

Syntheses and structures of two novel copper complexes constructed from unusual planar tetracopper(II) SBUs

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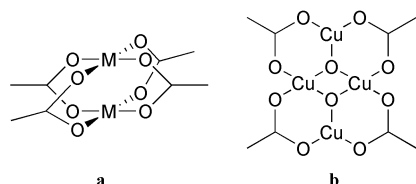
Two novel polymeric copper complexes constructed from unusual planar tetracopper(II) SBUs have been prepared and characterized.

In many cases it is quite difficult to design and synthesize a desired metal–organic framework (MOF) in a truly deliberate manner, due to the influence of many factors, such as the coordination geometry of the central metal ion and the shape, functionality, flexibility and symmetry of the ligand.¹ In principle, high dimensional coordination frameworks can be derived from low dimensional building blocks by the linkage of organic ligands through metal-to-ligand bonds. Hence, employing polynuclear metal clusters, which possess specific rigid geometries and potential to extend to a multi-dimensional framework, as secondary building blocks (SBUs) is helpful in directing the construction of a given structure.^{2–4} The most successful SBU used in the syntheses of MOFs is the paddle wheel dinuclear unit formed by carboxylate ligand $M_2(CO_2)_4$ (Scheme 1a), through which many interesting structures have been constructed in the past decade.^{5–7} Recently, Yaghi has extended the paddle wheel dinuclear unit into other conformation SBUs, such as triangular, tetrahedral, trigonal prismatic and octahedral SBUs.⁸ For instance, the use of an octahedral SBU has resulted in a series of porous materials, and one of them exhibited high capacity for methane storage.⁹ However, study on the use of a polynuclear cluster as an SBU in the construction of MOFs is still a challenge to chemists.¹⁰ Our synthetic approach starts by focusing on finding new SBUs as a target for synthesis and we hope to construct some novel structures different from the reported ones. We find a tetranuclear copper cluster (Scheme 1b), where the four copper atoms are locked by four bridging carboxylate groups and two μ_3 -OH bridges, may be a good candidate. A discrete tetranuclear copper cluster with such a structure was reported several years ago, and a SO_4^{2-} is present to stabilize the structure.¹¹ Our strategies to use the Cu_4 SBU are two-fold: employing multi-carboxylate ligands to extend the SBU into infinite MOFs and using other ligands to replace SO_4^{2-} . In this communication, we will report two novel copper complexes, $[Cu_4(OH)_2(SIPA)_2(bipy)_2 \cdot 2H_2O]_n$ (**1**) and $[Cu_4(OH)_2(SIPA)_2(py)_2 \cdot 4H_2O]_n$ (**2**) ($H_3SIPA = 5$ -sulfoisophthalic acid, $bipy = 4,4'$ -bipyridine, $py =$ pyridine), constructed from unusual planar tetracopper SBUs.

We first studied the reaction of NaH_2SIPA , $Cu(NO_3)_2 \cdot 6H_2O$ and $4,4'$ -bipyridine,[†] hoping to synthesize a high dimensional MOF constructed from the Cu_4 SBU through the bridging ability of the carboxylate ligand and $4,4'$ -bipyridine. Complex **1** was isolated as blue plate-like crystals in 65% yield. As expected, X-ray diffraction[‡] reveals **1** possesses a 1D chain structure constructed from planar tetranuclear Cu_4 SBUs. In **1**,

