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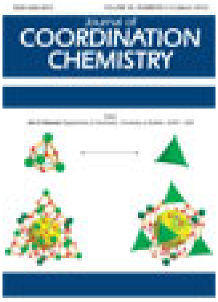

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Syntheses, structures, and properties of four Cu(II) complexes containing 2-(1H-imidazol-1-methyl)-1H-benzimidazole ligand

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Syntheses, structures, and properties of four Cu(II) complexes containing 2-(1*H*-imidazol-1-methyl)-1*H*-benzimidazole ligand

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Four Cu(II)-containing complexes based on 2-(1*H*-imidazol-1-methyl)-1*H*-benzimidazole (imb), $[Cu_2(imb)_2Cl_4]\cdot 2CH_3OH$ (**1**), $\{[Cu(imb)(bdic^{2-})]\cdot 1.5H_2O\cdot DMF\}_n$ (**2**), $\{[Cu(imb)(bdic^{2-})]\cdot 2H_2O\}_n$ (**3**), and $\{[Cu_3(imb)_2(Hbdc^{3-})_2]\cdot 2H_2O\}_n$ (**4**), where $H_2bdic = $ 1,3-benzenedicarboxylic acid and $H_4bdc = $ 1,2,4,5-benzenetetracarboxylic acid, have been synthesized and characterized by single-crystal diffraction. Dinuclear **1** is isolated by the reaction of imb with $CuCl_2\cdot 2H_2O$. When H_2bdic is added in the reaction with the other experimental conditions unchanged, **2** with a different structure is obtained. The $[Cu_2(imb)_2]$ dinuclear units are linked through $bdic^{2-}$ groups to form a 2-D structure. The imb reacts with $CuCl_2\cdot 2H_2O$ and H_2bdic at 80°C to give **3**, which exhibits a 2-D (4,4) network. With the replacement of H_2bdic with H_4bdc in the above reaction, **4** is formed featuring a 2-D structure in which $Hbdc^{3-}$ is a six-connecting group. Their IR spectra and thermogravimetric analyses are also investigated.

Keywords: Copper complex; 2-(1*H*-imidazol-1-methyl)-1*H*-benzimidazole; Crystal structure; Thermogravimetric analysis

1. Introduction

Design and construction of complexes with multidimensional structures are of interest due to their fascinating structures and potential applications as functional materials [1–5]. A large number of complexes have been reported but the exploration of synthetic strategies and routines is still a long-term challenge [6]. The structure of the framework is influenced by ligands, anions, temperature, geometric requirements of metal ions, etc. [7]. Ligands and anions play an important role in the construction of complexes with flexible ligands, since they have variable coordination modes and can adopt a variety of conformations according to restrictions imposed by the coordination geometry of the metal ions [8]. For instance, flexible multidentate ligands containing imidazole, benzimidazole, triazole, and benzotriazole have been widely employed to construct complexes with fascinating architectures and interesting properties [9]. Anions, especially carboxylates, are effective for constructing diverse complexes [4, 10, 11]

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with the number of the carboxylates, the positions of the carboxylates, and coordination to metals important [8]. For example, 1,2-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid, 1,2,3-benzenetricarboxylic acid, 1,3,5-benzenetricarboxylic acid, and 1,2,4,5-benzenetetracarboxylic acid assemble many attractive coordination architectures [12].

In this work, we select a flexible multidentate *N*-heterocyclic compound 2-(1*H*-imidazol-1-methyl)-1*H*-benzimidazole (imb) and investigate the effect of anions and temperature on the final structures. Four new complexes, $[Cu_2(imb)_2Cl_4] \cdot 2CH_3OH$ (**1**), $\{[Cu(imb)(bdic^{2-})] \cdot 1.5H_2O \cdot DMF\}_n$ (**2**), $\{[Cu(imb)(bdic^{2-})] \cdot 2H_2O\}_n$ (**3**), and $\{[Cu_3(imb)_2(Hbdc^{3-})_2] \cdot 2H_2O\}_n$ (**4**) ($H_2bdic = $ 1,3-benzenedicarboxylic acid, $H_4bdc = $ 1,2,4,5-benzenetetracarboxylic acid), are obtained and characterized by infrared (IR), thermogravimetric analysis (TGA), and single-crystal X-ray diffraction.

2. Experimental

2.1. *General information and materials*

The ligand 2-(1*H*-imidazol-1-methyl)-1*H*-benzimidazole (imb) was synthesized according to the literature method [13, 14]. All chemicals were commercially available and used without purification. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets from 400 to 4000 cm^{-1}. Elemental analyses were carried out on a FLASH EA 1112 elemental analyzer. TG measurements were performed by heating the sample from 30°C to 530°C (or 560°C, 590°C, 850°C) at a rate of 10°C min^{-1} in air on a NETZSCH STA 409 PC/PG differential thermal analyzer.

2.2. *Synthesis of* $[Cu_2(imb)_2Cl_4] \cdot 2CH_3OH$ *(1)*

A methanol solution (5 mL) of imb (0.1 mmol) was added dropwise into 3 mL methanol solution of $CuCl_2 \cdot 2H_2O$ (0.1 mmol) to give a clear solution. The mixture was put aside at room temperature for 4 weeks, and then a large number of blue block crystals were obtained. Anal. Calcd for $C_{24}H_{28}Cl_4Cu_2N_8O_2$ (%): C, 39.52; H, 3.87; N, 15.36. Found (%): C, 39.84; H, 3.75; N, 15.47. IR (KBr, cm^{-1}): 3448(m), 3128(w), 1623(m), 1523(s), 1460(m), 1425(w), 1336(w), 1282(m), 1235(m), 1097(s), 1051(w), 1027(w), 951(w), 846(m), 749(s), 651(m), 617(w), 482(w), 437(w).

