# Four Novel 3D Copper(II) Coordination Polymers with Different Topologies

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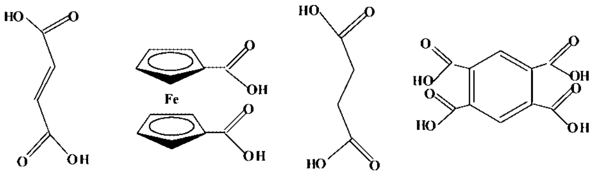
A series of $Cu^{II}$ coordination polymers with different topologies, namely $[CuL(L^1)]·2H_2O$ (**1**), $[CuL_{1.5}(L^2)]·3H_2O$ (**2**), $[CuL(L^3)]·3H_2O$ (**3**) and $[Cu_2L_{2.5}(L^4)(H_2O)]·10H_2O$ (**4**) [L = 1,1′-(1,4-butanediyl)bis(imidazole), $H_2L^1$ = fumaric acid, $H_2L^2$ = 1,1′-ferrocenedicarboxylic acid, $H_2L^3$ = succinic acid, and $H_4L^4$ = pyromellitic acid], are presented. Different polymeric frameworks are obtained by varying the polycarboxylate anions. These include the threefold interpenetrated diamond structure of **1**, the rare twofold interpenetrated $4^66^4$ network of **2**, and two planar four-connected networks of **3** and **4**, which display an unusual Archimedean-type $(6^58)(6^48^2)$ net containing two different types of nodes and a $(56^48)(5^26^28^2)_2(68^{4}10)(5^46^2)$ net containing four different types of nodes, respectively. Thermogravimetric analysis (TGA) curves of **1**, **2**, **3**, and **4** exhibit three similar weight-loss stages.

## Introduction

The construction of coordination networks with novel topologies is of particular current interest due to their intriguing structural diversity.[1] The analysis of network topology acts as an important role in the discussion and design of crystal structures. Wells has listed a large number of topologies in his classic monographs on networks.[2] Numerous reported fascinating archetypal structures, including diamond $(6^6)$,[3] $SrSi_2$ $(10^3$-a),[4] α-$ThSi_2$ $(10^3$-b),[5] $SiO_2$ $(6^48^2$-b),[6] and PtS $(4^28^4)$,[7] have provided experimental examples of these theoretical topologies. All of these extraordinary structures are of fundamental importance in structural design and in the understanding of structure–property correlations.

In recent years many rational synthetic strategies have been proposed for the design of metal-based coordination supramolecular structures. Application of these strategies allows the assembly of a target compound with novel topology.[8] However, general and precise principles for controlling the structures of the target products still need to be further classified and improved. An understanding of the factors that govern the assembly process is therefore necessary for the development of the synthetic strategies. In molecular self-assembly processes many factors influence the formation of the final architectures, such as the solvent system, template, central metal, and anion. We are particularly interested in the effects of anions on the architectures of the final complexes.[9] In an attempt to investigate the design and control of the preparation of coordination compounds, the first square-planar four-connected $(8^6)$ or (8,4) nets have been rationally synthesized by Tong et al. and us.[10] As a continuation of our work, we present here four novel coordination polymers with different organic anions, namely $[CuL(L^1)]·2H_2O$ (**1**), $[CuL_{1.5}(L^2)]·3H_2O$ (**2**), $[CuL(L^3)]·3H_2O$ (**3**), and $[Cu_2L_{2.5}(L^4)(H_2O)]·10H_2O$ (**4**) [L = 1,1′-(1,4-butanediyl)bis(imidazole), $H_2L^1$ = fumaric acid, $H_2L^2$ = 1,1′-ferrocenedicarboxylic acid,[11] $H_2L^3$ = succinic acid, and $H_4L^4$ = pyromellitic acid; see Scheme 1]. Single-crystal X-ray analyses show that the organic anions play an important role in directing the final structural motifs of the polymers.



$H_2L^1$ $H_2L^2$ $H_2L^3$ $H_4L^4$

Scheme 1.

## Results and Discussion

### Syntheses and Characterization

Complexes **1**–**4** are insoluble in water and common organic solvents, and crystals suitable for X-ray diffraction analysis cannot be obtained by evaporating an appropriate solution of **1**–**4**. We found that they can be dissolved in a concentrated solution of ammonia by segregating the ligands from $Cu^{II}$ cations owing to the coordinating role of ammonia toward the $Cu^{II}$ cation. Their crystals were there-

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fore obtained by an unusual crystallization process by evaporating an ammoniacal solution of **1**–**4**.

