

基于 5-磺酸基间苯二甲酸钠和双三唑烷烃的 Cu(II)配合物的合成、结构和性质

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摘要: 利用 5-磺酸基间苯二甲酸钠(NaH_2sip)和双三唑烷烃,合成了 3 个配合物 $[\text{Cu}_{0.5}(\text{btm})(\text{H}_2\text{O})](\text{H}_2\text{sip})\cdot\text{H}_2\text{O}]_n$ (**1**, btm=双三唑甲烷), $[\text{Cu}(\text{btp})_2(\text{H}_2\text{sip})(\text{H}_2\text{O})](\text{NO}_3)\cdot 4\text{H}_2\text{O}]_n$ (**2**, btp=双三唑丙烷) 和 $[\text{Cu}(\text{btb})_2(\text{Hsip})]_n$ (**3**, btb=双三唑丁烷)。化合物 **1** 为一维双链结构;化合物 **2** 为二维四方网络结构,多个二维层依次叠加形成三维超分子结构;化合物 **3** 也具有二维层状结构,其中金属铜离子和双三唑丁烷构成的一维双链结构经双齿 $\mu_2\text{-Hsip}^{2-}$ 配体连接构成了二维层状结构。同时对配合物的热稳定性和顺磁共振特性进行了讨论。

关键词: 双三唑甲烷; 双三唑丙烷; 双三唑丁烷; 5-磺酸基间苯二甲酸单钠盐; 超分子结构; 氢键

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Copper(II) Complexes Based on 5-Sulfoisophthalate and Bis(1,2,4-triazol-1-yl)alkanes: Syntheses, Structures, and Properties

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Abstract: The reaction of copper(II) nitrate with flexible bis (1,2,4-triazol-1-yl)alkanes and rigid ligand 5-sulfoisophthalic acid monosodium salt (NaH_2sip) affords three complexes $[\text{Cu}_{0.5}(\text{btm})(\text{H}_2\text{O})](\text{H}_2\text{sip})\cdot\text{H}_2\text{O}]_n$ (**1**, btm=bis(1,2,4-triazol-1-yl)methane), $[\text{Cu}(\text{btp})_2(\text{H}_2\text{sip})(\text{H}_2\text{O})](\text{NO}_3)\cdot 4\text{H}_2\text{O}]_n$ (**2**, btp=1,3-bis(1,2,4-triazol-1-yl)propane), and $[\text{Cu}(\text{btb})_2(\text{Hsip})]_n$ (**3**, btb=1,4-bis(1,2,4-triazol-1-yl)butane). Compound **1** contains one-dimensional (1D) double-strained chains. Compound **2** contains two-dimensional (2D) rectangular networks with (4,4) topology, in which the 2D planar nanogrid networks stacked in a step stacking fashion. **3** is also 2D layers, in which double-strained chains $[\text{Cu}(\text{btb})]_n$ are connected into 2D layer architectures by the $\mu_2\text{-Hsip}^{2-}$ linkers. The three compounds also are characterized by Elemental analysis, EPR, and thermal stability. CCDC: 1023688, **1**; 776320, **2**; 1023689, **3**.

Key words: bis(1,2,4-triazol-1-yl)methane; 1,3-bis-(1,2,4-triazol-1-yl)propane; 1,4-bis(1,2,4-triazol-1-yl)butane; 5-sulfoisophthalic acid monosodium salt; supramolecular structure; hydrogen-bond interaction

Coordination polymers have recently aroused much interest as materials, due to not only the structural diversity but also their attractive properties,

such as catalytic activity, magnetism, photochemical activity and electrical chemistry^[1-9]. One of the key steps for preparation of polymeric transition metal

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complexes is to select the multidentate bridging ligands or mixed coordination ligands^[10-14]. Currently, the rational construction of new structurally defined MOFs using the mixed-ligand strategy seems to be a marvelous success^[15-21].

Because of the diversity of the coordination modes and high structural stability, multi-carboxylic ligands with suitable spacers, especially benzoic acid based ligands are frequently used for metal-organic networks^[22-27]. Benzene-1,3,5-tricarboxylic acid (H_3btc , also known as trimesic acid) is a rigid, planar molecule and has been widely used as a bridging ligand in the synthesis of multidimensional MOFs. Compared to the widely used benzene-1,3,5-tricarboxylic acid, 5-sulfoisophthalic acid monosodium salt (NaH_2sip) has distinctive characteristics: (i) C_2 symmetry of the ligand may cause the generation of different structures; (ii) the sulfonate group is generally perceived as a weaker group with respect to their coordinating ability and has one more potentially coordinating oxygen atom; (iii) the weak coordination nature of $-SO_3$ makes its coordination mode very flexible and sensitive to the chemical environment.

