

Assembly of Seven Supramolecular Compounds with *p*-Sulfonatocalix[6]arene

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Received July 16, 2009; Revised Manuscript Received September 27, 2009

ABSTRACT: Seven supramolecular compounds comprising *p*-sulfonatocalix[6]arene and transition metals, {[Cu(Imz)(phen)(H₂O)]₄[C6AS]} · 10H₂O (**1**), {[Cu(Imz)₂(phen)]₂[Cu(Imz)(phen)(H₂O)]₂[C6AS]} · 13.3H₂O (**2**), {[M(phen)₂(H₂O)]-[M(phen)₂]₂[C6AS]} · *n*H₂O (**3** and **4**) (**3**: M = Co and *n* = 29.6; **4**: M = Zn and *n* = 29.9), {[Cu(phen)₂]₄[C6AS]}₂ · 13H₂O (**5**), [H₃O]₂[Co(phen)₃]₂[C6AS] · 10.7H₂O (**6**), and [Cu(phen)₂(H₂O)]₂{[Cu(phen)₂]₂[C6AS]} · 8H₂O (**7**) (phen = 1,10-phenanthroline, C6AS = *p*-sulfonatocalix[6]arene, Imz = imidazole), have been synthesized by a hydrothermal method and structurally characterized by IR spectroscopy, thermogravimetric-differential thermal analysis (TG-DTA), and single crystal X-ray diffraction. It is found that not only the acidity of the feeds plays an important role in the syntheses, but also the kind of metals, the molar ratio of the reactants, and the chelating ligands influence the final extended structures. The extended structures are featured with two-dimensional (2D) coordination layers, one-dimensional chains, or zero-dimensional fragments. Notably, the 2D metal-C6AS coordination layer was observed for the compounds of *p*-sulfonatocalix[6]arene for the first time. In these structures, all the C6AS ligands adopt a 1,2,3-alternate conformation.

Introduction

p-Sulfonatocalix[*n*]arenes (C*n*AS, *n* = 4, 5, 6, or 8), a well-known kind of water-soluble calixarene derivative, have been attracting increasing attention in supramolecular chemistry and coordination chemistry.^{1,2} Among them, *p*-sulfonatocalix[4]arenes (C4AS) has gained much attention, and a variety of structures composed of “Russian dolls”,³ “molecular capsules”,⁴ “ferris wheels”,⁵ hydrogen bonded polymers, and coordination polymers have been reported.⁶ In contrast to the flourishing study on C4AS, the solid-state supramolecular chemistry of the corresponding calix[5, 6, and 8]arenes is less well developed. For example, although *p*-sulfonatocalix[6]arenes (C6AS) possesses a profusion of active oxygen atoms from sulfonate and phenoxyl groups which might be helpful to coordinate various cationic units, it has not been used as a popular building block due to its flexible conformation and high charge. Raston and Atwood et al. reported some architectures in which C6AS can act as a ditopic receptor to specific guest molecules such as crown ether, pyridine N-oxide, 4,4'-dipyridine-*N,N'*-dioxide, lanthanide, transition metal and tetraphenylphosphonium cations to form extended supramolecular arrays and bimolecular capsules.⁷ Liu et al. prepared the inclusion compounds of C6AS with 1,10-phenanthroline (phen), 6,7-dihydro-5*H*-[1,4]diazepino-[1,2,3,4-*lmn*][1,10]-phenanthroline-4,8-dium, protonated quinoline and 8-hydroxyquinoline guests.⁸ Long and co-workers reported a supramolecular complex assembling from the building blocks of C6AS and cucurbit[6]uril through noncovalent bonding.⁹ Recently, our group prepared a copper/C6AS/phen supramolecular compound with one-dimensional (1D) [Cu₂-calixarene]_{*n*} coordination chains.¹⁰ However, as we know, the two- or three-dimensional (2D or 3D) coordination networks of C6AS were not reported. On the basis of our

previous work on the calixarenes,¹¹ we extended our research to the C6AS-phen system. Here we present the syntheses and structures of seven novel compounds {[Cu(Imz)(phen)(H₂O)]₄[C6AS]} · 10H₂O (**1**), {[Cu(Imz)₂(phen)]₂[Cu(Imz)(phen)(H₂O)]₂[C6AS]} · 13.3H₂O (**2**), {[M(phen)₂(H₂O)]-[M(phen)₂]₂[C6AS]} · *n*H₂O (**3** and **4**) (**3**: M = Co and *n* = 29.6; **4**: M = Zn and *n* = 29.9) {[Cu(phen)₂]₄[C6AS]}₂ · 13H₂O (**5**), [H₃O]₂[Co(phen)₃]₂[C6AS] · 10.7H₂O (**6**), and [Cu(phen)₂(H₂O)]₂{[Cu(phen)₂]₂[C6AS]} · 8H₂O (**7**) (phen = 1,10-phenanthroline, C6AS = *p*-sulfonatocalix[6]arene, Imz = imidazole). Among them, one can find a 2D metal-C6AS coordination network and some 1D metal-C6AS coordination chains. To the best of our knowledge, it is the first time the 2D coordination network for C6AS has been reported.

Experimental Section

Materials and Measurement. The sodium salt of *p*-sulfonatocalix[6]arene was synthesized according to the literature method,¹² and other reagents were purchased from commercial sources and used as received. The thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA-7000 instrument from 40 to 800 °C, with a heating rate of 10 °C min⁻¹ under a nitrogen flow. FT-IR (KBr pellets) spectra were recorded in the range of 225–4000 cm⁻¹ using a Perkin-Elmer Spectrum One FTIR spectrophotometer.