The elemental analysis data for the four compounds are in good agreement with the formulae [CuL(L$^1$)]·2 $H_2O$ (**1**), [CuL$_{1.5}$(L$^2$)]·3 $H_2O$ (**2**), [CuL(L$^3$)]·3 $H_2O$ (**3**), and [Cu$_2$L$_{2.5}$(L$^4$)($H_2O$)]·10 $H_2O$ (**4**). In order to characterize the compounds **1**–**4** more fully in terms of thermal stability, we studied them by TGA. Compounds **1**–**4** were heated from 35 to 750 °C under $N_2$. When crystals of **1**–**4** were removed from the mother liquor, they lost some of their water molecules. TGA was performed with these partially dehydrated samples. As expected, the TGA curves of compounds **1**–**4** exhibit three similar weight-loss stages. The first weight loss, corresponding to the remaining water molecules, is observed over the wide temperature ranges 35–96 °C, 35–90 °C, 35–92 °C, and 35–89 °C for **1**–**4**, respectively. The second weight loss is 46.2% (calculated 43.6%) for **1** in the range 237–477 °C, 43.4% (calculated 42.2%) for **2** in the range 232–340 °C, 45.9% (calculated 44.8%) for **3** in the range 233–468 °C, and 47.3% (calculated 45.2%) for **4** in the range 227–330 °C, assigned to the release of L molecules. Drastic weight losses corresponding to the removal of L$^1$, L$^2$, L$^3$, and L$^4$ were observed from 477 to 530 °C for **1**, from 340 to 528 °C for **2**, from 468 to 530 °C for **3**, and from 400 to 505 °C for **4**, respectively.

## Crystal Structures

Selected bond lengths and angles for complexes **1**–**4** are listed in Table 1. In the crystal structure of **1** there is one unique four-coordinate Cu$^{II}$ atom. Each Cu$^{II}$ center has a square-planar coordination sphere, with two nitrogen atoms from two L and two oxygen atoms from two L$^1$ ligands (see a in Figure 1), which provide the four-connected nodes resulting in an unsymmetrical adamantane-type $6^6$ net (see b in Figure 1). Water molecules are found in the cage of the adamantane unit and distortions of the unit can arise from the application of different ligands (L and L$^1$).[12] The distance between the Cu$^{II}$ centers is determined by the length of L (11.784 Å) or L$^1$ (9.714 Å). Three-fold interpenetration occurs for the $6^6$ nets of **1** to diminish the void volume of the structure. Figure 1 (see c) shows that three independent equivalent networks are interpenetrated within the structure of **1**. Each pair of nets (I and II, II and III) display a normal mode of interpenetration.[13] For example, four rods from the node of net II inside the cavity of one adamantane unit of net I penetrate one six-membered window of the adamantane unit of net I.

The coordination environment of the Cu$^{II}$ atom in **2** is shown in Figure 2 (see a). The copper(II) center adopts a distorted square pyramidal geometry by coordinating to three nitrogen atoms (N1, N3, and N5) from three L ligands and two oxygen atoms (O1 and O3A) from two L$^2$ ligands. The N1, N3, N5, and O1 atoms constitute the base of the pyramid, whereas O3A occupies the apical position at a Cu–O3A distance of 2.268(3) Å.

The Cu$^{II}$ cations in **2** are bridged by L to form 2D (6,3) networks (see b in Figure 2). These 2D (6,3) networks are further connected by bridging L$^2$ ligands to give rise to a 3D network which can be classified as a $4^{6}6^{4}$ topological type based on pure five-connected nodes (see c in Figure 2). It is noteworthy that this $4^{6}6^{4}$ net is topologically analogous to the inorganic network $B_2$ in $AlB_2$.[13] Interestingly, as shown in Figure 2 (see d), the identical $4^{6}6^{4}$ networks are twofold interpenetrated to form an interlocked 3D structure. To the best of our knowledge, this structural topology is very rare in coordination polymer chemistry.[14]

Table 1. Selected bond lengths [Å] and angles [°] for **1**–**4**.[a]