On the other hand, bis(1,2,4-triazol-1-yl)alkanes are highly flexible ligands. The flexibility and conformation freedoms of bistriazole alkanes can offer the possibility for the construction of unpredictable and interesting frameworks.

In this contribution, we describe a series of Cu(II) metal-organic frameworks constructed from rigid multi-carboxylic ligand NaH_2sip and flexible bistriazole alkanes. Three novel complexes $[Cu_{0.5}(btm)(H_2O)](H_2sip) \cdot H_2O$ (**1**), $[[Cu(btp)_2(H_2sip)(H_2O)](NO_3)4H_2O]$ (**2**), and $[[Cu(btb)_2(Hsip)]_n$ (**3**) were fabricated and structurally characterized by X-ray single crystal analyses. They exhibited novel framework structures varying from 1D chains, to 2D layers. The thermal stability and EPR spectra have also been discussed.

1 Experimental

1.1 General considerations

The reagents and solvents employed were commercially available and used as received without

further purification. Bis(1,2,4-triazol-1-yl)alkanes was synthesized as reported previously^[28]. The elemental analyses (C, H, and N) were carried out on a Perkin-Elmer elemental analyzer. TG experiments were performed on a NETZSCH TG 209 instrument with a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ under nitrogen conditions. EPR spectra were measured on a BRUKER EMX-6/1 EPR spectrometer.

1.2 Preparation

$[Cu_{0.5}(btm)(H_2O)](H_2sip) \cdot H_2O$ (**1**). A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (168 mg, 0.7 mmol), NaH_2sip (189 mg, 0.7 mmol), btm (91 mg, 0.7 mmol) and H_2O (12 mL) was added into a parr Teflon-lined stainless steel vessel (25 mL), and then the vessel was sealed and heated to $140\text{ }^\circ\text{C}$. After 3 days the autoclave was cooled to room temperature at a rate of $1.5\text{ }^\circ\text{C} \cdot \text{h}^{-1}$. Blue crystalline products **1** were filtered off, washed with distilled water and dried in air. Yield: 45% (based on Cu). Anal. Calcd.(%) for $C_{13}H_{15}Cu_{0.5}N_6O_9S$ (463.15): C 33.71, H 3.26, N 18.15. Found (%): C 33.38, H 3.55, N 18.46.

$[[Cu(btp)_2(H_2sip)(H_2O)](NO_3) \cdot 4H_2O]$ (**2**). Blue crystals of **2** were obtained by adopting the similar synthetic procedure as **1** except that btm was replaced by btp (111 mg, 0.7 mmol). Yield: 48% (based on Cu). Anal. Calcd.(%) for $C_{22}H_{35}CuN_{13}O_{15}S$ (817.25): C 32.33, H 4.32, N 22.29. Found (%): C 32.65, H 4.37, N 22.54.

$[Cu(btb)_2(Hsip)]_n$ (**3**). Blue crystals of **3** were obtained by adopting the similar synthetic procedure as **1** except that btm was replaced by btb (120 mg, 0.7 mmol). Yield: 43% (based on Cu). Anal. Calcd.(%) for $C_{12}H_{14}Cu_{0.5}N_6O_{3.5}S_{0.5}$ (346.10): C 41.64, H 4.08, N 24.29. Found(%): C 41.35, H 4.18, N 24.55.

1.3 X-ray crystallography

Single-crystal X-ray diffraction measurements of **1**~**3** were carried out with a Oxford Supernova CCD diffractometer and a graphite crystal monochromator situated in the incident beam for data collection at 150 (2) K. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97^[29-30]

programs. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and refined isotropically. Crystallographic data for **1~3** are

summarized in Table 1. Selected bond lengths and angles were summarized in Table 2.

CCDC: 1023688, **1**; 776320, **2**; 1023689, **3**.

