, Y.H. Zhao, Y.Q. Lan, Y. Wang, Y.Q. Qiu, K.Z. Shao, Z.M. Su, Inorg. Chem. Commun. 10 (2007) 720.
- [9] S. Belanger, A.L. Beauchamp, Acta Crystallogr., Sect. C 52 (10) (1996) 2588.
  [10] B.B. Ding, Y.Q. Weng, Y. Cui, X.M. Chen, B.H. Ye, Supramol. Chem. 17 (2005) 475.
- [11] R. Atencio, K. Ramrez, J.A. Reyes, T. Gonzalez, P. Silva, Inorg. Chim. Acta 358 (2005) 520.
- [12] L.N. Yang, J. Li, J.J. Liu, H. Jiao, F.X. Zhang, Chin. J. Inorg. Chem. 23 (2007) 133.
- [13] L.M. Gruia, F.D. Rochon, A.L. Beauchamp, Inorg. Chim. Acta 360 (2007) 1825.
- [14] I. Nagasawa, H. Amita, H. Kitagawa, Chem. Commun. (2009) 204.
- [15] G.M. Sheldrick, SHELXS-97 and SHELXL-97, Software for Crystal Structure Analysis, Siemens Analytical X-ray Instruments Inc., Wisconsin, Madison, USA, 1997.
- [16] G.M. Sheldrick, SHELXTL NT Version 5.1, Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [17] The Cambridge Structural Data Base: F.H. Allen, Acta Crystallogr., Sect. B 58 (2002) 380.