Journal of Chemical Crystallography, Vol. 37, No. 4, April 2007 (© 2007)
DOI: 10.1007/s10870-007-9179-8

Reaction of 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne and imidazole with Cu(II) generates a discrete complex not a coordination polymer: crystal structure of [μ-4,4′-(1,2-ethynediyl)-bis(pyridine-2,6-dicarboxylato)-N, O, O′-μ-N′, O″, O‴]-diaqua-bis(imidazole)-dicopper(II)

Yu Wang,(1) **Christopher G. F. Cooper,**(1) **Brian S. Luisi,**(2) **Brian Moulton,**(2)
and John C. MacDonald(1)*

Received August 1, 2006; accepted January 8, 2007

Reaction of 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne and imidazole with Cu(II) produces crystals containing a discrete complex of [μ-4,4′-(1,2-ethynediyl)-bis(pyridine-2,6-dicarboxylato)-N, O, O′-μ-N′, O″, O‴]-diaqua-bis(imidazole)-dicopper(II) complex (**1**), $[(C_{16}H_4N_2O_8)(C_3H_4N_2)_2(H_2O)_2Cu_2]$ instead of a linear coordination polymer. The complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 5.3763(8)$ Å, $b = 18.522(3)$ Å, $c = 11.4827(7)$ Å, $\beta = 93.705(3)^\circ$ and $Z = 2$. The complex sits on a center of symmetry such that the two halves of the molecule are related by inversion symmetry. The molecules pack in layers in which the molecules are joined by intermolecular N–H···O hydrogen bonds between imidazole and carboxylate groups and O–H···O hydrogen bonds between carboxylate groups and water.

KEY WORDS: 2,6-dicarboxypyridine; 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne; imidazole.

Introduction

We are investigating the design and synthesis of metal-organic frameworks using ligands that promote divergent assembly as a means to prepare porous crystalline solids. Solids that obtain their porosity from rigid frameworks of molecules joined by metal ions are receiving considerable attention because these materials exhibit useful properties such as permanent porosity, high thermal stability, large void volumes and pores with adjustable structures.[1–26] Accordingly, porous solids are promising materials for molecular storage, separation and sensing, production of nanoparticles, catalysis, and exchange of molecules and ions.[27–47] We have demonstrated previously that 2,6-dicarboxypyridine is a versatile ligand that coordinates a range of transition metals and that metal-ligand coordination can be used to promote assembly of molecules in solids[48–53] and on surfaces.[54,55] Based on this work, we are now investigating the utility of ligands containing multiple 2,6-dicarboxypyridine groups as building blocks for preparing 1-D, 2-D

(1) Department of Chemistry & Biochemistry, Worcester Polytechnic Institute, Worcester, MA 01609, USA.
(2) Department of Chemistry, Brown University, Providence, RI 02912, USA.
* To whom correspondence should be addressed; e-mail: jcm@wpi.edu

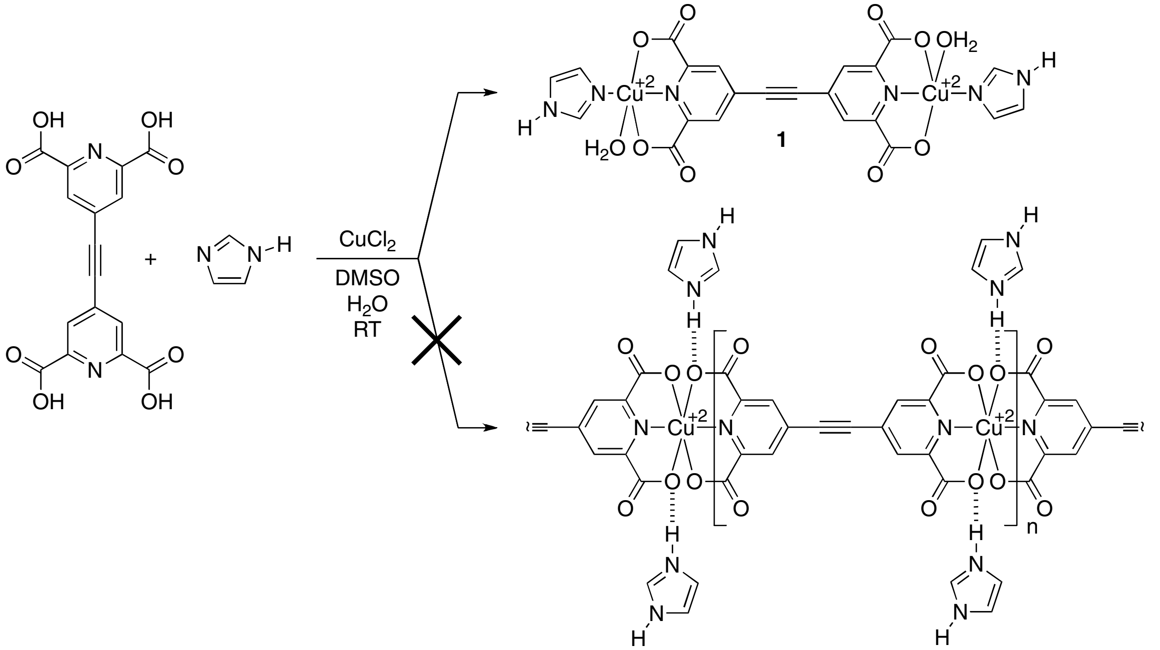


Fig. 1. Reaction of 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne and imidazole with CuCl$_2$ followed by crystallization gave crystals containing complex **1** (*top*) rather than a rigid 1-D metal-organic framework consisting of a linear coordination polymer (*bottom*).