Table 1 Crystallographic data and structure refinement for complexes **1~3**

Complex	1	2	3
Empirical formula	C ₁₃ H ₁₅ Cu _{0.5} N ₆ O _{9.5}	C ₂₂ H ₃₅ CuN ₁₃ O _{15.5}	C ₁₂ H ₁₄ Cu _{0.5} N ₆ O _{3.5} S _{0.5}
Formula weight	463.15	817.25	346.1
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$Ama2$
<i>a</i> / nm	0.862 3(1)	1.727 9 (2)	1.573 1(2)
<i>b</i> / nm	0.870 7(2)	1.189 6(2)	1.964 0(3)
<i>c</i> / nm	1.315 3(2)	1.670 0 (1)	0.881 1(2)
α / (°)	87.020(9)	90	90
β / (°)	72.764(10)	97.644(6)	90
γ / (°)	67.786(10)	90	90
<i>V</i> / nm ³	0.871 1(3)	3.402 1(4)	2.722 2(3)
<i>Z</i>	2	4	8
<i>D_c</i> / (Mg·m ⁻³)	1.766	1.596	1.824
Absorption coefficient / mm ⁻¹	0.847	0.791	1.689
<i>F</i> (000)	475	1 692	1 428
θ range / (°)	2.53~25.01	2.46~25.01	2.45~25.01
Limiting indices	$-10 \leq h \leq 7$, $-10 \leq k \leq 10$, $-15 \leq l \leq 15$	$-20 \leq h \leq 20$, $-14 \leq k \leq 9$, $-19 \leq l \leq 19$	$-18 \leq h \leq 17$, $-22 \leq k \leq 23$, $-10 \leq l \leq 6$
Reflns collected / unique	5 161/3 078(<i>R</i> _{int} =0.025 6)	12 843/5 985(<i>R</i> _{int} =0.062 5)	3 922/2 201(<i>R</i> _{int} =0.034 2)
Goodness-of-fit on <i>F</i> ²	1.140	0.845	1.038
<i>R</i> ₁ / <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.033 7 / 0.099 3	0.049 2 / 0.088 8	0.057 3 / 0.136 4
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.037 9 / 0.100 8	0.100 7 / 0.096 6	0.059 3 / 0.137 7

Table 2 Selected bond lengths (nm) and bond angles (°) for complexes **1~3**

1					
Cu1-N1	0.202 0(2)	Cu1-N4 ⁱⁱ	0.202 4(2)	Cu1-O1A	0.237 7(2)
Cu1-N1i	0.202 0(2)	Cu1-N4C	0.202 4(2)	Cu1-O1	0.237 7(2)
N1-Cu1-N1 ⁱ	180.0	N4 ⁱⁱ -Cu1-N4 ⁱⁱⁱ	180.00(10)	N1-Cu1-O1	91.48(7)
N1-Cu1-N4 ⁱⁱ	91.48(8)	N1-Cu1-O1i	88.52(7)	N4B-Cu1-O1	88.27(7)
N1A-Cu1-N4 ⁱⁱ	88.52(8)	N1A-Cu1-O1A	91.48(7)	N4C-Cu1-O1	91.73(7)
N1-Cu1-N4 ⁱⁱⁱ	88.52(8)	N4B-Cu1-O1A	91.73(7)	O1A-Cu1-O1	180.00(7)
N1i-Cu1-N4 ⁱⁱⁱ	91.48(8)	N4C-Cu1-O1A	88.27(7)		
2					
Cu1-N7	0.198 7(3)	Cu1-N12 ⁱⁱ	0.199 4(3)	Cu1-O8	0.244 8(3)
Cu1-N6 ⁱ	0.201 1(3)	Cu1-N1	0.201 2(3)	Cu1-O1	0.253 6(3)
N7-Cu1-N12 ⁱⁱ	90.82(13)	N12 ⁱ -Cu1-N1	173.43(14)	N6B-Cu1-O8	88.09(11)
N7-Cu1-N6i	176.42(13)	N6B-Cu1-N1	87.98(13)	N1-Cu1-O8	98.78(12)
N12 ⁱ -Cu1-N6i	92.57(13)	N7-Cu1-O8	90.87(12)		
N7-Cu1-N1	88.79(13)	N12A-Cu1-O8	87.78(12)		

Continued Table 2

3					
Cu1-N6 ⁱ	0.201 0(6)	Cu1-N1	0.201 3(6)	Cu1-O3D	0.220 6(8)
Cu1-N6 ⁱⁱ	0.201 0(6)	Cu1-N1C	0.201 3(6)	Cu1-O1	0.256 4(7)
N6 ⁱ -Cu1-N6 ⁱⁱ	88.6(4)	N6 ⁱⁱ -Cu1-N1	172.7(3)	N6A-Cu1-O3D	91.1(2)
N6 ⁱ -Cu1-N1	87.9(3)	N1-Cu1-N1C	94.9(4)	N1-Cu1-O3D	95.4(2)

Symmetry codes: Complex **1**: ⁱ $-x, -y, -z+1$; ⁱⁱ $x, y-1, z$; ⁱⁱⁱ $-x, -y+1, -z+1$; Complex **2**: ⁱ $-x+1, y+1/2, -z+1/2$; ⁱⁱ $-x, y+1/2, -z+1/2$; Complex **3**: ⁱ $x, y+1/2, z+1/2$; ⁱⁱ $-x+3/2, y+1/2, z+1/2$; ⁱⁱⁱ $-x+3/2, y, z$; ^{iv} $x, y+1/2, z-1/2$

