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Linking triangles: synthesis and structure of $[Cu_3(phen)_4(PPh_3)](BF_4)_3 \cdot X$ and $[Cu_5(phen)_7](BF_4)_5 \cdot 4(NO_2C_6H_5)$ (phen = 4,7-phenanthroline and X = Et_2O or 2 THF)

Jacqueline M. Knaust, Susan Lopez, Chad Inman, Steven W. Keller *

Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, USA

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Abstract

Two new coordination polymers containing Cu(I) and 4,7-phenanthroline (phen) have been synthesized and structurally characterized. **1a**, $[Cu_3(phen)_4(PPh_3)](BF_4)_3 \cdot 2(THF)$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.5407(6)$ Å, $b = 14.5687(7)$ Å, $c = 23.579(1)$ Å, $\alpha = 74.203(1)°$, $\beta = 80.530(1)°$, $\gamma = 83.998(1)°$, and $Z = 2$. **1b** (isostructural with **1a**), $[Cu_3(phen)_4(PPh_3)](BF_4)_3 \cdot Et_2O$, also crystallizes in the triclinic, space group $P\bar{1}$, with $a = 11.4920(6)$ Å, $b = 14.5074(8)$ Å, $c = 23.749(1)$ Å, $\alpha = 73.599(1)°$, $\beta = 79.871(1)°$, $\gamma = 83.814(1)°$, and $Z = 2$. **2**, $[Cu_5(phen)_7](BF_4)_3 \cdot 4(NO_2Ph)$, crystallizes in the triclinic space group $P\bar{1}$, with $a = 11.7867(9)$ Å, $b = 14.5076(1)$ Å, $c = 15.946(1)$ Å, $\alpha = 100.076(1)°$, $\beta = 106.637(1)°$, $\gamma = 95.612(1)°$, and $Z = 1$. Three unique copper atoms reside in the asymmetric units of all three compounds; each display trigonal Y-shaped coordination environments. For **1**, $(Cu_3phen_3)^{+3}$ bowl shaped triangles are linked through a phen bridge into one-dimensional chains. In **2**, two Cu(I) cations have similar coordination environments containing three bridging phen ligands, but the third Cu(I) cation is coordinated by two fully occupied phen ligands, as well as a one-half occupied phen ligand, or a one half-occupied BF_4^- anion which sit roughly on the same general position. The Cu(I) centers are linked through the phen ligands to form a ladder-like structure composed of two disordered chains (similar to those seen in **1**) fused together. Extensive π–π stacking interactions are observed in both **1** and **2**.

Keywords: Synthesis; Coordination polymers; Crystal structures; 4,7-Phenanthroline; Cu(I)

1. Introduction

Self-assembly of metals cations and bridging multifunctional ligands into structures with specific geometric shapes continues to be widely pursued [1]. Coordination polymers containing many different polygonal motifs have been described, including squares [2], rectangles [3], pentagons [4], and hexagons [5]. Though the literature contains many reports of isolated triangular metallomacrocycles [6], to date there are few reports of coordination polymers containing triangular units. Xiong and coworkers [7] have recently prepared a 2-D network of fused hexagons with chiral triangular cavities, but to the best of our knowledge only Evans and Lin [8] have reported coordination polymers with triangular units. They prepared three pillared, three-dimensional Cd(II)–isonicotinate coordination networks where "*pseudo*-trigonal sheets" of Cd(II) centers and *exo*-tridentate isonicotinate ligands are linked to adjacent sheets by additional *exo*-tetradentate isonicotinate ligands.

As previously described by others [1,6], there are only two possible ways to construct triangular metallomacrocycles (Scheme 1). Most triangular molecular structures are of type I [6a–6f], where the ligands form the corners of the triangle; Lin's Cd(II)–isonicotinate triangles are of this type. The other possibility (type II) occurs when the metal cations occupy the corners of the triangle. Structures of type II do not exist with linear rod-like ligands due to the impossibility of generating 60° ligand–metal–ligand angles. However, flexible or bent organic ligands allow for the formation of type II [6g–6l] structures where the ligand–metal–ligand corner

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* Corresponding author. Tel.: +1-573-884-6893; fax: +1-573-882-2754.

E-mail address: KellerS@missouri.edu (S.W. Keller).

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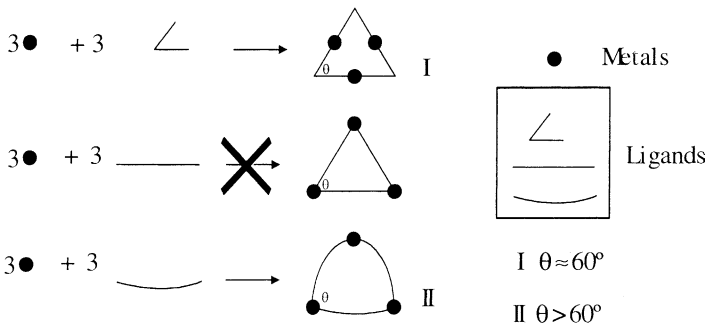


Scheme 1. Possible ways to construct triangular metallomacrocycles.

angles are much larger than 60°. Lippert and co-workers [6g] recently reported the structures of several molecular triangles of 2,2′-bipyrazine with Pt and Pd where the N–M–N corner angles are roughly 90°.

