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Assembly and structures of five new Cu(II) complexes based on the V-shaped building block [Cu(dbsf)]

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Abstract

Five new copper(II) complexes $[Cu(dbsf)(H_2O)]_n \cdot 0.5n(i\text{-}C_3H_7OH)$ (**1**), $[Cu(dbsf)(4,4'\text{-bpy})_{0.5}]_n \cdot nH_2O$ (**2**), $[Cu(dbsf)(2,2'\text{-bpy})(H_2O)]_2 \cdot (n\text{-}C_3H_7OH) \cdot 0.5H_2O$ (**3**), $[Cu(dbsf)(phen)(H_2O)]_2 \cdot 1.5H_2O$ (**4**) and $[Cu(dbsf)(2,2'\text{-bpy})(H_2O)]_n \cdot n(i\text{-}C_3H_7OH)$ (**5**) (H_2dbsf = 4,4′-dicarboxybiphenyl sulfone, 4,4′-bpy = 4,4′-bipyridine, 2,2′-bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, $i\text{-}C_3H_7OH$ = isopropanol, $n\text{-}C_3H_7OH$ = *n*-propanol) have been synthesized under hydro/solvothermal conditions. All of the complexes are assembled from V-shaped building blocks, [Cu(dbsf)]. Complex **1** is composed of 1D double-chains. In complex **2**, $dbsf^{2-}$ ligands and 4,4′-bpy ligands connect Cu(II) ions into catenane-like 2D layers. These catenane-like 2D layers stack in an ABAB fashion to form a 3D supramolecular network. Complexes **3** and **4** are 0D dimers, in which two [Cu(dbsf)] units encircle to form dimetal macrocyclic molecules. However, in complex **5**, the V-shaped building blocks [Cu(dbsf)] are joined head-to-tail, resulting in the formation of infinite tooth-like chains. The different structures of complexes **3** and **5** may be attributed to the different solvent molecules included.

Keywords: 4,4′-Dicarboxybiphenyl sulfone; V-shaped building block; Cu(II) complex; Hydro/solvothermal synthesis; Auxiliary ligand; Solvent molecule

1. Introduction

Porous metal-organic frameworks (MOFs) have attracted much interest of chemists in the field of crystal engineering and chemistry materials, for their intriguing structures and molecular topologies [1], as well as their potential applications in catalysis, gas storage, ion exchange and molecular recognition [2]. The building block method [1a,1b,3], because of its directive function of the target structures as well as the expected physical properties, has become one of the most important synthetic strategies. Yaghi et al. have successfully constructed plenty of porous MOFs using metal carboxylate cluster building blocks [4], and some novel MOFs have been constructed from linear building blocks [5]. However, there are few reports of MOFs constructed by V-shaped building blocks [6,7].

As far as we know, the formation of MOFs is influenced by many factors, such as metal ions, organic ligands, counterions, solvent molecules and pH of the reaction mixture, etc. [8]. Among these factors, the selection of organic ligands is one of the most important aspects [1a,9]. The configuration, rigidity, substituent and coordination modes of organic ligands have an important effect on the final structures. Generally, polycarboxylate ligands feature prominently in the construction of coordination compounds, and the reported coordination polymers are mostly constructed by rigid polycarboxylate ligands [1b,4,10]. Recently, more and more attention has been paid to the flexible polycarboxylate ligands [11], but studies about semi-rigid V-shaped dicarboxylate ligands are relatively few [6,7].

4,4′-Dicarboxybiphenyl sulfone (H_2dbsf) is a typical example of semi-rigid V-shaped dicarboxylate ligands. To the best of our knowledge, there has been no report about its coordination compounds. Under hydro/solvothermal conditions, H_2dbsf and the Cu(II) ion can form the

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V-shaped building block [Cu(dbsf)]. Using these V-shaped building blocks, with the help of different auxiliary ligands, we have successfully obtained five new copper coordination compounds: $[Cu(dbsf)(H_2O)]_n \cdot 0.5n(i\text{-}C_3H_7OH)$ (**1**), $[Cu(dbsf)(4,4'\text{-bpy})_{0.5}]_n \cdot nH_2O$ (**2**), $[Cu(dbsf)(2,2'\text{-bpy})(H_2O)]_2 \cdot (n\text{-}C_3H_7OH) \cdot 0.5H_2O$ (**3**), $[Cu(dbsf)(phen)(H_2O)]_2 \cdot 1.5H_2O$ (**4**) and $[Cu(dbsf)(2,2'\text{-bpy})(H_2O)]_n \cdot n(i\text{-}C_3H_7OH)$ (**5**).

2. Experimental

2.1. Materials and apparatus

All reagents were used as received without further purification (H_2dbsf from TCL). The C, H, N microanalyses were carried out with a Vario EL elemental analyzer. The IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer using the KBr pellet technique. The thermal analyses were performed on a ZRY-2P thermal analyzer using a heating rate of 20 °C/min from room temperature to 900 °C.

2.2. Synthesis

2.2.1. Synthesis of $[Cu(dbsf)(H_2O)]_n \cdot 0.5n(i\text{-}C_3H_7OH)$ (1)

A mixture of $CuCl_2 \cdot 6H_2O$ (0.017 g, 0.1 mmol), H_2dbsf (0.030 g, 0.1 mmol), NaOH aqueous solution (0.05 mL, 0.65 M), HCl aqueous solution (0.05 mL, 1.20 M), distilled water (5 mL), isopropanol (5 mL) and *N*,*N*-dimethyl formamide (0.1 mL) was sealed in a Teflon-lined stainless vessel (25 mL) and heated at 180 °C for 72 h under autogenous pressure. The vessel was then cooled slowly to room temperature. Blue strip crystals were obtained by filtration, washed with distilled water and isopropanol, and dried in air. Yield: 0.002 g (4.8%). Additionally a lot of blue polycrystals were also obtained (~50%. Found: C, 42.09; H, 4.11%). *Anal.* Calc. for $C_{15.5}H_{14}CuO_{7.5}S$ (415.87): C, 44.77; H, 3.39. Found: C, 44.70; H, 3.64%. IR data (KBr pellet, cm^{-1}): 3441s, 1633s, 1409s, 1169m, 1140w, 1100w, 742m, 727w, 523w.

