SPECIAL ISSUE PAPER



JOURNAL OF THE CHINESE **CHEMICAL SOCIETY** 

# The structures of MOFs prepared from 1,3,5-tris [4-pyridylethynyl]-benzene and a copper(I) perchlorate complex

En-Che Yang<sup>1</sup> | Chen-Ming Wu<sup>1</sup> | Pei-Jia Pan<sup>1</sup> | Gene-Hsiang Lee<sup>2</sup> | Hwo-Shuenn Sheu<sup>3</sup> | Chung-Kai Chang<sup>3</sup>

<sup>1</sup>Department of Chemistry, Fu Jen Catholic University, New Taipei City, Taiwan

<sup>2</sup>Instrumentation Center, College of Science, National Taiwan University, Taipei, Taiwan

<sup>3</sup>National Synchrotron Radiation Research Center Hsinchu Science Park, Hsinchu, Taiwan

#### Correspondence

En-Che Yang, Department of Chemistry, Fu Jen Catholic University, Hsinchuang, New Taipei City 24205, Taiwan, Republic of China. Email: 071549@mail.fju.edu.tw

**Funding information** Ministry of Science and Technology, Taiwan, Grant/Award Number: MOST106-2113-M-030-008

# **1 | INTRODUCTION**

# Metal-organic frameworks (MOFs) have become an important topic in chemistry due to their wide application in gas storage,<sup>[1]</sup> chromatography,<sup>[2]</sup> heterogeneous catalysis,<sup>[3]</sup> chemical sensing,<sup>[4]</sup> fluorescence,<sup>[5]</sup> and drug delivery.<sup>[6]</sup> In addition to these extensive applications, the discovery of MOFs with new structures is itself a great challenge in crystal engineering as most new frameworks are produced by self-assembly. Fine tuning the reaction conditions can sometimes have a profound influence on the final structure as well as the properties of the final product. Based on a review of the history of this subject, MOFs can be classified as (a) strongly linked materials that are largely ligated by the oxygen atoms of carboxylic acids, (b) weakly linked materials that include MOFs containing coordinated, nitrogencontaining compounds (pyridine and derivatives thereof). A recent review article concluded that because carboxylic groups coordinate complexes that bind metal ions tightly

### Abstract

Two copper(I)-based frameworks of complexes  $\{[Cu(L)_2(ClO_4)] \cdot CH_3CN\}(2)$  and  $\{[Cu(L)(ClO_4)] \cdot 2CH_3CN\}$  (3) (L = 1,3,5-tris(4-pyridylethynyl) benzene) were produced by reacting [Cu(MeCN)<sub>4</sub>(ClO<sub>4</sub>)] with different amounts of a ligand (L) using a hydrothermal method at temperatures of up to 130°C. The nitrogen atoms in the pyridine moieties of the ligand coordinate to the Cu(I) ion. The charge on the Cu(I) ion can be stabilized by extending the degree of conjugation in the system and by taking advantage of its highly symmetrical structure. The large degree of conjugation also supports numerous  $\pi$ - $\pi$  interactions in the framework.

#### **KEYWORDS**

 $\pi$ - $\pi$  interactions, interpenetrating, MOF

and rigidly, and because the negative charges on the oxygen atoms can be balanced with positive charges on metal ions, large MOF structures can be formed without the anion being held in the channel of the complex. On the other hand, because pyridine complexes bind weakly with metal ions, supramolecular structures are typically formed. Among the carboxylic acid-coordinated compounds, benzene-1,-3,5-tricarboxylic acid (H<sub>3</sub>BTC) and benzene-1,-4-dicarboxylic acid (H<sub>2</sub>BDC) are two typical examples. They both form secondary building units (SBUs) or MOFs with efficient gas absorption properties. In particular, both findings that the H<sub>3</sub>BTC combines Cu to give HKUST-1,<sup>[7]</sup> and that  $H_2BDC$  combines with Zn to produce MOF-5<sup>[8]</sup> triggered a series of studies of these materials for use in gas storage.