Preparation of Compounds 1–7. [Cu(Imz)(phen)(H₂O)]₄[C6AS] · 10H₂O (**1**) and [Cu(Imz)₂(phen)]₂[Cu(Imz)(phen)(H₂O)]₂[C6AS] · 13.3H₂O (**2**). A suspension of CuCl₂ · 2H₂O (34.0 mg, 0.2 mmol), Na₆C6AS (62.4 mg, 0.05 mmol), phen (39.6 mg, 0.2 mmol), and imidazole (34.0 mg, 0.5 mmol) in water (10 mL) was transferred into a Teflon-lined stainless-steel autoclave. The autoclave was heated to 130 °C in 90 min, kept at that temperature for 4 days, and then cooled gradually to room temperature at about 4 °C h⁻¹. The final pH value of the solution was 6.6. Green block crystals of **1** and blue block crystals of **2** suitable for X-ray diffraction analysis were isolated. Yield: 28% for **1** and 10% for **2** with respect to C6AS.

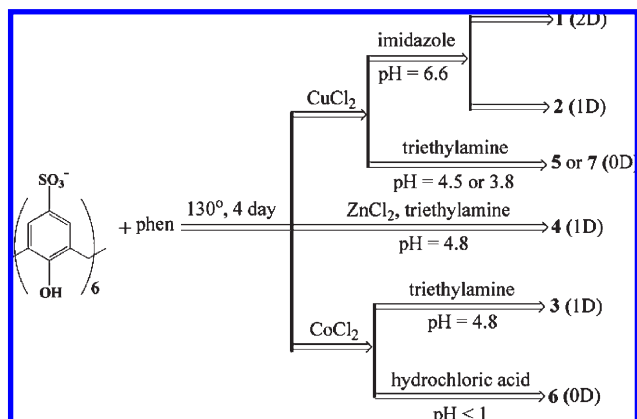
{[M(phen)₂(H₂O)]-[M(phen)₂]₂[C6AS]} · *n*H₂O (**3**: M = Co and *n* = 29.6; **4**: M = Zn and *n* = 29.9). Orange block crystals of **3** and colorless block crystals of **4** were obtained by hydrothermal treating the

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Table 1. Crystallographic Data for Compounds 1–7

	1	2	3	4	5	6	7
formula	C ₁₀₂ H ₁₀₄ Cu ₄ N ₁₆ O ₃₈ S ₆	C ₁₀₈ H _{118.50} Cu ₄ N ₂₀ O _{41.25} S ₆	C ₁₃₈ H _{169.06} Co ₄ N ₁₆ O _{55.53} S ₆	C ₁₃₈ H _{169.74} Zn ₄ N ₁₆ O _{55.87} S ₆	C ₁₃₈ H ₁₁₈ Cu ₄ N ₁₆ O ₃₇ S ₆	C ₁₁₄ H _{105.32} Co ₂ N ₁₂ O _{36.66} S ₆	C ₁₃₈ H ₁₁₂ Cu ₄ N ₁₆ O ₃₄ S ₆
formula wt	2608.53	2803.25	3368.51	3400.40	3039.00	2540.20	2984.96
<i>T</i> (K)	186(2)	187(2)	187(2)	186(2)	187(2)	173(2)	187(2)
cryst. syst.				triclinic			monoclinic
space group				P $\bar{1}$			P2 ₁ /c
<i>a</i> (Å)	13.3935(5)	12.8498(5)	12.1344(5)	12.1579(4)	16.0944(9)	11.2771(5)	20.5525(7)
<i>b</i> (Å)	14.9472(5)	13.3198(5)	15.4172(6)	15.4571(5)	16.1653(8)	15.4311(7)	14.8671(5)
<i>c</i> (Å)	15.8144(6)	17.2996(7)	20.3397(7)	20.2944(7)	26.696(2)	16.2779(7)	25.5502(7)
α (deg)	67.904(1)	82.762(1)	80.495(1)	99.640(1)	91.654(1)	85.799(1)	90
β (deg)	69.399(1)	82.390(1)	85.236(1)	94.916(1)	105.849(1)	82.086(1)	127.511(2)
γ (deg)	66.590(1)	84.626(1)	89.904(1)	90.071(1)	98.066(1)	75.895(1)	90
volume (Å ³)	2614.6(2)	2902.5(2)	3739.6(2)	3745.7(2)	6598.9(6)	2718.8(2)	6192.8(3)
<i>Z</i>	1	1	1	1	2	1	2
<i>D_c</i> /g cm ⁻³	1.654	1.600	1.490	1.507	1.529	1.551	1.601
μ /mm ⁻¹	1.021	0.929	0.616	0.813	0.821	0.516	0.872
<i>F</i> (000)	1344	1442	1744	1773	3132	1317	3072
total data	18978	17765	35910	22998	39928	14721	44011
unique data	9166	10165	13161	13158	23085	9521	10915
<i>R</i> _{int}	0.0324	0.0240	0.0363	0.0273	0.0311	0.0252	0.0497
GOF	1.066	1.060	1.078	1.088	1.021	1.055	1.088
<i>R</i> ¹ _a [<i>I</i> > 2σ(<i>I</i>)]	0.0428	0.0409	0.0615	0.0594	0.0978	0.0437	0.0460
<i>wR</i> ² _b	0.1217	0.1081	0.1863	0.1912	0.2481	0.1052	0.1484

$$^a R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad ^b wR2 = \frac{\{\sum [w(F_o^2 - F_c^2)^2]\}}{\{\sum [w(F_o^2)^2]\}}^{1/2}.$$

Scheme 1. Syntheses of Compounds 1–7

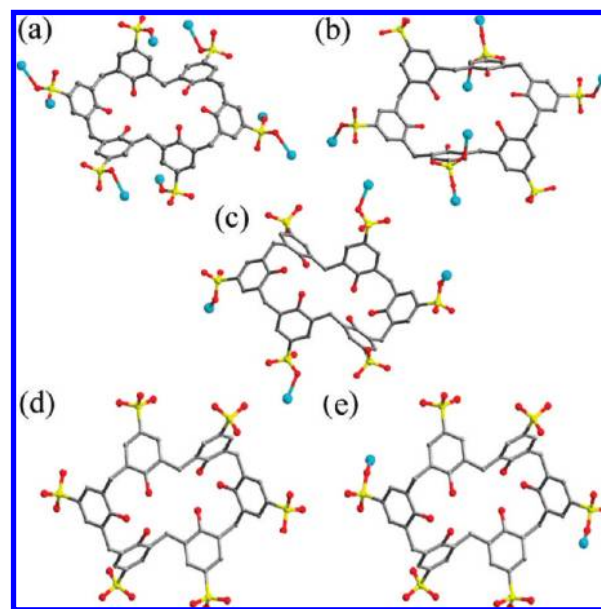
suspension of CoCl₂·6H₂O (24 mg, 0.1 mmol) or ZnCl₂ (13.6 mg, 0.1 mmol), Na₆C₆AS (62.4 mg, 0.05 mmol), and phen (39.6 mg, 0.2 mmol) in 10 mL of deionized water (whose pH value was adjusted by 0.4 mol/L triethylamine aqueous solution to 5.2) following similar procedures for the syntheses of **1** and **2**. The final pH value was 4.8. Yield: 24% for **3** and 31% for **4**.