We have previously described several one-dimensional coordination polymers with Cu(I) and 4,7-phenanthroline (phen) [9]. Though Cu(I) is generally found in a four-coordinate tetrahedral environment, in no case did we observe more than three phen ligands coordinated to one copper center, presumably due to the steric bulk of this rigid ligand. In the cases in which Cu(I) centers displayed tetrahedral environments, the coordination spheres were completed with one or two solvent molecules (MeCN or PhCN) or anions ($SO_3CF_3^-$). Two of the seven structures reported contained the rather rare three-coordinate Y-shaped geometry about the Cu(I) centers, and another contained alternating linear and tetrahedral Cu(I) centers within the same one-dimensional chain. We found that solvent choice, the nature of the counter anion, and aromatic π–π stacking effects were significant factors in determining the final crystal structure; much more so than the metal coordination geometry preferences typically found for Cu(I).

Herein we report the synthesis and crystal structures of two new coordination polymers of phenanthroline-linked Cu(I)–phen triangles where the triangles are of type II; again we see that at most three phen ligands are coordinated to the any of the Cu(I) centers all of which display distorted trigonal planar geometries. The influence of extensive π–π stacking interactions will also be discussed.

2. Experimental

2.1. Materials and methods

Cu_2O (ACROS), triphenylphosphine (Aldrich), 4,7-phenanthroline (GFS Chemicals and Aldrich), nitrobenzene, tetrahydrofuran, diethyl ether, and acetonitrile (Fisher) were used without further purification. $[Cu(MeCN)_4]BF_4$ [10a] and $[Cu(PhCN)_4]BF_4$ [10b] were synthesized by literature methods. $[Cu(MeCN)_2]BF_4$ was used to prepare $[Cu(MeCN)_2(PPh_3)_2]BF_4$ [11]. Thermogravimetric analyses were performed on a TA Instruments Q500 TGA with an N_2 flow rate of 100 cc/min and a heating rate of 10°/min.

2.2. Preparation of $[Cu_3(phen)_4(PPh_3)](BF_4)_3 \cdot 2THF$ (**1a**)

In a small 5-dram vial $[Cu(MeCN)_2(PPh_3)_2]BF_4$ (30.4 mg, 0.040 mmol) was dissolved in nitrobenzene (1 ml) to which was added 4,7-phenanthroline (10.9 mg, 0.060 mmol). The small open vial was then placed in a larger 20-dram vial containing 3 ml of THF. The large vial was sealed, and the THF was allowed to diffuse into the solution at room temperature. Yellow, rectangular column-like crystals were harvested after several days.

2.3. Preparation of $[Cu_3(phen)_4(PPh_3)](BF_4)_3 \cdot Et_2O$ (**1b**)

In a small 5-dram vial $[Cu(MeCN)_2(PPh_3)_2]BF_4$ (32.2 mg, 0.043 mmol) was dissolved in nitrobenzene (3 ml) and 4,7-phenanthroline (11.9 mg, 0.066 mmol) was added to the solution. The small open vial was then placed in a larger 20-dram vial containing 3 ml of diethyl ether. The large vial was sealed, and the ether was allowed to diffuse into the solution at room temperature. Yellow column-like crystals were harvested after several days.

2.4. Preparation of $[Cu_5(phen)_7](BF_4)_5 \cdot 4(PhNO_2)$ (**2**)

In a small 5-dram vial $[Cu(PhCN)_4]BF_4$ (29.4 mg, 0.052 mmol) was dissolved in PhCN (0.5 ml) and diluted with nitrobenzene (3 ml). 4,7-phenanthroline (95.2 mg, 0.51 mmol) was added to the solution. The small open vial was then placed in a larger 20-dram vial containing 5 ml of THF. The large vial was sealed, and the THF was allowed to diffuse into the solution at room temperature. Yellow plate-like crystals were harvested after several days.

2.5. Crystal structure determination

Single crystals, as determined by polarized optical microscopy, were placed in inert oil and then mounted with silcone grease to a thin glass fiber. Full hemispheres of data were collected at −100 °C using a Siemens SMART system equipped with a CCD area detector (Mo(Kα) = 0.71073 Å). Absorption corrections were applied after integration [12], and all structures were solved using SHELXS direct methods [13], and refined using a full least squares treatment on F^2 [14].

