Two New Zeolite-Like Supramolecular Copper Complexes

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Assembly of sodium 5-sulfoisophthalate (NaH_2SIPA) with copper(II) nitrate in the presence of an amine results in the formation of two new types of supramolecular copper complexes $[\{Cu(H_2O)_2(HSIPA)\}\cdot 2H_2O\cdot(PIP)_{1/2}]_n$ (**1**) and $[\{Cu(H_2O)_3(HSIPA)\}\cdot 6H_2O\cdot(hmt)_{1/2}]_n$ (**2**). Both complexes have 1D zigzag chain structures formed by the interconnection of four- or five-coordinate copper ions by carboxylate ligands. The 3D supramolecular architectures are dependent on the guest amine.

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Introduction

Crystal engineering of supramolecular architectures or metal-organic coordination polymers is a maturing field and has attracted much attention in the past decades.[1−4] With the recent development of self-assembly supramolecular chemistry, it is possible to rationally design and synthesize supramolecular architectures or metal-organic coordination polymers based on covalent or supramolecular contacts (such as hydrogen bond, π-π interactions etc.).[5−7] However, the assembly of porous materials from organic ligands and metal-ion building blocks to generate new supramolecular architectures is still a challenge.[8−10] Based on the different interactions between building blocks, two principle methods can be achieved to construct open supramolecular architectures: one is based upon covalent bonds and the other on supramolecular contacts.[11] The use of covalent bonds to engage metal ions and organic ligands, such as polycarboxylic acids or 4,4′-bipy, has resulted in a large number of porous frameworks with various dimensionalities and topologies.[12−15] In contrast, the use of supramolecular contacts to construct porous supramolecular frameworks is much less common, although a few examples have been reported.[16−20]

Currently, one of the problems when constructing porous networks is the presence of an interpenetrated network if the void is more than 50% of the crystal by volume.[21] The use of guest molecules as templates — as in zeolite-like metal phosphates — can reduce the interpenetration, and this has been well documented.[4,21,22] Furthermore, the porous architectures can be tailored by changing the structure of the guest molecules.[23] In this paper, we report two new zeolite-like supramolecular copper(II) complexes, $[\{Cu(H_2O)_2(HSIPA)\}\cdot 2H_2O\cdot(PIP)_{1/2}]_n$ (**1**) and $[\{Cu(H_2O)_3(HSIPA)\}\cdot 6H_2O\cdot(hmt)_{1/2}]_n$ (**2**) (H_3SIPA = 5-sulfoisophthalic acid, PIP = piperazine, hmt = hexamethylenetetramine), constructed by a combination of coordination and hydrogen bonds. These two complexes possess quite different architectures based on the guest amine molecules.

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Results and Discussion

Complexes **1** and **2** were prepared in the presence of an amine in solution at room temperature. X-ray diffraction shows that both **1** and **2** possess one-dimensional zigzag chain structures and the hydrogen-bond interactions between chains make them three-dimensional channel-like frameworks in which the guest amine molecules reside.

Complex **1** possesses a one-dimensional zigzag chain structure. As shown in Figure 1, the central copper ion is coordinated by two oxygen atoms from two different $HSIPA^{2-}$ ligands and two coordinated water molecules — with the average $Cu-O_{SIPA}$ distance being 1.951(5) and $Cu-O_w$ being 1.965(7) Å — in a square -planar geometry, whereas the protonated sulfonate group does not participate in the coordination. Thus, every copper ion is linked by two $HSIPA^{2-}$ ligands to form a one-dimensional zigzag chain. The organic amine molecules (PIP) are found on the same side of the chain. Three kinds of strong hydrogen bonds are found between the chains: a) hydrogen bonds between uncoordinated carboxylate oxygen atoms and coordinated water molecules (O···O distances: 2.626 and 2.756 Å); b) hydrogen bonds between sulfonate oxygen atoms and the coordinated water molecules (O···O distances: 2.660 Å); and c) hydrogen bonds between uncoordinated carboxylate or sulfonate oxygen atoms and the guest amine or water molecules. The hydrogen-bond interactions between chains

make the complex a three-dimensional open supramolecular architecture with channels along the *a* axis (Figure 2). These channels possess approximate dimensions of 11.016 × 9.894 Å and are occupied by amine and free water molecules that form hydrogen bonds with the oxygen atoms of the sulfonate group and with coordinated water molecules (O···O distance: 2.636−2.819 Å; O···N distance: 2.819 Å).