{[Cu(phen)₂]₄[C₆AS]₂·13H₂O (**5**). Green block crystals of **5** were obtained by similar experiments for the syntheses of **3** and **4** but with CoCl₂·6H₂O or ZnCl₂ replaced by CuCl₂·2H₂O (17 mg, 0.1 mmol). The pH value of the feed was first adjusted to about 5 and the final pH value was 4.5. Yield: 23% for **5**.

[H₃O]₂[Co(phen)₃]₂[C₆AS]·10.7H₂O (**6**). The synthesis of **6** was similar to that of **3**, but the pH value was adjusted using hydrochloric acid (1 mol/L) to 1.5 first. The final pH value of the solution was less than 1. Yield: 41% for **6**.

[Cu(phen)₂(H₂O)]₂[[Cu(phen)₂]₂[C₆AS]]·8H₂O (**7**). Green block crystals of **7** were obtained by similar experiments for the syntheses of **3** and **4** but with CoCl₂·6H₂O or ZnCl₂ replaced by CuCl₂·2H₂O (17 mg, 0.1 mmol). The pH value of the feed was first adjusted to about 4.5 and the final pH value was 3.8. Yield: 17% for **7**.

X-ray Crystal Structure Analysis. The X-ray intensity data for compounds **1**–**7** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) operated at 2.0 kW (50 kV, 40 mA). The crystal structure was solved by means of Direct Methods and refined

Scheme 2. Coordinations of C₆AS in Compounds 1–7: (a) **1**; (b) **2**–**4**; (c) **5**; (d) **6**; and (e) **7**

employing full-matrix least-squares on *F*² (SHELXTL Program).¹³ All non-hydrogen atoms except some disordered water molecules were refined anisotropically, and hydrogen atoms of the phen and C₆AS were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The refinement details for these compounds are given in Table 1.

Crystallographic data for these structures reported here have been deposited in Cambridge Crystallographic Data Center with CCDC reference numbers 733763–733768 and 737591 for compounds **1**–**7**.

Results and Discussion

Syntheses. Compounds **1**–**7** were prepared under similar hydrothermal conditions, and their formations were governed by the reaction conditions such as the reactants, the

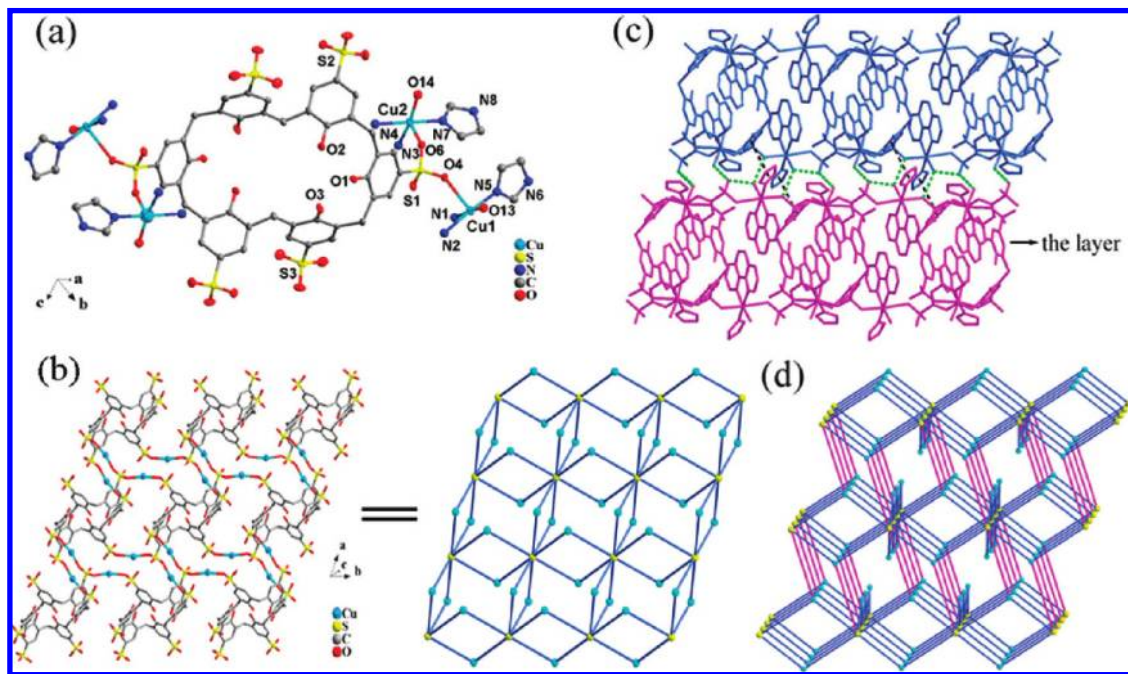


Figure 1. Compound **1**: (a) molecular structure (carbon atoms of phen ligands, water molecules and hydrogen atoms are omitted for clarity); (b) a ball-and-stick plot (left; phen and imidazole molecules are omitted for clarity) and the topological representation of the 2D coordination layer (right; C6AS: yellow; copper atoms: blue); (c) the stacking of the coordination layers through hydrogen bonds (green dotted lines) and $\pi \cdots \pi$ stacking interactions (black dotted lines); (d) topological representation of the extended structure (purple line, $\pi \cdots \pi$ stacking interactions).

molar ratio of the reactants, cochelating ligands, and the pH value of the reaction system. The synthesis conditions of compounds **1–7** are summarized in Scheme 1.