The disordered THF molecules in **1a** were refined with geometric constraints and isotropic thermal parameters; the diethyl ether molecule in **1b** was also refined with isotropic thermal parameters. All other non-hydrogen atoms of both **1a** and **1b** were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and refined as riding models with fixed $U_{\mathrm{iso}} = 1.2U_{\mathrm{iso}}$ of the carbon atoms to which they are bonded. One of the copper centers and one of the included nitrobenzene solvent molecules in **2** were found to be disordered over the inversion center; therefore atoms Cu2, O3S, O4S, N2S, and C7S–12S were assigned site occupancies of 0.50. The phenanthroline ligand bridging Cu2 and Cu3 and the BF_4 coordinated to Cu3 sit in roughly the same position and are also disordered over the inversion center. Atoms N1C, C2C–C13C, and N14C and B1D and F1D–F4D were split into parts and given site occupancies of 0.50. Due to the aforementioned disorder of Cu2 a one-half occupied BF_4 is necessary for overall charge balance. Both included nitrobenzene solvent molecules were refined with geometric constraints and isotropic thermal parameters fixed at 0.30. In figures, only one orientation of the nitrobenzene molecules are shown. One of the BF_4 anions was disordered over two positions related by an approximate C_2 rotation about the B1–F1 bond, therefore atoms F2–F4 and F2′–F4′ were spit into two parts and refined to site occupancies of 0.52 and 0.48, respectively. The phenanthroline ligand bridging Cu1 and Cu2 was found to be disordered over two positions. The atoms were split into parts and show site occupancies of 0.74 (N1A, C2A–C13A, and N14A) and 0.26 (N1B, C2B–C13B, and N14B). The rings containing N1A, N14A, N1B and N14B were slightly distorted and constrained to be hexagonal. In the figures presented, only the higher occupied orientation of this phenanthroline is shown. Atoms N1B, C2B–C13B, N14B, N1C, C2C–C13C, N14C, B1D, F1D–F4D, O1S–O4S, N1S, N2S, C1S–C12S were refined with isotropic thermal parameters; all other non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were included in calculated positions as described above for **1a** and **1b**. Selected bond lengths and bond angles, and crystallographic details are given in Tables 1 and 2, respectively; full details are listed in the supplementary material.

Table 1
Selected bond lengths and angles for compounds **1a**, **1b**

	1a	**1b**
Bond lengths		
Cu1–N1	1.991(5)	1.999(5)
Cu1–N3	2.060(5)	2.036(6)
Cu1–P1	2.1888(2)	2.189(2)
Cu2–N4	2.097(5)	2.092(5)
Cu2–N5	1.939(4)	1.943(4)
Cu2–N7	1.950(4)	1.945(4)
Cu3–N2	2.096(4)	2.103(5)
Cu3–N6	1.945(4)	1.934(4)
Cu3–N8	1.944(4)	1.938(4)
Bond angles		
N1–Cu1–N3	100.8(2)	100.5(3)
N1–Cu1–P1	143.5(2)	143.9(2)
N3–Cu1–P1	114.01(4)	114.4(2)
N4–Cu2–N5	108.0(2)	109.0(2)
N4–Cu2–N7	101.6(2)	103.3(2)
N5–Cu2–N7	150.3(2)	147.5(2)
N2–Cu3–N6	104.4(2)	104.2(2)
N2–Cu3–N8	106.6(2)	107.0(2)
N6–Cu3–N8	148.9(2)	148.8(2)

3. Results and discussion

3.1. Description of the crystal structures

The asymmetric unit of **1** contains three unique Cu(I) centers each displaying a distorted, three-coordinate Y-shaped geometry. The coordination sphere for Cu(1) includes two bridging phen ligands and one PPh_3 (N–Cu1–N angles: 100.8(2)° and 114.01(4)° and N–Cu1–P angle: 143.5(2)°). Cu2 and Cu3 have similar coordination spheres comprised of three bridging phen ligands (N–Cu(2)–N angles: 101.6(2)°, 108.0(2)°, 150.3(2)° and N–Cu3–N angles: 104.4(2)°, 106.6(2)°, 148.9(2)°). As seen in Fig. 1 the three Cu(I) cations (corners) and three of the phen ligands (sides) assemble to form a nearly regular equilateral triangle with Cu–Cu distances ranging from 7.3 to 7.8 Å and Cu–Cu–Cu angles between 57° and 60°. The N–Cu–N angles at the corners of the triangle are much larger than 60° (100.8(2)°, 101.6(2)°, 106.6(2)°) as expected for a type II triangle.

The remaining phen ligand (N5, N6) connects the bowl-shaped triangles to form a 1-D chain (Fig. 2). **1a** and **1b** display isostructural linear networks, although the number and type of solvent molecules included in each differs; **1a** contains two THF molecules; whereas, **1b** has only one diethyl ether molecule. Packing of the anions (shortest Cu–F distance ca. 3.8 Å) and solvent molecules is quite similar for **1a** and **1b**, the only noticeable difference being the additional THF in **1b.**

In all of our previously reported one-dimensional Cu(I)/phen structures, $[Cu(MeCN)_4]X$ (X = PF_6^-, BF_4^- or $CF_3SO_3^-$) was used as the starting material; in this case $[Cu(MeCN)_2(PPh_3)_2]BF_4$ was used as the starting