2.3. *Synthesis of* $\{[Cu(imb)(bdic^{2-})] \cdot 1.5H_2O \cdot DMF\}_n$ *(2)*

A methanol solution (5 mL) of imb (0.1 mmol) and H_2bdic (0.1 mmol) was added dropwise into 3 mL methanol solution of $CuCl_2 \cdot 2H_2O$ (0.1 mmol), then 1 mL DMF was added to give a light blue solution. The mixture was put aside at room temperature for 6 weeks, and then a large number of blue block crystals were obtained. Anal. Calcd for $C_{22}H_{24}CuN_5O_{6.5}$ (%): C, 50.24; H, 4.60; N, 13.31. Found (%): C, 49.97; H, 4.75; N, 13.07. IR (KBr, cm^{-1}): 3435(s), 3134(m), 2922(w), 2787(w), 1667(s), 1620(s), 1607(w), 1561(m), 1383(s), 1344(s), 1233(m), 1092(m), 1051(w), 868(w), 747(s), 655(m), 623(w), 481(w).

2.4. *Synthesis of* $\{[Cu(imb)(bdic^{2-})]\cdot 2H_2O\}_n$ *(3)*

A mixture of $CuCl_2 \cdot 2H_2O$ (0.1 mmol), H_2bdic (0.1 mmol), imb (0.1 mmol), and water (10 mL) was placed in a 25 mL Teflon-lined stainless steel vessel and heated at 80°C for 72 h, then cooled to room temperature. Blue rod crystals were collected, washed with distilled water, and dried in air. Anal. Calcd for $C_{19}H_{18}CuN_4O_6$ (%): C, 49.40; H, 3.93; N, 12.13. Found (%): C, 49.52; H, 3.81; N, 12.47. IR (KBr, cm^{-1}): 3466(m), 3140(w), 2370(w), 1608(s), 1557(s), 1527(w), 1465(w), 1436(w), 1394(w), 1361(s), 1279(m), 1241(w), 1109(m), 1030(w), 953(w), 868(w), 750(s), 725(w), 657(m), 622(w), 577(w).

2.5. *Synthesis of* $\{[Cu_3(imb)_2(Hbdc^{3-})_2]\cdot 2H_2O\}_n$ *(4)*

The preparation of **4** was similar to that of **3** except that H_4bdc was used instead of H_2bdic. Blue block crystals of **4** were collected. Anal. Calcd for $C_{42}H_{30}Cu_3N_8O_{18}$ (%): C, 44.83; H, 2.69; N, 9.96. Found (%): C, 44.97; H, 2.65; N, 9.77. IR (KBr, cm^{-1}): 3461(m), 3152(w), 1635(s), 1543(w), 1486(m), 1466(w), 1427(w), 1381(s), 1324(m), 1283(m), 1188(w), 1135(w), 1038(m), 930(w), 846(w), 743(m), 709(m), 669(m), 628(w), 597(w).

2.6. *Single-crystal structure determination*

A suitable single crystal of each complex was carefully selected and glued to a thin glass fiber. Crystal structure determinations by X-ray diffraction were performed on a Rigaku Saturn 724 CCD area detector with a graphite monochromator for the X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. The data were collected in ω scan mode at 293(2) K; the crystal-to-detector distance was 45 mm. An empirical absorption correction was applied. The data were corrected for Lorentz-polarization effects. The structures were solved by direct methods and completed by difference Fourier syntheses and refined by full-matrix least-squares using SHELXS-97 [15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined using a riding model. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restraints. Crystallographic parameters and structural refinement for these complexes are summarized in table 1. Selected bond lengths and angles of the four complexes are listed in table 2 and H-bonds in table 3.

3. Results and discussion

3.1. *IR spectroscopy of 1–4*

IR spectra show bands at 3448 cm^{-1} for **1**, 3435 cm^{-1} for **2**, 3466 cm^{-1} for **3**, and 3461 cm^{-1} for **4** attributed to O–H stretch. Absorptions at 3128 cm^{-1} for **1**, 3134 cm^{-1} for **2**, 3140 cm^{-1} for **3**, and 3152 cm^{-1} for **4** can be attributed to Ar–H stretch. Absorptions at 749 and 651 cm^{-1} for **1** could be associated with modes involving chlorides. Separations (Δ) between ν_a (COO) and ν_s (COO) are different for the unidentate and bridging complexes. In **2**, carboxylates exhibit ν_a (COO) and ν_s (COO)

Table 1. Crystal data and structural refinement of **1–4**.