As Atwood et al. reported,¹⁴ the pK_{a1-2} values for the phenolic hydroxyls of C6AS are 4.76 and 3.44, respectively. At a higher pH value, the phenolic hydroxyl groups should be deprotonated more easily and the coordination number of the C6AS ligand might become larger. The coordinations of C6AS in compounds **1–7** are shown in Scheme 2. It can be found that the metals bonded to C6AS become less in number with the increasing acidity of the feeds and even reach none when the pH value of the feed is below 1. The 2D networks or 1D chains formed when the pH value of the feed was higher than 4.5, while 0D fragments formed with the pH value being < 4.5 . The effect of the cochelating ligands has also been studied. In the syntheses of **1** and **2**, no target crystals were obtained if there was no imidazole added in the feeds. Similarly, in the syntheses of compounds **3** and **4**, if phen was substituted by 2,2'-bipy, only pellucid solution was observed. This means that the organonitrogen ligands not only act as the chelants but also play an important role in the stacking of the extended structures. It is also found that different metals led to different structures in the similar condition such as compounds **3(4)** and **5**. The effect of the molar ratio of the reactants was obvious. When the amount of phen was reduced by half and no triethylamine aqueous solution was used to adjust the acidity of the feed in the synthesis of compound **5**, another compound $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})]\{[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2][\text{C6AS}]\} \cdot 2.5\text{H}_2\text{O}$ (**8**) was obtained.¹⁰

Description of Crystal Structures. Single-crystal X-ray analysis reveals that compounds **1–6** crystallize in a triclinic system with space group $P\bar{1}$ and compound **7** crystallizes in a monoclinic system with space group $P2_1/c$. The C6AS molecules in all these seven compounds adopt a similar

1,2,3-alternate conformation which is stabilized by the intramolecular hydrogen bonds between the phenolic hydroxyl groups of the C6AS.

Compound 1. The characteristic feature of **1** is given by the 2D $\{[\text{Cu}(\text{Imz})(\text{phen})(\text{H}_2\text{O})_4][\text{C6AS}]\}_n$ neutral layers in which the C6AS molecule acts as an octadentate ligand to bond eight copper cations through six sulfonate groups. To the best of our knowledge, it is the first example with 2D C6AS-metal coordination polymers and also the first example for C6AS acting as an octadentate ligand. The extended structure is stacked by these layers along the c axis through supramolecular stacking interactions such as hydrogen bonds and $\pi \cdots \pi$ stacking interactions.

There are two crystallographically independent Cu centers in an asymmetric unit, both of which are six-coordinated in similar coordination environments. Both Cu(1) and Cu(2) sites are coordinated by two sulfonate oxygen atoms (with the Cu–O distances being in the range of 2.30–2.61 Å) from two C6AS ligands, three nitrogen atoms (with the Cu–N distances being of 1.96–2.02 Å) from one phen and one imidazole ligand and one water molecule (with the Cu–O distance being of 1.99 or 2.01 Å). Notably, Cu(1) and Cu(2) atoms are bonded to the same sulfonate group in an asymmetric unit, as shown in Figure 1a. The adjacent C6AS molecules are bridged by Cu(1) atoms into the chains along the [010] direction, and the Cu(2) atoms link the chains into a 2D puckery framework parallel to the (001) face (Figure 1b). The extended structure can be best described as the stacking of these 2D layers along the c axis by the $\pi \cdots \pi$ stacking interactions between the imidazole ligands bonded to Cu(1) atom and the aromatic ring of C6AS (π imidazole ring (N5, N6, C47–C49) $\cdots \pi$ aromatic ring (C1–C5, C19): 3.78 Å), and the hydrogen-bonding interactions between the intermolecular sulfonate groups and the water molecules bonded to Cu(1) and Cu(2) atoms (the shortest O(4) \cdots O(13): 2.74 Å)