Table 2
Crystallographic data for **1a**, **1b**, and **2**

	1a	**1b**	**2**
CCDC deposit number	190310	190311	190312
Empirical formula	$Cu_3C_{74}H_{63}B_3F_{12}N_8O_2P$	$Cu_3C_{70}H_{57}B_3F_{12}N_8OP$	$Cu_5C_{108}H_{76}B_5F_{20}N_{18}O_8$
Formula weight (g/mol)	1578.4	1508.26	2505.7
Crystal system, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
T (K)	173(2)	173(2)	173(2)
Unit cell dimensions (Å, °)	$a = 11.5407(6)$ $b = 14.5687(7)$ $c = 23.579(1)$ $\alpha = 74.203(1)$ $\beta = 80.530(1)$ $\gamma = 83.998(1)$	$a = 11.4920(6)$ $b = 14.5074(8)$ $c = 23.749(1)$ $\alpha = 73.599(1)$ $\beta = 79.871(1)$ $\gamma = 83.814(1)$	$a = 11.7867(9)$ $b = 14.576(1)$ $c = 15.946(1)$ $\alpha = 100.076(1)$ $\beta = 109.637(1)$ $\gamma = 95.612(1)$
V (Å^3)	3755.2(3)	3723.7(7)	2504.0(3)
Z	2	2	1
ρ, Calculated (g/cm^3)	1.396	1.342	1.580
Absorption coefficient (mm^{-1})	0.943	0.944	1.146
$F(000)$	1608	1532	1200
Crystal size (mm)	0.40 × 0.18 × 0.18	0.60 × 0.20 × 0.20	0.50 × 0.20 × 0.20
Θ range for data collection (°)	1.46 to 27.12	1.47 to 23.26	1.39 to 27.11
Limiting indices	$-14 \leqslant h \leqslant 14$ $-18 \leqslant k \leqslant 18$ $-30 \leqslant 1 \leqslant 30$	$-12 \leqslant h \leqslant 12$ $-15 \leqslant k \leqslant 16$ $-22 \leqslant 1 \leqslant 26$	$-15 \leqslant h \leqslant 13$ $-18 \leqslant h \leqslant 17$ $-20 \leqslant 1 \leqslant 20$
Reflections collected/unique	26,945/16,165 [$R_{int} = 0.0315$]	19,502/10,656 [$R_{int} = 0.02701$]	17,925/10,750 [$R_{int} = 0.0313$]
Max. and min. transmission	1.000 and 0.758379	1.000 and 0.770801	1.000 and 0.798133
Data/restraints/parameters	1615/19/880	10,656/0/861	10,750/109/550
Final R indices [$I > 2\sigma(I)$][a,b]	$R_1 = 0.0668$, $wR_2 = 0.2081$	$R_1 = 0.0753$, $wR_2 = 0.2468$	$R_1 = 0.1055$, $wR_2 = 0.2976$
R indices (all data)	$R_1 = 0.1150$, $wR_2 = 0.2300$	$R_1 = 0.1000$, $wR_2 = 0.2638$	$R_1 = 0.1606$, $wR_2 = 0.3167$
Largest differential peak and hole (e A^{-3})	1.869 and −0.480	1.907 and −0.576	1.056 and −0.784

Structures were refined on F_o^2 using all data.

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.

[b] $wR_2 = [\sum(|F_o - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

material. We have reported similar reactions with $[Cu(MeCN)_2(PPh_3)_2]X$ ($X = BF_4$, or PF_6) and 4,4′-bipyridine [4a] or 1,2-*bis*(4-pyridyl)ethylene [5a], but had not seen such distinctly different coordination environments within these structures. In fact, with bpy and bpe the previous structures were either linear chains with each tetrahedral Cu(I) coordination environment containing two bridging ligands and two terminal phosphine ligands (no loss of phosphine), or they were layered networks of fused hexagons with each Cu(I) center coordinated by three bridging ligands and one terminal phosphine ligand (loss of one phosphine from each Cu(I)). Here however, we find that not only is each copper center three-coordinate, but only one out of three is coordinated by a phosphine ligand. Though we did not expect to coordinate more than three phenanthroline ligands to any one copper atom, the complete replacement of phosphine on two-thirds of the copper centers was unexpected. Notably, here we observed that varying the copper:4,7-phenanthroline stoichiometry from 1:1 to 1:8 has no effect on the structure produced. Regardless of the amount of phenanthroline added, only one phosphine per three copper cations is retained in the final structure, and the last phosphine is not displaced even with an eight-fold excess of phenanthroline.

The factors influencing the stabilization of three-coordinate copper(I) are not yet fully understood, Blake et al. [15] have recently argued that the face-to-face π–π stacking interactions of 2,9-dimethyl-1,10-phenanthroline (dmp) in the complex $[Cu(dmp)L]^+$ promotes a planar three-coordinate geometry because it causes the cations to pack in a parallel fashion. We have also seen such face-to-face stacking interactions between the ligands in several of our previous Cu–phen networks and have argued that ligand–ligand interactions are the dominant factor influencing the formation of the final structure [9]. In **1**, we see π–π stacking interactions between two phenanthroline ligands on neighboring chains (plane-to-plane distance 3.3 Å) (Fig. 3). This interaction is possible in part due to one large N–Cu–N angle (ca. 150°) about each copper center allowing the phenanthroline ligands (N5, N6 and N7, N8) forming the chain to lie roughly in the same plane. It is the phenanthroline ligand that bridges Cu2 and Cu3 within the triangle that