2 Results and discussion

2.1 Description of crystal structure of $\{[\text{Cu}_{0.5}(\text{btm})(\text{H}_2\text{O})](\text{H}_2\text{sip}) \cdot \text{H}_2\text{O}\}_n$ (**1**)

1 is double-stranded chains which are composed of ribbons of 16-membered rings, each ring involving two copper atoms and two btm molecules, in which the Cu (**1**) atom is in a general position (Fig.1). The metal coordination sphere is octahedral, with four nitrogen atoms from four btm ligands and two oxygen atoms from two water molecules. The four nitrogen atoms make up the equatorial plane, whereas the two oxygen atoms occupy the apical positions. The Cu-N bonds in **1** are in the normal range, and the axial Cu1-O1 distance (0.237 7(5) nm) is a little longer than the normal Cu-O distances, which can be attributed to Jahn-Teller elongation.

The btm ligand exhibits *cis* conformation and works as shorter spacers (N \cdots N 0.581 4 nm). Acting as bidentate chelating-bridging ligands, a pair of btm ligands chelate the Cu1 center by triazolyl N donors with the Cu \cdots Cu separation being 0.870 7(4) nm, which leads to an infinite 1D chain (Fig.1b).

In the framework of **1**, free H₂sip and lattice water molecules constitute 1D supramolecular double-chains along the crystallographic *a*-axis through classical hydrogen-bonding interactions (O2-H2A \cdots O9^{vi}, O9-H9A \cdots O8ⁱⁱ, O9-H9B \cdots O4^{viii}; Symmetry code: ^{vi} $-x+2, -y, -z$; ⁱⁱ $x, y-1, z$; ^{viii} $-x+1, -y+1, -z$; Table 3), which further links the 1D btm-Cu chains into 3D supramolecular architecture (Fig.1c and 1d). The btm-Cu chains carry positive charges, whereas the H₂sip⁻-H₂O supramolecular chains have negative charge. Thereupon, the 3D supramolecular structure is

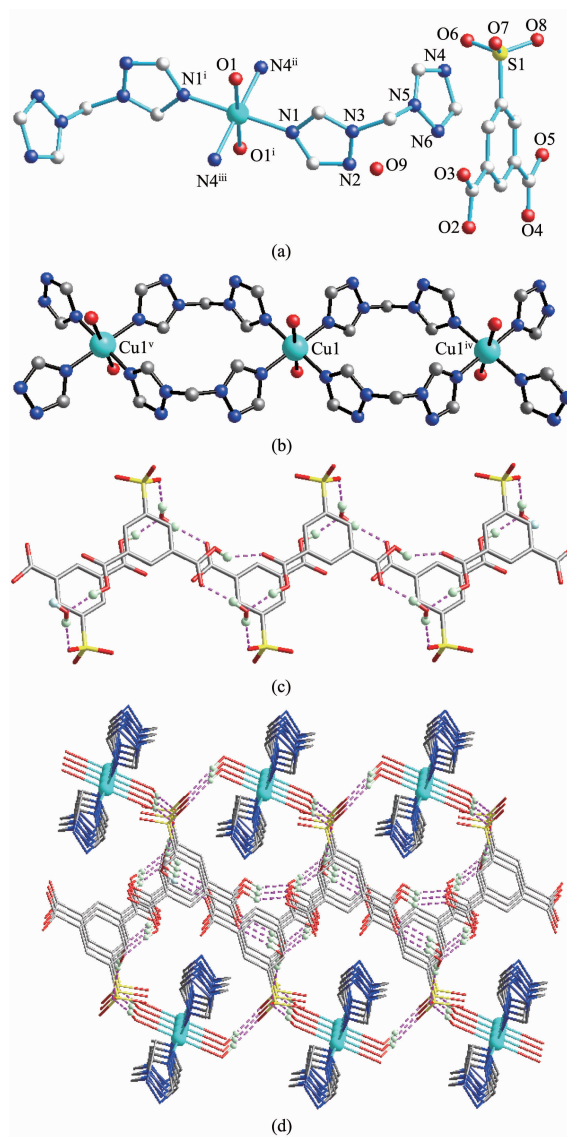


Fig.1 (a) Molecule structure of **1**, showing the coordination environments of Cu²⁺, btm and H₂sip⁻ ligands; (b) 1D chain of **1**; Symmetry Codes: ^{iv} $x, y+1, z$; ^v $x, y-1, z$; (c) Extended 1D supramolecular double-chain linked with hydrogen-bonding interactions in **1**; (d) 3D supramolecular structure of **1** viewed from *b* direction (dashed line: hydrogen bonding)