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{24}H_{28}Cl_4Cu_2N_8O_2$	$C_{22}H_{24}CuN_5O_{6.5}$	$C_{19}H_{18}CuN_4O_6$	$C_{42}H_{30}Cu_3N_8O_{18}$
Formula weight	729.42	526.00	461.91	1125.36
Temperature (K)	293(2)	293(2)	293(2)	273(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*P2(1)/c*	*P2(1)/c*	*C2/c*
Unit cell dimensions (Å, °)				
a	43.561(9)	9.4939(19)	10.015(2)	11.691(2)
b	9.810(2)	20.064(4)	16.727(3)	18.186(4)
c	14.406(3)	12.907(3)	13.349(5)	20.347(4)
α	90	90	90	90
β	91.08(3)	108.23(3)	118.27(2)	102.20(3)
γ	90	90	90	90
Volume (Å^3), *Z*	6155(2), 8	2335.2(9), 4	1969.5(9), 4	4228.6(15), 4
F(000)	2960	1088	948	2276
Crystal sizes (mm^3)	$0.19 \times 0.19 \times 0.12$	$0.21 \times 0.18 \times 0.16$	$0.14 \times 0.12 \times 0.09$	$0.22 \times 0.21 \times 0.19$
R(int)	0.0563	0.0339	0.0429	0.0422
Data/restraints/parameters	5372/1/348	4349/0/316	3655/0/271	4040/0/322
Goodness-of-fit on F^2	1.074	1.095	1.092	1.077
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0724$	$R_1 = 0.0450$	$R_1 = 0.0423$	$R_1 = 0.0461$
	$wR_2 = 0.1986$	$wR_2 = 0.1180$	$wR_2 = 0.1007$	$wR_2 = 0.1076$
R indices (all data)	$R_1 = 0.0833$	$R_1 = 0.0488$	$R_1 = 0.0510$	$R_1 = 0.0529$
	$wR_2 = 0.2093$	$wR_2 = 0.1209$	$wR_2 = 0.1061$	$wR_2 = 0.1127$

at 1620 and 1383 cm^{-1} ($\Delta = 217$ cm^{-1}), comparable to those of unidentate complexes [16]. Similar to **2**, carboxylates in **3** also coordinate to Cu(II) unidentate, and the separation (Δ) between ν_a (COO) and ν_s (COO) is 214 cm^{-1} (1608 cm^{-1}, 1394 cm^{-1}). In **4**, unidentate and bridging carboxylates are observed; the unidentate carboxylates exhibit ν_a (COO) and ν_s (COO) at 1635 and 1381 cm^{-1} ($\Delta = 254$ cm^{-1}), whereas the bridging carboxylates exhibit ν_a (COO) and ν_s (COO) at 1543 and 1427 cm^{-1} ($\Delta = 116$ cm^{-1}). The above analyses are consistent with the results of the X-ray diffraction.

3.2. *Crystal structures of complexes*

3.2.1. Crystal structure of [$Cu_2(imb)_2Cl_4$]·2CH_3OH (1). The imb reacts with $CuCl_2 \cdot 2H_2O$ to give **1** at room temperature. Single-crystal X-ray diffraction reveals that it crystallizes in monoclinic *C2/c* space group. There are two Cu(II) ions, two imb, four coordinated chlorides, and two uncoordinate methanol molecules in the asymmetric unit. As shown in figure 1(a), both Cu1 and Cu2 adopt slightly distorted quadrangular coordination. Each Cu1 is four-coordinate with two nitrogen atoms from two imb (Cu1–N3 = 1.987(5), Cu1–N5 = 1.980(5) Å) and two chlorides (Cu1–Cl1 = 2.246(2), Cu1–Cl2 = 2.259(2) Å). The environment of Cu2 is similar with Cu1, but with different bond lengths and bond angles. The Cu–Cl and Cu–N bond lengths are similar to the reported literature [17]. Two imb ligands in *cis*-conformation (N1–C4–C5–N3 = 26.3°, N5–C15–C16–N7 = 24.8°) link two Cu(II) ions to form a dinuclear complex with Cu1–Cu2 distance of 5.237 Å. Three kinds of hydrogen bonds exist between methanol molecules, between dinuclear units, and between methanol molecules

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

1					
Cu(1)–N(5)	1.980(5)	Cu(1)–N(3)	1.987(5)	Cu(1)–Cl(1)	2.246(2)
Cu(1)–Cl(2)	2.259(2)	Cu(2)–N(1)	1.979(5)	Cu(2)–N(7)	1.980(4)
Cu(2)–Cl(4)	2.2462(19)	Cu(2)–Cl(3)	2.2767(17)	N(5)–Cu(1)–N(3)	158.6(2)
N(5)–Cu(1)–Cl(1)	94.23(16)	N(3)–Cu(1)–Cl(1)	90.59(17)	N(5)–Cu(1)–Cl(2)	93.75(16)
N(3)–Cu(1)–Cl(2)	91.37(17)	Cl(1)–Cu(1)–Cl(2)	152.80(14)	N(1)–Cu(2)–N(7)	158.6(2)
N(1)–Cu(2)–Cl(4)	92.87(15)	N(7)–Cu(2)–Cl(4)	93.75(14)	N(1)–Cu(2)–Cl(3)	93.94(15)
N(7)–Cu(2)–Cl(3)	89.99(14)	Cl(4)–Cu(2)–Cl(3)	151.20(8)		
2					
Cu(1)–O(4)#1	1.951(2)	Cu(1)–O(1)	1.9477(19)	Cu(1)–N(1)	1.986(2)
Cu(1)–N(3)#2	1.996(2)				
O(4)#1–Cu(1)–O(1)	160.83(9)	O(4)#1–Cu(1)–N(1)	89.82(9)	O(1)–Cu(1)–N(1)	91.90(9)
O(4)#1–Cu(1)–N(3)#2	90.05(9)	O(1)–Cu(1)–N(3)#2	92.77(9)	N(1)–Cu(1)–N(3)#2	166.12(10)
3					
Cu(1)–O(2)	1.947(2)	Cu(1)–O(3)#1	1.962(2)	Cu(1)–N(1)	1.967(2)
Cu(1)–N(3)	1.991(2)	O(2)–Cu(1)–O(3)#1	152.75(10)	O(2)–Cu(1)–N(1)	91.45(9)
O(3)#1–Cu(1)–N(1)	91.78(9)	O(2)–Cu(1)–N(3)	97.20(9)	O(3)#1–Cu(1)–N(3)	92.08(9)
N(1)–Cu(1)–N(3)	152.93(11)				
4					
Cu(1)–O(2)#1	1.988(2)	Cu(1)–O(6)#2	1.990(2)	Cu(1)–O(5)#3	2.000(2)
Cu(1)–O(1)	2.029(2)	Cu(1)–N(3)	2.150(3)	Cu(1)–Cu(1)#1	2.7328(10)
Cu(2)–O(3)#4	1.921(2)	Cu(2)–O(3)	1.921(2)	Cu(2)–O(7)#3	1.930(2)
Cu(2)–O(7)#5	1.929(2)	O(2)–Cu(1)#1	1.988(2)	O(5)–Cu(1)#6	2.000(2)
O(6)–Cu(1)#7	1.990(2)	O(7)–Cu(2)#8	1.929(2)	O(2)#1–Cu(1)–O(6)#2	91.09(10)
O(2)#1–Cu(1)–O(5)#3	168.21(9)	O(6)#2–Cu(1)–O(5)#3	86.37(10)	O(2)#1–Cu(1)–O(1)	85.67(10)
O(6)#2–Cu(1)–O(1)	163.62(9)	O(5)#3–Cu(1)–O(1)	93.54(10)	O(2)#1–Cu(1)–N(3)	91.70(10)
O(6)#2–Cu(1)–N(3)	100.53(10)	O(5)#3–Cu(1)–N(3)	100.09(10)	O(1)–Cu(1)–N(3)	95.61(10)
				O(3)#4–Cu(2)–O(3)	90.43(14)
O(3)#4–Cu(2)–O(7)#3	175.34(10)	O(3)–Cu(2)–O(7)#3	87.04(10)	O(3)#4–Cu(2)–O(7)#5	87.04(10)
O(3)–Cu(2)–O(7)#5	175.34(10)	O(7)#3–Cu(2)–O(7)#5	95.75(14)		