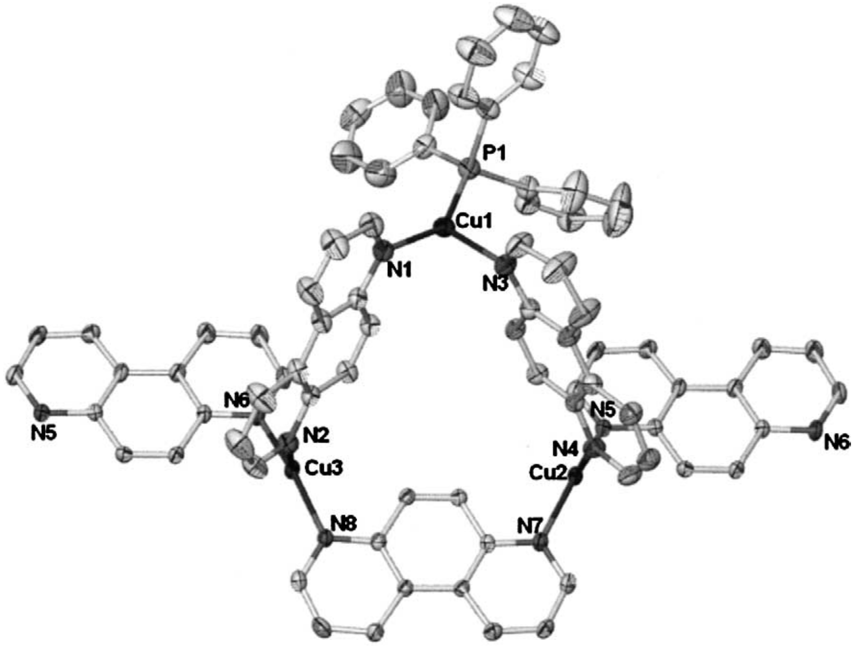


Fig. 1. Copper coordination environment in **1** with all atoms shown as 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

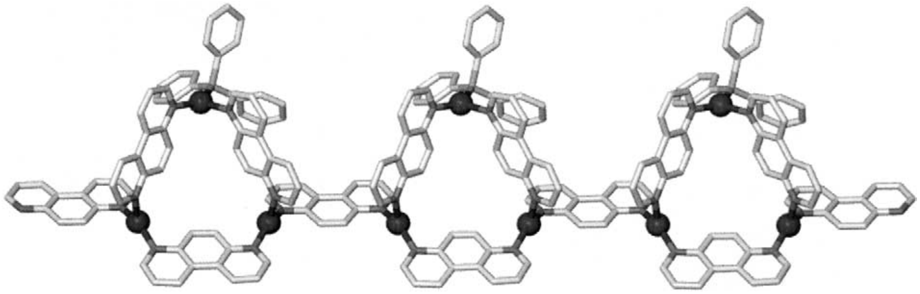


Fig. 2. Stick diagram of the one-dimensional chains in **1**. Cu atoms shown as spheres, N atoms are dark gray, C atoms are light gray, P atoms are dark gray, and hydrogen atoms have been omitted for clarity.

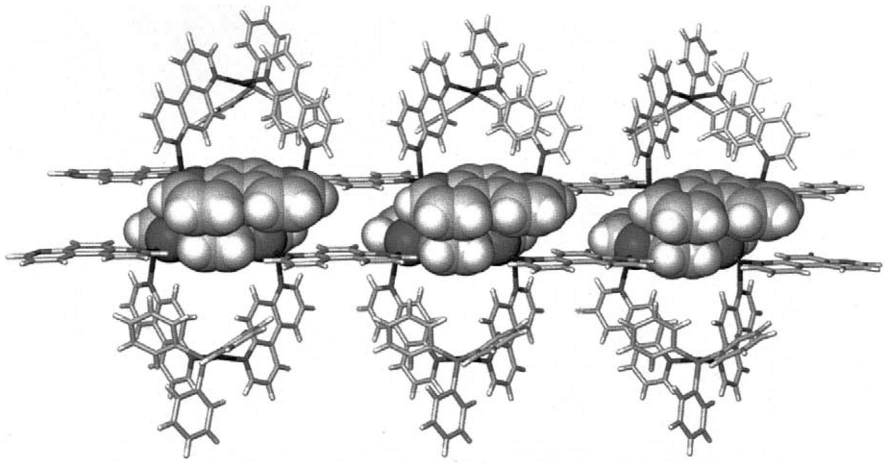


Fig. 3. Stick representation of the ligand–ligand π–π stacking interactions between neighboring chains in **1**. The phenanthroline ligands involved in interchain π–π interactions are represented as space-filling spheres.

interacts with the identical phen on an adjacent chain (rotated by 180° and slightly offset) [16].

Inclusion of neutral molecules within macrocyclic cavities is well known. For example calix[4]arenes are know to include toluene [17] or anisole [18], and nitromethane and diethyl ether have been included within the cavities of metallated cyclotriveratrylenes [19]. Considering the bowl-shaped cavity formed by these $(Cu_3phen_3)^{+3}$ triangles, one would expect to see something within the bowl. In fact, a phosphine phenyl ring from a neighboring chain resides in the cavity. H5 and H6 of this ring are involved in an edge-to-face stacking interaction with one of the phenanthroline ligands of the bowl (N3, N4) (Fig. 4).