and 3-D frameworks. Our objective is to develop a library of poly(2,6-dicarboxypyridin-4-yl) ligands that form frameworks with a range of architectures and porosity that can be selected based on the geometry of the ligand and the choice of transition or lanthanide metals. Toward this goal, we are investigating ligands substituted with two, three or four 2,6-dicarboxypyridine units attached covalently to a central core by rigid linkers that consist of alkynyl groups and benzene rings. Here we report results from initial efforts to prepare a linear framework by reacting 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne with Cu(II) metals ions in the presence of imidazole. We chose to study 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne as a candidate for preparing linear frameworks for the following reasons: (1) 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne contains two 2,6-dicarboxypyridine groups bonded at either end of ethyne, as shown in Fig. 1; (2) the rigid ethyne group holds the 2,6-dicarboxypyridine groups in a linear arrangement with metal-binding sites oriented facing in opposite directions; (3) this ligand is known to bind lanthanide metals and form coordination networks in solution.[56] Our previous studies of bis(imidazolium 2,6-dicarboxypyridine) M(II) complexes (M = Mn, Co, Ni, Cu, and Zn),[50–53] bis(2-methylimidazolium 2,6-dicarboxypyridine) M(II) complexes (M = Mn, Co, Ni, Cu, and Zn)[49] and bis(imidazolium 2,4,6-tricarboxypyridine) M(II) complexes (M = Co, Ni, Cu, and Zn)[48] established that imidazole functioned not as a ligand, but as a base. In each family of complexes, we found that imidazole deprotonated one carboxyl group on each 2,6-dicarboxypyridine ligand when an equimolar amount of imidazole was present during formation of the metal complex. The resulting imidazolium cations played an important structural role by linking adjacent metal complexes into hydrogen-bonded layers via N–H· · ·O interactions with carboxylate groups. A consistent feature of the layers was the presence of large (e.g., 17Å × 21Å) holes. We reasoned it should be possible to form solids with open channels by tethering two 2,6-dicarboxypyridine units covalently in order to align the holes in adjacent layers.

Shown at the bottom in Fig. 1 is the structure of a coordination polymer with pendant imidazolium cations that we targeted by reacting reacting 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne and imidazole with Cu(II) ions. Our attempts to prepare porous solids from these components unexpectedly yielded a discrete coordination complex. In this report, we present the crystal structure of [μ-4,4′-(1,2-ethynediyl)-bis(pyridine-2,6-dicarboxylato)-N, O, O′-μ-N′, O″, O‴]-diaqua-bis (imidazole)-dicopper(II) complex (**1**).

Experimental

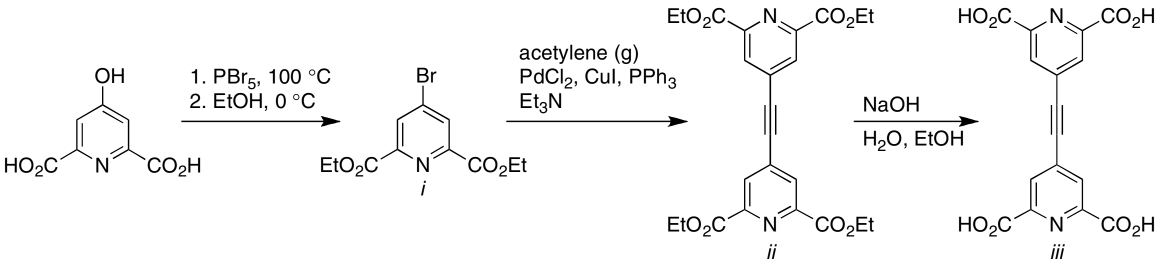
All reagents and solvents were purchased from Aldrich or Acros and were used without further purification. Bis(2,6-dicarboxypyridin-4-yl)ethyne was synthesized in three steps (Scheme 1) by adapting procedures reported previously by Latva *et al.* as described below.[56] Acetylene (30% in acetone) was purchased from Mattheson Gas, Inc. Phosphorous pentabromide was prepared freshly via addition of bromine and phosphorous tribromide. The resulting yellow solid was reslurried in *tert*-butyl methyl ether several times until the filtrate was no longer yellow in color, and was used immediately after. NMR spectra were obtained with a 400 MHz Avance Bruker spectrometer. Mass spectra were measured by SynPep Corporation. Ionization was performed using electrospray, with acetonitrile as the carrier solvent, and nitrogen as a curtain gas.

*Preparation of 4-bromo-2,6-bis (ethoxycarbonyl)pyridine (**i**)*

Chelidamic acid (23.9 *g*, 100 mmol) was combined with phosphorous pentabromide (43.1 *g*, 100 mmol) under an N_2 atmosphere. The mixture was heated gently at 100°C for 0.5 h. The reaction was cooled to RT, and the solid was dissolved in ether (150 mL). The ethereal solution was then added dropwise to a stirred solution of absolute ethanol (100 mL) at 0°C. Recrystallization of the product from 30 % nitric acid yielded 22.0 *g* (66.1 % yield) of **i** as white needles.^{1}H NMR (*d6*-DMSO) δ (ppm) 1.30 (t, 6 H), 4.29 (q, 4 H), 9.0 (s, 2 H).

*Preparation of bis[2,6-bis(ethoxycarbonyl) pyridin-4-yl]ethyne (**ii**)*

Compound **i** (22.0 *g*, 66.1 mmol) was dissolved in triethyl amine (200 mL) under an N_2 atmosphere, and $PdCl_2$ (1.1 *g*, 6.6 mmol), CuI (2.5 *g*, 13.2 mmol), and triphenyl phosphine (1.7 *g*, 6.6 mmol) were added. Acetylene was bubbled through the reaction mixture, and the mixture stirred for 18 h at RT. The resultant mixture was poured into water (400 mL), and extracted three times with ethyl acetate (900 mL total). The organic fractions were combined, washed twice with citric acid, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The



Scheme 1.

resulting crude product was purified over silica gel (40% ethyl acetate:hexane) to give 10.2 *g* of **ii** (33.0% yield) as a white powder. ^{1}H NMR (*d6*-DMSO) δ (ppm) 1.25 (t, 12 H), 4.38 (q, 8 H), 8.6 (s, 4 H).