four copper ions are engaged by two μ_3 -OH and four carboxylate groups of $SIPA^{3-}$ to form a planar tetranuclear copper SBU (Scheme 1b), which sits on a crystallographic twofold axis that passes through the Cu_2 and Cu_{2A} . Two crystallographically independent four-coordinate copper atoms are present: $Cu(1)$ and $Cu(2)$. Both copper atoms reside in square pyramidal coordination environments with two oxygen atoms from $SIPA^{3-}$, one nitrogen atom from $4,4'$ -bipy and one hydroxyl for $Cu(1)$, and two carboxylate oxygen atoms and two μ_3 -OH groups for $Cu(2)$, respectively. To our knowledge, a number of tetranuclear copper examples have been reported, but the geometry in these cases invariably approximates to tetrahedral;^{12,13a,b,f} far fewer examples containing a planar tetranuclear copper unit have been documented.^{11,13c} In **1**, the four copper ions are located in a plane and the largest deviation of the two μ_3 -bridge hydroxyl groups from the $Cu(1)Cu(2)Cu(1B)Cu(2B)$ plane is 0.6955 Å. The distance between Cu_2 and Cu_{2A} is 2.919 Å, whereas the distance between Cu_2 and Cu_1 bridged by the carboxylate group is 3.288 Å. Interestingly, the $4,4'$ -bipy ligand acts as a mono-dentate ligand to take part in coordination and the dihedral angle of the two pyridine rings of $4,4'$ -bipy is 2.5°. The structure can be simply described as a one-dimensional linear chain constructed from the planar Cu_4 SBUs through sharing $SIPA^{3-}$ ligands (Fig. 1), in which all the phenyl rings of $SIPA^{3-}$ ligands are located almost in the same plane. The sulfonate group of $SIPA^{3-}$ does not take part in coordination but balances the charge by being deprotonated.

In order to synthesize different structures constructed from the same Cu_4 SBUs, pyridine was employed to replace $4,4'$ -bipy and complex **2** was isolated as blue block-like crystals in 35% yield. X-ray diffraction[‡] reveals **2** possesses a three-dimensional channel-like framework constructed from the planar tetranuclear Cu_4 SBUs. The mono-dentate coordinated $4,4'$ -bipy in **1** is replaced by the pyridine molecule in **2**, and the Cu_2 – Cu_{2A} distance is 3.030 Å, slightly longer than that observed in **1**. In a difference from **1**, the Cu_1 atom is five-coordinate, where the fifth coordination comes from a sulfonate oxygen atom of the $SIPA^{3-}$ ligand from another tetranuclear unit, in a square pyramidal geometry. The largest deviation of the two μ_3 -bridge hydroxyl groups from the $Cu(1)Cu(2)Cu(1B)Cu(2B)$ plane is 0.4939 Å, slightly shorter than that in **1**. The Cu_4 SBUs are linked by the $SIPA^{3-}$ ligand to give rise to a one-dimensional chain (Fig. 2), as observed in **1**. The one-dimensional chain is further linked by the sulfonate oxygen atom of $SIPA^{3-}$ from another chain to complete the square pyramidal coordination



Scheme 1

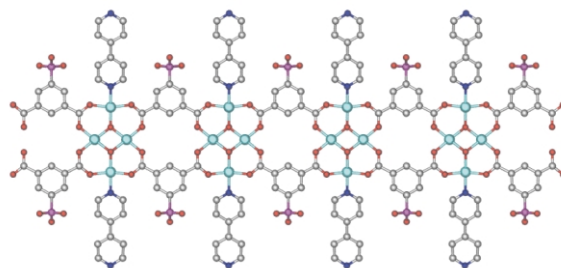


Fig. 1 The 1D band-like architecture of **1**.

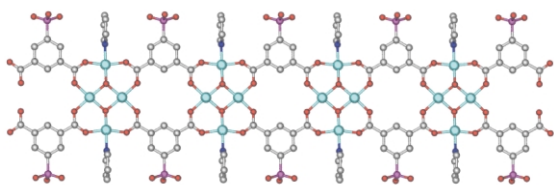


Fig. 2 The 1D band-like architecture in **2**.

environments of CuI ions and result in the formation of the final three-dimensional channel-like framework. As shown in Fig. 3, the 1D chains are perpendicular to each other and every four of them constitute a square channel along the *c* axis; the channels possess approximate dimensions of $11.453 \times 8.672 \text{ \AA}$ and are occupied by free water molecules.

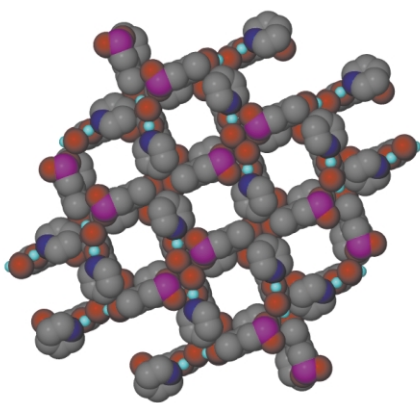


Fig. 3 Space-filling views of the three-dimensional framework of **2**.