Table 3 Selected hydrogen bond data for 1~3

	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H}\cdots\text{A} / (^{\circ})$
1				
O1-H1B \cdots O6 ⁱⁱ	0.085 0	0.191 0	0.275 9	178.19
O2-H2A \cdots O9 ^{vi}	0.090 8	0.169 8	0.259 1	167.15
O5-H5 \cdots O3 ^{viii}	0.083 1	0.197 4	0.259 6	131.04
O9-H9A \cdots O8 ⁱⁱ	0.085 1	0.194 5	0.278 5	169.26
O9-H9B \cdots O4 ^{viii}	0.085 1	0.193 3	0.277 9	172.25
O1-H1A \cdots O8 ^{ix}	0.085 1	0.199 6	0.284 1	171.48
2				
O4-H4C \cdots O3 ^{viii}	0.083 8	0.183 0	0.263 5	160.34
O7-H7C \cdots O15 ^{iv}	0.084 6	0.174 7	0.258 5	170.80
O8-H8B \cdots O9 ^v	0.085 0	0.178 4	0.263 1	174.70
O8-H8C \cdots O12	0.084 8	0.195 8	0.279 4	168.09
O12-H12C \cdots N2 ^{vi}	0.085 2	0.205 1	0.285 4	156.66
O13-H13A \cdots O3 ^{viii}	0.085 0	0.205 9	0.285 7	156.02
O14-H14A \cdots O2 ^{viii}	0.085 2	0.189 8	0.274 0	169.43
O15-H15A \cdots O8 ^{vi}	0.085 2	0.198 1	0.283 1	175.48
O15-H15B \cdots O13 ^{vi}	0.084 8	0.191 6	0.273 1	161.00
3				
O6-H6A \cdots O2 ^{vi}	0.085 1	0.199 2	0.274 6	147.21

Symmetry codes: Complex 1: ⁱⁱ $x, y-1, z$; ^{vi} $-x+2, -y, -z$; ^{viii} $x-1, y+1, z$; ^{viii} $-x+1, -y+1, -z$; ^{ix} $-x+1, -y+1, -z+1$; Complex 2: ^{viii} $x, -y+5/2, z-1/2$; ^{iv} $x-1, y+1, z$; ^v $x, -y+3/2, z+1/2$; ^{vi} $-x+1, y-1/2, -z+1/2$; ^{viii} $x, y-1, z$; Complex 3: ^{vi} $-x+3/2, y, z-1$

consolidated by interchain hydrogen bonding interactions as well as electrostatic interactions (Fig.1d).

2.2 Description of crystal structure

$[\{\text{Cu}(\text{btp})_2(\text{H}_2\text{sip})(\text{H}_2\text{O})\}(\text{NO}_3)\cdot 4\text{H}_2\text{O}]_n$ (2)

Compound **2** crystallizes in the $P2_1/c$ space group, and structural determination reveals it as 2D layers linked by μ_2 -btp ligands. The repeated unit in **2** consists of one crystallographically independent Cu^{2+} ion. As viewed in Fig.2a, Cu1 is six-coordinated in a distorted octahedral coordination sphere that is defined by two different oxygen atoms (one from water, the other two from H_2sip^-) occupying the axial positions, while the equatorial positions are finished by four nitrogen donors from four btp ligands. The bond distances of Cu1-O8 and Cu1-O1 which occupy the axial positions of the octahedron, are 0.253 6(3) nm and 0.244 5(2) nm, respectively. This axial elongation could be attributed to the Jahn-Teller effect. The other Cu-O and Cu-N bonds in **2** are in the normal range.

All of the btp ligands adopt *trans* conformation with the N \cdots N distances of 0.743 2 nm (to which N1

belongs) and 0.844 6 nm (to which N7 belongs) between the two donor atoms and a dihedral angle of the two triazole rings of 66.9° and 111.7°, respectively. Each Cu(II) ion is linked by four btp ligands, leading to 2D tetragonal layer structures with Cu \cdots Cu separations of 1.002 6 nm (to which N1 belongs) and 1.131 4 nm (to which N7 belongs), as depicted in Fig.2b. The structures provide a very nice example of interdigitation. The sheets occur in which one of the uncoordinated carboxylic groups penetrate the rectangular windows of the partner, as can be clearly seen in Fig. 2c. Whats more, the interdigitating units lead to a 3D supramolecular architecture through the hydrogen-bond interactions(O4-H4C \cdots O3^{viii} (^{viii} $x, -y+5/2, z-1/2$)) (Table 3).