*Preparation of bis(2,6-dicarboxypyridin-4-yl) ethyne (**iii**)*

Compound **ii** (10.2 *g*, 21.7 mmol) was dissolved in 10% aqueous ethanol (300 mL), and sodium hydroxide (1.6 *g*, 65.1 mmol) was added. The reaction mixture was heated to reflux for 3 h, with progress being monitored via TLC. The reaction mixture was cooled to RT, and solvent removed under reduced pressure. The crude product was dissolved in water (500 mL), and extracted twice with TBME (500 mL total). The pH of the aqueous layer was adjusted to 6 with ammonium chloride, and the product was extracted three times with methylene chloride (250 mL per wash). The organic fractions were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give 6.2 *g* of **iii** (80% yield) as a white solid. ^{1}H NMR (*d6*-DMSO) δ (ppm) 9.3 (s, 4 H), 12.6 (bs, ~ 4 H). ESI-MS, m/z $[M+H]^* = 357.1$, $[M+Na]^* = 379.8$.

*Preparation of [μ-4,4′-(1,2-ethynediyl)-bis(pyridine-2,6-dicarboxylato)-N, O, O′-μ-N′, O″, O‴]-diaqua-bis(imidazole)-dicopper(II) complex (**1**)*

A solution containing 10 *mg* (0.028 mmol) of compound **iii** and 3.7 *mg* (0.054 mmol) imidazole in 10 mL of 1:1 DMSO/H_2O (v/v) was placed in a glass vial. Ten mL of 1:1 DMSO/H_2O (v/v) were carefully layered on top followed by 20 mL of H_2O. A solution containing 4.6 *mg* (0.0027 mmol) of $CuCl_2{\cdot}2H_2O$ in 5 mL of H_2O was added as a fourth layer. The vial was covered and allowed to sit undisturbed until crystals of **1** formed as green plates in solution after one week. Single crystals were removed from solution and dried on filter paper.

Crystal structure determination

A crystal of **1** having approximate dimensions 0.11 mm × 0.10 mm × 0.03 mm was placed on a glass fiber that was mounted on a Siemens SMART/CCD diffractometer equipped with an LT-II low temperature device. Diffraction data were collected at 90(2) K using graphite monochromated Mo-K_α radiation with the omega-scan technique. Diffraction data were corrected for absorption using the SADABS program.[57] The unit cell and space group were determined using the SAINT+ program.[57] The structure was solved by direct methods and refined by full matrix least-squares using the SHELXTL program on a PC platform.[57] Refinement was based on F^2 using all reflections. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on oxygen atoms were located and refined with isotropic thermal parameters. Hydrogen atoms on oxygen atoms on the molecules of water bonded to Cu were located in the difference Fourier map, the coordinates constrained to ride on the coordinates of the bonded oxygen atom, and refined isotropically with thermal parameters based upon the corresponding attached oxygen atoms [U(H) = 1.2 Ueq (O)]. The remaining hydrogen atoms on carbon were fixed in calculated positions and refined isotropically with thermal parameters based upon the corresponding attached carbon atoms [U(H) = 1.2 Ueq (C)].

Results and discussion

The molecular structure of **1** with thermal ellipsoids and atomic numbering is shown in Fig. 2. A view of crystal packing perpendicular to the 103 plane is shown in Fig. 3. A summary of the crystallographic information is given in Table 1. Selected bond lengths and bond angles are given in Table 2.

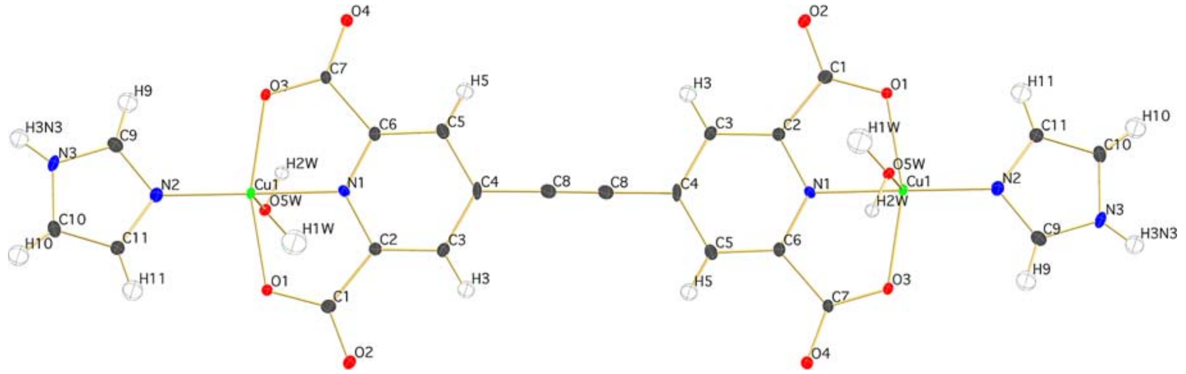


Fig. 2. Molecular structure of **1**, ellipsoids at 50% probability.