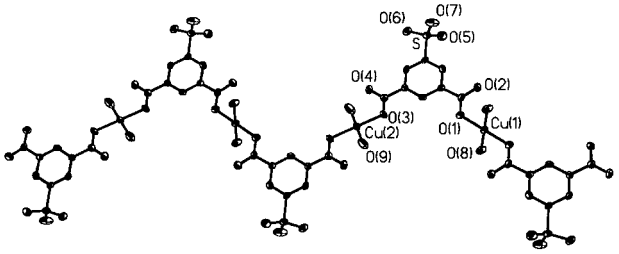

Figure 1. The one-dimensional zigzag chain structure of **1**, showing the coordination environment of the central metal ion

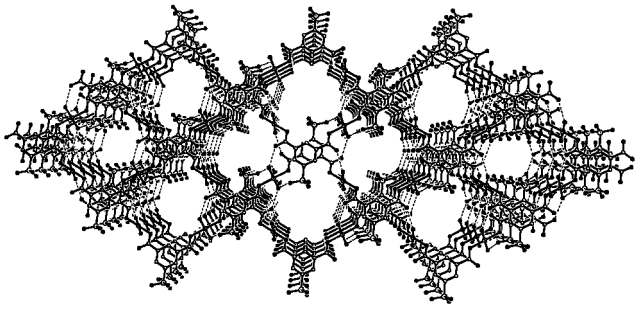

Figure 2. The 3D channel-like supramolecular architecture of **1** along the *a* axis; guest amine and water molecules are omitted for clarity

Complex **2** also has a one-dimensional zigzag chain, different from **1**, where the central copper ion is coordinated by two oxygen atoms from two different $HSIPA^{2-}$ ligands and three coordinated water molecules — with the average $Cu-O_{SIPA}$ distance being 1.960 Å, $Cu-O_w$ being 2.068 Å — in a pyramidal geometry (Figure 3). Two carboxylate oxygen atoms and two coordinated water molecules form the equatorial plane, and another coordinated water molecule occupies the axial position. As in $[Zn(ta)(phen)(H_2O)]_n$ and other similar complexes,[24,25] an axial elongation of the M−O bonds is observed [$Cu-O_w$ distance: 2.241(7) Å which is much longer than others]. Similar to **1**, every copper ion is linked by two $HSIPA^{2-}$ ligands to form a one-dimensional zigzag chain and the amine molecules (hmt) are found on the same side of the chain. Three kinds of hydrogen bonds are observed in **2**: a) hydrogen bonds between uncoordinated carboxylate oxygen atoms and coordinated water molecules (O···O distances: 2.634−2.729 Å); b) hydrogen bonds between sulfonate oxygen atoms and the free water molecules (O···O distances: 2.746−2.954 Å); and c) hydrogen bonds between sulfonate oxygen atoms or coordinated water molecules and the guest amine molecules. The chain is linked by hydrogen bonds of type *a* to generate a two-dimensional porous layer structure (Figure 4), which is further linked by hydrogen bonds of type *b* in an $O_{SIPA}\cdots O_w\cdots O_{SIPA}$ fashion to form a 3D open supramolecular framework with channels along the *c* axis (Figure 5). These channels, with approximate dimensions of 16.445 × 6.474 Å, are occupied by amine (hmt) and free water molecules that form hydrogen bonds with the oxygen atoms of the sulfonate group and with coordinated water molecules (O···O distance: 2.644−2.788 Å; O···N distance: 2.711−2.879 Å).