2.3 Description of crystal structure

$[\text{Cu}(\text{btb})_2(\text{Hsip})]_n$ (3)

3 crystallizes in the space group $Ama2$. In **3**, the Cu1 atom and S1 atom lie on a twofold axis and the twofold axis is parallel to the *b* axis. What's more, the H_2sip^- ligand is coordinated to the Cu1 with O1 from

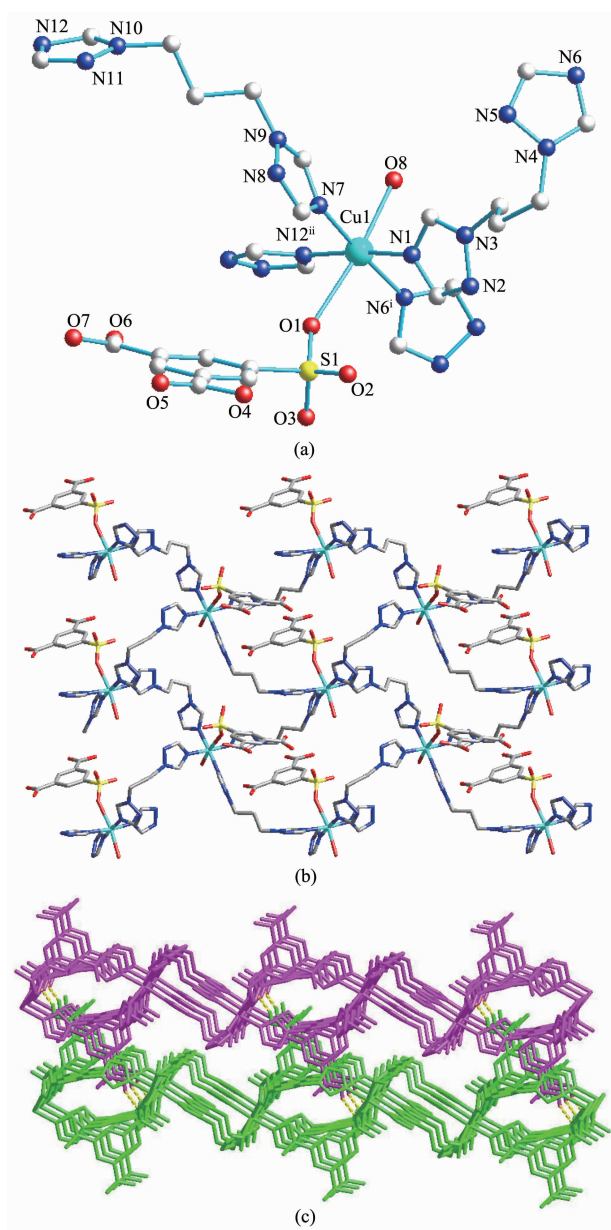


Fig.2 (a) Molecule structure of **2**, showing the coordination environments of Cu^{2+} , H_2sip^- and btp ligands; (b) 2D layer of compound **2** in *ab* plane; (c) 3D supramolecular structure of **2** viewed from a direction

the $-\text{SO}_3$ group and O3 from COO^- group, so the central atom Cu1 is unsymmetric (Fig.3). That is the reason why compound **3** belongs to non-centrosymmetric space group of *Ama2*.

The coordination environment of Cu(II) ions is presented in Fig.3(a). Every central Cu(II) ion is six-coordinated by two oxygen atoms from two Hsip^- ligands, four nitrogen atoms from four btp ligands, which is in a highly distorted octahedral coordination

sphere. The bond distances of Cu(II) ions with two Hsip^{2-} oxygen atoms are 0.220 6(8) nm and 0.256 4(7) nm, respectively. This axial elongation could also be