TGA study of **2** shows that there is a one-step weight loss (found: 6.94%) from 60 to 140 °C, corresponding to the loss of free water molecules (calcd: 7.16%) and leading to a framework of $[\text{Cu}_4(\text{OH})_2(\text{SIPA})_2(\text{py})_2]_n$. This framework is stable up to 280 °C where the decomposition starts and ends above 900 °C. After heating the sample of **2** at 140 °C over 1 h, the guest water molecules are removed from the sample; X-ray powder diffraction (XRPD) determination shows that most of the important peaks of the heated sample possess the same positions as those of the original one although slight shifts and broadening of some peaks are observed. These results illustrate that the framework of **2** may be retained upon removal of the guest water molecules.

Although clusters with cubane-like tetranuclear Cu_4 units in which four metal ions are linked by hydroxo, alkoxo, azido, sulfido, or iminato bridges have been widely studied in the past,^{12,13a,bf} only two cubane-like tetracopper units have been extended into a 1D chain or 2D layer by the linkage of organic ligands.¹⁴ To the best of our knowledge, complexes **1** and **2** are the first two polymeric compounds constructed from planar tetracopper SBUs. Further study on this subject, such as magnetic properties and the application of other polycarboxylates, is underway and will be reported in a full paper.

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Notes and references

† Preparation of $[\text{Cu}_4(\text{OH})_2(\text{SIPA})_2(\text{bipy})_2 \cdot 2\text{H}_2\text{O}]_n$ (**1**): $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.06 g, 0.25 mmol) and NaH_2SIPA (0.033 g, 0.125 mmol) in 10 mL of distilled water were placed in the bottom of a 25 mL stainless-steel reactor with a Teflon liner, on which a solution of 4,4'-bipy (0.05 g, 0.25 mmol) in 6 mL of benzene was layered. The stainless-steel reactor was heated at 140 °C for 3 days; deep blue plate-like crystals were obtained in 65% yield.

Calc. for $\text{C}_9\text{H}_7\text{CuNO}_{4.5}\text{S}_{0.5}$: C 38.51, H 2.51, N 4.99%; Found: C 38.38, H 2.35, N 5.05%.

$[\text{Cu}_4(\text{OH})_2(\text{SIPA})_2(\text{py})_2 \cdot 4\text{H}_2\text{O}]_n$ (**2**): A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.06 g, 0.25 mmol) and NaH_2SIPA (0.033 g, 0.125 mmol) in a mixed solution of DMF (20 mL), nitrobenzene (2 mL) and pyridine (0.2 mL) was stirred at 60 °C for 5 hours. A blue precipitate was formed; after filtration, ethyl ether was allowed to diffuse in the filtrate until blue block-like crystals were obtained in 35% yield. But the attempt to synthesize complex **2** by hydrothermal reaction failed. Calc. for $\text{C}_{6.5}\text{H}_{6.5}\text{CuNO}_{0.5}\text{S}_{0.5}$: C 31.08, H 2.61, N 2.79%; Found: C 30.98, H 2.64, N 2.69%.

‡ Crystal data for **1**: $\text{C}_9\text{H}_7\text{CuNO}_{4.5}\text{S}_{0.5}$, orthorhombic, space group *Pnmm*, $a = 10.9368(10)$, $b = 16.2104(16)$, $c = 10.7803(10) \text{ \AA}$, $U = 1911.2(3) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 8$, $D_c = 1.951 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, 5971 reflections measured, 1802 unique which are used in all calculations. $R1 = 0.0574$ and $wR2 = 0.1032$ for $I > 2\sigma(I)$. CCDC 205535.

Crystal data for **2**: $\text{C}_{6.5}\text{H}_{6.5}\text{CuNO}_{0.5}\text{S}_{0.5}$, orthorhombic, space group *Pnmm*, $a = 12.5451(5)$, $b = 15.8535(6)$, $c = 10.8885(2) \text{ \AA}$, $U = 2165.55(13) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 8$, $D_c = 1.541 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, 6367 reflections measured, among which 2014 unique are used in calculations. $R1 = 0.0845$ and $wR2 = 0.2406$ for $I > 2\sigma(I)$. CCDC 205536. See <http://www.rsc.org/suppdata/cc/b3/b302692b/> for crystallographic data in .cif or other electronic format.

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