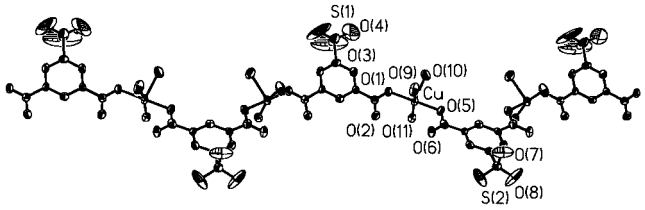

Figure 3. The one-dimensional zigzag chain structure of **2**, showing the coordination environment of the central metal ion

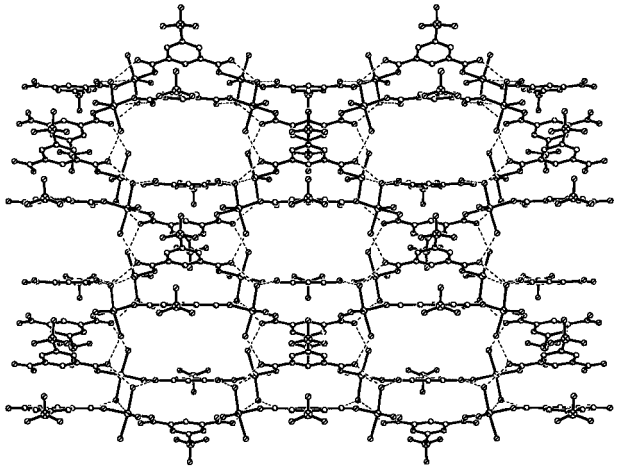

Figure 4. The 2D porous supramolecular architecture of **2** along the *c* axis

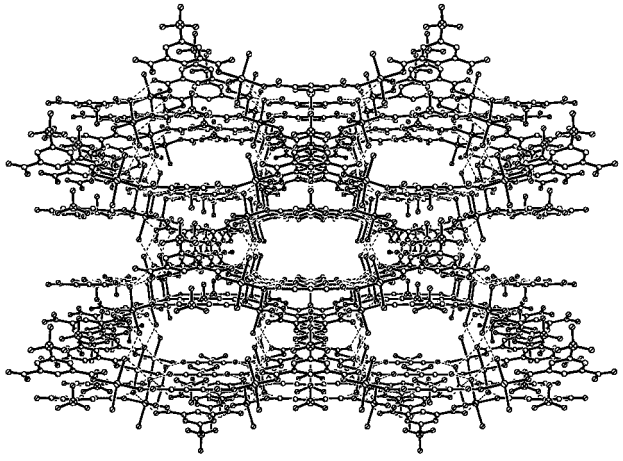

Figure 5. The 3D channel-like supramolecular architecture of **2** along the *c* axis; guest amine and water molecules are omitted for clarity

Thermogravimetric analysis (TGA) determined the thermal stability of complexes **1** and **2**. For **1**, the weight loss of 4.41% from 25 to 93 °C is equivalent to the loss of one uncoordinated water molecule (calcd. 3.71%). A total weight loss of 12.02% is achieved at 280 °C, which corresponds to the loss of another uncoordinated water molecule and 0.5 guest amine molecules per formula unit (calcd. 12.55%). However, the loss of the coordinated water molecules in **1** is not observed before 300 °C where the decomposition starts; decomposition ends above 800°C. For **2**, there is three-step weight loss in the range from 25 to 800 °C. The first weight loss of 21.20% from 25 to 145 °C corresponds to the loss of the six free water molecules per formula unit (calcd. 20.38%); the second weight loss of 12.80% from 145 to 300 °C corresponds to the loss of 0.5 guest amine molecules per formula unit (calcd. 13.21%) and the third weight loss of 10.25% from 300 to 325 °C corresponds to the loss of the coordinated water molecules (calcd. 10.19%); after 325 °C, complex **2** starts to decompose and the decomposition ends above 800 °C. This result may indicate that the guest molecules are difficult to remove from the host molecules due to the existence of strong hydrogen bonds between the host and guest molecules.