Symmetry transformations used to generate equivalent atoms: For **2**: #1: $x-1, y, z$; #2: $-x+1/2, y+1/2, -z+3/2$. For **3**: #1: $-x+1, y-1/2, -z+1/2$. For **4**: #1: $-x+1, y, -z+3/2$; #2: $x-1/2, y-1/2, z$; #3: $-x+3/2, y-1/2, -z+3/2$; #4: $-x+2, y, -z+3/2$; #5: $x+1/2, y-1/2, z$; #6: $-x+3/2, y+1/2, -z+3/2$; #7: $x+1/2, y+1/2, z$; #8: $x-1/2, y+1/2, z$.

Table 3. Hydrogen bonds of **1**–**4**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	(D–H···A) (°)
1				
N(4)–H(4C)···O(1)#1	0.81	2.03	2.826(14)	169.3
N(8)–H(8B)···Cl(3)#2	0.86	2.48	3.222(5)	145.2
O(1)–H(1)···O(1)#3	0.79	2.25	2.79(2)	127.1
2				
N(4)–H(4A)···O(5)	0.86	1.90	2.753(4)	169.0
N(8)–H(8B)···Cl(3)#2	0.85	1.98	2.811(3)	164.6
O(5)–H(2W)···O(1)#5	0.85	2.09	2.891(3)	157.7
3				
N(4)–H(4C)···O(5)#4	0.86	1.93	2.776(3)	165.6
O(6)–H(3W)···O(1)#1	0.85	2.28	3.128(5)	179.9
O(5)–H(2W)···O(2)	0.96	2.19	3.072(3)	151.3
O(6)–H(4W)···O(4)#6	0.89	1.93	2.812(4)	170.4
O(5)–H(1W)···O(1)#5	0.75	2.05	2.794(4)	175.7
4				
O(8–H(8)···O(7)#1	0.82	2.51	2.993(4)	119.2
O(9)–H(1W)···O(4)#4	0.85	2.00	2.851(5)	175.3
N(4)–H(4C)···O(4)#9	0.86	1.99	2.835(4)	169.7
O(8)–H(8)···N(1)#8	0.82	2.08	2.711(4)	133.7

Symmetry transformations used to generate equivalent atoms: For **1**: #1: x, $y+1$, $z-1$; #2: $-x+1/2$, $y-1/2$, $-z+1/2$; #3: $-x$, y, $-z+3/2$. For **2**: #2: $-x+2$, $-y$, $-z+2$; #5: $-x+1$, $-y$, $-z+2$. For **3**: #1: $x+1$, y, z; #4: $-x-1$, $y-1/2$, $-z+1/2$; #5: x, $-y-1/2$, $z-1/2$; #6: $x+2$, $-y-1/2$, $z+1/2$. For **4**: #1: $-x+1$, y, $-z+3/2$; #4: $-x+2$, y, $-z+3/2$; #8: $x-1/2$, $y+1/2$, z; #9: $x-1/2$, $-y+1/2$, $z-1/2$.

and dinuclear units. $Cu_2(imb)_2Cl_4$ units are connected by these hydrogen bonds and π–π interactions between benzimidazole rings which are parallel to each other and have an interplanar distance of 3.4537 Å leading to the 3-D structure (figure 1b). Although these interactions are weak compared to coordination bonds, they are important in the complex assembly.