2.2.2. Synthesis of $[Cu(dbsf)(4,4'\text{-bpy})_{0.5}]_n \cdot nH_2O$ (2)

A mixture of $CuCl_2 \cdot 6H_2O$ (0.017 g, 0.1 mmol), H_2dbsf (0.030 g, 0.1 mmol), $4,4'\text{-bpy} \cdot 2H_2O$ (0.019 g, 0.1 mmol), NaOH aqueous solution (0.05 mL, 0.65 M), HCl aqueous solution (0.05 mL, 1.20 M), distilled water (5 mL) and *N*,*N*-dimethyl formamide (0.1 mL) was sealed in a Teflon-lined stainless vessel (25 mL) and heated at 180 °C for 72 h under autogenous pressure. The vessel was then cooled slowly to room temperature. Green strip crystals were obtained by filtration, washed with distilled water and dried in air. Yield: 0.015 g (32.3%). *Anal.* Calc. for $C_{19}H_{14}CuNO_7S$ (463.91): C, 49.19; H, 3.04; N, 3.02. Found: C, 49.48; H, 3.18; N, 3.05%. IR data (KBr pellet, cm^{-1}): 3439s, 1644s, 1608m, 1570m, 1408s, 1326w, 1302w, 1169m, 1100m, 1015w, 739s, 726w, 620w, 520m.

2.2.3. Synthesis of $[Cu(dbsf)(2,2'\text{-bpy})(H_2O)]_2 \cdot (n\text{-}C_3H_7OH) \cdot 0.5H_2O$ (3)

The synthesis of complex **3** was the same as that for complex **2** but substituting 2,2′-bpy (0.016 g, 0.1 mmol) for $4,4'\text{-bpy} \cdot 2H_2O$, and *n*-propanol (5 mL) was also added to the reaction mixture. Blue block crystals were obtained by filtration, washed with distilled water and *n*-propanol, and dried in air. Yield: 0.020 g (34.7%). *Anal.* Calc. for $C_{25.5}H_{22.5}CuN_2O_{7.75}S$ (576.55): C, 53.13; H, 3.92; N, 4.86. Found: C, 53.56; H, 4.34; N, 4.53%. IR data (KBr

Table 1
Crystal data and structure refinement parameters of complexes **1**–**5**

Complex	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{15.5}H_{14}CuO_{7.5}S$	$C_{19}H_{14}CuNO_7S$	$C_{25.5}H_{22.5}CuN_2O_{7.75}S$	$C_{26}H_{19.5}CuN_2O_{7.75}S$	$C_{27}H_{26}CuN_2O_8S$
Formula weight	415.87	463.91	576.55	579.54	602.10
Crystal system	orthorhombic	orthorhombic	triclinic	triclinic	monoclinic
Space group	*Cmcm*	*Cmcm*	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	22.073(5)	12.694(4)	6.936(4)	6.975(5)	6.8069(9)
b (Å)	12.689(2)	13.983(4)	12.137(6)	12.115(10)	16.574(2)
c (Å)	11.592(2)	21.823(7)	16.324(9)	16.749(13)	23.762(3)
α (°)	90	90	79.717(9)	82.469(13)	90
β (°)	90	90	88.063(10)	85.658(12)	92.146(2)
γ (°)	90	90	73.418(9)	74.148(13)	90
V (Å^3)	3246.9(12)	3874(2)	1295.5(12)	1348.5(18)	2678.8(6)
Z	8	8	2	2	4
F(000)	1696	1888	593	593	1244
D_{calc} (Mg m^{-3})	1.701	1.591	1.478	1.427	1.493
T (K)	293(2)	293 (2)	293(2)	293(2)	293(2)
θ Range (°)	1.85–26.30	1.87–26.46	1.78–25.01	2.26–25.01	1.50–26.39
μ (mm^{-1})	1.514	1.278	0.974	0.937	0.946
Goodness-of-fit	1.054	1.087	1.073	1.020	1.046
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0413$, $wR_2 = 0.1036$	$R_1 = 0.0617$, $wR_2 = 0.1221$	$R_1 = 0.0570$, $wR_2 = 0.1550$	$R_1 = 0.0562$, $wR_2 = 0.1475$	$R_1 = 0.0374$, $wR_2 = 0.0852$

pellet, cm^{-1}): 3431s, 1600s, 1560s, 1474w, 1447w, 1398s, 1319w, 1297m, 1163s, 1133m, 1101m, 1054w, 1012w, 773w, 744s, 731m, 718w, 692w, 624m, 576w.

2.2.4. *Synthesis of* $[Cu(dbsf)(phen)(H_2O)]_2 \cdot 1.5H_2O$ *(**4**)*

The synthesis of complex **4** followed a similar process as for complex **2** except that 4,4′-bpy · $2H_2O$ was replaced by phen·H_2O (0.020 g, 0.1 mmol), and isopropanol (5 mL) was added to the reaction mixture. Blue strip crystals were obtained by filtration, washed with distilled water and isopropanol, and dried in air. Yield: 0.031 g (53.5%). *Anal.* Calc. for $C_{26}H_{19.5}CuN_2O_{7.75}S$ (579.54): C, 53.89; H, 3.39; N, 4.83. Found: C, 53.53; H, 3.76; N, 4.74%. IR data (KBr pellet, cm^{-1}): 3423s, 1604s, 1563s, 1518w, 1426m, 1398s, 1380s, 1344m, 1298m, 1161s, 1102m, 856w, 746s, 724s, 624m, 585w.