Some successful cases have been reported in which the pyridine-coordinated ligands with a three-fold C<sub>3</sub> symmetry can be applied to some functional organic site FOCs. Following this route, a new ligand referred to as 1,3,5-tris

© 2019 The Chemical Society Located in Taipei & Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

2

(pyridine-4-ylethynyl) benzene (L, see Scheme 1) was first developed by Prof. Sanders and his coworkers in 1995.<sup>[9]</sup> Thereafter, a series of supramolecules synthesized using L have been published by Prof. Peter J Stang.<sup>[10]</sup> In 2006, this ligand was used by Prof. Edwin Weber along with some hexafluoroacetylacetonate (hfacac) derivatives to synthesize a two-dimensional coordination polymer.<sup>[11]</sup> Prof. Schmittel et al. then used a similar ligand 1,3,5-trimethyl-2,4,6-tris (4-pyridylethynyl)benzene to bind Cu(II) ions and form a number of different supramolecules.<sup>[12]</sup> Furthermore, the self-assembled structure and computational chemistry of ligand (L) was reported and the results indicated the existence of hydrogen bonding, and a special arrangement of atoms at the solid-liquid interface.<sup>[13]</sup> MOFs that are prepared using only L have not been reported. In the current article, we report on the preparation of and structures of two new pure ligand L-linked Cu(I) MOFs, where complex 2 was prepared using L and cuprous ions in a 3:4 ratio, with a [4 + 2] mutual penetration structure being produced. MOF 3, however, was isolated in a similar reaction, but using a ligand L to cuprous ion ratio of 11:1, resulting in the formation of a [3 + 3] penetration structure.

# 2 | RESULTS AND DISCUSSION

### 2.1 | Ligand and synthesis

The ligand used in this article is 1,3,5-tris(4-pyridylethynyl) benzene that is abbreviated as "L". The synthesis of this ligand was developed by Masashi Kijima et al.<sup>[14]</sup> The most important aspect of the synthesis of the ligand is that the procedure is air-sensitive. Any leakage in the Schlenk line can cause a dramatic drop in the yield of the product. To avoid damage caused by minor impurities in the nitrogen gas, the use of an argon atmosphere is suggested in this reaction. The ligand produced is quite stable in air. The ligand possesses a regular triangle planar geometry with an extensive conjugated system and three pyridines. The regular triangle geometry facilitates the formation of facets of polyhedrons. The

conjugated system displays a variety of  $\pi$ - $\pi$  interactions that are mutually penetrating stabilizing the layered structure.

Ligands that are used to prepare MOFs can be roughly classified into three categories according to Stang et al. survey of 2013.<sup>[15]</sup> They are (a) supramolecular coordination complexes (SCC), (b) SCC and MOFs, and (c) MOFs that contain a ligand "L" as its pyridine sites providing weak linkages between metal ions, and are classified into the SCC category. Nevertheless, when a low charge metal ion center Cu(I) with a lower coordination number is used, a variety of different MOFs' framework is formed. The metal ion source used in this study was  $[Cu(MeCN)_4(ClO_4)]$ . Scheme 2 shows the synthetic strategies that were used in this study, where in the first route, a 3:4 metal to ligand ratio was used and the reaction was conducted in a sealed tube at 130°C for 3 days. The second route used a metal to ligand ratio of 11:1 and was also heated in a sealed tube at 130°C for 3 days. Both conditions give different three dimensional MOF frameworks. The extended conjugated system of the ligand L with a variety of  $\pi$ - $\pi$  stacking forces leads to the formation of different types of interpenetrating networks, with layered structures. Structural data obtained for these materials are discussed below.

#### 2.2 | Structural analysis and discussion

Both MOFs were characterized using X-ray crystallography. Their experimental conditions are summarized in Table 1.

# 2.2.1 | {[Cu(L)<sub>2</sub>(ClO<sub>4</sub>)]·CH<sub>3</sub>CN}<sub>n</sub> (2)

Compound **2** crystallizes in a triclinic space group of  $P\bar{1}$  and the repeating unit per unit cell contains one Cu(I) ion, two crystallographically distinguishable ligands, one perchlorate as the counter ion, and one acetonitrile molecule as the packing solvent whose formula is given as [Cu(L)<sub>2</sub>(ClO<sub>4</sub>)]. CH<sub>3</sub>CN. All of the Cu(I) ions have tetrahedral coordination environments that are ligated to four pyridine groups that