For the synthesis of **2**, $[Cu(PhCN)_4]BF_4$ was used in a reaction similar to those we have previously reported with $[Cu(RCN)_4]X$ (R = Ph or Me, X = BF_4^-, PF_6^- or $CF_3SO_3^-$) [9]. Again we see a one-dimensional structure which in this case contains Cu(I)/phenanthroline triangles quite similar to those seen in **1**. However, the terminal PPh_3 seen in **1** is replaced by a bridging phen ligand in **2** leading to a complicated ladder-like structure. As in **1** the asymmetric unit of **2** contains three unique Cu(I) centers displaying distorted, trigonal, Y-shaped geometry, but in this case disorder of one Cu(I) center, a BF_4^- anion, and a phenanthroline over the inversion center results in a very complex structure. Cu1 and Cu2 have similar coordination environments comprised of three bridging phen ligands (N–Cu1–N angles 101.3(2)°, 105.1(2)°, and 153.6(3)° and N–Cu2–N angles 105.5(4)°, 114.3(4)°, and 140.1(2)°). Cu2 is disordered over the inversion center; in either position it is coordinated to a phenanthroline ligand (N1C, N14C) also disordered over the inversion (Fig. 5). Though Cu3 appears to be coordinated to four ligands – three phenanthroline ligands and one BF_4^- anion – one of the phen ligands is the disordered phenanthroline. This ligand and a BF_4^- anion sit in the roughly the same position, and both have only half-occupancy. The half-occupied BF_4^- anion (B1D) in addition to the two other fully occupied anions is necessary to maintain charge balance with the half-occupied disordered copper(I) cation, Cu2, and the two fully occupied copper(I) cations, Cu1 and Cu3. The closest Cu–F distance for the non-coordinating BF_4 anions is 3.5 Å. The position in which Cu2 is situated dictates the position of the disordered phenanthroline ligand (either directed up or down in Fig. 5) and thereby determines whether Cu3 (top or bottom in Fig. 5) is coordinated to the this phen ligand or the BF_4^- anion.

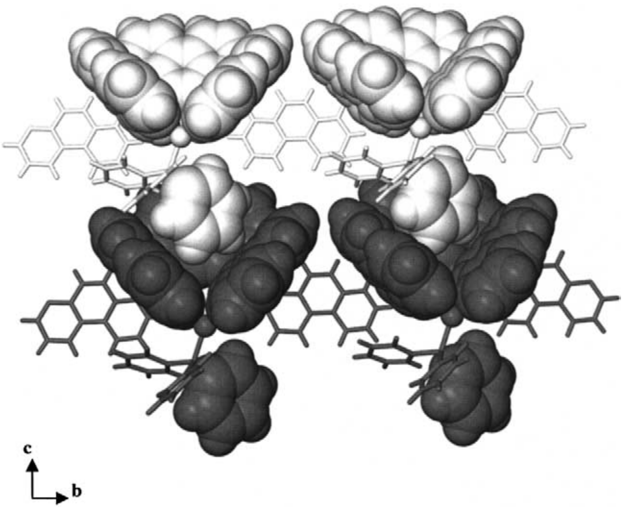


Fig. 4. Stick representation of phosphine phenyl ring situated in the cavity of a bowl on a neighboring chain in **1**. The bowl shaped trimer and included phenyl ring are shown as space-filling spheres.

As seen for **1** the three Cu(I) atoms (corners) and three of the phen ligands (sides) in **2** assemble to form a nearly regular equilateral bowl-shaped triangle. The ligand geometry in the triangle is quite similar to that seen for 1 with Cu–Cu distances of 7.4–7.7 Å and Cu–Cu–Cu angles of 61°–66° (slightly larger that those seen in 1), and again the N–Cu–N angles of the triangle are much larger than 60° (98.3(3)°, 101.2(2)°, and 114.2(4)°). The ladder-like nature of **2** can be seen in Fig. 6 where the phen–Cu–phen "rings" bridge a Cu1 on one side of the ladder to a symmetry-related Cu1 on the opposite side, and the sides consist of Cu2–phen(N1, N2)–Cu3–phen(N3, N4) chains.

There are significant similarities between the structures of **1** and **2**. The sides of the ladders in **2** are remarkably comparable to the chains in **1** as shown in Scheme 2a. Removing the terminal phosphine groups from two separate chains in **1** and then fusing the pair together (as in Scheme 2b) can assemble the ladder observed in **2**. However, the central copper atom of the ladder, Cu1, cannot bond to all four phen ligands, (presumably due to steric requirements as discussed previously) and is therefore disordered over two positions, bonding to only three phen ligands in either position. In either position it is coordinated to a disordered phenanthroline ligand, but which position it resides dictates whether Cu(3) is coordinated to the phenanthroline ligand or the BF_4^- anion. In other words, where there is a "missing" phenanthroline ligand the coordination sphere of Cu3 is completed with the BF_4^- anion, necessary for charge balance. In each case there is only one complete Cu/phen triangle per unit (Scheme 2c). This disorder of Cu2, the phenanthroline (N1C, N14C) ligand and BF_4 (B1D) anion appears to be a completely random arrangement; no supercell reflections were observed to indicate long-range ordering.