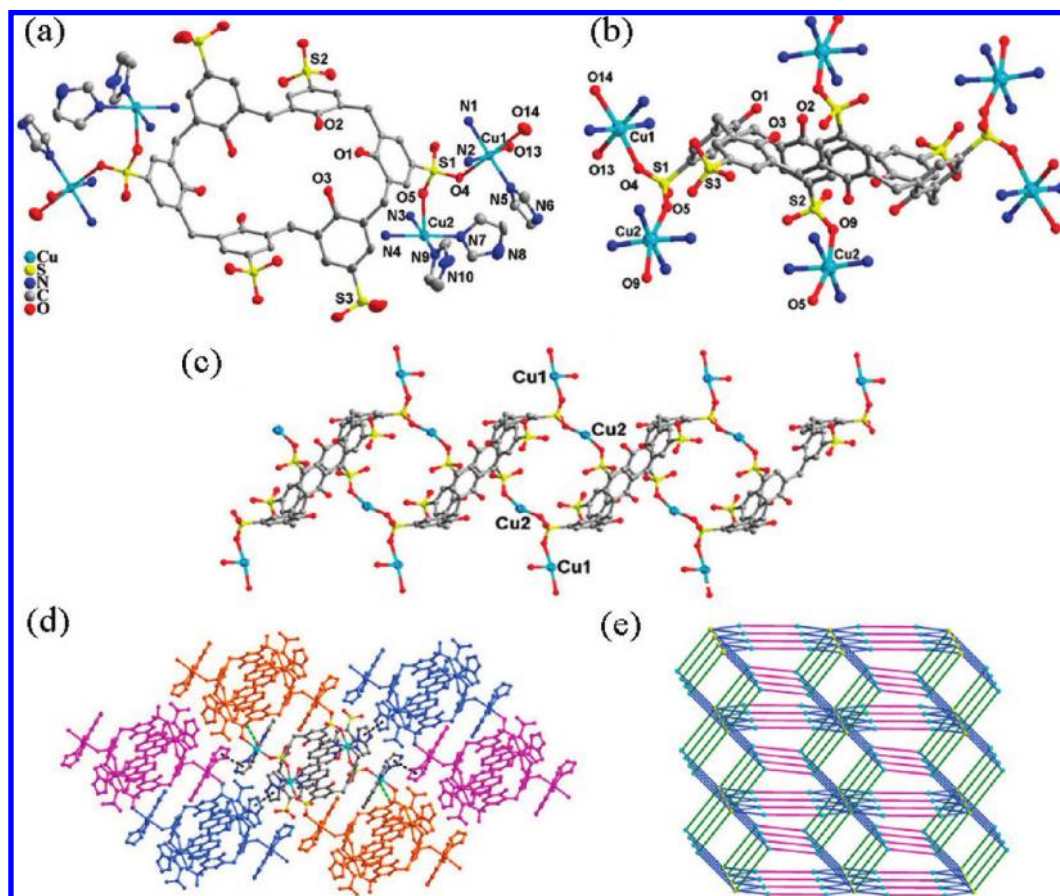


Figure 2. Compounds **2**: (a) molecular structure (carbon atoms of phen ligands, water molecules, and hydrogen atoms are omitted for clarity); (b) the coordination of C6AS; (c) a 1D M_2 -C6AS chain; (d) $\pi \cdots \pi$ stacking interactions (green dotted lines) and hydrogen bonds (black dotted lines) between one linear chain and its six neighbors; (e) schematic drawing of the 3D supramolecular topology (cyan line, yellow and blue nodes, coordination polymer chains; purple line, $\pi \cdots \pi$ stacking interactions (interaction A); green line, hydrogen bonds (interaction B); the same hereafter).

(see Table S1, Supporting Information) (Figure 1c). A better insight of this attractive structure can be obtained by reducing this multidimensional structure to a simple node-and-linker reference net known as the topological approach. If the 2D layers are thought as ball-and-stick representation (cyan line, yellow and blue nodes) and the $\pi \cdots \pi$ stacking interactions as the spacers (purple line, 12.60 Å), the 3D topological network can be shown in Figure 1d.

Compounds 2–4. The structures of compounds **2–4** are featured by the 1D neutral chains in which the C6AS molecule acts as a hexadentate ligand and bonds six metal atoms simultaneously. However, the chains in **2** are different from those in **3** and **4**. To be exact, the chains in **2** are better called the “belts” or “ladders” because all the calixarenes are bridged into the 1D fragments by the metals through four opposite sulfonate groups. Differently, those in **3** and **4** are exact chains in which the calixarenes are interconnected by the metals through two opposite sulfonate groups. All these three extended structures are stacked by the 1D chains through $\pi \cdots \pi$ stacking interactions and hydrogen bonds. Some solvent water molecules are found in the interstices.

In all three compounds, there are two crystallographically independent metal centers in an asymmetric unit, both of which are six-coordinated but in different coordination environments (Figures 2 and 3). In compound **2**, Cu(1) atom is coordinated by one sulfonate group (with the Cu–O distance being 2.31 Å), three nitrogen atoms from one phen

and one imidazole ligand (with the Cu–N distances being in the range of 1.97–2.03 Å) and two water molecules (with the Cu–O distance being 2.00 and 2.01 Å). In compounds **3** and **4**, M(1) site is coordinated by one sulfonate group (with the distance Co(1)–O(8) = 2.09 Å and Zn(1)–O(8) = 2.10 Å), four nitrogen atoms from two phen ligands (with the M–N distances being in the range of 2.11–2.19 Å) and one water molecule (with the M–O distance being 2.09 Å in **3** and 2.11 Å in **4**). All the Cu(2) in **2** and M(2) in **3** and **4** are coordinated by two sulfonate groups from two different C6AS ligands (with the M–O distance being 2.39 and 2.57 Å in **2**; 2.09 and 2.15 Å in **3** and 2.11 and 2.16 Å in **4**, respectively) and two phen ligands (with the M–N distances being in the range of 1.98–2.03 Å in **2**; 2.11–2.14 Å in **3** and 2.11–2.13 Å in **4**, respectively).

In compound **2**, Cu(1) and Cu(2) atoms are bonded to a same sulfonate group in the asymmetric unit as in compound **1**. Different from the Cu(1) site which is coordinated by one Imz, one phen and two water molecules and hung on a C6AS molecule, Cu(2) is coordinated by one phen, two Imz and another sulfonate group from another C6AS molecule. So the Cu(2) atoms bridge the C6AS molecules into a belt along the *a* axis (Figure 2c) which is similar to that in the reported structure.¹⁰ The 3D supramolecular structure can be best described as the arrangement of these belts with six others by the $\pi \cdots \pi$ stacking interactions between the imidazole molecules bonded Cu(1) and Cu(2) (with a face-to-face distance being 3.63 and 3.73 Å), and the hydrogen bonds between the