2.2.5. *Synthesis of* $[Cu(dbsf)(2,2'\text{-}bpy)(H_2O)]_n \cdot n(i\text{-}C_3H_7OH)$ *(**5**)*

The synthesis of complex **5** followed the same procedure as that for complex **2** except using 2,2′-bpy (0.016 g, 0.1 mmol) instead of 4,4′-bpy · $2H_2O$, and isopropanol (5 mL) was added to the reaction mixture. Blue board crystals were obtained by filtration, washed with distilled water and isopropanol, and dried in air. Yield: 0.051 g (84.7%). *Anal.* Calc. for $C_{27}H_{26}CuN_2O_8S$ (602.10): C, 49.69; H, 3.07; N, 3.05. Found: C, 49.72; H, 3.11; N, 3.01%. IR data (KBr pellet, cm^{-1}): 3418s, 1600s, 1560s, 1475w, 1447m, 1399s, 1298m, 1163s, 1133m, 1101m, 744m, 731w, 623w.

In the syntheses of the complexes **1**–**5**, HCl and NaOH solutions were added to adjust the pH of the reaction system. Propanol and DMF were added to enhance the solubility of the H_2dbsf ligand. Complexes **1**, **4** and **5** were synthesized in the mixed solvent of water, isopropanol and DMF, and **2** was formed in the mixed solvent of water and DMF, while complex **3** was obtained in the mixed solvent of water, *n*-propanol and DMF, showing that selectivity of the solvent plays an important role in the formation of the complexes.

2.3. *X-ray diffraction determination*

Diffraction data for complexes **1**–**5** were collected at 294 K on a Bruker SMART 1000 CCD diffractometer with a graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å), using the ω and φ scan technique. A semi-empirical absorption correction was applied with the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs [12–14], respectively. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. Crystallographic data for complexes **1**–**5** are summarized in Table 1, and selected bond lengths (Å) and bond angles (°) are listed in Table 2 while selected hydrogen bond lengths (Å) and bond angles (°) are presented in Table 3.

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **1**–**5**[a]

Complex 1			
Cu(1)–O(1)	1.952(3)	Cu(1)–O(3)#2	1.981(3)
Cu(1)–O(4)	2.153(4)		
O(1)–Cu(1)–O(4)	100.9(1)	O(1)#1–Cu(1)–O(3)#2	89.8(1)
O(1)–Cu(1)–O(1)#1	89.9(2)	O(3)#2–Cu(1)–O(4)	90.1(1)
O(1)–Cu(1)–O(3)#2	168.8(1)	O(3)#2–Cu(1)–O(3)#3	88.3(2)
Complex 2			
Cu(1)–O(1)	1.987(5)	Cu(2)–O(2)	1.966(5)
Cu(1)–N(2)#4	2.10(1)	Cu(2)–N(1)	2.12(1)
O(1)–Cu(1)–O(1)#1	88.7(3)	O(2)–Cu(2)–O(2)#1	90.0(3)
O(1)–Cu(1)–O(1)#2	89.9(3)	O(2)–Cu(2)–O(2)#2	88.9(3)
O(1)–Cu(1)–O(1)#3	167.6(3)	O(2)–Cu(2)–O(2)#3	168.8(3)
O(1)–Cu(1)–N(2)#4	96.2(1)	O(2)–Cu(2)–N(1)	95.6(1)
Complex 3			
Cu(1)–O(1)	1.929(4)	Cu(1)–N(1)	1.992(5)
Cu(1)–O(7)	2.303(4)	Cu(1)–N(2)	1.996(5)
Cu(1)–O(5)#1	1.924(4)		
O(1)–Cu(1)–O(7)	95.5(2)	O(5)#1–Cu(1)–N(1)	93.3(2)
O(1)–Cu(1)–N(1)	169.8(2)	O(5)#1–Cu(1)–N(2)	164.7(2)
O(1)–Cu(1)–N(2)	93.5(2)	N(1)–Cu(1)–O(7)	93.0(2)
O(5)#1–Cu(1)–O(1)	90.6(2)	N(1)–Cu(1)–N(2)	80.4(2)
O(5)#1–Cu(1)–O(7)	101.0(2)	N(2)–Cu(1)–O(7)	93.4(2)
Complex 4			
Cu(1)–O(1)	1.951(4)	Cu(1)–N(1)	2.014(4)
Cu(1)–O(7)	2.353(4)	Cu(1)–N(2)	2.020(4)
Cu(1)–O(5)#1	1.941(4)		
O(1)–Cu(1)–O(7)	95.1(2)	O(5)#1–Cu(1)–N(1)	92.6(2)
O(1)–Cu(1)–N(1)	171.8(2)	O(5)#1–Cu(1)–N(2)	167.1(2)
O(1)–Cu(1)–N(2)	92.5(2)	N(1)–Cu(1)–O(7)	91.1(2)
O(5)#1–Cu(1)–O(1)	91.9(2)	N(1)–Cu(1)–N(2)	81.8(2)
O(5)#1–Cu(1)–O(7)	98.9(2)	N(2)–Cu(1)–O(7)	92.8(2)
Complex 5			
Cu(1)–O(1)	1.943(2)	Cu(1)–N(1)	2.011(2)
Cu(1)–O(8)	2.273(2)	Cu(1)–N(2)	2.016(2)
Cu(1)–O(5)#1	1.955(2)		
O(1)–Cu(1)–O(8)	96.82(8)	O(5)#1–Cu(1)–N(1)	91.20(9)
O(1)–Cu(1)–O(5)#1	92.52(8)	O(5)#1–Cu(1)–N(2)	162.82(8)
O(1)–Cu(1)–N(1)	168.43(8)	N(1)–Cu(1)–O(8)	93.83(8)
O(1)–Cu(1)–N(2)	93.04(8)	N(1)–Cu(1)–N(2)	80.41(9)
O(5)#1–Cu(1)–O(8)	94.18(8)	N(2)–Cu(1)–O(8)	101.28(8)