Once again it appears that π–π interactions (ligand–ligand, solvent–ligand, and solvent–solvent) are the dominant features in the packing of the ladders, and that the metal coordination is quite flexible. In **2** the disordered phenanthroline (N1C, N14C) is the only ar-

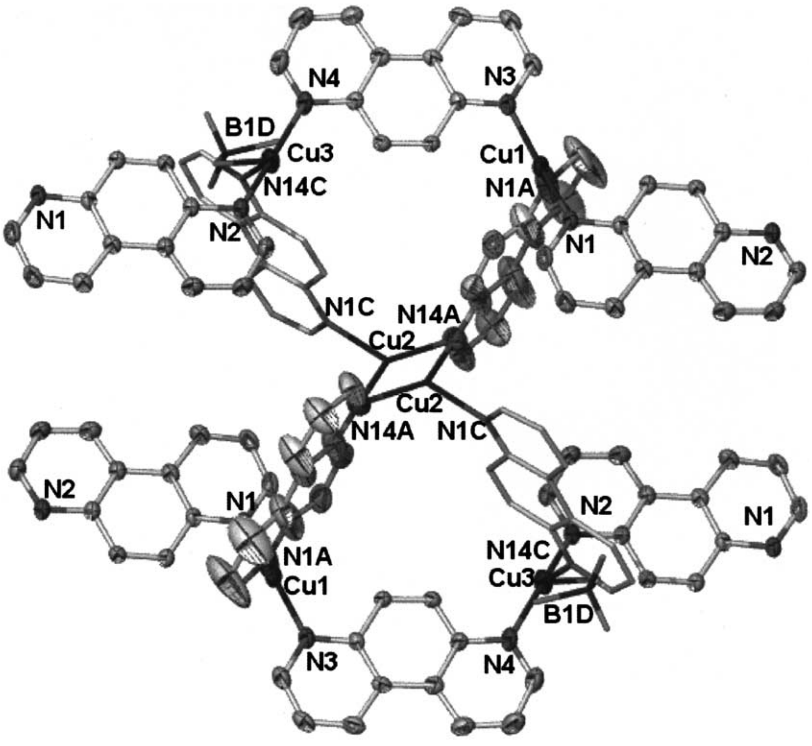


Fig. 5. Copper coordination environment in **2** with labeling scheme. All atoms excluding those that are disordered are shown as 50% probability thermal ellipsoids. Atoms shown as sticks have only 50% occupancy.

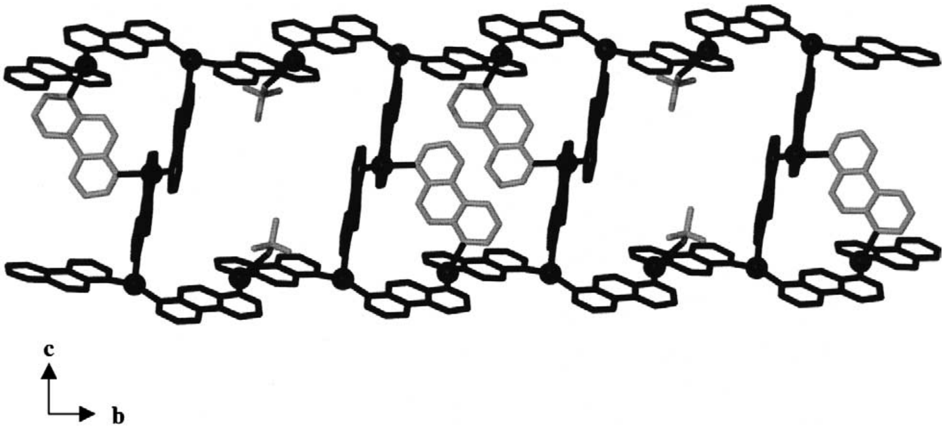
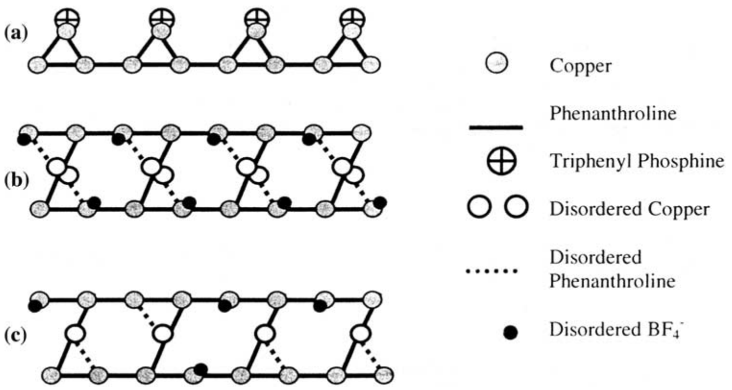


Fig. 6. Stick representation of the ladder-like nature of **2**. The ladder is shown in black with the disordered phenanthroline and BF_4 shown in gray.

omatic molecule in the structure *not* involved in π–π stacking. As seen for **1**, the large N–Cu–N angles for the sides of the ladder (N1–Cu1–NS, 153.6(3)° and N2–Cu3–N–4, 157.4(3)°) allow for these phenanthrolines to lie nearly flat in the same plane. Fig. 7 shows the π–π interactions between the sides of two adjacent ladders. A phen (N1, N2) of one ladder, interacts with a phen (N3, N4) of a neighboring ladder in a slightly offset parallel fashion. The included nitrobenzene solvent molecules are also involved in stacking interactions. One of the phenanthroline ligands (N1A, N14A) of the bowl π–π stacks with an included nitrobenzene, which in turn stacks with the identical phenanthroline on an adjacent ladder. The other included nitrobenzene π–π stacks with this same this same phenanthroline and also itself (Fig. 8).