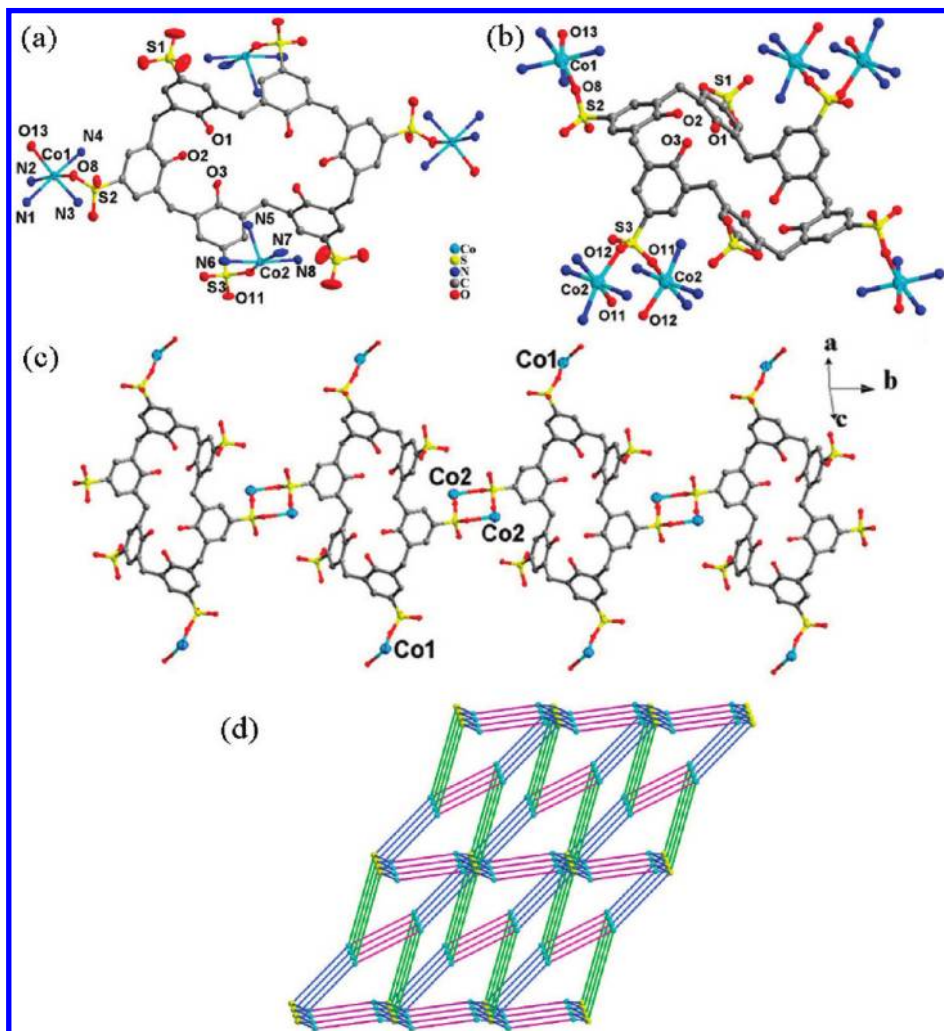


Figure 3. Compounds **3** and **4**: (a) molecular structure (carbon atoms of phen ligands, water molecules, and hydrogen atoms are omitted for clarity); (b) the coordination of C6AS; (c) a 1D M_2 -C6AS chain; and (d) schematic drawing of the 3D supramolecular topology.

intermolecular sulfonate groups and water molecules coordinated to Cu(1) and Cu(2) atoms (see Table S1, Supporting Information and Figure 2d). If the C6AS molecules and Cu atoms are perceived as nodes and the $\pi \cdots \pi$ stacking interactions (interaction A: 7.86 and 8.33 Å) and hydrogen bonds (interaction B: 11.18 Å) as spacers, the 3D topological structure can be obtained (shown in Figure 2e).

In isomorphous compounds **3** and **4**, M(1) and M(2) atoms are bonded to two adjacent sulfonate groups of a C6AS molecule in an asymmetric unit (Figure 3a). Except the sulfonate group, M(1) is also coordinated by two phen molecules and one water molecule. However, M(2) is bonded to two sulfonate groups from two C6AS ligands so that it connects the C6AS ligands into some 1D chains along the *b* axis (Figure 3c). Each chain is arrayed with six others by the $\pi \cdots \pi$ stacking interactions between the phen molecules bonded M(1) and M(2) (with a face-to-face distance being of 3.78, 3.75, and 3.75 Å in **3**; 3.77, 3.70, and 3.75 Å in **4**), and the hydrogen bonds between the intermolecular sulfonate groups and water molecules coordinated to M(1) atoms (see Table S1 and Figure S1, Supporting Information) to form a 3D supramolecular network (Figure 3d).

It should be noted that, although all the compounds **2–4** exhibit M_2 -C6AS- M_2 -C6AS chains which contain two parallel metal lines, there is significant difference in their topologies.

In compound **2**, each C6AS bridges the copper atoms into the belts through four sulfonate groups, while in compounds **3** and **4** each C6AS bridges the copper atoms into the 1D chain through two sulfonate groups each of which bonds two bridge metals simultaneously. By comparing the structures of compounds **2** and **3**(**4**), one can find that the pH value of feeds and the kind of cochelating ligand play a key role in constructing the extended structures.

Compound 5. Single-crystal X-ray diffraction revealed there are two similar tetranuclear units in an asymmetric unit as shown in Figure 4a, which have some small difference in bond length and bond angle. There are four crystallographically independent Cu centers in an identical coordination environment. All the Cu atoms are coordinated by one sulfonate group from the C6AS ligand (with the Cu–O distances being 2.06–2.14 Å) and two phen ligands (with the Cu–N distances being in the range of 1.96–2.14 Å). C6AS acts as a tetragonal tetradentate ligand and is bonded to four metal atoms through four sulfonate groups, which exhibits some similarity to those in the reported structure.¹⁰ However, C6AS adopts a 1,2,3-alternate conformation here but an uncommon up–up double cone conformation in the reported complex.¹⁰

All the tetranuclear units are stacked by the $\pi \cdots \pi$ stacking interactions between the phen molecules (with face-to-face

distances being 3.56–3.93 Å; Figure S2, Supporting Information), and the extended structure can be simplified into a 3D topology as shown in Figure 4c if the C6AS molecules and the copper atoms are thought as the nodes and the coordination and supramolecular interactions as spacers.

Compound 6. In an asymmetric unit, there is one cobalt site, one C6AS molecule, and some isolated water solvent molecules. As shown in Figure 5, the C6AS molecule also adopts the 1,2,3-alternate conformation but bonds no metal