**SCHEME 1** Ligand (L) simplified in topology structure of the ligand (L)



**SCHEME 2** Synthetic procedure for preparing the two complexes

#### TABLE 1 Crystal data and structure refinement

Identification code	(2)	(3)
Empirical formula	C <sub>56</sub> H <sub>33</sub> ClCuN <sub>7</sub> O <sub>4</sub>	C31H21ClCuN5O4
Formula weight	966.88	626.52
Crystal system	Triclinic	Orthorhombic
Space group	P-1	Pna2 <sub>1</sub>
Unit cell dimensions	$a = 11.0963(6)\text{\AA}$ $\alpha = 88.6860(18)^{\circ}$ $b = 12.1939(7)\text{\AA}$ $\beta = 73.5469(18)^{\circ}$ $c = 17.8188(9)\text{\AA}$ $\gamma = 86.699(2)^{\circ}$	a = 16.9224(11)  Å $\alpha = 90^{\circ}$ b = 29.1720(19)  Å $\beta = 90^{\circ}$ c = 7.2751(5)  Å $\gamma = 90^{\circ}$
Z	2	4
D (mg/m <sup>3</sup> )	1.391	1.159
Absorption coefficient (mm <sup>-1</sup> )	0.588	0.719
F(000)	992	1,280
Theta range for data collection	2.384 to 25.000°	2.407 to 27.500°
Index ranges	$-13 \le h \le 13$ $-14 \le k \le 14$ $-21 \le l \le 21$	$-20 \le h \le 21$ $-37 \le k \le 37$ $-9 \le 1 \le 9$
Reflections collected	16,145	25,689
Independent reflections	8,124 [R(int) = 0.0102]	8,044 [R(int) = 0.0369]
Max. and min. Transmission	0.7452, 0.7196	0.7456, 0.6802
Data/restraints/parameters	8,124/20/664	8,044/73/398
Goodness-of-fit on F2	1.043	1.159
Final <i>R</i> indices $[I > 2$ sigma $(I)$ ]	R1 = 0.0561, w $R2 = 0.1566$	R1 = 0.0712, w $R2 = 0.1963$
R indices (all data)	R1 = 0.0621, wR2 = 0.1627	R1 = 0.0757, wR2 = 0.1991

arise from different ligands. Details of the coordination mode can be seen in Figure 1(a). The observed coppernitrogen bond lengths are in the range of approximately 2.003-2.074 Å. In the meantime, two crystallographically distinguishable ligands have the same coordination pattern, which is illustrated in Figure 1(b). Each ligand has a ligating



**FIGURE 1** (a) Copper-centered structure showing the coordination mode for compund **2**. (b) Compound **2** grid showing copper-copper distance

mode of  $\mu_2$ -bridging coordinating to two Cu(I) ions from two different pyridines, respectively. The remaining pyridine group then acts as the dangling arm, as shown in Figure 1(b).

It can also be seen from Figure 1(b) that the ligand L ligates in a quite special coordination pattern. The Cu(I) ions form pleated wrinkles with a two-dimensional (4,2) grid structure. The topography contains dangling arms on both sides of the grid plane. The network has Cu(I)-Cu(I) ions on the  $16.0 \times 16.9$  Å grid surface. It is important to note that the interpenetrating holes have the same size in the network. The final result is that the two crimp planes are selfinterpenetrating with respect to each other to form a thick double layer. A detailed plot of this aspect can be seen in Figure 2(a) and (b), which indicates the pyridine groups are double interpenetrating wove in the grid network. It is also quite important that the arms are dangling on both sides of a double-layer interpenetrating grid. The arms act as an adhesive and form perfect  $\pi$ - $\pi$  interactions with the pyridine functional groups that are adjacent to the double interpenetrating grid, which is illustrated in Figure 2 (c). The



**FIGURE 2** (a) Topology structure of compound **2**, blue and red represent different layers, (b) topology side view shows that each of the two layers are interpenetrating. (c) Interpenetrating groups composed of two layers (blue and red), and different types of pyridine-pyridine  $\pi$ - $\pi$  interactions

adjacent double-layer interpenetrating grid planes accumulate in the self-assembly to form a perfect supramolecular grid thin wall. The grids are separated by a distance that is sufficient to accommodate perchlorate ions.

The network of compound 2 is further analyzed using program ToposPro that provides structure extension analysis and simplification.<sup>[16]</sup> The autoCN module was used after reading the crystal coordinates of the binding atoms and considering the hydrogen bonding when the new bond is added. The auto mode was then used to determine a simplified adjacent matrix to simplify the structure and delete the atoms. This left only atoms that contain more than two bonds with the nonlinear bonding atoms being removed. All hydrogens and carbon-bonded hydrogens, sp<sup>2</sup> carbons, sp hybridized carbons were deleted. Finally, an ADS analysis was carried out for the full molecule with Schläfli symbol and topographical analysis. The results of the products (2) and (3) are summarized in Table 2, which show compound 2 has an octet grid with (4,2) nodes. And there are four  $12^4$  loops (12 nodes in shortest loops, 4 loops) and two 18 loops  $(18^2)$ at each Cu(I) center.