| | | | |
|---|---|---|---|
| [CuL(L$^1$)]·2 $H_2O$ (**1**) | | | |
| N(1)-Cu(1) | 2.016(2) | O(1)-Cu(1) | 1.996(2) |
| O(1)–Cu(1)–O(1)$^{i}$ | 93.0(1) | O(1)–Cu(1)–N(1) | 174.61(7) |
| O(1)$^{i}$–Cu(1)–N(1) | 91.02(8) | N(1)–Cu(1)–N(1)$^{i}$ | 85.2(1) |
| [CuL$_{1.5}$(L$^2$)]·3 $H_2O$ (**2**) | | | |
| Cu(1)–N(1) | 1.990(4) | Cu(1)–N(3) | 2.087(4) |
| Cu(1)–N(5) | 1.966(4) | Cu(1)–O(1) | 2.016(3) |
| Cu(1)–O(3)$^{i}$ | 2.268(3) | | |
| N(5)–Cu(1)–N(1) | 176.1(2) | N(5)–Cu(1)–O(1) | 89.5(1) |
| N(1)–Cu(1)–O(1) | 88.0(1) | N(5)–Cu(1)–N(3) | 94.0(2) |
| N(1)–Cu(1)–N(3) | 89.8(2) | O(1)–Cu(1)–N(3) | 144.6(2) |
| N(5)–Cu(1)–O(3)$^{i}$ | 90.0(1) | N(1)–Cu(1)–O(3)$^{i}$ | 89.0(2) |
| O(1)–Cu(1)–O(3)$^{i}$ | 123.8(1) | N(3)–Cu(1)–O(3)$^{i}$ | 91.5(1) |
| [CuL(L$^3$)]·3 $H_2O$ (**3**) | | | |
| Cu(2)–N(1) | 1.970(4) | Cu(1)–N(3) | 1.970(3) |
| Cu(1)–O(2) | 1.956(2) | Cu(2)–O(3) | 2.000(3) |
| O(2)–Cu(1)–N(3) | 91.2(1) | O(2)$^{i}$–Cu(1)–N(3) | 90.5(1) |
| N(1)$^{ii}$–Cu(2)–O(3) | 90.2(1) | N(1)–Cu(2)–O(3) | 89.8(1) |
| [Cu$_2$L$_{2.5}$(L$^4$)($H_2O$)]·10 $H_2O$ (**4**) | | | |
| Cu(1)–N(2) | 1.949(3) | Cu(2)–N(3) | 2.009(3) |
| Cu(3)–N(6) | 1.975(3) | Cu(2)–N(7) | 1.996(3) |
| Cu(2)$^{i}$-N(10) | 1.998(3) | Cu(1)–O(2) | 1.928(2) |
| Cu(2)–O(4) | 1.974(2) | Cu(3)–O(5) | 1.981(2) |
| Cu(2)-Ow1 | 2.311(3) | | |
| O(2)–Cu(1)–N(2) | 91.4(1) | O(2)$^{ii}$–Cu(1)–N(2) | 88.7(1) |
| O(4)–Cu(2)–N(10)$^{iii}$ | 89.9(1) | N(7)–Cu(2)–N(10)$^{iii}$ | 89.7(1) |
| O(4)–Cu(2)–N(3) | 89.3(1) | N(7)–Cu(2)–N(3) | 89.9(1) |
| N(10)$^{iii}$–Cu(2)–N(3) | 170.5(1) | O(4)–Cu(2)–Ow1 | 92.0(1) |
| N(7)–Cu(2)–Ow1 | 95.6(1) | N(10)$^{iii}$–Cu(2)–Ow1 | 96.4(1) |
| N(3)–Cu(2)–Ow1 | 93.1(1) | O(4)–Cu(2)–N(7) | 172.4(1) |
| N(6)$^{iv}$–Cu(3)–O(5)$^{iv}$ | 89.5(1) | N(6)–Cu(3)–O(5)$^{iv}$ | 90.5(1) |
| N(6)$^{iv}$–Cu(3)–O(5) | 90.5(1) | N(6)–Cu(3)–O(5) | 89.5(1) |

[a] Symmetry codes for **1**: $^{i}$ $-x + 2, y, -z + 1/2$. Symmetry codes for **2**: $^{i}$ $x - 1, y, z$. Symmetry codes for **3**: $^{i}$ $-x + 1/2, y, -z + 1/2$; $^{ii}$ $-x + 1, -y, -z + 1$. Symmetry codes for **4**: $^{i}$ $x + 1, y, z$; $^{ii}$ $-x - 3, -y + 1, -z - 1$; $^{iii}$ $x - 1, y, z$; $^{iv}$ $-x, -y + 2, -z$.

The structure of **3** contains two crystallographically unique Cu$^{II}$ cations, two unique L ligands, and one unique L$^3$ ligand. As shown in part a of Figure 3, each Cu$^{II}$ cation is four-coordinate in a square-planar four-connected geometry with two nitrogen atoms from two L molecules and two oxygen atoms from two L$^3$ ligands. There exist some unique shortest six- and eight-membered circuits through Cu$^{II}$ cations in **3** (see Figures S1–S4 in the Supporting Information). Figure 3 (see b) shows the unusual network displayed by the structure of **3**. This net contains two types of nodes (Cu1 and Cu2). For Cu1, each of four sets of *cis* links is contained in a six-membered ring (circuit II), and each of two sets of *trans* links is contained in an eight-membered