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

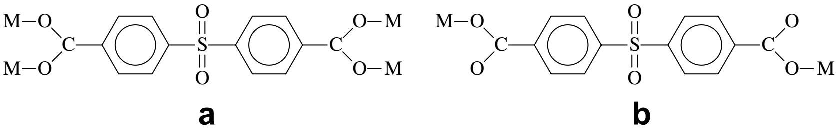
3. Results and discussion

3.1. *Description of the structures*

In complexes **1**–**5**, the $dbsf^{2-}$ ligands are completely deprotonated and are largely bent at the sulfone-sulfur sites (C–S–C = 103.0(2)–106.5(3)°, O–S–O = 119.1(2)–120.2(3)°). Each of them displays a V-shaped configuration, and assembles with the Cu(II) ion to form the V-shaped building block [Cu(dbsf)]. The coordination

Table 3
Selected hydrogen bond lengths (Å) and bond angles (°) for complexes **1**–**5**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA	Symmetry code
Complex 1					
O(4)–H(4A)···O(5wA)	0.849	1.998	2.785	153.62	[*x*, *y*, *z*−1]
O(4)–H(4A)···O(5′wB)	0.849	2.133	2.905	150.97	[−*x*, *y*, −*z* + 1/2]
O(4)–H(4A)···O(5′wB)	0.849	2.133	2.905	150.97	[*x*, *y*, *z* − 1]
O(4)–H(4B)···O(3)	0.852	2.172	3.013	169.44	[*x*, −*y* + 1, −*z*]
Complex 3					
O(7)–H(7B)···O(6)	0.850	2.337	2.803	114.87	[−*x*, −*y*, −*z* + 1]
C(13)–H(13)···O(4)	0.930	2.547	3.232	130.80	[−*x* + 1, −*y* − 1, −*z* + 1]
C(22)–H(22)···O(3)	0.930	2.376	3.253	157.30	[−*x* + 1, −*y*, −*z*]
C(21)–H(21)···O(6)	0.930	2.403	3.318	168.00	[*x* − 1, *y* + 1, *z*−1]
Complex 4					
O(7)–H(7B)···O(6)	0.849	2.346	2.784	112.58	[−*x*, −*y* + 1, −*z* + 2]
O(7)–H(7A)···O(8w)	0.849	1.995	2.825	165.52	[−*x*, −*y* + 1, −*z* + 1]
C(19)–H(19)···O(6)	0.930	2.487	3.130	126.40	[*x* − 1, *y* + 1, *z*−1]
C(20)–H(20)···O(6)	0.930	2.683	3.228	118.10	[*x* − 1, *y* + 1, *z*−1]
C(4)–H(4)···O(2)	0.930	2.542	3.304	99.70	[*x* + 1, *y*, *z*]
Complex 5					
O(7)–H(7A)···O(6)	0.820	2.152	2.914	154.48	[−*x* − 1/2, *y* − 1/2, −*z* + 1/2]
O(8)–H(8A)···O(6)	0.845	1.920	2.720	157.58	[−*x* + 1/2, *y* − 1/2, −*z* + 1/2]
O(8)–H(8B)···O(2)	0.845	1.996	2.788	155.72	[*x* + 1, *y*, *z*]
C(4)–H(4)···O(2)	0.930	2.306	3.197	160.30	[−*x* + 1, −*y* + 1, −*z*]



Scheme 1. The coordination modes of the dbsf^{2-} ligand in complexes **1**–**5**.

modes of the dbsf^{2-} ligand in complexes **1**–**5** are represented in Scheme 1.

3.1.1. [Cu(dbsf)(H_2O)]$_n$ · 0.5n(i-C_3H_7OH) (1)

In complex **1**, each Cu(II) ion is coordinated to five oxygen atoms, four oxygen atoms from four dbsf^{2-} ligands and one oxygen atom from a water molecule, as shown in Fig. 1a. O(1), O(1C), O(3B) and O(3C) atoms form an equatorial plane and one oxygen atom (O(4)) occupies the axial position, giving a slightly distorted square-pyramidal geometry. In complex **1**, each dbsf^{2-} ligand adopts a bis(bridging-bidentate) mode (Scheme 1a) to coordinate to four Cu(II) ions. V-Shaped building blocks [Cu(dbsf)] are joined to form 1D double-chains, as shown in Fig. 1b. The single 1D double-chain possesses rhombic voids with dimensions of about 8 × 8 Å. All these double-chains are parallel to each other. Along the *c*-axis, these double-chains are arranged in an ABAB fashion and there is a displacement between the adjacent chains, which leads to the formation of small 1D channels (Fig. 1c). Hydrogen bonds are observed between the coordinated water molecules and the carboxylate oxygen atoms of dbsf^{2-} ligands among the adjacent chains along the *c*-axis (Table 3), and there are π–π stacking interactions in the *ab*-plane, with a distance of 3.507 Å between the phenyl rings of dbsf^{2-} ligands. Hydrogen bonds and π–π stacking interactions result in the formation of the porous supramolecular network of complex **1**. Isopropanol molecules are accommodated in the channels (see Fig. 1c). There are hydrogen bonds between the oxygen atom (O(5w)) of isopropanol molecules and coordinated water molecules of the chains (Table 3).