3.2.2. Crystal structure of $\{[Cu(imb)(bdic^{2-})]\cdot 1.5H_2O\cdot DMF\}_n$ (2). When the mixture of imb and H_2bdic are added into solution of $CuCl_2\cdot 2H_2O$, **2** with a different structure than **1** is obtained. In **2**, 1,3-benzenedicarboxylates take the place of chlorides of **1**. As illustrated in figure 2(a), Cu(II) coordinates two nitrogen donors (N1, N3A) from two imb ligands and two unidentate carboxylate oxygen atoms from two bdic^{2-} groups. The Cu–N bond lengths (1.986(2), 1.996(2) Å) are similar to those in **1** and Cu–O bond lengths (1.9477(19), 1.951(2) Å) are close to those in $[Cu(\mu_2\text{-hep})(\text{hep-H})]_2\cdot 2PF_6$ (hep-H = 2-(2-hydroxyethyl)pyridine) [18]. The bond angles around the Cu(II) ion are 89.82°(9), 90.05°(9), 91.90°(9), 92.77°(9), 160.83°(9), and 166.12°(10), respectively. So Cu(II) exhibits distorted quadrangular coordination. Similar to **1**, imb are *cis* (N1–C4–C5–N3 = 41.9°) and coordinate to Cu(II) to generate dinuclear units $[Cu_2(imb)_2]$ with Cu1–CuA distance of 4.940 Å. These units are further linked by bdic^{2-} groups to furnish a 2-D layer (figure 2b). The π–π interactions between benzimidazole rings of adjacent layers can further stabilize the structure of **2** in the solid state, and the

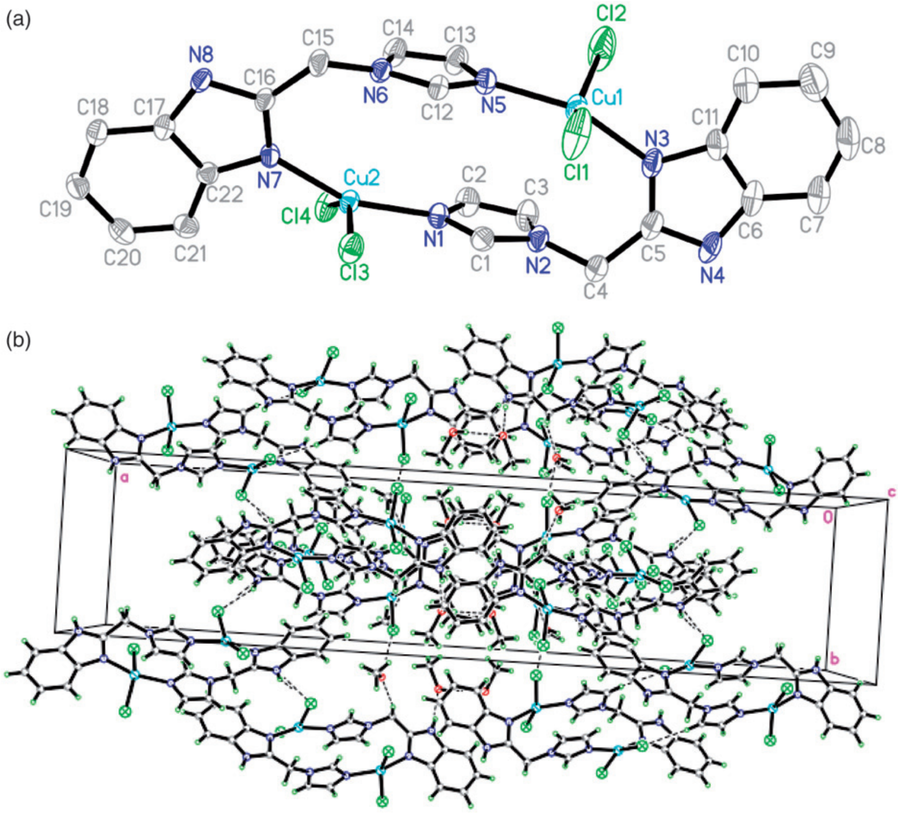

Figure 1. (a) Coordination environment of Cu(II) in **1** with the atom numbering scheme. Hydrogen atoms and methanol molecules are omitted for clarity; (b) 3-D structure of **1** in the solid state supported by hydrogen bonds and π–π interactions.

interplanar distance is 3.3617 Å (figure 2c). In addition, there are two kinds of hydrogen bonds between carboxylates and between imb and carboxylates.

3.2.3. Crystal structure of $\{[Cu(imb)(bdic^{2-})]\cdot 2H_2O\}_n$ (3). The imb reacts with $CuCl_2 \cdot 2H_2O$ and H_2bdic at 80°C to give **3** with a different structure than **2**. From figure 3(a) central Cu(II) coordinates two nitrogen atoms from imb and two unidentate carboxylates from two bdic^{2-} to form quadrangular environment; N1, N3A, O1, O4A, Cu1 are almost located in the same plane (the mean deviation from plane is 0.0984 Å). The Cu–N bond lengths (1.967(2), 1.991(2) Å) and Cu–O bond lengths (1.947(2)–1.962(2) Å) are close to those in **2**. As shown in figure 3(b), different from **1** and **2**, imb bridge Cu(II) in *trans*-conformation (N1–C4–C5–N3 = 168.4) to form a 1-D chain ($\cdots$Cu–imb–Cu–imb$\cdots$) parallel to the *b* direction. Each bdic^{2-} bridges Cu(II) centers to form another 1-D chain ($\cdots$Cu–bdic^{2-}–Cu–bdic$^{2-}\cdots$) parallel to the *a* direction. The two intersecting chains further generate a 2-D network. The interplanar distance of adjacent layers with parallel benzimidazole rings is 3.405 Å, which is in the range of common distances for π–π interactions between two aryl rings [19]. In addition, there