Although both **1** and **2** have three-dimensional supramolecular architectures, they are quite different due to the influence of the amine molecules. In **1**, the central copper ion is four-coordinate in a square planar geometry, and the uncoordinated carboxylate oxygen atoms, which act as hydrogen-bond acceptors, point toward different sides of the chain (Figure 6a), which makes the angle of the zigzag chain almost 90°. The chains are superimposed above each other in a staggered arrangement through hydrogen bonds between the uncoordinated carboxylate oxygen atoms and coordinated water molecules (Figure 7a). In **2**, the copper ion is five-coordinate in a pyramidal geometry, and the uncoordinated carboxylate oxygen atoms, which act as hydrogen-bond acceptors, point toward the same side of the chain (Figure 6b), which makes the angle of the zigzag chain about 120°. The superposition of the chains in **2** is quite different from that in **1**: first, two chains are linked by hydrogen bonds in staggered arrangement to form a double chain, which is further linked to generate a 2D porous layer. Secondly, the hydrogen bonds between the oxygen atoms of the sulfonate group and free water molecules in an $O_{SIPA}\cdots O_w\cdots O_{SIPA}$ fashion give rise to the final 3D open framework (Figure 7b). We propose that the structural differences between **1** and **2** arise from the influence of the guest amine molecules: the difference in the backbone of the guest molecules results in a difference of the coordination modes of the central metal ions, which further influences the arrangement of the hydrogen-bond acceptor, and leads to the difference in the final 3D supramolecular architectures. This result indicates that the host structures assembled are greatly affected by the guests,[23] and therefore changing the guest molecule, even only slightly, should lead to different structural supramolecular complexes constructed from covalent or supramolecular contacts, or a combination of the two.

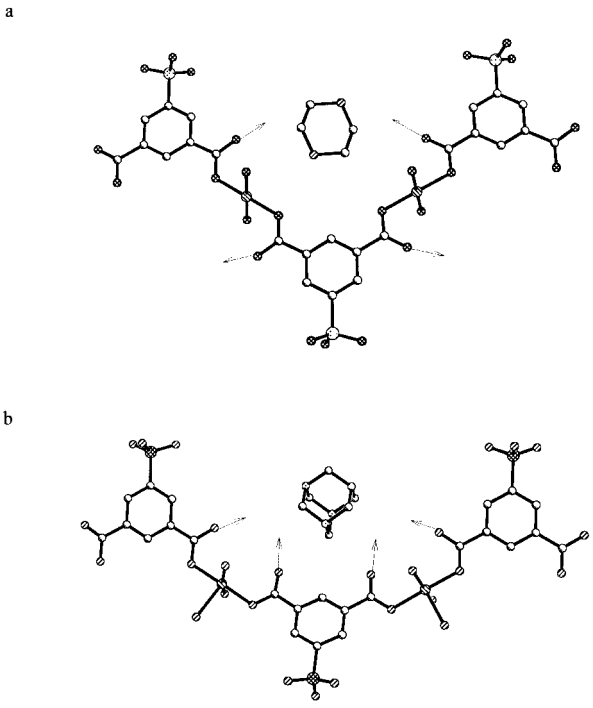

Figure 6. The different arrangement of the uncoordinated carboxylate oxygen atoms for **1** (a) and **2** (b)

Conclusion

In conclusion, two new zeolite-like supramolecular copper complexes have been prepared in the presence of amines at room temperature. Although both complexes possess one-dimension zigzag chain structures, the different guest amines result in different three-dimensional supramolecular architectures. Although guest-dependent supramolecular structures are known, their construction is still a challenge to chemists and will be an active field in the future.