3.1.2. [Cu(dbsf)(4,4′-bpy)$_{0.5}$]$_n$ · nH_2O (2)

In complex **2**, there are two kinds of crystallographically independent Cu(II) ions, as shown in Fig. 2a. Both Cu(1) and Cu(2) are five-coordinated, and their coordination environments are similar but the bond lengths and bond angles around Cu(1) and Cu(2) are different. Each Cu(II) ion is coordinated to four oxygen atoms of four different dbsf^{2-} ligands and one nitrogen atom of one 4,4′-bpy molecule. In complex **2**, the dbsf^{2-} ligands adopt a bis(bridging-bidentate) mode (Scheme 1a), linking the Cu(II) ions into a 1D double-chain structure along the *a*-axis, which is similar to that in complex **1**. However, because of the introduction of 4,4′-bpy molecules, these 1D [Cu(dbsf)]$_n$ double-chains are pillared to generate 2D square-grids (Fig. 2b). Unexpectedly, two such grids interpenetrate each

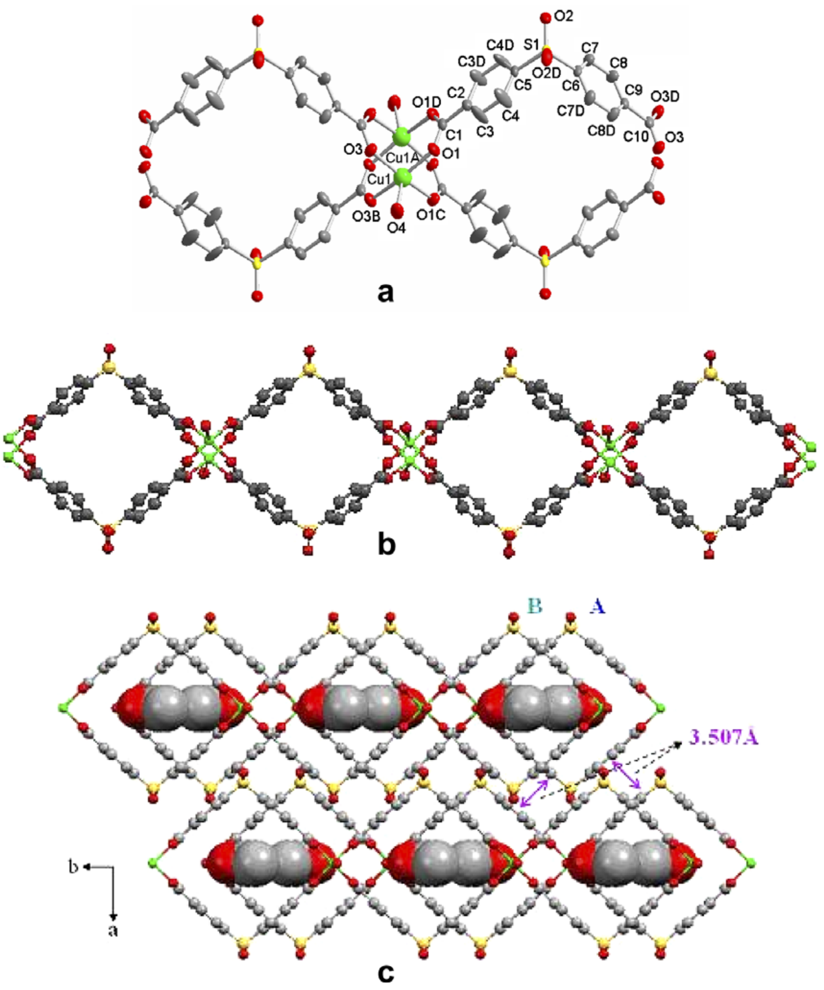


Fig. 1. (a) The coordination environment of the Cu(II) ion in complex **1** with 30% thermal ellipsoids, all hydrogen atoms are omitted for clarity. (b) The 1D double-chain structure with rhombic voids. (c) View of the supramolecular network of complex **1** along the *c*-direction (space-filling model represents isopropanol molecules).

other to generate a novel catenane-like 2D layer (Fig. 2c). Such catenane-like layers are unusual [15]. These catenane-like 2D structures stack in an ABAB fashion along the *c*-axis with some displacement between A and B, resulting in the formation of a 3D supramolecular network. There are lattice water molecules accommodated between the layers.

3.1.3. $[Cu(dbsf)(2,2'\text{-}bpy)(H_2O)]_2 \cdot (n\text{-}C_3H_7OH) \cdot 0.5H_2O$ (3) and $[Cu(dbsf)(phen)(H_2O)]_2 \cdot 1.5H_2O$ (4)

X-ray diffraction analysis reveals that complexes **3** and **4** possess similar structures, except that the 2,2′-bpy ligand in complex **3** is replaced by a phen ligand in complex **4**, and the guest molecules are different in the two complexes (n-C_3H_7OH and H_2O for **3**, H_2O for **4**). So only the structure of complex **3** will be described here. The coordination environment of the Cu(II) ion in complex **3** is shown in Fig. 3a. The Cu(II) ion is five-coordinated, with two oxygen atoms from two $dbsf^{2-}$ ligands, two nitrogen atoms from one 2,2′-bpy ligand and one oxygen atom from a coordinated water molecule. The coordination geometry of the Cu(II) ion can be described as a distorted square-pyramid. The Cu–N bond lengths are 2.014(4) and 2.020(4) Å, and the Cu–O bond lengths are in the range of 1.941(4)–2.353 (4) Å (the Cu–N bond lengths are 1.992(5) and 1.996(5) Å, and the Cu–O bond lengths are in the range of 1.924(4)–2.303 (4) Å for complex **4**). In complex **3**, every $dbsf^{2-}$ ligand adopts a bis(monodentate) mode (Scheme 1b), so that two V-shaped building blocks encircle to form a macrocyclic dimer unit (Fig. 3a). All the dimer units are parallel, and plenty of hydrogen bonds exist between them. Along the *a*-axis, there exists O–H···O hydrogen bonds [O(7)–H(7B)···O(6)] between the coordinated water molecule and the oxygen atom of the uncoordinated carboxyl group. In addition, three kinds of C–H···O hydrogen bonds, such as C(13)–H(13)···O(4), C(22)–H(22)···O(3) and C(21)–H(21)···O(6) exist in the adjacent dimers in the *bc*-plane. Moreover, a π–π stacking interaction exists between 2,2′-bpy ligands (the face-to-face distance is 3.639 Å). These hydrogen bonds and π–π stacking interactions lead to the