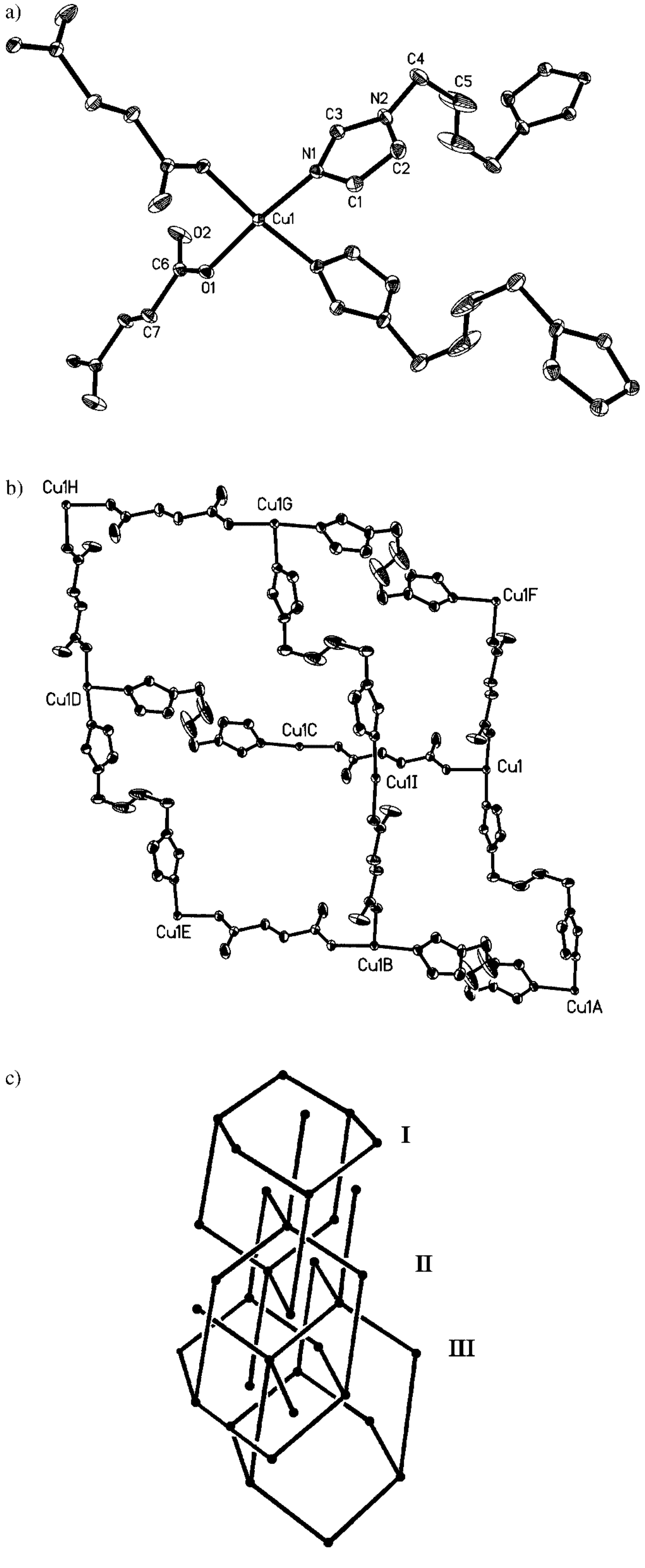

Figure 1. (a) ORTEP view of complex **1** showing 30% thermal probability ellipsoids. (b) View of the adamantane unit of **1**. (c) A schematic representation of the threefold interpenetration mode in **1**.

ring (circuit IV), so the square-planar four-connected Cu1 cation serves as an NbO-like node that also exists in the network of quartz (Schläfli symbol $6^48^2$).[15] For Cu2, each of four sets of *cis* links and one set of two *trans* links can be used to construct a six-membered ring (circuits I and II), and the other set of *trans* links is contained in an eight-membered ring (circuit III). Thus, the Cu2 cation can be described as a $CdSO_4$-like node (Schläfli symbol $6^58$).[15] Structures based solely on rare NbO or $CdSO_4$ have been explored, but networks containing both an NbO node and a $CdSO_4$ node have not previously been reported in coordination polymers.[15] The network of **3** based on Cu1 and Cu2 cations can be symbolized as an Archimedean-type $(6^58)(6^48^2)$ net with planar four-connected nodes.[2]

In the structure of **4**, there exist three crystallographically unique $Cu^{II}$ cations (Cu1, Cu2, and Cu3), two unique $L^4$ ligands, and three unique L molecules. As shown in Figure 4a, each of the Cu1 and Cu3 cations is four-coordinate in a square-planar geometry with two nitrogen atoms from two L molecules and two oxygen atoms from two $L^4$ anions, while the Cu2 cation center has a distorted square-pyramid coordination sphere defined by one carboxylate oxygen atom, one water molecule, and three nitrogen atoms from three L molecules. The two unique $L^4$ anions display different coordination modes: one coordinates to four $Cu^{II}$ cations through four carboxylate groups, acting as a tetradentate ligand, while the other coordinates to two $Cu^{II}$ cations using two *para*-carboxylate groups and is a bidentate ligand.