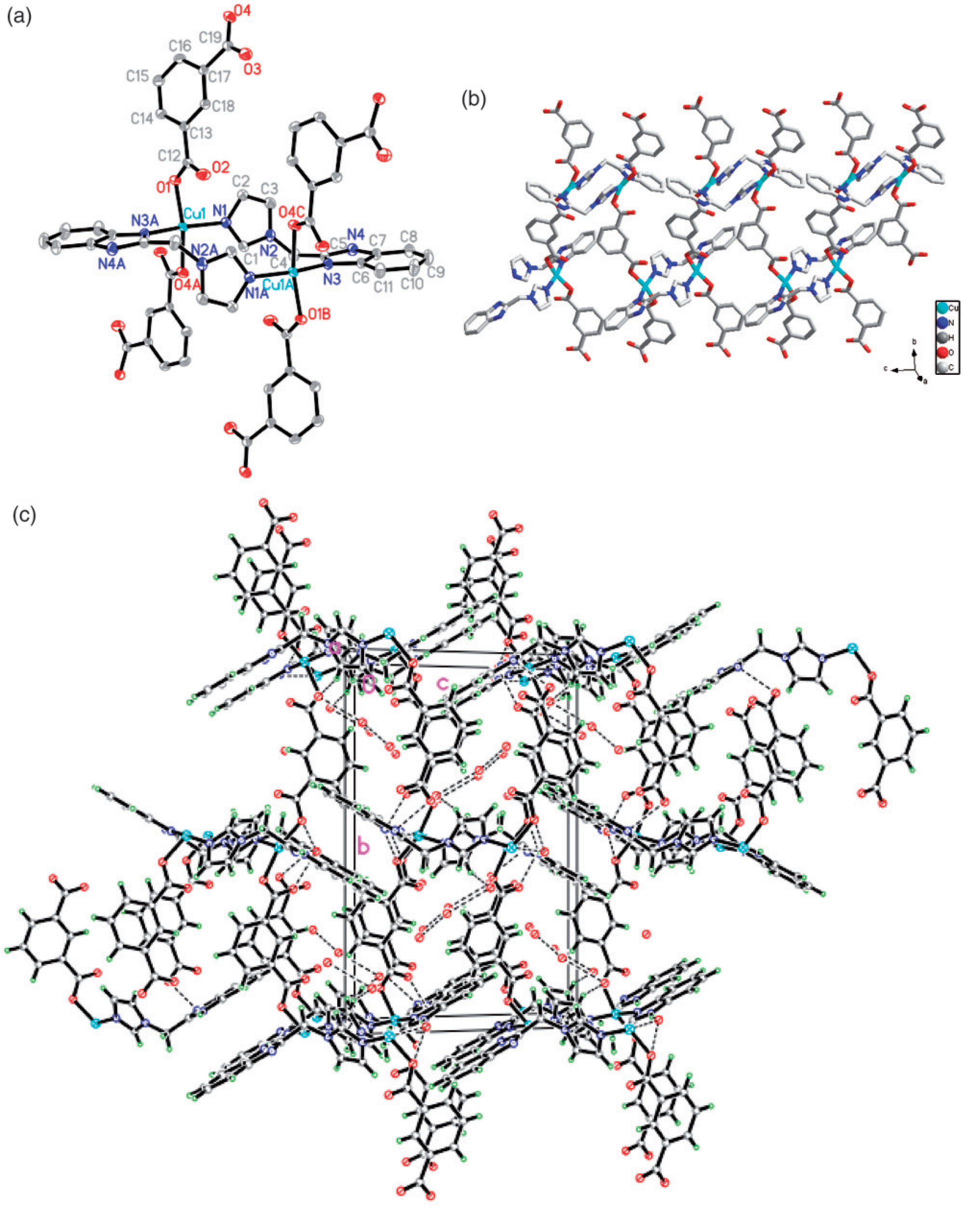

Figure 2. (a) Coordination environment of Cu(II) in **2** with the atom numbering scheme. Hydrogen atoms, water molecule, and DMF are omitted for clarity; (b) The view of the 2-D network structure of **2**; (c) 3-D structure of **2** linked through hydrogen-bonding and π–π interactions indicated by dashed lines.

are hydrogen-bonding interactions between water molecules and carboxylates. The existence of hydrogen bonds further stabilizes the 3-D structure (figure 3c).

3.2.4. Crystal structure of $\{[Cu_3(imb)_2(Hbdc^{3-})_2]\cdot 2H_2O\}_n$ (4). When H_4bdc group, instead of H_2bdic, was used with the other experimental conditions unchanged, **4** with a