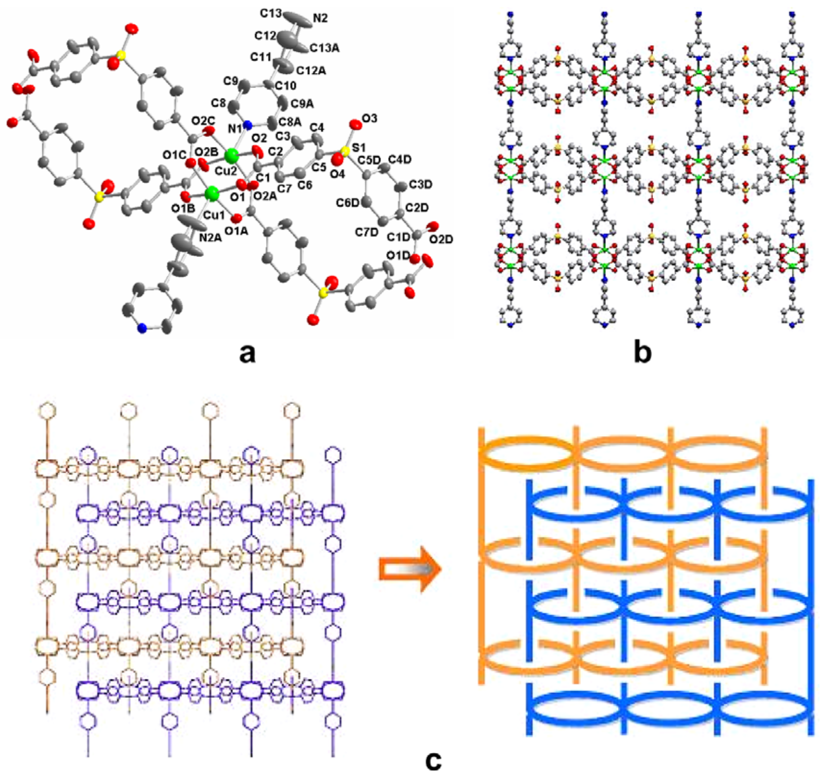


Fig. 2. (a) The coordination environments of the Cu(II) ions in complex **2** with 30% thermal ellipsoids, all hydrogen atoms are omitted for clarity. (b) The 2D layer framework of complex **2**. (c) Interpenetrated catenane-like 2D layers and its schematic view.

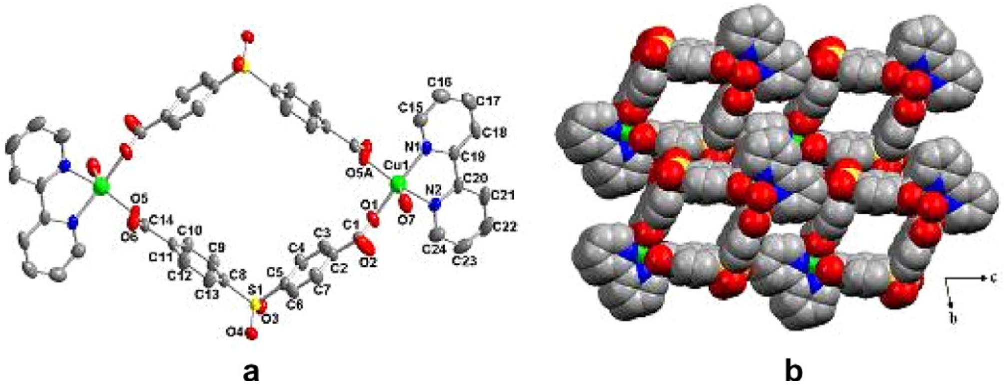


Fig. 3. (a) The coordination environment of the Cu(II) ion in complex **3** with 30% thermal ellipsoids, all hydrogen atoms are omitted for clarity. (b) View of the 3D porous supramolecular structure along the *a*-axis, all the atoms except hydrogen atoms are shown as a space-filling model.

formation of a 3D porous supramolecular architecture [16], as shown in Fig. 3b. Water molecules and *n*-propanol molecules alternately occupy the 1D channels along the *a*-axis. But they are so far away from the dimers that no hydrogen bonds are formed between the guest molecules and the dimers.