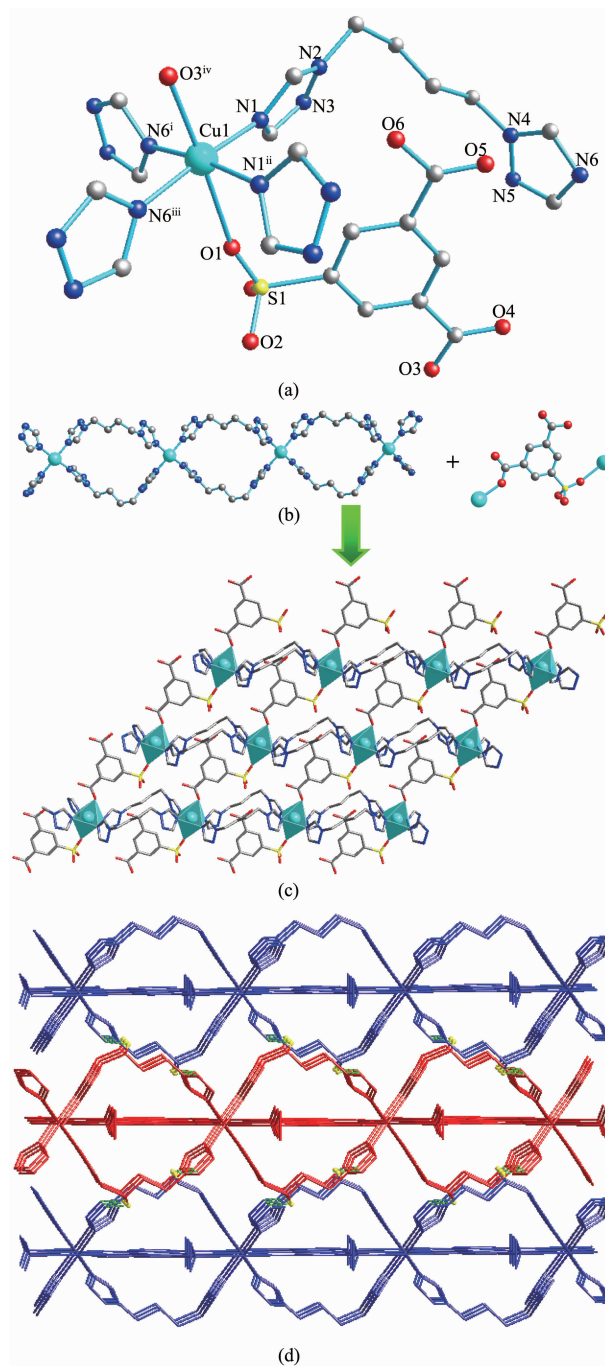


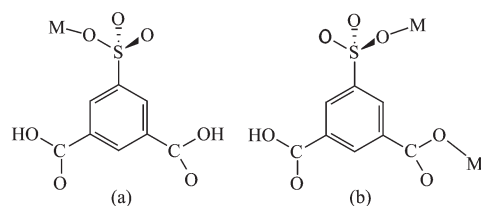
Fig.3 (a) Molecule structure of **3**, showing the coordination environments of Cu^{2+} , Hsip^{2-} and btp ligands and building unit with 30% thermal ellipsoids; (b) 1D double-stranded chain and μ_2 - Hsip^{2-} ligand in **3**; (c) 2D layer of **3** viewed from a direction; (d) 3D supramolecular structure of **3** viewed from *c* direction (dashed line: hydrogen bonding)

attributed to the Jahn-Teller distortion of copper(II) ions. All of the other Cu-O and Cu-N bonds are in the normal range.

The btb ligands adopt *cis* conformation with the N...N distances of 0.817 1 nm between the two donor atoms and a dihedral angle of the two triazole rings of 83°. Two strands of btb ligands are wrapped around each other and are held together by Cu(II) ions, also forming double-stranded chains like compound **1** (Fig. 3b). But the Cu...Cu separation across the bridging btb ligand is 1.076 3 nm which is longer than that in **1**. In the *bc* plane, the double-stranded chains are connected into a 2D layer by the link of the μ_2 -Hsip²⁻ ligands. What's more, the 2D layers lead to a 3D supramolecular architecture through the weak hydrogen-bond interactions (C12...N5^v 0.330 4 nm, C12-H12B...N5^v 126.98°, Symmetry code: ^v 1-x, -y+3/2, z-1/2)).

2.4 Comparison of structures

In the construction of compounds **1**~**3**, the difference coordination modes (Scheme 1) of the ligand NaH₂sip have an important influence on the resulting supramolecular architectures. In **1**, the H₂sip⁻ ligand did not coordinated to the central Cu²⁺, it is only as counter ion. In compound **2**, H₂sip⁻ ion acts as monodentate ligand, and mode a is observed. In **3**, Hsip²⁻ ion coordinated to Cu²⁺ ion in mode b as a bidentate ligand. In addition, the versatile conformations of bistriazole alkanes have an important influence on the resulting frameworks. So compound **1** is double-stranded chains; compounds **2** and **3** are two different kinds of 2D frameworks. This work can be compared with our previous results^[19,31-34], in which we used flexible bistriazole and rigid multicarboxylic ligands to obtain 1D, 2D, 3D and interpenetrated complexes. In all these complexes, although bistriazole ligands adopted the same μ_2 linking mode, ligand conforma-

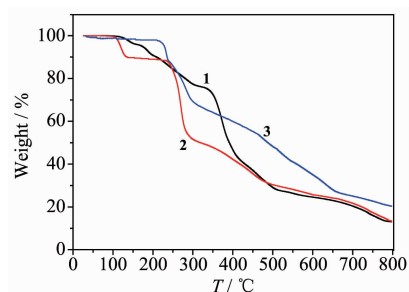


Scheme 1 Coordination modes of ligand NaH₂sip in **2** and **3**

tions, deprotonating degree and coordination modes of the aromatic multi-carboxylic ligands are important for various framework structures in crystal engineering.