Molecular structure of 1

Reaction of 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne and imidazole with copper(II) chloride in DMSO/H_2O gave the corresponding [μ-4,4′-(1,2-ethynediyl)-bis(pyridine-2,6-dicarboxylato)-N, O, O′-μ-N′, O″, O‴]-diaqua-bis(imidazole)-dicopper(II) complex, **1**. As shown in Fig. 2, this complex has a structure in which both Cu ions coordinate to ligands in a distorted square pyramidal geometry. The Cu ions bond to 1,2-bis(2,6-dicarboxypyridin-

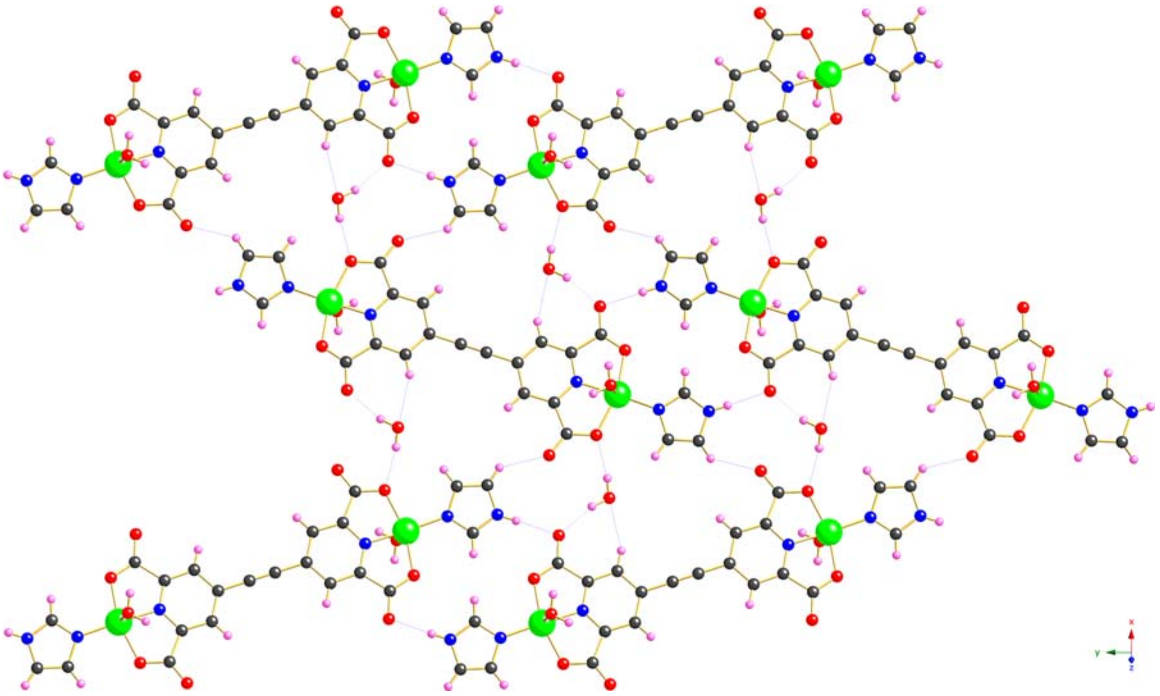


Fig. 3. A hydrogen-bonded layer in the crystal structure of **1** viewed perpendicular to the 103 plane. Isolated molecules of water shown within the layer are bonded to metal complexes that have been omitted for clarity. Thin blue lines represent hydrogen bonds.

Table 1. Crystallographic Data and Refinement Information for **1**

Empirical formula	$C_{22}H_{16}N_6O_{10}Cu_2$
CCDC deposit no.	CCDC 615638
Formula weight	651.48
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal description	green plate
Unit cell dimensions	
a(Å)	5.3763(8)
b(Å)	18.522(3)
c(Å)	11.4827(17)
β(deg)	93.705(3)
Volume (Å^3)	1141.1(3)
Z	2
Density$_{\text{calc}}$(g/cm^3)	1.896
Temperature (K)	90(2)
F(000)	656
θ range for data collection (°)	2.09–28.28
Absorption coefficient (mm^{-1})	1.940
Reflections collected	9892
Independent reflections	2707 [$R_{\text{int}} = 0.1240$]
Reflections [$I > 2\sigma(I)$]	2054
Data/restraints/parameters	2707/0/183
Goodness of fit on F^2	1.001
R [$I > 2\sigma(I)$]	$R_1 = 0.0560$, $wR_2 = 0.0945$
R (all data)	$R_1 = 0.0881$, $wR_2 = 0.1042$
Max. and min. peaks in final diff. map (eÅ^{-3})	0.872, – 0.646

4-yl)ethyne in a meridonial arrangement and to one molecule of imidazole and one molecule of water. The carboxylic acid groups at both ends of 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne lose protons to form negatively charged carboxylate groups that balance the 2+ charge of the Cu metal ions. The least squares planes of the pyridine rings are parallel but separated by 0.3Å because the central C≡C bond bends out of the planes of the rings by 2.7°. The carboxylate groups are nearly coplanar with the pyridine ring and rotate by just 1.2° [O(1)-C(1)–O(2)] and 2.1° [O(3)–C(7)–O(4)] out of the plane of the ring. The Cu ion bonds to 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne via one Cu–N bond [Cu(1)–N(1) = 1.910(3)Å] to the pyridine ring and two Cu-O bonds [Cu(1)–O(1) = 2.022(3)Å, Cu(1)–O(3) = 2.033(3)Å] to the carboxylate groups. In addition, the metal ion bonds to imidazole via one Cu–N bond [Cu(1)–N(2) = 1.926(3)Å] and to the oxygen of a molecule of water via one Cu–O bond [Cu(1)–O(5W) = 2.342(3)Å].