## 2.2.2 | $[Cu(L)(ClO_4)] \cdot 2CH_3CN(3)$

Compound **3** crystallized in an orthorhombic space group, Pna2<sub>1</sub>, which contains one copper monovalent ion Cu(I), one perchlorate ion as the counter ion, and three

 TABLE 2
 Summary of topological analysis based on

 TOPOSPRO

Crystal	2	3
Crystal system	Triclinic	Orthorhombic
Space group	P-1	Pna2 <sub>1</sub>
Formula	[Cu(L) <sub>2</sub> (ClO <sub>4</sub> )] CH <sub>3</sub> CN	$[Cu(L)(ClO_4)] \cdot 2CH_3CN$
Grid	Octet	Hexagon
Node	(4,2)	(3,3)
TOPOSpro build	The topospro analysis shows that, Schälfli symbols, the Cu(I) center of compound (2) has four 12-member loops $12^4$ (12 of nodes in shortest loop, four times of loop) and two 18-member loops, $18^2$  Point symbols for net: $\{0\}2\{12^4.18^2\}$ $\{3.12.13\}4\{3\}2$ point symbols for net with loops: $\{12^4.18^2\}$ $\{3.12.13\}4\{3\}4$ 1,3,3,4-c net with stoichiometry (1-c)2 (3-c)4(3-c)2(4-c); 4-nodal net	There are four planes mutually penetrating in a $[2 \times 2]$ form. They form a spiral shape along the C- axis, repeating for every 7.28 Å. [0,0,1] (7.28 A)  NISE: Nontranslating interpenetration symmetry elements  1:2(1) $[0,0,1]$  IC: $[0,0,2][1,0,1]$ [1,1,0] (IICVR = 2) Zt = 2; Zn = 2 Class IIIa Z = 4[2 × 2]

indistinguishable L ligands but can be regarded as one L ligand per repeating unit and two acetonitrile molecules in the crystallographic repeating unit. This gives a formula of  $\{[Cu(L)(ClO_4)]\cdot 2CH_3CN\}_n$ . In compound **3**, each Cu (I) has a planar triangular geometry, connecting three different L ligands, which are displayed in Figure 3(a). Each L unit adopts a  $\mu_3$ -bridge mode and coordinates with three different Cu (I) ions, respectively. The copper–nitrogen bond lengths



**FIGURE 3** (a) Copper-centered structure showing the coordination mode, (b) copper-centered structure showing the Cu–N bond lengths

are in the range of 1.9537 to 2.0203 Å. The ligand with a bond length of 2.0203 Å forms a twist angle with the other two ligands. This arrangement is shown in Figure 3(b).

The three Cu(I) ions ligated in the same  $\mu_3$ -L have Cu...Cu distances of 16.7694. 17.7780, and 18.4200 Å. respectively (see Figure 4(a)). This arrangement is quite different from the two-dimensional, infinitely extended hexagonal honeycomb formed by the general (3,3) network. The three Cu(I)–Cu(I) and the three L units form a spiral shape at an angle of 60° along the C-axis and overlap with another Cu(I) ion in the C-axis to form a unique three-dimensional honeycomb structure. The structure is very similar to the quadruple helix along the C-axis in a DNA structure in which the network forms hexagon helices that are separated by a distance of 14.5502 Å along the C-axis, as illustrated in Figure 4(b). Here, each honeycomb structure that is formed along the C-axis will have two parallel L-planes and one twisted L plane. After using the TOPOSPRO program to simplify the structure, the results show that this material has a three-dimensional honeycomb structure. The threedimensional pores are formed by the interpenetrating sixring honeycomb structure. In this self-assembly synthesis, up to four single-layer structures are possible. Each layer is separated from the next layer by 14.5502 Å along the Caxis. Based on the simplified structure obtained by using the ToposPro program, we also conclude from Figure 5(a) that the spiral extension plane forms a unit. In this threedimensional honeycomb structure, each Cu(I) ion is related to two acetonitrile molecules. The closest distance between the Cu(I) ions and perchlorate ions is 5.626 Å. This means that every three copper ions form a spiral honeycomb unit that contains six acetonitrile molecules and three perchlorate ions, as shown in Figure 5(b).