Experimental Section

General Remarks: All chemicals were used as purchased without purification. Thermogravimetric experiments were performed using a TGA/SDTA851 instrument (heating rate of 10 °C/min, argon stream). IR spectra were recorded on a Magna 750 FT-IR spectrophotometer as KBr pallets. Elementary analyses were carried out in the elementary analysis group of this institute.

Synthesis of $[\{Cu(H_2O)_2(HSIPA)\}\cdot 2H_2O\cdot(PIP)_{1/2}]_n$ (1): NaH_2SIPA (0.034 g, 0.125 mmol) was dissolved in 15 mL water and $Cu(NO_3)_2\cdot 5H_2O$ (0.06 g, 0.25 mmol) was added with stirring at 60 °C. After stirring for 15 min, a solution of PIP (0.02 g, 0.25 mmol) in ethanol (5 mL) was added, and 15 min later a blue precipitate had formed. After filtration, the light-blue solution was allowed to stand in air at room temperature until blue prism-like crystals were obtained. Yield: 40%. $C_{10}H_{16}CuNO_{11}S$ (485.38): calcd. C 28.51, H 3.83, N 3.33; found C 28.60, H 3.75, N 3.40. IR (KBr): $\tilde{\nu}$ = 3211

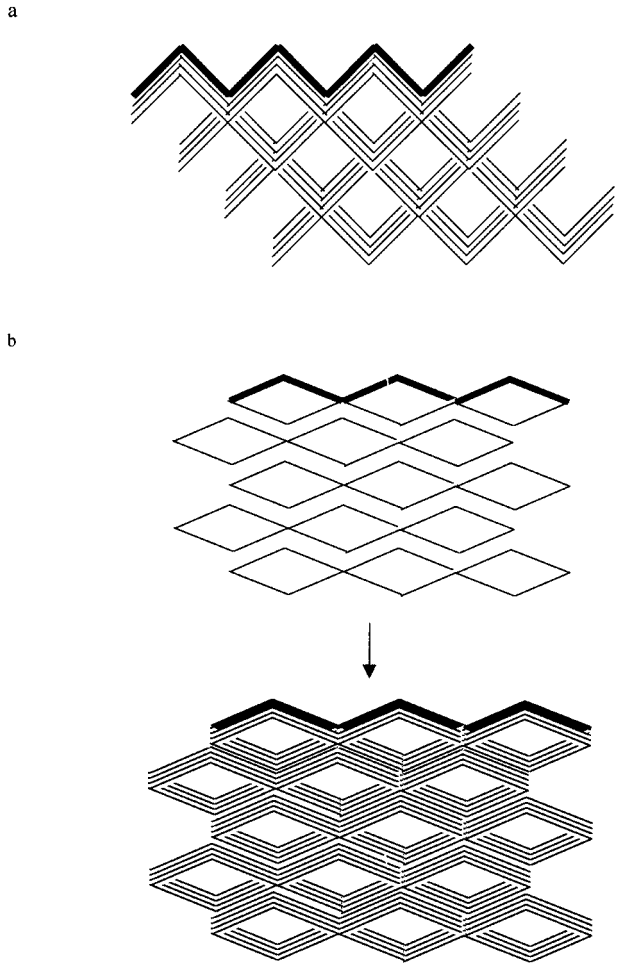

Figure 7. Schematic representation of the arrangement of the chains constructed by hydrogen bonding in **1** (a) and **2** (b)

cm^{-1} (vs), 3035 (vs), 2829 (s), 1605 (vs), 1556 (vs), 1444 (s), 1362 (vs), 1174 (s), 1043 (vs), 771 (s), 733 (m), 623 (s).

Synthesis of $[\{Cu(H_2O)_3(HSIPA)\}\cdot 6H_2O\cdot(hmt)_{1/2}]_n$ (2): The procedure was the same as that for **1** except that PIP was replaced by hmt. Yield: 50%. $C_{11}H_{26}CuN_2O_{15.5}S$ (529.94): calcd. C 24.95, H 4.95, N 5.29; found C 24.70, H 5.10, N 5.50. IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (vs), 3120 (vs), 1637 (vs), 1574 (s), 1441 (vs), 1358 (vs), 1259 (s), 1178 (vs), 1109 (s), 1047 (vs), 1024 (s), 976 (m), 775 (s), 725 (vs), 633 (s).