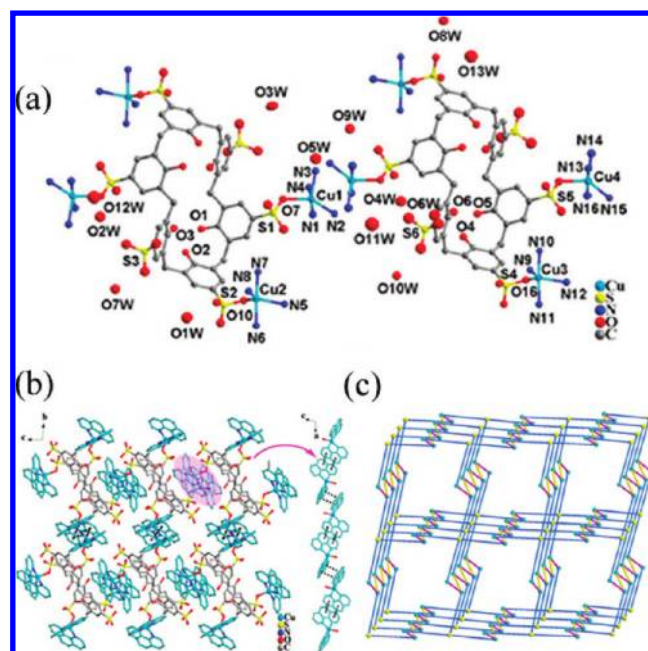


Figure 4. Compounds 5: (a) molecular structure; (b) view of the extended structure along the *a* axis showing a layered structure in which the $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})]^{2+}$ units are interconnected into some linear chains by the $\pi \cdots \pi$ stacking interactions; (c) schematic drawing of the 3D supramolecular topology.

atoms. The cobalt cations are coordinated by three phen molecules, and all bond distances and angles around the metal centers are close to those reported in the literature.¹⁶

The interesting structural feature of **6** is given by the calixarene layers separated by the zigzag-like $[\text{Co}(\text{phen})_3]^{2+}$ cation layers. That is, the C6AS molecules are interconnected to each other through hydrogen bonds between the sulfonate groups and phenolic hydroxy groups into some 1D chain-like structure along the *c* axis and then these supramolecular chains are linked into the 2D layers through $\text{C}-\text{H} \cdots \text{O}$ hydrogen-bonds (see Table S4, Supporting Information and Figure 5c). The 2D calixarene layers parallel to the (*ac*) plane are further stacked along the *b* axis to form a 3D supramolecular structure. Notably, all the adjacent C6AS anion layers are separated by the zigzag-like $[\text{Co}(\text{phen})_3]^{2+}$ cation layers which are interconnected by the $\pi \cdots \pi$ stacking interactions between the phen molecules (with face-to-face distances being 3.85 Å), and hydrogen bonding interactions between solvent water molecules and the carbon atoms of phen (see Table S1 and Figure S3, Supporting Information). As shown in Figure 5b, these intertwining 2D architectures are interconnected to each other through the $\pi \cdots \pi$ stacking interactions (Figure S4, Supporting Information) between the phen molecules and the aromatic groups of the C6AS molecules (with face-to-face distances being 3.85 and 3.84 Å). The 3D simplified topology structure is shown in Figure 5d. In addition, two H^+ cations are compensated by the charge balance.

Compound 7. This compound crystallizes in a monoclinic system with space group $P2_1/c$, which is different from compound **5** and the previously reported samples.¹⁰ There are two crystallographically independent Cu sites in an asymmetric unit, both of which are five-coordinated but in a different coordination environment. The Cu(1) atom is bonded to two phen molecules (with the Cu–N distances being 1.97–2.12 Å) and one sulfonate oxygen atom (with the Cu–O distance being 2.02 Å), while the Cu(2) atom is coordinated by two phen ligands (with the Cu–N distances being in the range of 1.97–2.11 Å) and one solvent water

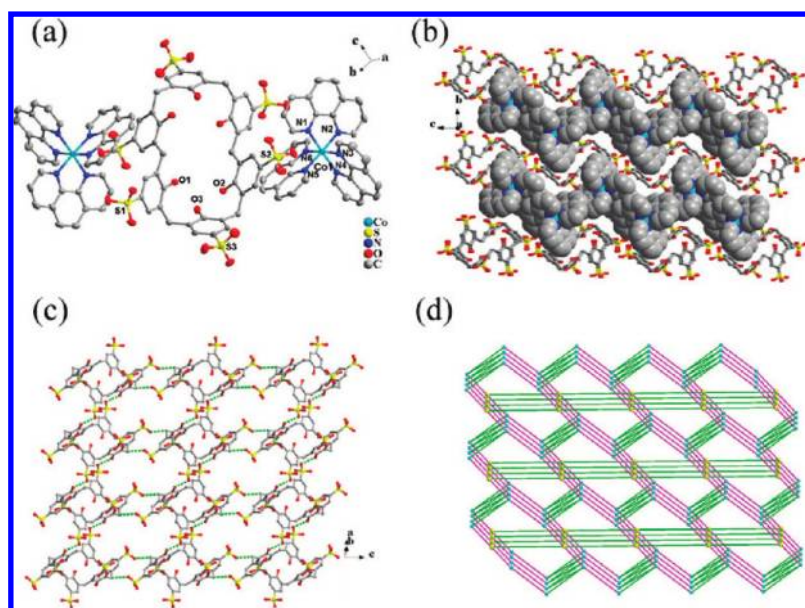


Figure 5. Compound 6: (a) Molecular structure; (b) the alternate stacking of C6AS anion layers and zigzag-like $[\text{Co}(\text{phen})_3]^{2+}$ cation layers along the *b* axis; (c) the 2D supramolecular C6AS anion layer showing hydrogen bonds; (d) schematic drawing of the 3D supramolecular topology.