Because this ligand (L) contains four aromatic rings, strong  $\pi$ - $\pi$  stacking with the adjacent two layers of ligand L was displayed. A detailed image of the  $\pi$ - $\pi$  stacking is shown in Figure 6(a).

Hereafter, the term Py is used to denote a pyridine unit and Bz a benzene ring.<sup>[17]</sup> In Figure 6, the blue Py and green



FIGURE 4 (a) L-centered indicates  $\mu_3$ -coordination in compound 3, (b) bond length between copper without the same plan



5

**FIGURE 5** (a) Structure of compound (3), as simplified by the ToposPro program. (b) C-axis view showing the position of acetonitrile molecules and perchlorate ions

Bz form a Py–Bz (+)  $\pi$ – $\pi$  stacking, the orange Py and green Bz are involved in Py–Bz (–) $\pi$ – $\pi$  stacking. Each L ligand has a pyridine ring above and below, leading to positive and negative Py...Bz  $\pi$ - $\pi$  interactions. The remaining Py forms  $\pi$ - $\pi$  interactions with the alkynyl moieties of two other ligand layers, causing the layers to overlap at nearly the same distance to form a relatively stable three-dimensional structure. The structural analysis based on the ToposPro program gave a hexagon grid with (3,3) nodes. There are four interpenetrating planes, in the form of  $2 \times 2$  planes in



**FIGURE 6** (a) Blue Py and green Bz form py–Bz (+),  $\pi$ – $\pi$ distance is 3.303 Å, orange Py and green Bz are with py–Bz (–) $\pi$ – $\pi$ stacking of 3.348 Å, Py forms  $\pi$ - $\pi$  interactions with alkynyl moieties of two other layers ligands with distances of 3.610 and 3.672 Å. (b) the topos view shows four interpenetrating planes

6

Figure 6(b), spiraling up the C-axis that are repeated at an interval of 7.28 Å.

Table 2 shows the summary of topological analysis based on TOPOSPRO.

### **2.3** | Elemental analysis of compound (3)

It should be noted here that the elemental analysis for compound (3) was not very reproducible. This can be attributed to the fact that the guest acetonitrile molecule is easily lost from the complex, even at room temperature. To determine the solvent loss behavior, thermogravimetric analyses (TGA) were performed and the results are shown in Figure 7. It can be seen that the solvent loss can occur at temperatures lower than 50°C. The mass decreases with increasing temperature up to 150°C and then reaches the first plateau. Solvent loss is estimated to be two acetonitrile guest molecules per unit of complex, making a weight loss of 86.7%. However, the experimental data indicate a loss of 93.9%. This must be due to the loss of solvent molecules during the interval between removing the sample from the mother liquid but before inserting it in the TGA chamber.

The integrity of the bulky sample was confirmed by powder X-ray diffraction measurements carried out using the mother liquor. Figure 8 shows a comparison between the experimental data (upper) and a theoretical simulation based on single crystal data (bottom). Except for the base line caused by the mother liquid, the simulated values and the experimental data are in quite good agreement. This result strongly indicates two points: (a) the bulk sample is pure and (b) the sample is quite stable in the mother liquid.



FIGURE 7 Thermogravimetric analysis (TGA) of compound (3)



**FIGURE 8** Powder X-ray diffraction patterns of compound (3) obtained using the mother liquid ( $\lambda = 0.826$  nm)

## **3** | EXPERIMENTAL

All the chemicals were of commercial grade and were used without further purification.

## **3.1** | $[Cu(MeCN)_4(ClO_4)]$ (1)

Cu(ClO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O (1.5 g, 5.93 mmol) was dissolved in 50.0 mL of MeCN and 0.75 g (11.81 mmol) powdered elemental copper was then added to the solution. The mixture was heated at 60°C for 30 min and then filtered while the solution was still hot. The resulting filtrate was stored in a refrigerator overnight, resulting in the formation of colorless crystals (1). IR spectrum(KBr cm<sup>-1</sup>): 3,437(m), 2,926(w), 2,268(w), 2,016(m), 1,625(m), 1,385(w), 1,366(w), 1,145 (s), 1,114(s), 1,086(s), 946(m) 699(w), 636(m), and 625 (s) (elemental analysis: exp. [calc.], C29.34% [29.55%], N17.11% [17.17%], and H3.67% [3.70%]).