For complex **4**, the benzene ring of the tetradentate $L^4$ anion can be considered as a four-connected node, thus there exist four kinds of planar four-connected nodes in the framework (Cu1, Cu2, Cu3 and the benzene ring of the $L^4$ anion). There exist some unique shortest five-, six-, eight-, and ten-membered circuits through nodes in **4** (see Figures S5–S12 in the Supporting Information). For Cu1, each of four sets of *cis* links is contained in a six-membered ring (circuit II), while two sets of *trans* links are contained in a five-membered ring (circuit I) and an eight-membered ring (circuit **III**), respectively (see Figure S13 in the Supporting Information). Thus, the Cu1 cation has the Schläfli symbol $56^48$. For Cu2, each of two sets of *cis* links is contained in a five-membered ring (circuit I), while each of the other two sets of *cis* links is contained in a six-membered ring (circuit IV); each of two sets of *trans* links is contained in an eight-membered ring (circuit V and circuit VI; see Figure S14 in the Supporting Information). Thus, the Cu2 cation has the Schläfli symbol $5^26^28^2$. For Cu3, each of four sets of *cis* links is contained in an eight-membered ring (circuit VI), while two sets of *trans* links are contained in a six-membered ring (circuit IV) and a 10-membered ring (circuit VII; see Figure S15 in the Supporting Information). Thus, Cu3 has the Schläfli symbol $68^410$. For the benzene ring of the tetradentate $L^4$ ligand, each of four sets of *cis* links is contained in a five-membered ring (circuit I), while each of two sets of *trans* links is contained in a six-membered ring (circuits II and VIII; see Figure S16 in the Supporting Information). Thus, the benzene ring of the tetradentate $L^4$ anion has the Schläfli symbol $5^46^2$. The molar ratio of these four kinds of nodes is 1:2:1:1, thus the network of complex **4** can be described as an Archimedean-type net with four kinds of nonequivalent points: $(56^48)(5^26^28^2)_2(68^410)(5^46^2)$

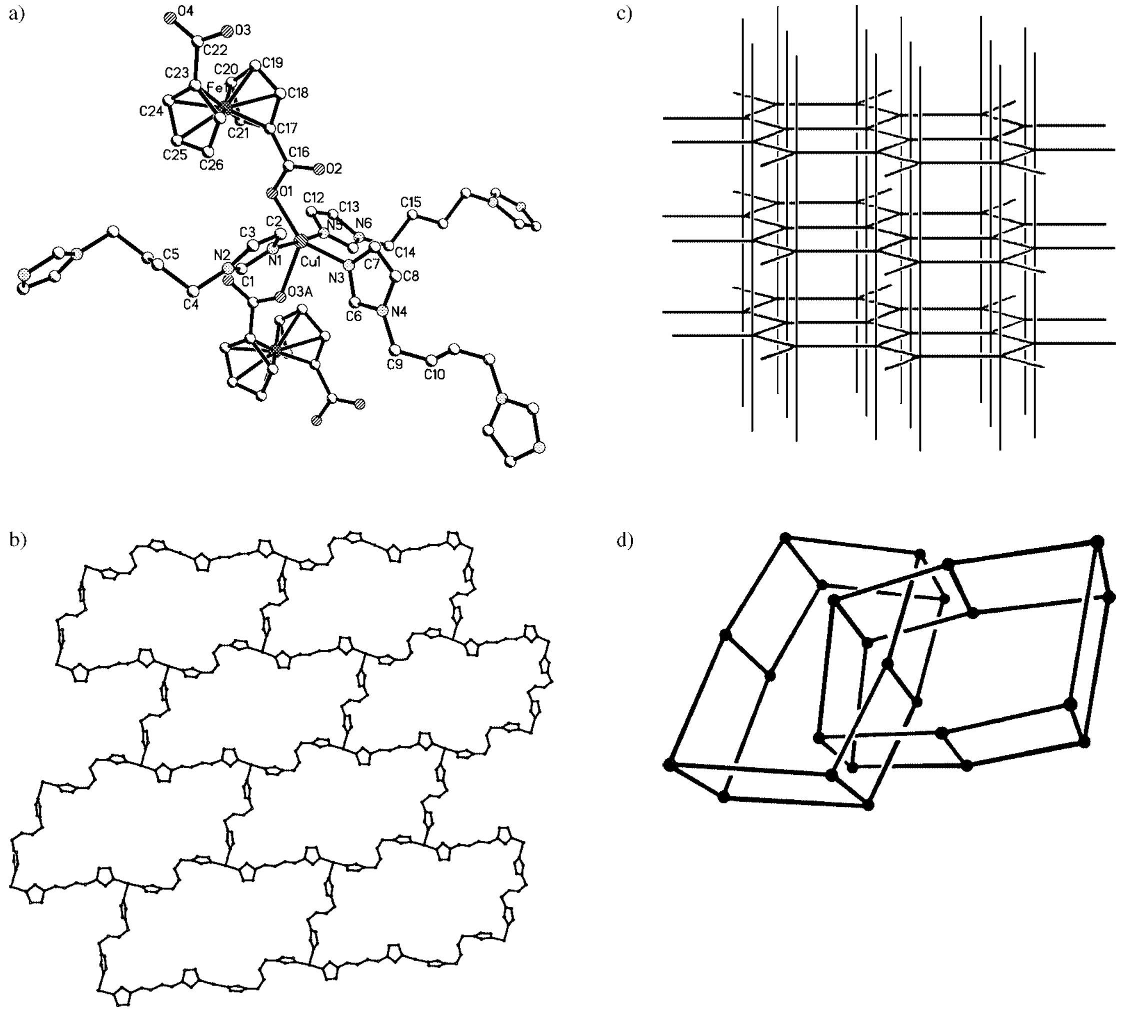

Figure 2. (a) Coordination environment of the copper(II) cation in **2**. (b) 2D (6,3) network containing $Cu^{II}$ cations and L in **2**. (c) A schematic representation of the $4^6 6^4$ network of **2**. (d) A schematic representation of the twofold interpenetration mode in **2**.