To compare the Cu-N and Cu-O bond distances and coordination in the 2,6-dicarboxypyridine moiety of **1** to those reported previously in the crystallographic literature, we searched the Cambridge Structural Database (CSD) for complexes that contained Cu bonded to at least one 2,6-dicarboxypyridine moiety.[58] The search, which allowed for substituents other than hydrogen on carbons 3, 4 and 5 on the pyridine ring, yielded 36 crystal structures of complexes that featured 52 Cu–N bonds and 101 Cu–O bonds that were unique crystallographically. The Cu–N bond distances ranged from 1.844–2.034Å with an average distance of 1.931(48)Å. The Cu–O bond distances ranged from 1.987–2.536Å with an average distance of 2.131(144)Å. By comparison, the Cu–N and Cu–O bond lengths in the structure of **1** fall within one e.s.d. of the average Cu–N and Cu–O distances, and thus are average within experimental error. Twelve of the structures from the CSD had Cu ions coordinated to two 2,6-dicarboxypyridine ligands; the other 24 had Cu ions coordinated to one 2,6-dicarboxypyridine ligand and to nitrogen and oxygen atoms on other ligands that included various derivatives of pyridine, pyrazine, pyrimidine, bipyridine, terpyridine, phenanthroline, propane-1,3-diamine, imidazole, imidazole-N-oxide, methanol and water.

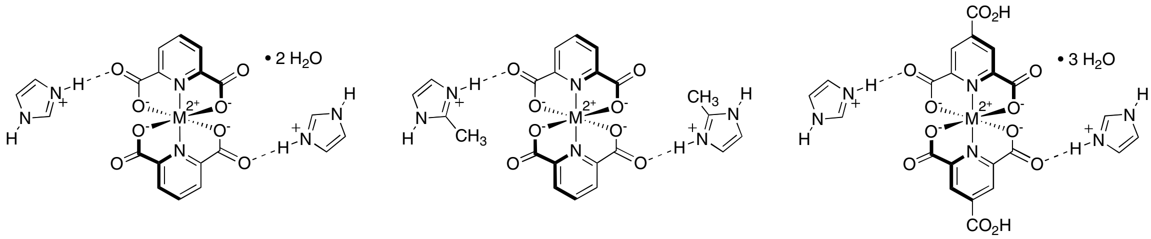
It was surprising to find Cu ions coordinated to molecules of imidazole in addition to the 2,6-dicarboxypyridine groups. We reported previously that transition metals coordinate to two 2,6-dicarboxypyridine ligands in bis(imidazolium 2,6-dicarboxypyridine) M(II) dihydrate complexes,[50–53] bis(2-methylimidazolium 2,6-dicarboxypyridine) M(II) dihydrate complexes[49] and bis(imidazolium 2,4,6-tricarboxypyridine) M(II) trihydrate complexes (where M = Mn, Co, Ni, Cu or Zn).[48] The chemical structures of those complexes are shown in Fig. 4. Those studies established that 2,6-dicarboxypyridine is a versatile ligand that reliably coordinates to a variety of first-row transition metal ions in an

Table 2. Bond Lengths (Å) and Angles (°) for **1**

Cu(1)–N(1)	1.909(3)	O(1)–Cu(1)–O(5W)	88.84(11)
Cu(1)–N(2)	1.926(3)	O(3)–Cu(1)–O(5W)	95.96(11)
Cu(1)–O(1)	2.022(3)	C(6)–N(1)–C(2)	123.6(3)
Cu(1)–O(3)	2.034(3)	C(6)–N(1)–Cu(1)	118.9(3)
Cu(1)–O(5W)	2.343(3)	C(2)–N(1)–Cu(1)	117.3(3)
N(1)–C(6)	1.329(5)	C(9)–N(2)–C(11)	105.5(4)
N(1)–C(2)	1.343(5)	C(9)–N(2)–Cu(1)	127.7(3)
N(2)–C(9)	1.328(5)	C(11)–N(2)–Cu(1)	126.8(3)
N(2)–C(11)	1.383(5)	C(9)–N(3)–C(10)	107.8(4)
N(3)–C(9)	1.332(5)	C(1)–O(1)–Cu(1)	114.7(2)
N(3)–C(10)	1.369(5)	C(7)–O(3)–Cu(1)	114.4(2)
O(1)–C(1)	1.288(5)	O(2)–C(1)–O(1)	126.0(4)
O(2)–C(1)	1.223(5)	O(2)–C(1)–C(2)	119.9(4)
O(3)–C(7)	1.271(5)	O(1)–C(1)–C(2)	114.1(3)
O(4)–C(7)	1.249(5)	N(1)–C(2)–C(3)	119.5(4)
C(1)–C(2)	1.513(6)	N(1)–C(2)–C(1)	112.4(3)
C(2)–C(3)	1.385(6)	C(3)–C(2)–C(1)	128.1(4)
C(3)–C(4)	1.400(6)	C(2)–C(3)–C(4)	118.5(4)
C(4)–C(5)	1.403(6)	C(3)–C(4)–C(5)	120.2(4)
C(4)–C(8)	1.436(6)	C(3)–C(4)–C(8)	119.5(4)
C(5)–C(6)	1.383(5)	C(5)–C(4)–C(8)	120.3(4)
C(6)–C(7)	1.527(6)	C(6)–C(5)–C(4)	118.2(4)
C(8)–C(8)#1	1.189(8)	N(1)–C(6)–C(5)	120.1(4)
C(10)–C(11)	1.341(6)	N(1)–C(6)–C(7)	110.9(3)
N(1)–Cu(1)–N(2)	169.56(15)	C(5)–C(6)–C(7)	128.8(4)
N(1)–Cu(1)–O(1)	80.96(13)	O(4)–C(7)–O(3)	125.6(4)
N(2)–Cu(1)–O(1)	97.94(13)	O(4)–C(7)–C(6)	119.2(3)
N(1)–Cu(1)–O(3)	80.31(13)	O(3)–C(7)–C(6)	115.2(3)
N(2)–Cu(1)–O(3)	99.58(13)	C(8)#1–C(8)–C(4)	177.0(7)
O(1)–Cu(1)–O(3)	160.64(11)	N(2)–C(9)–N(3)	110.8(4)
N(1)–Cu(1)–O(5W)	89.77(12)	C(11)–C(10)–N(3)	106.5(4)
N(2)–Cu(1)–O(5W)	100.60(13)	C(10)–C(11)–N(2)	109.4(4)