### 3.2 | 1,3,5-tris(4-pyridylethynyl)benzene (L)

CuI (100 mg, 0.52 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (600 mg, 0.52 mmol), 1,3,5-triethynylbenzene (1.3)g, 8.6 mmol), and 4-bromopyridine hydrochloride (7.6 g, 39.0 mmol) were placed in a round bottom flask under an atmosphere of argon. A solution of 100 mL of tetrahydrofurane (THF) and 50 mL of triethyl amine (Et<sub>3</sub>N) was placed in a second flask under an atmosphere of argon. The solutions were then mixed with one another and stirred at ambient temperature for 24 hr under argon. The resulting solution was heated at 50°C for 24 hr and then evaporated to dryness, after which, 150 mL of CH<sub>2</sub>Cl<sub>2</sub> was added and the solution was shaked

by ultrasound wave for 30 min. The resulting solution was washed three times with 150 mL of distilled water and the resulting product was then purified by silica gel chromatography by elution with  $CH_2Cl_2:EA = 1:2$  to give 2.7 g of a pale yellow product, yield = 82%. IR spectrum (KBr cm<sup>-1</sup>): 3,431(s), 3,035(s), 2,889(w), 2,431(w), 2,216(m), 1,938(w), 1,848(w), 1,774(w), 1,596(s), 1,539(m), 1,490(m), 1,407(s), 1,321(w), 1,286(w), 1,215(s), 1,123(w), 1,091(w), 1,067(w), 990(m), 968(m), 926(w), 882(s), 833(s), 819(s), 744(s), 681 (s), 610(w), 544(s), and 527(s); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.38$  (d, 6H),  $\delta = 7.74$  (s, 3H),  $\delta = 8.63$  (d, 6H);  ${}^{13}$ C NMR (300 MHz, CDCl3):  $\delta = 149.81$ ,  $\delta = 135.19, \delta = 130.68, \delta = 125.52, \delta = 123.33, \delta = 91.49,$ and  $\delta = 88.20$  (elemental analysis: exp. [calc.], C84.05% [84.94%], N10.94% [11.01%], and H3.98% [3.93%]). MASS  $(Z = 1 C_{27}H_{16}N_3 = 382.1339)$ 

## 3.3 | {[Cu(L)<sub>2</sub>(ClO<sub>4</sub>)]·CH<sub>3</sub>CN}<sub>n</sub> (2)

Compound (1) (110.0 mg, 0.34 mmol) was dissolved in 30 mL of acetonitrile and 160 mg (0.43 mmol) of ligand L was then added. The resulting solution was placed in a sealed tube under a nitrogen atmosphere. The reactor was then heated at 130°C for 3 days and then allowed to cool to room temperature at a rate of  $13^{\circ}$ C/hr, orange color crystals suitable for X-ray analysis were obtained. Yield 3.7%. IR spectrum (KBr cm<sup>-1</sup>): 3,413(m), 3,062(m), 2,217(m), 1,944 (w), 1,603(s), 1,536(s), 1,489(s), 1,410(s), 1,322(m), 1,214 (s), 1,098(s), 1,058(s), 1,008(m), 987(m), 966(m), 879(s), 819(s), 747(w), 678(s), 622(s), and 599(w). (Elemental analysis: exp. [Calc.], C 69.58% [69.50%], N 10.00% [10.14%], and H 3.38% [3.41%]).

## **3.4** + [Cu(L)(ClO<sub>4</sub>)] 2CH<sub>3</sub>CN (3)

Compound (1) (1.50 g, 4.59 mmol) was dissolved in 30 mL of acetonitrile. Ligand L 150 mg (0.41 mmol) was then added. The solution was placed in a sealed tube under a nitrogen atmosphere and then heated at 130°C for 3 days. The solution was then allowed to cool to room temperature at a rate of 13°C/hr. An amount of 50 mg of pale yellow block-shaped crystals was obtained. Yield 3%. IR spectrum (KBr cm<sup>-1</sup>): 3,414(s), 2,442(m), 2,218(s), 1,605(s), 1,537 (m), 1,492(s), 1,417(s), 1,291(w), 1,213(s), 1,115(s), 1,086 (s), 1,019(s), 968(s), 888(s), 826(s), 754(w), 682(s), and 626 (s) 547(s). (Elemental analysis: exp. [calc.], C 57.23% [57.22%], N 12.91% [9.94%], and H 3.96% [3.35%]).