(see b in Figure 4). To the best of our knowledge, complex **4** is the first example of a coordination polymer which displays a $(56^48)(5^26^28^2)_2(68^410)(5^46^2)$ topology.[1]

## Role of the Anions in the Self-Assembly Processes

From the above descriptions it is clear that the choice of anions is critical in determining the molecular structures of the resultant complexes. In this study, the nature of the anions such as rigidity, flexibility, and the length of the spacer is the underlying reason behind the differences in the structure of this series of copper(II) complexes:·$L^1$ possesses rigidity due to the presence of a –C=C– spacer between the two carboxylate moieties, whereas $L^3$ possesses flexibility owing to the presence of a $–CH_2CH_2–$ spacer between the two carboxylate moiety;·$L^2$ is a ferrocene-based ligand, which can freely rotate around the organoferrocene "ball-joint" to meet the requirements of the coordination geometries of metal ions in the assembly process. Compared with $L^1$, $L^2$, and $L^3$, $L^4$ is a planar multi-carboxylate anion, which can adopt various coordination modes.

The ratios of Cu:$L^n$ ($n$ = 1, 2, 3, and 4) are determined by the negative charges of the anions. Thus, the ratios of Cu:$L^n$ ($n$ = 1, 2 and 3) are 1:1, and the ratio of Cu:$L^4$ is 2:1. Since the compounds are isolated by evaporation of the corresponding solutions, the Cu:L ratios of 1:1 for **1** and **3**, 1:1.5 for **2**, and 1:1.25 for **4** may be affected by the solubility of the compounds. The different network topologies of the compounds are related to the Cu:L:$L^n$ ratios ($n$ = 1, 2, 3 and 4). The topological difference between **1** and **3** should result from the structural features of $L^1$ and $L^3$: $L^3$ is more flexible than $L^1$, and due to its flexibility $L^3$ forms a $(6^58)(6^48^2)$ network with less void volume, and the rigid ligand $L^1$ forms a $6^6$ network of **1** with large void volume, which is eliminated by the interpenetration. In addition, it should be pointed out that the change of copper(II) and L compositions used in the preparations of these complexes cannot have an effect on their final structures. Thus, the formation of these different frameworks is due solely to the effects of the organic anions.

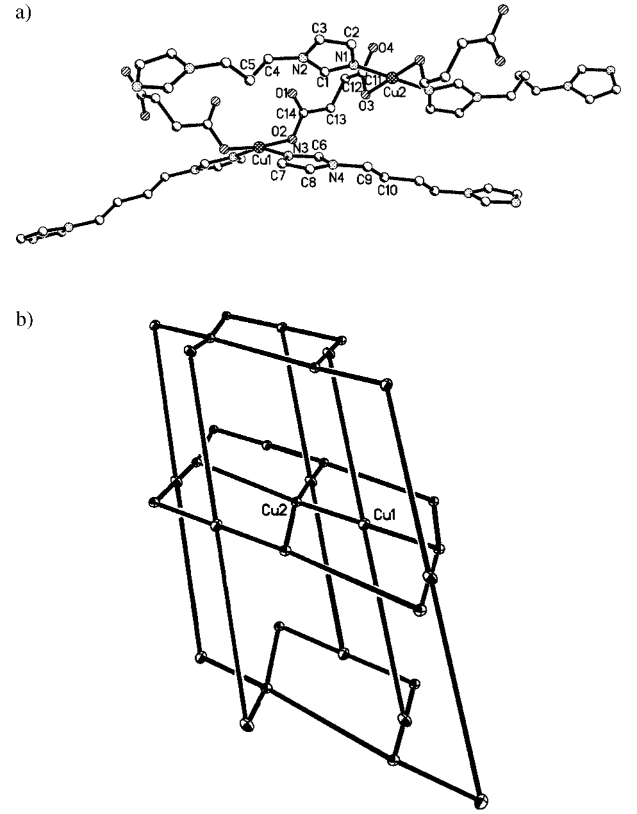

Figure 3. (a) View of the local coordination geometries of complex **3**. (b) The square-planar four-connected $(6^58)(6^48^2)$ net containing both NbO-like and $CdSO_4$-like nodes in complex **3**.