3.1.4. $[Cu(dbsf)(2,2'\text{-}bpy)(H_2O)]_n \cdot n(i\text{-}C_3H_7OH)$ (**5**)

The X-ray crystallographic analysis shows that complex **5** possesses 1D tooth-like chains. There is one crystallographically independent Cu(II) center in the crystal structure. As shown in Fig. 4a, the Cu(II) ion is five-coordinated and displays a distorted square-pyramidal geometry, which is completed by two nitrogen atoms from one chelating 2,2′-bpy ligand, two oxygen atoms from two $dbsf^{2-}$ ligands, and one oxygen atom from one coordinated water molecule. In complex **5**, the $dbsf^{2-}$ ligands adopt a bis(monodentate) mode (Scheme 1b), the same as that in complex **3**, but they connect the Cu(II) ions into a completely different structure. V-Shaped building blocks are joined head-to-tail to form infinite tooth-like chains (Fig. 4b). Among these chains, there are plenty of hydro-

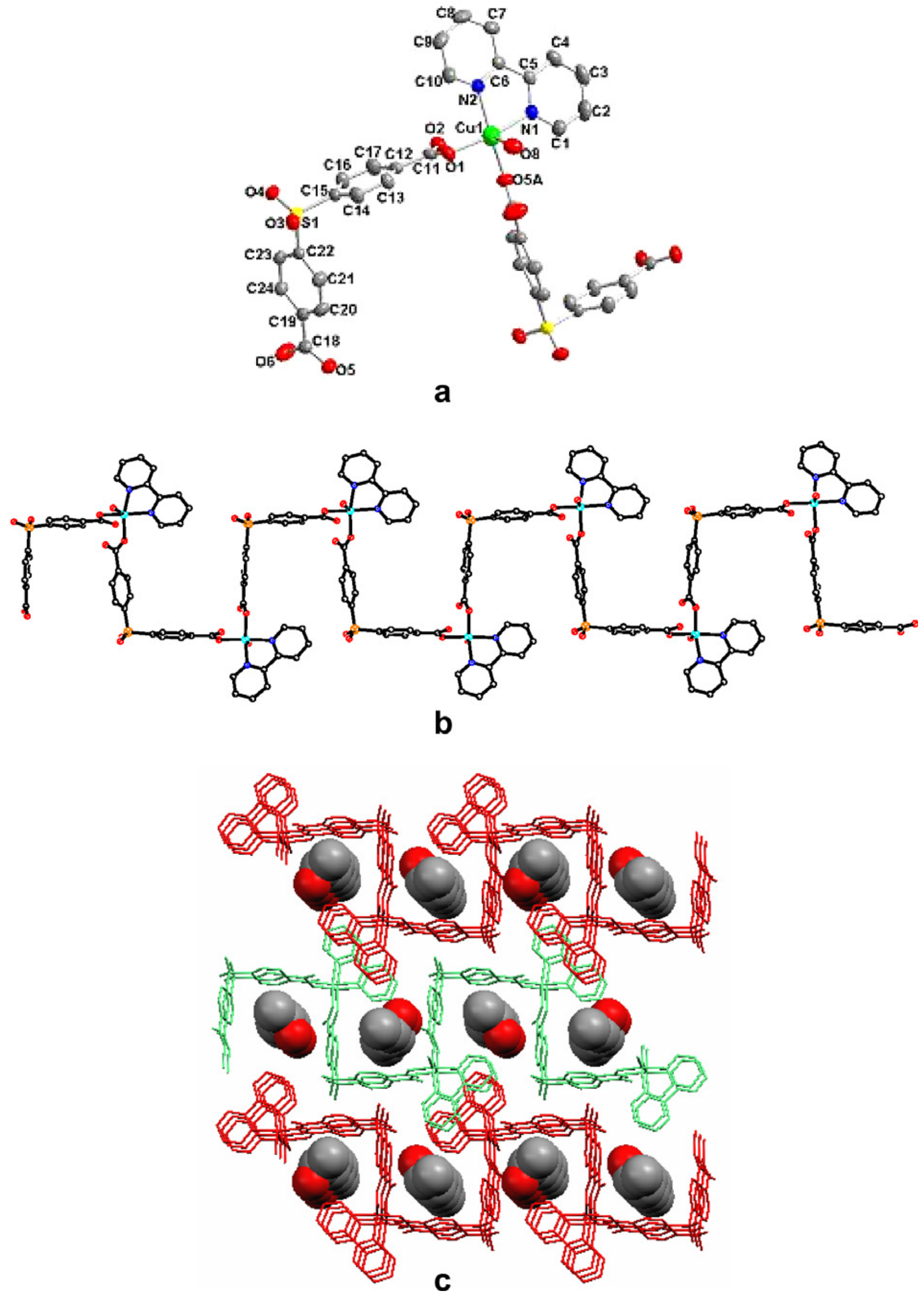
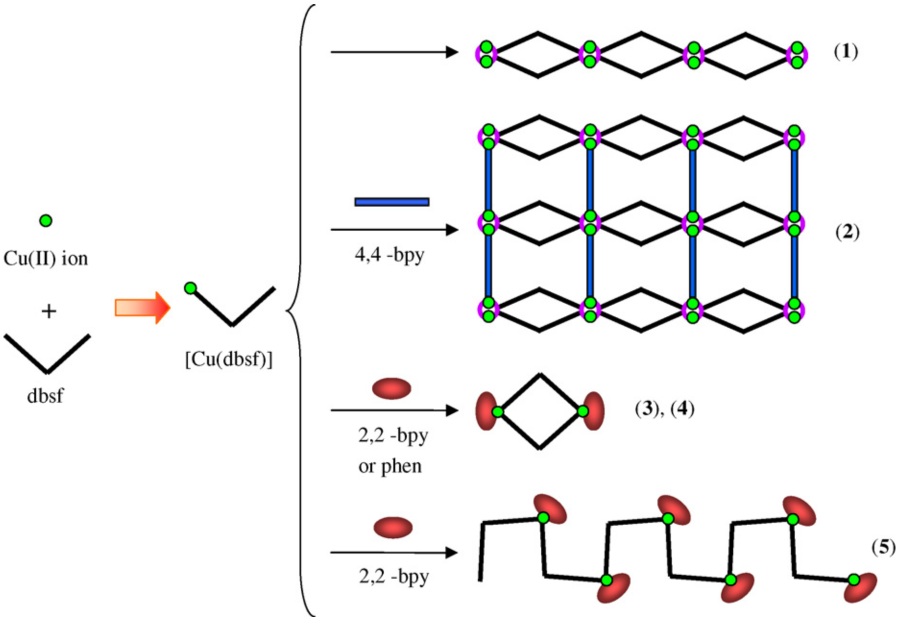