### **3.5** | Physical property measurements

NMR spectra were recorded using a Bruker AV-300 spectrometer. Infrared spectra were recorded using KBr pellets on a Perkin Elmer 1,600 spectrometer in the  $450-4,000 \text{ cm}^{-1}$  range. The elemental analysis and mass spectroscopy were conducted at Instrumentation Center, College of Science, National Taiwan University. The powder X-ray diffraction was carried out at National Synchrotron Radiation Research Center.

## 3.6 | X-ray crystallography

Good quality crystals of compounds 2 and 3 were selected and mounted on the tip of a glass fiber. A Bruker Kappa 4CCD diffractometer was employed that was equipped with graphite monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073$ ). The temperature was maintained at 150 K by an Oxford Cryosystems Cryostream Cooler. The area detector was located at a distance of 5.00 cm from the crystal. Data reduction was done by the multiscan method using the HKL SCALEPACK. Empirical absorption correction was done using the SADABS program.<sup>[18]</sup> The structural analysis was performed on a personal computer using the SHELXTL program package. The structures were solved by the SHELXS-97 program<sup>[19]</sup> and further refined by the *Shelxl-97* program using full matrix least-square fitting of F<sup>2.[20]</sup>Nonhydrogen atoms were refined anisotropically, whereas hydrogen atoms were located at the calculated positions and refined by the riding mode. The perchlorate ion in compound 2 was disordered in a 0.55:0.45 ratio, and the same disorder was observed for the pyridine in compound 2.

# **4** | **CONCLUSIONS**

Based on the experimental conditions, we speculate that a high ratio of metal ions can cause the complexes tend to form low coordinating frameworks. This is an intuitive conclusion in which we assume that a high metal ion ratio would increase the number of collisions between metal ions, and this, in turn, would decrease the number of reactions between ligands and metal ions. The tris(4-pyridylethynyl) benzene ligand described here can be used to produce MOFs with different structures by using different ratios of reactants. The  $\pi$ - $\pi$  stacking that can occur in such a special conjugate system as this can be quite diverse. In addition to the common benzene ring and pyridine, some other  $\pi$ - $\pi$  forces such as ethyne-Py or ethyne-Bz can also be involved. Armed with these  $\pi$ - $\pi$  interactions, such materials can form interpenetrating planes and even lead to highly symmetrical structures. It should be noted here that numerous reports have appeared concerning the formation of general complex and cage compounds using this ligand. Nevertheless, MOFs purely prepared using this ligand (L) are unprecedented. With the current work, we report two new MOF structures formed by using this tris(4-pyridylethynyl)benzene ligand. Compounds 2 and 3, each has its own special framework. Compound 2 forms an octet with a (4,2) node network and compound 3 forms a hexagonal structure with a (3,3) node network. Given these findings, we conclude that they will stimulate the development of a new research branch and that the findings will open up the gate to the formation of other types of such complexes.

#### ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology of Taiwan (MOST106-2113-M-030-008). Supporting information Compound (2) and compound (3) have been deposited with CambridgeCrystallographic Data Centre,CCDC number 1871203 and 1871204. The ligand LTGA(Figure 1S) have been attached.Powder X-ray (Figure 2S), NMR H spectra(Figure 3S),ORTEPs, ESI-MASS(5S) for ligand L(Figure 4S). Furthermore, Crystal data(table 1S to 10S) about compound(2)and compound (3) was specificallyrecorded.

#### ORCID

En-Che Yang b https://orcid.org/0000-0002-2987-2131

#### REFERENCES

- (a) O. K. Farha, A. Özgür Yazaydın, I. Eryazici, C. D. Malliakas,
   B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr,
   J. T. Hupp, *Nat. Chem.* **2010**, *2*, 944. (b) J. A. Mason,
   M. Veenstra, J. R. Long, *Chem. Sci.* **2014**, *5*(1), 32.
- [2] (a) B. Chen, C. Liang, J. Yang, D. S. Contreras, Y. L. Clancy,
  E. B. Lobkovsky, O. M. Yaghi, S. Dai, *Angew. Chem. Int. Ed.* **2006**, 45(9), 1390. (b) Z.-Y. Gu, C.-X. Yang, N. Chang, X.-P. Yan, *Acc. Chem. Res.* **2012**, 45(5), 734.
- [3] (a) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*(5), 1450. (b) C.-D. Wu, A. Hu, L. Zhang, W. Lin, J. Am. Chem. Soc. **2005**, *127*(25), 8940. (c) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **2012**, *112*(2), 1196.
- [4] (a) Z. Hu, B. Deibert, J. Li, *Chem. Soc. Rev.* 2014, *43*(16), 5815.
  (b) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* 2012, *112*(2), 1105.
- [5] B. Gole, A. K. Bar, P. S. Mukherjee, *Chem. Commun.* 2011, 47, 12137.
- [6] (a) B. Chen, S. Xiang, G. Qian, Acc. Chem. Res. 2010, 43(8), 1115. (b) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastré, J. Mater. Chem. 2006, 16 (7), 626.
- [7] S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* 1999, 283(5405), 1148.