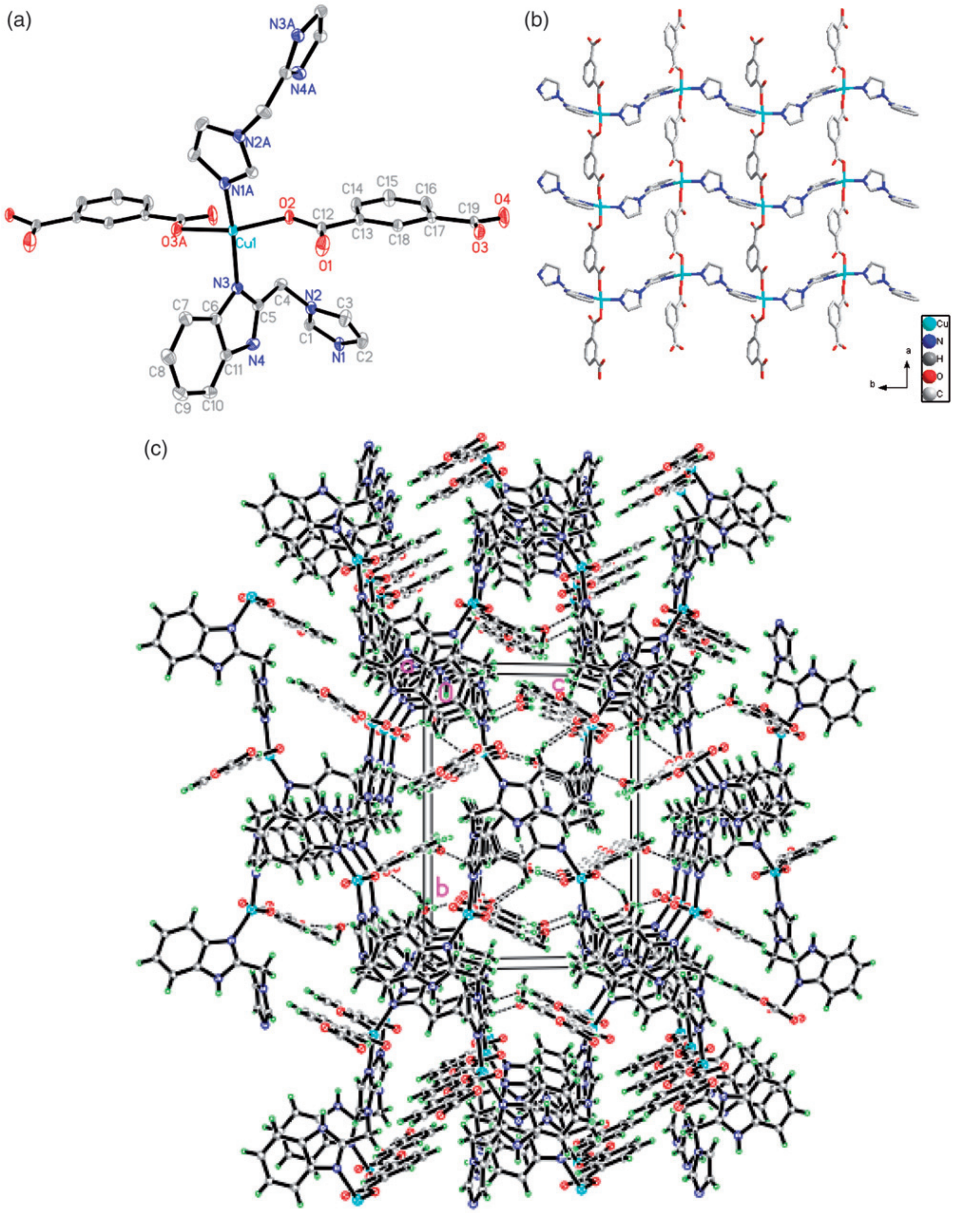

Figure 3. (a) Coordination environment of Cu(II) in **3** with the atom numbering scheme. Hydrogen atoms and water molecules are omitted for clarity; (b) The 2-D network structure of **3**; (c) 3-D structure of **3** linked through hydrogen-bonding and π–π interactions indicated by dashed lines.

different structure than **2** and **3** is obtained. The single-crystal X-ray diffraction analysis shows that **4** crystallizes in the monoclinic *C2*/*c* space group. The asymmetric unit contains one Cu1, a half of Cu2, one imb, one $Hbdc^{3-}$, and one uncoordinated water molecule. As depicted in figure 4(a), Cu1 is five-coordinate by one nitrogen from imb

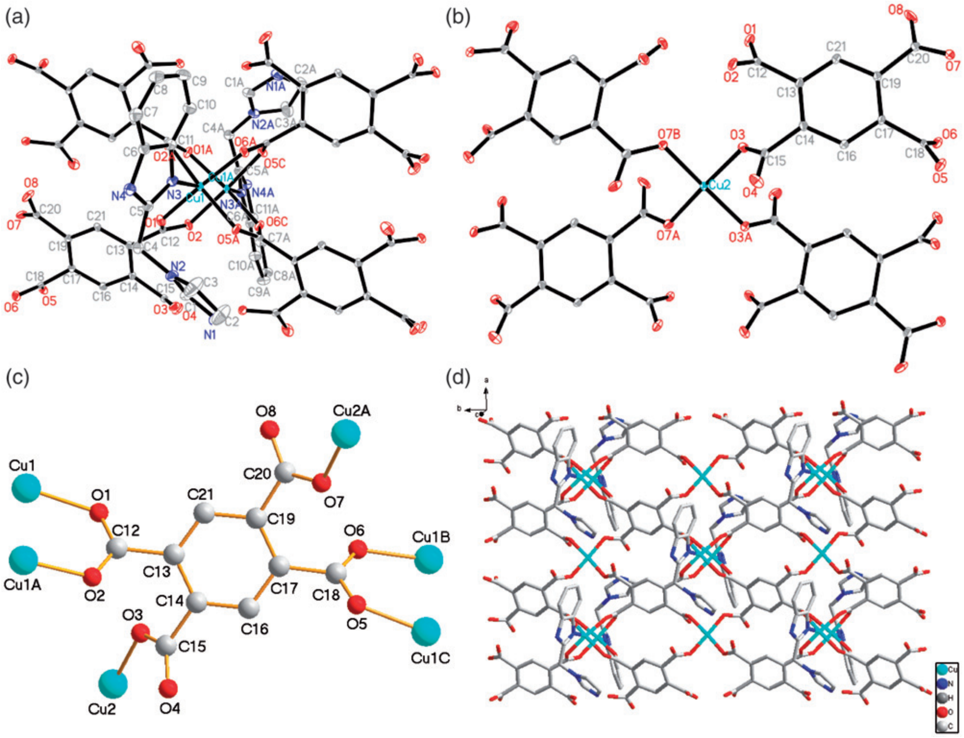

Figure 4. (a) Coordination environment of Cu1 in **4** with the atom numbering scheme; (b) Coordination environment of Cu2 in **4** with the atom numbering scheme. Hydrogen atoms and water molecules are omitted for clarity; (c) Coordination mode of $Hbtc^{3-}$ in **4**; (d) The 2-D network structure of **4**.