Note. Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z$.

octahedral arrangement in which the metal ion is encapsulated by two ligands. Moreover, this work showed that imidazole and 2-methylimidazole did not compete with 2,6-dicarboxypyridine or 2,4,6-tricarboxypyridine in coordinating to metal ions when both ligands were present in solution



M = Zn, Cu, Ni, Co, Mn

M = Zn, Cu, Ni, Co, Mn:Cu (7:3)

M = Zn, Cu, Ni, Co

Fig. 4. Chemical structures of bis(imidazolium 2,6-dicarboxypyridine) M(II) dihydrate complexes,[50–53] bis(2-methylimidazolium 2,6-dicarboxypyridine) M(II) complexes[49] and bis(imidazolium 2,4,6-tricarboxypyridine) M(II) trihydrate complexes.[48]

prior to addition of the metal ion. Instead, imidazole acted as a base by deprotonating carboxylic acid groups on the pyridine ligands. The resulting imidazolium cations served as hydrogen-bonding donors that promoted formation of 2-D networks of hydrogen bonds involving carboxylate acceptors. Accordingly, we expected 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne ligands to coordinate Cu preferentially in a 1:1 ratio, thereby forming linear coordination polymers with pendant imidazolium cations hydrogen bonded along the backbone (Fig. 1). The structure of complex **1**, while unexpected, is not unprecedented. For example, several structures featuring Cu(II) ions coordinated by 2,6-dicarboxypyridine and substituted imidazole ligands, [Cu(2,6-dicarboxypyridine)(L)], where L = 1-methylimidazole, 2-methylimidazole and 4-methylimidazole, have been reported with coordination similar to that in complex **1**.[59–61] In one study, Su investigated the structure and electronic properties of the complex with 1-methyl imidazole and proposed that monodentate bonding of imidazoles with the ring coplanar to the pyridine ligand is necessary to maximize π-donation of electron density from the imidazole to the pyridine ring.[61] The structure of complex **1** is consistent with this finding in that the imidazole coordinates to Cu so that the two rings are nearly coplanar (the imidazole ring twists 11.4° out of the plane of the pyridine ring). In a recent study, we found that the monodentate ring nitrogen of 2,6-dicarboxypyrazine rings in coordination polymers of *catena*-[diaqua-(μ-pyrazine-2,6-dicarboxylato-N,O,O′-μ-N′)-copper(II) also bond to Cu(II) ions in a coplanar arrangement with adjacent 2,6-dicarboxypyrazine rings.[62] It is notable that 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne, Cu and imidazole were incorporated into complex **1** in a 1:2:2 molar ratio, respectively, from solutions containing the three components in a 1:1:2 molar ratio. Considering that half of the 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne molecules remained uncomplexed in solution, these results indicate there is a significant driving force for selective formation of discrete complexes with mixed ligands over coordination polymers. In related work, we recently reported that reaction and crystallization of 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne with Co(II) ions in the absence of imidazole produced a discrete complex of 4-(2,6-dicarboxypyridin-4-yl)ethynylpyridine-2,6-dicarboxylatotriaqua cobalt(II) monohydrate, $[Co(C_{16}H_6N_2O_8)(H_2O)_3] \cdot H_2O$.[63] That complex featured a Co ion coordinated octahedrally to a single 2,6-dicarboxypyridine group at one end of the ligand and three molecules of water, leaving the second 2,6-dicarboxypyridine group uncomplexed. We hypothesize that coordination of the positive Co ion by one 2,6-dicarboxypyridine group withdraws enough electron density from the second 2,6-dicarboxypyridine group through the conjugated acetylenic backbone to inhibit coordination to a second Co ion. Differences in the relative ratio of ligand to metal and modes of coordination between the Co complex and complex **1** likely are determined by the presence or absence of imidazole in solution during reaction of the components. The fact that Cu ions coordinate to both ends of the 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne ligand in complex **1** can be explained by considering that imidazole behaves as a π-donor that stabilizes mixed ligand Cu complexes with 2,6-dicarboxypyridine (a π-acceptor) by donating electron density to the complex.[61] In the absence of imidazole, we expect 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne and Cu ions to form a discrete complex similar to that of the Co complex. Accordingly, we predict that formation of linear coordination polymers is unlikely to occur with 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne or related ligands in which two electron-deficient 2,6-dicarboxypyridine groups are linked electronically via a conjugated backbone.

The molecule of water coordinated to Cu sits in an axial position with respect to the 2,6-dicarboxypyridine and imidazole moieties. Water also was present in a similar arrangement in four of the five structures of mixed ligand Cu complexes with 2,6-dicarboxypyridine and substituted imidazoles present in the CSD.[59–61] We did not attempt to prepare crystals of **1** from solvents other than DMSO/H_2O mixtures; therefore it is not known what effect solvents other than water might have on the composition of the final product. Our earlier investigation of bis(imidazolium 2,6-dicarboxypyridine) M(II) dihydrate complexes[50–53] and bis(imidazolium 2,4,6-tricarboxypyridine) M(II) trihydrate complexes[48] revealed that water was included in all structures as hydrates (i.e., not coordinated to metal ions) regardless of whether DMSO, water or a mixture of DMSO and water was used as the solvent for crystallization. In contrast, we found water coordinated to the metal ions in the structures of *catena*-[diaqua-(μ-pyrazine-2,6-dicarboxylato-N,O,O′-μ-N′)-copper(II) and 4-(2,6-dicarboxypyridin-4-yl)ethynylpyridine-2,6-dicarboxylatotriaqua cobalt(II) monohydrate.[62,63] It is likely that coordination of water will occur in other solvents to form complexes of **1** unless water is rigorously excluded.