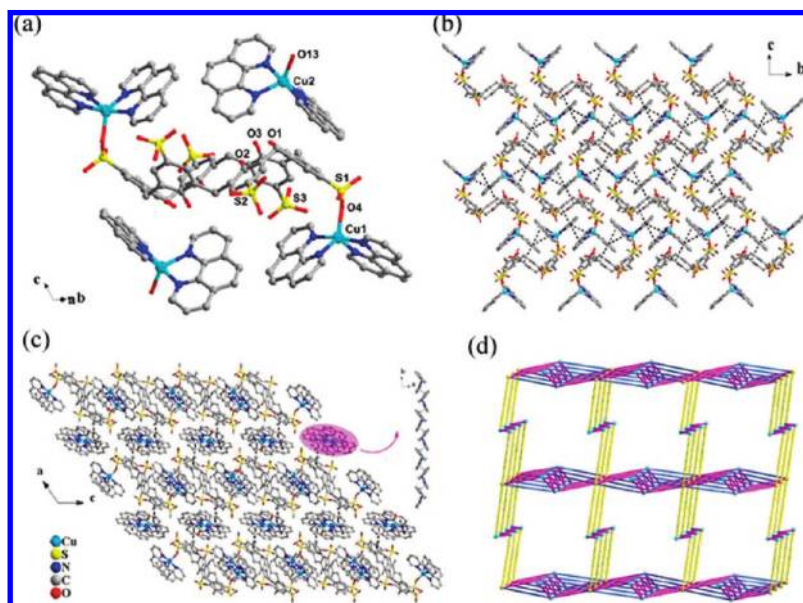


Figure 6. Compound 7: (a) Molecular structure; (b) the 2D supramolecular $\{[\text{Cu}(\text{phen})_2]_2[\text{C6AS}]\}^{4-}$ anionic layer showing $\pi \cdots \pi$ stacking interactions; (c) the layered extended structure showing the $\{[\text{Cu}(\text{phen})_2]_2[\text{C6AS}]\}^{4-}$ anionic layers separated by the $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})]^{2+}$ cationic chains; (d) schematic drawing of the 3D supramolecular topology.

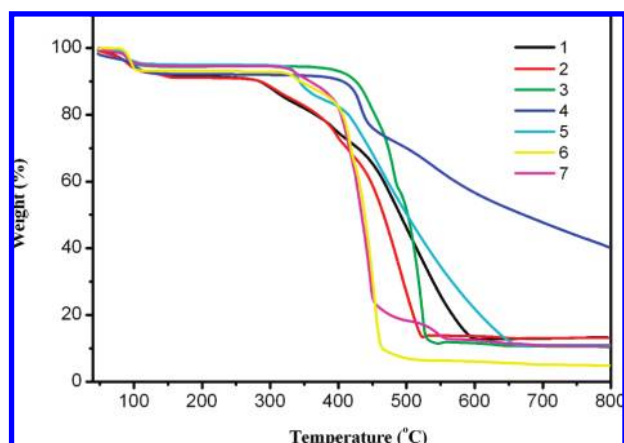


Figure 7. TGA curves of compounds 1–7.

molecule (with the Cu–O distance being 2.02 Å). As shown in Figure 6a, two Cu(1) atoms are bonded to a C6AS molecule to form a binuclear unit, while the Cu(2) atoms with phen and water molecules form some isolated $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})]^{2+}$ cations.

The binuclear units is interconnected to form a 2D layer via $\pi \cdots \pi$ stacking interactions between the aromatic rings of C6AS and the heterocycle rings of phen ligands coordinated to Cu(1) ions (with face-to-face distances being 3.86 Å, interaction A: spacers, 8.87 Å) or the aromatic and heterocycle rings of phen ligands coordinated to Cu(1) ions (with a face-to-face distances being 3.59 and 3.92 Å, interaction A: spacers, 7.97 Å) (Figure 6b). On the other hand, the isolated $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})]^{2+}$ cationic units are interconnected to each other via $\pi \cdots \pi$ stacking interactions (with a face-to-face distances being 3.85 Å, interaction B: spacers, 7.61 Å) between the phen ligands coordinated to Cu(2) atoms to form some infinite 1D chain along the *b* axis. Furthermore, viewed along the *b* axis, they are linked by the $\pi \cdots \pi$ interactions (with a face-to-face distance being 3.72 Å, interaction B: spacers, 8.44 Å), which further connect the

layers into a 3D network (Figure 6c). Upon close examination of the extended structure, one can find that the 3D supramolecular network can be regarded as the alternant stacking of the $\{[\text{Cu}(\text{phen})_2]_2[\text{C6AS}]\}^{4-}$ anionic layers and the $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})]^{2+}$ cationic chains. A novel topology structure of compound 7 is shown in Figure 6d if the C6AS⁸⁻ and Cu ions are considered as nodes and the coordination and supramolecular interactions as spacers, which is quite different from 5.

Thermal Analysis and IR Spectrum of Compounds 1–7.

The TGA curves of 1–7 are similar and that for compound 1 was discussed as an example (Figure 7). It is roughly divided into two stages. The former one in the range of 50–180 °C can be assigned to the release of all lattice water and coordination water molecules. The observed weight loss of 8.9% is close to the calculated value (9.7%). The latter stage after 280 °C can be attributed to the gradual decomposition of compound 1. The total weight loss is about 86.8% at 600 °C, but the final products are not identified. We suggest that the residual is mainly composed of CuSO_4 and CuO . The IR curves of 1–7 are also similar, and compound 1 was also chosen as an example (Figure S5, Supporting Information). The features in IR spectra of 1 at 1640–556 cm^{-1} can be attributed to the *p*-sulfonatocalix[6]arene and phen molecules. Peaks at about 1035, 1154 cm^{-1} are attributed to the vibration of the $-\text{SO}_3$ group, while the strong and broad peak at about 3433 cm^{-1} may be assigned to the contributions of the $-\text{OH}$ group from both C6AS and water molecules.

Conclusion

Seven novel M/C6AS/phen (or mixed phen and imidazole) compounds have been successfully synthesized by a hydrothermal route and structurally determined by X-ray analysis. It is found that not only the acidity of the feeds plays an important role in the syntheses, but also the metals and the cocatalyzing ligands influence the final extended structures. The 2D metal-C6AS coordination layer was observed for the first time in the presence of 1,10-phenanthroline and imidazole. Three structures with the rarely reported 1D metal-C6AS

coordination chains were also successfully obtained. The C6AS ligand adopts a 1,2,3-alternate conformation in all these compounds. However, with the increasing acidity of the feeds, the coordination ability of C6AS became less; that is, the coordination number of C6AS became less and less and even reached zero when the pH value of the feed was below 1, which leads to the fragments in different dimensions.

Acknowledgment. This work was supported by National Natural Science Foundation of China (Nos. 50704029, 20971119), S&T Development Program of Jilin Province (No. 20080116) and the project sponsored by SRF for ROCS, Ministry of Education of China.

Supporting Information Available: Additional table and figures, X-ray crystallographic information files (CIF) for 1–7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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