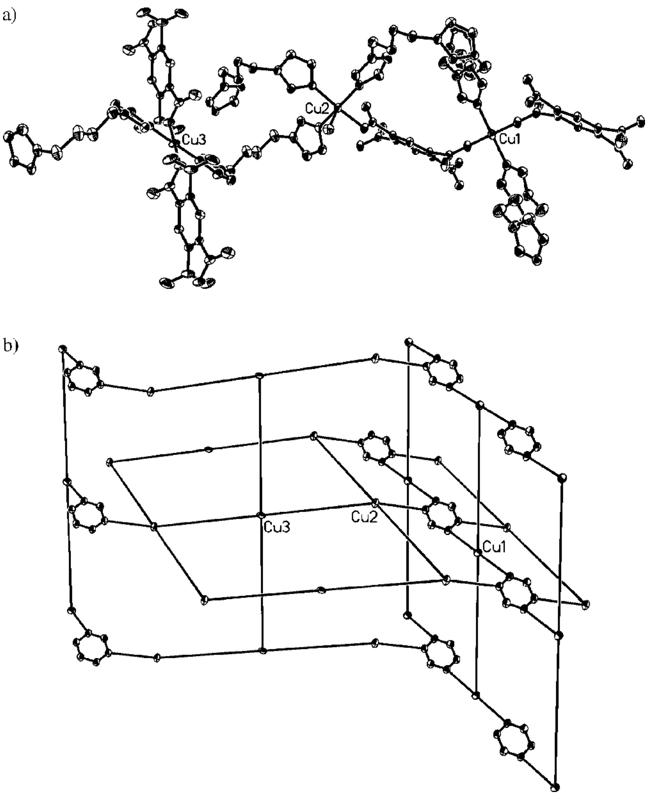

Figure 4. (a) View of the local coordination geometries of the $Cu^{II}$ cations in **4**. (b) The planar four-connected $(56^48)(5^26^28^2)_2$-$(68^410)(5^46^2)$ net in **4**.

## Conclusions

A series of $Cu^{II}$ coordination polymers with different topologies has been synthesized due to the effect of the organic anions on the formation of the final frameworks. When $L^1$ was used as the bidentate carboxylate anion, a coordination polymer **1** with a threefold interpenetrated diamond structure was obtained. Coordination polymer **2**, containing a $Cu^{II}$ atom and $L^2$, displays a rare twofold interpenetrated $4^66^4$ topology. Two planar, four-connected $Cu^{II}$ coordination polymers **3** (with $L^3$) and **4** (with $L^4$) display an interesting Archimedean-type $(6^58)(6^48^2)$ net containing two different types of square-planar nodes and a $(56^48)(5^26^28^2)_2(68\,^410)(5^46^2)$ net containing four different types of square-planar nodes, respectively.

## Experimental Section

**Materials and Methods:** All reagents and solvents for syntheses were purchased from commercial sources and used as received. A Perkin–Elmer 240 elemental analyzer was used to collect microanalytical data. TGA was performed on a Perkin–Elmer TG-7 analyzer in nitrogen. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 $cm^{-1}$ on a Mattson Alpha-Centauri spectrometer.

**Synthesis of 1,1′-(1,4-Butanediyl)bis(imidazole) (L):** A mixture of imidazole (3.4 g, 50 mmol) and NaOH (2.0 g, 50 mmol) in DMSO (10 mL) was stirred at 60 °C for 1 h, and then 1,4-dichlorobutane (3.2 g, 25 mmol) was added. The mixture was cooled to room temperature after stirring at 60 °C for 2 h and then poured into 200 mL of water. A white solid formed immediately, which weighed 4.1 g (86%) after drying in air. $C_{10}H_{14}N_4$ (190.25): calcd. C 63.16, H 7.37, N, 29.47; found C 63.11, H 7.42, N 29.31.

**Synthesis of $[CuL(L^1)]\cdot 2H_2O$ (1):** A mixture of $CuCl_2\cdot 2H_2O$ (0.171 g, 1 mmol), NaOH (0.080 g, 2 mmol), and fumaric acid ($H_2L^1$; 0.116 g, 1 mmol) in water was stirred for 10 min at 60 °C, then 1,1′-(1,4-butanediyl)bis(imidazole) (L; 0.190 g, 1 mmol) was added to the mixture. After stirring for 30 min, the blue precipitate was collected and dissolved in a minimum amount of ammonia (14 M). Blue single crystals of **1** were obtained by slow evaporation of the ammoniacal solution at ambient temperature. Yield: 66% (266 mg). $C_{14}H_{20}CuN_4O_6$ (403.88): calcd. C 41.60, H 4.99, N 13.87; found C 40.89, H 4.60, N 13.49. IR (KBr): 3436 $cm^{-1}$ (s), 3125 (w), 2950 (m), 1619 (s), 1526 (m), 1451 (m), 1285 (w), 1238 (s), 1107 (vs), 948 (w), 849 (w), 771 (w), 756 (m), 664 (m).