Crystal packing and hydrogen bonding in **1**

Complex **1** crystallizes in the monoclinic space group $P2_1/n$ with the asymmetric unit consisting of half the complex. The complex sits on a center of symmetry such that the two halves of the compound are related by inversion symmetry. Packing in the solid is dominated by hydrogen bonding involving imidazole, water and carboxylate groups. Each molecule is joined to two adjacent molecules by four symmetry equivalent N–H···O interactions between imidazole and carboxylate groups [N(3)···O(4) = 2.843(4)Å, H(3N3)···O(4) = 1.98Å, N(3)–H(3N3)···O(4) = 177.8°] that form hydrogen-bonded rings with graph set $R_2^2(16)$.[64,65] These interactions form on both sides of each molecule, thereby generating chains of molecules with graph set $C_2^2(16)[R_2^2(16)]$. Adjacent chains are joined into layers (103 plane) via O–H···O hydrogen bonds between the coordinated molecule of water and carboxylate groups, as shown in Fig. 3. Water forms O–H···O interactions to carboxylate oxygen atoms distal [O(5W)···O(4) = 2.881(4)Å, H(2W)···O(1) = 1.95Å, O(5W)-H(2W)···O(1) = 170.7°] and proximal [O(5W)···O(1) = 2.880(4)Å, H(2W)···O(1) = 2.00Å, O(5W)-H(2W)···O(1) = 164.0°] to Cu on opposite sides of the 2,6-dicarboxypyridine groups at both ends of the molecule that generate 3-D networks of hydrogen bonds.

Conclusions

Our attempts to prepare a crystalline solid containing a 1-D metal-organic framework by reacting 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne and imidazole with Cu metal ions resulted in an unexpected metal complex. Instead of forming a linear coordination polymer composed of alternating Cu metal ions and 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne ligands, Cu metal ions coordinated to molecules of 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne, imidazole and water, forming discrete complex **1**.

Supplementary Materials CCDC 615638 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44(0)1223–336033.

Acknowledgements

Acknowledgement is made to the U. S. Army Research Office (grant # W911NF-05-0293) and to the Donors of The Petroleum Research Fund (grant # 34604-B3), administered by the American Chemical Society, for support of this research at Worcester Polytechnic Institute.

References

1. Kitagawa, S.; Kitaura, R.; Noro, S.-I. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375.
2. Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem. Int. Ed.* **2004**, *43*, 1466–1496.
3. Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 428–431.