2.5 TGA and EPR characterization for **1**~**3**

The thermal behaviors of these new crystalline materials were studied by thermogravimetric analysis (TGA) under nitrogen atmosphere (Fig.4). Because of the existence of free H₂sip anion in **1**, it is very unstable and decomposes gradually above 115 °C. The TGA result of **2** displays two steps weight losses. For **2**, the first weight loss of 11.00% from 105 to 135 °C should be attributed to the loss of water molecules (Calcd. 11.01%), and the second weight loss is ascribed to the loss of organic ligands and NO₃⁻ anions. The decomposition of the coordination framework of **2** occurs immediately when the temperature is above 235 °C. The TG curve for **3** reveals that it is stable up to 210 °C. With further heating, rapid mass loss occurs, which is assigned to the decomposition of organic ligands.



Sample was heated to 800 °C at the heating rate of 10 °C·min⁻¹

Fig.4 TGA curves for **1**~**3**

The EPR spectra of powdered samples of **1**~**3** have been measured at the room temperature and are shown in Fig.5. The simulations were carried out by the EasySpin software. The obtained spectra are characteristic for the copper(II) centers, which are simulated assuming the axial symmetry of *g* and *A* tensors. The simulated spectra were obtained by employing the following parameters: *g*_∥=2.21, *g*_⊥=2.05, *A*₁=50 G, *A*₂=5 G and *A*₃=5 G for compound **1**; *g*₁=2.23, *g*₂=2.05, *g*₃=2.03, *A*₁=90 G, *A*₂=25 G and *A*₃=10 G for compound **2**; *g*₁=2.24, *g*₂=2.08, *g*₃=2.05, *A*₁=120 G, *A*₂=0 G and *A*₃=10 G for compound **3**. Both **2** and **3** have three *g* values, so the Cu(II) ions in them exist as unsymmetrically

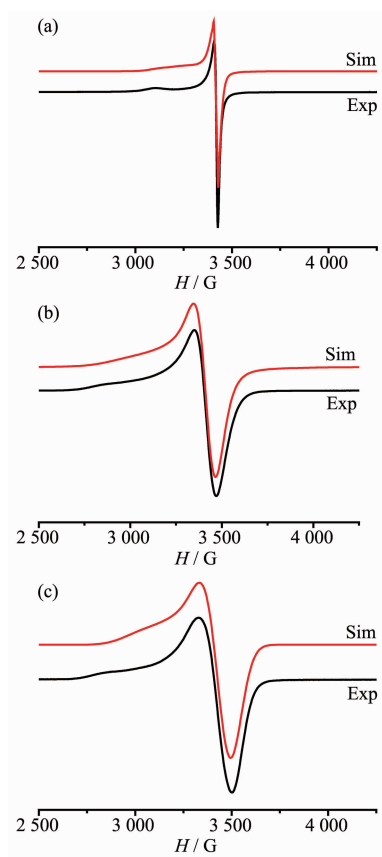


Fig.5 Experimental and simulated X-band EPR spectra of a powdered sample of **1** (a), **2** (b), and **3** (c) at room temperature

octahedral structures. Unlike **2** and **3**, the coordination environment of Cu(II) ions in **1** appear as symmetrically octahedron, and they only have two g values. The obtained values ($g_{\parallel} > g_{\perp} > 2.0023$) for **1** indicate that the unpaired electron is located in the $d_{x^2-y^2}$ ground state, which is in agreement with the crystal structure and the square-pyramidal coordination around Cu atom.

3 Conclusions

In summary, three novel inorganic-organic frameworks have been constructed from aromatic polycarboxylate acid (NaH_2sip) and $\text{Cu}(\text{NO}_3)_2$ in the presence of btm, btp and btb ligands with an increase of the length of $-(\text{CH}_2)-$. **1** features as 1D double-stranded chains. What's more, the free H_2sip^- and water molecules in **1** constitute into a supramolecular 1D chain through classical hydrogen-bonding interactions ($\text{O}-\text{H} \cdots \text{O}$). **2** has two-dimensional (2D) rectangular networks with a (4,4) topology, which contain 2D planar nano

grid networks stacked in a step stacking fashion. In compound **3**, the flexible btb ligands and Cu^{2+} ions also gives 1D double-strained chains like that in **1**, while the double-strained chains constitute to novel 2D layers by the link of $\mu_2\text{-Hsip}$. Structural analyses indicate that the difference in coordination modes of the aromatic polycarboxylic acids NaH_2sip and the versatile conformations of bistriazole alkanes have important influences on the resulting frameworks. Meanwhile, the weak hydrogen-bonding interactions also play important roles in the formation of complexes.

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