(Cu1–N3 = 2.150(3) Å) and four oxygen atoms from four bridging carboxylates (Cu(1)–O(1) = 2.029(2), Cu(1)–O(2)A = 1.988(2), Cu(1)–O(5)A = 2.000(2), Cu(1)–O(6)A = 1.990(2) Å), exhibiting a distorted square pyramidal coordination environment. The four nearly coplanar atoms O1, O2A, O5A, and O6A (the mean deviation from plane of 0.0403 Å) form the tapered bottom and the nitrogen (N3) is located in the conic node. The distance from the conic node to the tapered bottom is 0.245 Å. The Cu–N bond length (2.150(3) Å) is longer than those in **1**, **2**, and **3** due to the Jahn–Teller effect [20]. The carboxylates bridge two Cu1 ions to form a dinucler unit $[Cu_2(imb)_2]$, and the Cu1–Cu1A distance of 2.7328 Å is close to those in $\{[Cu_2(glu)_2(bpmp)] \cdot 4H_2O\}_n$ (glu = glutarate, bpmp = N,N'-bis(4-pyridyl)piperazine) [21] and $[Cu_2(L)_4(CH_3OH)_2](CH_3OH)$ (L = anthracene-9-carboxylic acid) [22]. As illustrated in figure 4(b), the coordination environment of Cu2 is different from Cu1, four-coordinate by four oxygen atoms from four unidentate carboxylates (Cu(2)–O(3) = 1.921(2), Cu(2)–O(3)A = 1.921(2), Cu(2)–O(7)A = 1.930(2), Cu(2)–O(7)B = 1.929(2) Å) in a slight distorted square geometry. The four O atoms (O3, O3A, O7A, O7B) and the central Cu2 ion are nearly located in the same plane (the mean deviation from plane is 0.0984 Å). The bond angles around Cu2 are close to 90° or 180°. As shown in figure 4(c), each $Hbdc^{3-}$ contains two unidentate carboxylates and two bridging carboxylates, and coordinates to six Cu(II) ions simultaneously. The bridging carboxylate links adjacent Cu1 ions and the unidentate carboxylate groups join Cu2 ions forming a 2-D layer, as depicted in figure 4(d). There are three kinds of hydrogen bonds, between carboxylate and water molecule, between carboxylate and imb, and between carboxylates. The hydrogen bonds further stabilize the structure of **4**.

3.3. *Thermogravimetric analysis*

TGA was performed in air at 10°C min^{-1} on **1**, **2**, **3**, and **4**. For the TG curve of **1**, the first weight loss of 4.40% occurred between 30°C and 150°C, corresponding to the release of methanol molecule (Calcd 4.39%). Consecutive weight loss from 190°C to 719°C corresponds to the release of chlorides and decomposition of methanol and imb. A plateau is observed from 719°C to 850°C. A black granular residue of CuO (observed 21.08%, Calcd 21.81%) was obtained. The TG curve of **2** reveals a weight loss of 18.76% from 132°C to 176°C, which can be assigned to the release of DMF and water (Calcd 19.03%). Continuous weight loss from 252°C to 492°C corresponds to the decomposition of imb and 1,3-benzenedicarboxylate, respectively. A plateau is observed from 492°C to 590°C. The residue is 15.25%, which should be CuO (Calcd 15.12%). The TG data of **3** shows that the first weight loss of 6.83% occurred between 55°C and 168°C, corresponding to the release of water molecule (Calcd 6.82%). Then there is a loss in the range of 240–497°C, corresponding to the decomposition of imb and 1,3-benzenedicarboxylate. Finally, a plateau region is observed from 497°C to 560°C. The remnants are 17.32%, which should be CuO (Calcd 17.22%). The TG curve of **4** indicates first weight loss of 3.2% between 61°C and 174°C, corresponding to the release of water molecule (Calcd 3.3%). Then there is loss from 236°C to 485°C, assigned to the decomposition of imb and 1,2,4,5-benzenetetracarboxylate. A plateau region is observed from 485°C to 610°C. The residues of 21.15% should be CuO (Calcd 21.20%). All these results are in agreement with the crystal structures.

4. Conclusion

We studied the Cu(II)-imb system in the presence of chloride, 1,3-benzenedicarboxylic acid or 1,2,4,5-benzenetetracarboxylic acid. Complex **1** exhibits dinuclear structure, the other three complexes display 2-D networks. Change of anions and temperature influence the coordination environment of Cu(II) and the conformation of imb, and thus influence the detailed architectures of the complexes. To some extent, this work enriches the field of complexes.

Supplementary material

Crystallographic data for the structures reported in this article in the form of CIF files have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 821311, 821426, 821313, and 821312 for **1**–**4**, respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union

Road, Cambridge CB2 IEZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk).

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