4. Ishii, Y.; Takenaka, Y.; Konishi, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 2702–2705.
5. Serre, C.; Millange, F.; Surble, S.; Ferey, G. *Angew. Chem. Int. Ed.* **2004**, *43*, 6286–6289.
6. Wu, C.-D.; Lin, W. *Angew. Chem. Int. Ed.* **2005**, *44*, 2–5.
7. Bowes, C. L.; Ozin, G. A. *Adv. Mater.* **1996**, *8*, 13–28.
8. Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330.
9. Ferey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217–225.
10. Shmilovits, M.; Diskin-Posner, Y.; Vinodu, M.; Goldberg, I. *Cryst. Growth Des.* **2003**, *3*, 855–863.
11. Lu, J.; Shen, E.; Li, Y.; Xiao, D.; Wang, E.; Xu, L. *Cryst. Growth Des.* **2005**, *5*, 65–67.
12. Lu, K.-L.; Chen, Y.-F.; Liu, Y.-H.; Cheng, Y.-W.; Liao, R.-T.; Wen, Y.-S. *Cryst. Growth Des.* **2005**, *5*, 403–405.
13. Ferey, G. *Chem. Mater.* **2001**, *13*, 3084–3098.
14. Zheng, X.-J.; Wang, Z.-M.; Gao, S.; Liao, F.-H.; Yan, C.-H.; Jin, L. P. *Eur. J. Inorg. Chem.* **2004**, 2968–2973.
15. Dybtsev, D. N.; Chun, H.; Kim, K. *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 5033–5035.
16. Ma, J.-F.; Yang, J.; Zheng, G.-L.; Li, L.; Liu, J.-F. *Inorg. Chem.* **2003**, *42*, 7531–7534.
17. Du, M.; Guo, Y.-M.; Chen, S.-T.; Bu, X.-H.; Batten, S. R.; Ribas, J.; Kitagawa, S. *Inorg. Chem* **2004**, *43*, 1287–1293.
18. Kondo, M.; Irie, Y.; Shimizu, Y.; Miyazawa, M.; Kawaguchi, H.; Nakamura, A.; Naito, T.; Maeda, K.; Uchida, F. *Inorg. Chem* **2004**, *43*, 6139–6141.
19. Saied, O.; Maris, T.; Wuest, J. D. *J. Am. Chem. Soc.* **2005**, *125*, 14956–14957.
20. Liao, Y.-C.; Liao, F.-L.; Chang, W.-K.; Wang, S.-L. *J. Am. Chem. Soc.* **2004**, *126*, 1320–1321.
21. Rowsell, J. L. C.; Yaghi, O. M. *Microporous and Mesoporous Materials* **2004**, *73*, 3–14.
22. Rosseinsky, M. J. *Microporous and Mesoporous Materials* **2004**, *73*, 15–30.
23. Burrows, A. D.; Cassar, K.; Friend, R. M. W.; Mahon, M. F.; Rigby, S. P.; Warren, J. E. *CrystEngComm* **2005**, *7*, 548–550.
24. Zhang, J.-P.; Lin, Y.-Y.; Zhang, W.-X.; Chen, X.-M. *J. Am. Chem. Soc.* **2005**, *127*, 14162–14163.
25. Ferey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I. *Science* **2005**, *309*, 2040–2042.
26. Sun, D.; Ke, Y.; Mattox, T. M.; Ooro, B. A.; Zhou, H.-C. *Chem. Commun.* **2005**, 5447–5449.
27. Snurr, R. Q.; Hupp, J. T.; Nguyen, S. T. *AIChE Journal* **2004**, *50*, 1090–1095.
28. Cheetham, A. K.; Rao, C. N. R. *MRS Bulletin* **2005**, *30*, 93–98.
29. Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469–472.
30. Ward, M. D. *Science* **2003**, *300*, 1104–1105.
31. Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127–1129.
32. Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762–1765.
33. Liu, S. Q.; Konaka, H.; Kuroda-Sowa, T.; Suenaga, Y.; Ito, H.; Ning, G. L.; Munakata, M. *Inorg. Chim. Acta* **2004**, *357*, 3621–3631.
34. Hu, A.; Ngo, H. L.; Lin, W. *Angew. Chem. Int. Ed.* **2003**, *42*, 6000–6003.
35. Maji, T. K.; Uemura, K.; Chang, H.-C.; Matsuda, R.; Kitagawa, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 3269–3272.
36. Moon, H. R.; Kim, J. H.; Suh, M. P. *Angew. Chem. Int. Ed.* **2005**, *44*, 1261–1265.
37. Rowsell, J. L. C.; Eckert, J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 14909–14910.
38. Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982–986.
39. Wang, Z.; Zhang, B.; Kurmoo, M.; Green, M. A.; Fujiwara, H.; Otsuka, T.; Kobayashi, H. *Inorg. Chem* **2005**, *44*, 1230–1237.
40. Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 32–33.
41. Uemura, K.; Kitagawa, S.; Fukui, K.; Saito, K. *J. Am. Chem. Soc.* **2004**, *126*, 3817–3828.
42. Rowsell, J. L. C.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666–5667.
43. Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940–8941.
44. Hermes, S.; Schroter, M.-K.; Schmid, R.; Khodeir, L.; Muhler, M.; Tissler, A.; Fischer, R. W.; Fischer, R. A. *Angew. Chem. Int. Ed.* **2005**, *44*, 6237–6241.
45. Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238–241.
46. Mori, W.; Takamizawa, S.; Kato, C. N.; Ohmura, T.; Sato, T. *Microporous and Mesoporous Materials* **2004**, *73*, 31–46.
47. Schichte, K.; Kratzke, T.; Kaskel, S. *Microporous and Mesoporous Materials* **2004**, *73*, 81–88.
48. Yigit, M. V.; Biyikli, K.; Moulton, B.; MacDonald, J. C. *Cryst. Growth Des.* **2005**, *6*, 63–69.
49. MacDonald, J. C.; Luo, T.-J. M.; Palmore, G. T. R. *Cryst. Growth Des.* **2004**, *4*, 1203–1209.
50. MacDonald, J. C.; Dorrestein, P. C.; Pilley, M. M.; Foote, M. M.; Lundburg, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 11692–11702.
51. MacDonald, J. C.; Dorrestein, P. C. *ACA Trans.* **1998**, *33*, 121–131.
52. Luo, T.-J. M.; MacDonald, J. C.; Palmore, G. T. R. *Chem. Mater.* **2004**, *16*, 4916–4927.
53. Luo, T.-J. M.; MacDonald, J. C.; Palmore, G. T. R. *ACA Trans.* **2004**, *39*, 1–10.
54. Cooper, C. G. F.; MacDonald, J. C.; Soto, E.; McGimpsey, W. G. *J. Am. Chem. Soc.* **2004**, *126*, 1032–1033.
55. Soto, E.; MacDonald, J. C.; Cooper, C. G.; McGimpsey, W. G. *J. Am. Chem. Soc.* **2003**, *125*, 2838–2839.
56. Latva, M.; Takalo, H.; Simberg, K.; Kankare, J. *J. Chem. Soc. Perkin Trans.* **1995**, *2*, 995–999.
57. Bruker,(1997). SAINT (Version 6.12), SHELXTL (Version 6.12) for WNT/2000. Bruker AXS Inc., Madison, Wisconsin, USA.
58. Allen, F. H. *Acta Cryst.* **2002**, *B58*, 380–388.
59. Ang, H. G.; Kwik, W. L.; Hanson, G. R. *J. Chem. Soc. Dalton Trans.* **1991**, 3193–3201.
60. Liu, S.-H.; Li, Y.-Z.; Meng, Q.-J. *Acta Cryst.* **2005**, *E61*, m1183-m1184.
61. Su, C.-C.; Chiu, S.-Y. *Polyhedron* **1996**, *15*, 2623–2631.
62. Yigit, M. V.; Wang, Y.; Moulton, B.; MacDonald, J. C. *Cryst. Growth Des.* **2006**, *6*, 829–832.
63. Yigit, M. V.; Cooper, C. G. F.; Wang, Y.; Moulton, B.; MacDonald, J. C. *J. Chem. Cryst.* **2006**, *36*, 371–379.
64. Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N.-L. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1555–1573.
65. Etter, M. C.; MacDonald, J. C.; Bernstein, J. *Acta Cryst.* **1990**, *B46*, 256–262.