X-ray Crystallographic Study: $C_{10}H_{16}CuNO_{11}S$ (**1**), M_r = 485.38, triclinic, $P\bar{1}$, a = 7.5666(4), b = 10.4595(3), c = 10.5323(5) Å, α = 75.387(2), β = 76.875(2), γ = 87.483(2)°, V = 785.44(6) $Å^3$, Z = 2, D_c = 2.052 $g\cdot cm^{-3}$, μ(Mo-K_α) = 2.901 mm^{-1}, T = 293(2) K, R [$I < 2\sigma(I)$] = 0.0753, wR = 0.1807 for 2749 independent reflections with $F \geq 2.0\ \sigma(F_o)$.
$C_{11}H_{26}CuN_2O_{15.50}S$ (**2**), M_r = 529.94, monoclinic, $C2/m$, a = 15.3759(3), b = 18.8359(6), c = 14.1292(2) Å, β = 90.324(2)°, V = 4092.02(16) $Å^3$, Z = 8, D_c = 1.720 $g\cdot cm^{-3}$, μ(Mo-K_α) = 1.251 mm^{-1}, T = 293(2) K, R [$I < 2\sigma(I)$] = 0.0864, wR = 0.1939 for 3711 independent reflections with $F \geq 2.0\ \sigma(F_o)$.

The intensity data were collected on a Smart CCD diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation at room temperature in the ω-2θ scan mode. An empirical absorption correction was applied to the data using the SADABS program. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated in idealized positions. All calculations were performed using the SHELXTL program. Selected bond lengths and angles for the two complexes are given in Table 1.
CCDC-189986 (**1**) and -189987 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Selected bond lengths [Å] and angles [°] for **1** and **2**

1[a]			
Cu(1)−O(1)#1[a]	1.969(5)	Cu(2)−O(3)	1.933(5)
Cu(1)−O(1)	1.969(5)	Cu(2)−O(3)#2	1.933(5)
Cu(1)−O(8)#1	1.983(5)	Cu(2)−O(9)	1.946(7)
Cu(1)−O(8)	1.983(5)	Cu(2)−O(9)#2	1.946(7)
O(1)#1−Cu(1)−O(1)	180.0	O(3)−Cu(2)−O(3)#2	180.0(3)
O(1)#1−Cu(1)−O(8)#1	87.0(2)	O(3)−Cu(2)−O(9)	88.8(2)
O(1)−Cu(1)−O(8)#1	92.9(2)	O(3)#2−Cu(2)−O(9)	91.2(2)
O(1)#1−Cu(1)−O(8)	93.0(2)	O(3)−Cu(2)−O(9)#2	91.2(2)
O(1)−Cu(1)−O(8)	87.0(2)	O(3)#2−Cu(2)−O(9)#2	88.8(2)
O(8)#1−Cu(1)−O(8)	180.0(3)		
2			
Cu−O(5)	1.955(5)	Cu−O(11)	1.988(6)
Cu−O(1)	1.964(5)	Cu−O(10)	2.241(7)
Cu−O(9)	1.975(6)		
O(5)−Cu−O(1)	177.9(2)	O(9)−Cu−O(11)	165.3(3)
O(5)−Cu−O(9)	93.2(3)	O(5)−Cu−O(10)	90.0(2)
O(1)−Cu−O(9)	88.8(3)	O(1)−Cu−O(10)	89.1(2)
O(5)−Cu−O(11)	87.4(2)	O(9)−Cu−O(10)	96.0(3)
O(1)−Cu−O(11)	90.8(2)	O(11)−Cu−O(10)	98.7(2)

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

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