- [9] H. L. Anderson, C. J. Walter, A. Vidal-Ferran, R. A. Hay, P. A. Lowden, J. K. M. Sanders, *J. Chem. Soc, Perk.* **1995**, *1*(18), 2275.
- [10] (a) M. Schweiger, T. Yamamoto, P. J. Stang, D. Bläser, R. Boese, J. Org. Chem. 2005, 70(12), 4861. (b) K. Ghosh, J. Hu, H. S. White, P. J. Stang, J. Am. Chem. Soc. 2009, 131(19), 6695. (c) H.-B. Yang, K. Ghosh, N. Das, P. J. Stang, Org. Lett. 2006, 8 (18), 3991. (d) H.-B. Yang, K. Ghosh, B. H. Northrop, P. J. Stang, Org. Lett. 2007, 9(8), 1561.
- [11] S. Winter, E. Weber, L. Eriksson, I. Csöregh, New J. Chem. 2006, 30(12), 1808.
- [12] S. Neogi, G. Schnakenburg, Y. Lorenz, M. Engeser, M. Schmittel, *Inorg. Chem.* 2012, 51(20), 10832.
- [13] (a) A. Ciesielski, W. R. Szabelski, A. Cadeddu, T. R. Cook, P. J. Stang, P. Samorì, J. Am. Chem. Soc. 2013, 135(18), 6942.
  (b) D. Ecija, S. Vijayaraghavan, W. Auwärter, S. Joshi, K. Seufert, C. Aurisicchio, D. Bonifazi, J. V. Barth, ACS Nano 2012, 6(5), 4258. (c) D. Trawny, P. Schlexer, K. Steenbergen, J. P. Rabe, B. Paulus, H.-U. Reissig, ChemPhysChem 2015, 16 (5), 949. (d) S. Vijayaraghavan, W. D. Ecija, S. Auwärter, K. Joshi, M. Seufert, D. Drach, P. Nieckarz, C. Szabelski, D. Aurisicchio, J. V. B. Bonifazi, Chem.-Eur. J. 2013, 19(42), 14143. (e) Q.-N. Zheng, X.-H. Liu, T. Chen, H.-J. Yan, T. Cook, D. Wang, P. J. Stang, L.-J. Wan, J. Am. Chem. Soc. 2015, 137 (19), 6128.
- [14] N. Kobayashi, M. Kijima, J. Mater. Chem. 2008, 18(9), 1037.
- [15] T. R. Cook, Y.-R. Zheng, P. J. Stang, *Chem. Rev.* 2013, 113 (1), 734.
- [16] V. A. Blatov, A. P. Shevchenko, D. M. Proserpio, *Cryst. Growth Des.* 2014, 14(7), 3576.
- [17] (a) E. G. Hohenstein, C. D. Sherrill, J. Phys. Chem. A 2009, 113 (5), 878. (b) B. K. Mishra, N. Sathyamurthy, J. Phys. Chem. A 2005, 109(1), 6.
- [18] G. M. Sheldrick, SADABS: Version 2.03, University of Göttingen, Göttingen, Lower Saxony, Germany, 2002.
- [19] G. M. Sheldrick, Acta Crystallogr. A 1990, 46, 467.
- [20] G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Lower Saxony, Germany, 1997.

#### SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Yang E-C, Wu C-M, Pan P-J, Lee G-H, Sheu H-S, Chang C-K. The structures of MOFs prepared from 1,3,5-tris [4pyridylethynyl]-benzene and a copper(I) perchlorate complex. *J Chin Chem Soc*. 2019;1–8. <u>https://doi.org/</u> 10.1002/jccs.201900022