**Synthesis of $[CuL_{1.5}(L^2)]\cdot 3H_2O$ (2):** The same procedure was used to synthesize compound **2** from 1,1′-ferrocenedicarboxylic acid ($H_2L^2$). Yield: 72% (324 mg). $C_{27}H_{35}CuFeN_6O_7$ (675.00): calcd. C 48.04, H 5.23, N 12.45; found C 48.43, H 5.63, N 12.79. IR (KBr): 3439 $cm^{-1}$ (vs), 3127 (w), 2941 (m), 1606 (vs), 1561 (s), 1527 (m), 1454 (m), 1363 (s), 1237 (m), 1103 (s), 758 (m), 655 (m).

**Synthesis of $[CuL(L^3)]\cdot 3H_2O$ (3):** The same procedure was used to synthesize compound **3** from succinic acid ($H_2L^3$). Yield: 78% (331 mg). $C_{14}H_{24}CuN_4O_7$ (423.91): calcd. C 39.63, H 5.71, N 13.22; found C 39.29, H 5.60, N 13.49. IR (KBr): 3437 $cm^{-1}$ (vs), 3123 (w), 2952 (m), 1617 (s), 1526 (m), 1453 (m), 1286 (w), 1240 (s), 1102 (vs), 952 (w), 846 (w), 773 (w), 659 (m).

**Synthesis of $[Cu_2L_{2.5}(L^4)(H_2O)]\cdot 10H_2O$ (4):** The same procedure was used to synthesize compound **4** from pyromellitic acid ($H_4L^4$).

Table 2. Summary of X-ray crystallographic data for complexes **1**–**4**.

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Formula | $C_{14}H_{20}CuN_4O_6$ | $C_{27}H_{35}CuFeN_6O_7$ | $C_{14}H_{24}CuN_4O_7$ | $C_{35}H_{59}Cu_2N_{10}O_{19}$ |
| Mol. mass | 403.88 | 675.00 | 423.91 | 1051.00 |
| Space group | $C2/c$ | $P2_1/c$ | $P2/n$ | $P\bar{1}$ |
| $a$ [Å] | 14.272(3) | 10.368(2) | 8.9023(18) | 10.702(2) |
| $b$ [Å] | 11.363(2) | 18.377(4) | 8.7362(17) | 11.186(2) |
| $c$ [Å] | 11.432(2) | 15.845(3) | 24.059(5) | 22.584(5) |
| $\alpha$ [°] | 90.00 | 90.00 | 90.00 | 93.80(3) |
| $\beta$ [°] | 115.15(3) | 96.86(3) | 93.75(3) | 90.13(3) |
| $\gamma$ [°] | 90.00 | 90.00 | 90.00 | 115.57(3) |
| $V$ [Å$^3$] | 1678.2(6) | 2997.6(10) | 1867.1(6) | 2431.9(8) |
| $Z$ | 4 | 4 | 4 | 2 |
| $D_{\text{calcd.}}$ [g cm$^{-3}$] | 1.598 | 1.496 | 1.508 | 1.435 |
| $F(000)$ | 836 | 1400 | 884 | 1098 |
| Reflections obsd. [$I > 2\sigma(I)$] | 1549 | 2405 | 2075 | 5975 |
| GOF on $F^2$ | 1.072 | 0.819 | 0.821 | 0.928 |
| $R_1$, w$R_2$ (obsd.) | 0.0349, 0.0895 | 0.0485, 0.0742 | 0.0439, 0.1154 | 0.0498, 0.1335 |

Yield: 81% (340 mg). $C_{35}H_{59}Cu_2N_{10}O_{19}$ (1051.0): calcd. C 39.97, H 5.66, N 13.33; found C 39.71, H 5.53, N 13.48. IR (KBr): 3441 cm$^{-1}$ (vs), 3133 (w), 2947 (m), 1609 (vs), 1559 (s), 1530 (m), 1452 (m), 1367 (s), 1240 (m), 1106 (s), 653 (m).

**X-ray Crystallography:** Single-crystal X-ray diffraction data for complexes **1**–**4** were recorded on a Rigaku RAXIS-RAPID image-plate diffractometer using the $\omega$-scan technique with Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073Å). Absorption corrections were applied using the multi-scan technique. All structures were solved by direct methods with SHELXS-97[16] and refined by full-matrix least-squares techniques using the SHELXL-97 program.[17] All non-hydrogen atoms were refined with anisotropic temperature parameters; the hydrogen atoms of the ligands were refined as rigid groups. Further details of the structural analysis are summarized in Table 2.

CCDC-253915 (for **1**), -228776 (for **2**), -216566 (for **3**), and -216568 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Powder X-ray Diffraction Analyses:** The powder X-ray diffraction patterns for the polymers **1**–**4** agree well with those simulated. The diffraction peaks of both experimental and simulated patterns match well in position, thus indicating the phase purity of polymers **1**–**4**. The difference in reflection intensities between the simulated and experimental patterns is due to the different orientation of the crystals in the powder samples.

**Supporting Information:** Figures of circuits around the copper cations of **3** and **4** (Figures S1–S16).

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