Fig. 4. (a) The coordination environment of the Cu(II) ion in complex **5** with 30% thermal ellipsoids, all hydrogen atoms are omitted for clarity. (b) The infinite 1D chain structure formed by V-shaped building blocks of [Cu(dbsf)]. (c) View of the 3D supramolecular structure along *a*-axis (space-filling model represents solvent molecules).

gen bonds. O–H···O hydrogen bonds are observed between the uncoordinated oxygen atoms (O(6)) and coordinated water molecules of the adjacent chains. Additionally, C–H···O hydrogen bonds are observed between C···H (H(4)) of the 2,2′-bpy molecule and the other uncoordinated carboxylate oxygen atoms (O(2)) of the adjacent chain (Table 3). The 2,2′-bpy molecules also participate in face-to-face π–π stacking interactions with a separation at the closest contact of 3.267 Å, and the pyridyl planes of the 2,2′-bpy ligands are parallel to ones in the adjacent chains. Thus a 3D supramolecular structure is formed via hydrogen bonds and π–π stacking interactions. In the 1D channels along the *a*-axis, isopropanol molecules are accommodated (Fig. 4c). They form O–H···O hydrogen bonds with the non-coordinated oxygen atoms (O(6)) of the dbsf^{2-} ligands. The formation of these hydrogen bonds prevents the dbsf^{2-} ligands encircling to form a dimer fragment. Besides, isopropanol molecules occupy the voids of the tooth-like chains, functioning as important supports to the shape of the chains.

*3.1.5. Comparison of the structures of complexes **1–5***

By self-assembly from V-shaped building blocks [Cu(dbsf)], we obtained five new complexes with structure described as



Scheme 2. The simplified representation of the structures of the five complexes.

0D metallocyclic, 1D chain and 2D catenane-like layer. From the above descriptions, it is obvious that the introducing of different auxiliary ligands has a crucial effect on the assembly of the [Cu(dbsf)] building block and the formation of the final structures. The simplified structures of these five complexes are represented in Scheme 2. In complexes **1**–**5**, the $dbsf^{2-}$ ligand shows two coordination modes (Scheme 1). It adopts a bis(bridging-bidentate) mode (Scheme 1a) in complexes **1** and **2**, and the bis(monodentate) mode (Scheme 1b) in complexes **3**–**5**. In complex **1**, V-shaped building blocks [Cu(dbsf)] are joined to form 1D double-chains. While in complex **2**, when the bridging auxiliary ligand 4,4′-bpy is introduced, these 1D double-chains are pillared into 2D layers. When terminal auxiliary ligands phen/2,2′-bpy were introduced into the Cu/dbsf system, 0D dimeric complexes **3** and **4** were obtained, in which every two V-shaped building blocks [Cu(dbsf)] encircle to form metallocyclic units in which the terminal ligands phen/2,2′-bpy prevent the structures extending to a higher dimension.

In addition, solvent molecules impact the structure too. It is worth noting that complexes **3** and **5** were obtained from the same reactants in different solvents, they possess very different structures [17]. Complex **3** is composed of dimetal macrocyclic molecules with two V-shaped building blocks of [Cu(dbsf)], while in complex **5**, V-shaped building blocks of [Cu(dbsf)] are linked in a head-to-tail model, and 1D tooth-like chains are organized. This may be attributed to the dissimilar solvent molecules included. In complex **5**, the free isopropanol molecules form hydrogen bonds with the main chain so as to prevent the $dbsf^{2-}$ ligands encircling to form dimer fragments (see Fig. 4c), occupying the voids of the tooth-like chains, and acting as important supports to the shape of the chains.

3.2. Thermal analyses

Thermogravimetric analyses of the complexes **2**–**5** were carried out to examine their thermal stabilities. The observed TG curve reveals that complex **2** looses its lattice water molecules at the first weight loss of 3.0% (calc. 3.8%) from 64 °C to 172 °C. For complex **3**, the TG curve shows that the uncoordinated solvent molecules and coordinated water molecules are lost at the first weight loss, 9.0% (calc. 9.1%) from 109 °C to 201 °C. While for complex **4**, the uncoordinated and coordinated water molecules are lost from 73 °C to 112 °C at the first weight loss of 6.2% (calc. 5.4%). In complex **5**, the first weight loss of 9.9% from 169 °C to 206 °C corresponds to the loss of uncoordinated isopropanol molecules (calc. 9.9%).

The TG curves of the complexes **3** and **5** show that further decomposition starts when the solvent was removed, indicating that the host framework collapses when the solvent is absent.

4. Conclusions

In summary, a series of Cu/dbsf complexes were prepared under hydro/solvothermal conditions. The crystal structures of the title complexes are the first report on metal complexes of 4,4′-dicarboxybiphenyl sulfone. Different structures of complexes **1**–**5** indicate that the V-shaped dicarboxylate ligand $dbsf^{2-}$ has the ability of adjusting its coordination configuration in different reaction systems intelligently. Complexes **1**–**5** are all built up from V-shaped building blocks [Cu(dbsf)] with diverse auxiliary ligands. Our studies show that the configuration of the building blocks of [Cu(dbsf)] together with the help of auxiliary ligands has a crucial effect on the topology and configuration of the final structures of the Cu(II) complexes. Additionally, the solvent molecule acting as a guest is another notable factor for the arrangement of the 3D supramolecular networks.

5. Supplementary material

CCDC 611527, 611528, 611529, 611530 and 611531 contain the supplementary crystallographic data for **1**, **2**, **3**, **4** and **5**. These data can 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.

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