We believe the dominance of π–π interactions in structures containing 4,7-phenanthroline is in part due to its increased attractive forces arising from the three fused aromatic rings compared to some of the other nitrogen containing aromatics we have used such as 3,3′-bipyridine [20] and 4,4′-bipyridine [4a], and



Scheme 2. Cartoon representation of the relationship between **1** and **2**. (a) The chains of linked triangles in **1**. (b). Removal of triphenyl phosphine from **1** and fusion of two chains showing all disordered parts in both possible orientations of **2**. (c) Random removal of one-half the disordered copper atoms, phenanthroline ligands, and anions to show what one of the ladders in **2** may look like.

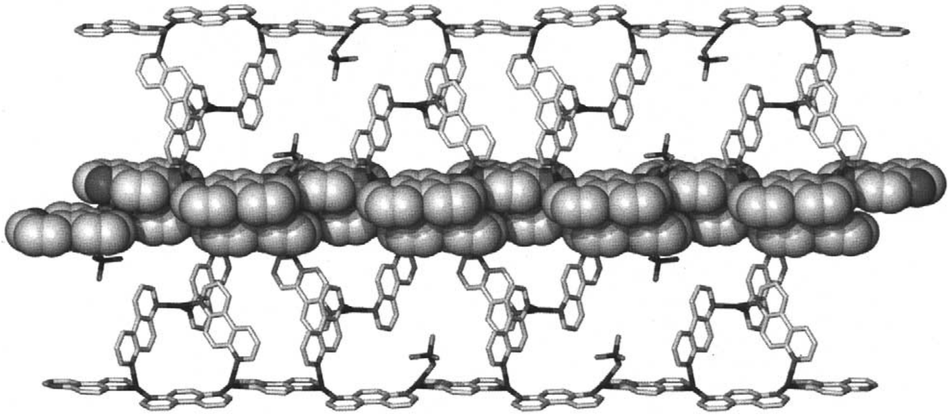


Fig. 7. Stick representation of ligand–ligand π–π stacking interactions between neighboring chains in **2**. The phenanthroline ligands (N1, N2 and N3, N4) involved in π–π interactions are represented as space-filling spheres.

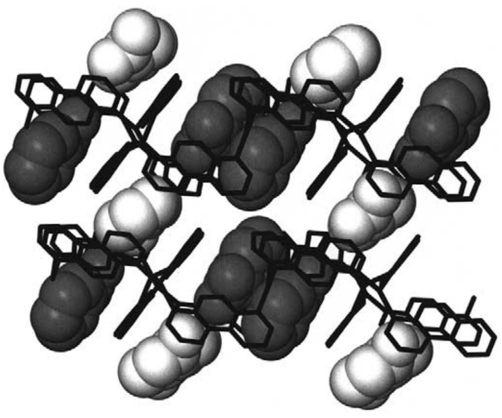
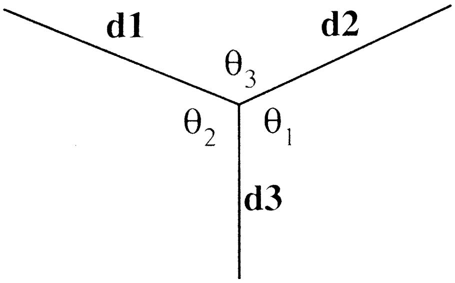


Fig. 8. Stick representation of π–π interactions between nitrobenzene solvent molecules and phenanthroline ligands of **2**. Nitrobenzene solvent molecules are shown in space-filling representation. Those shown in white π–π stack with the same phenanthroline (N1A, N14A) of two different bowls on adjacent ladders, and those shown in gray stack with that same phen and adjacent solvent molecules.

bis(4-pyridyl)ethylene [5a]. While structures with these other ligands do display π–π interactions, they do not appear to be the dominant interactions. The Cu(I) centers in those examples have the expected distorted tetrahedral coordination environments.

Although trigonal Cu(I) is rare [20] we have seen this type of coordination environment in several of our previous phenanthroline-containing structures. Munakata et al. [21] have developed a correlation between bond angles and bond distances, concluding that for Y- and T-shaped complexes as the angle θ_3, approaches 180° from 120°, d_3 lengthens and shortens as θ_3 approaches 0° from 120° (Scheme 3). Due to the nature of the mixed ligand coordination environment and the bulk of the phosphine ligand in **1** a relationship between bond angle and distance is not apparent for Cu(1). However for Cu(2), with $d_3 = 2.097(5)$, $d_2 = 1.950(4)$, and $d_1 = 1.939(4)$, and Cu(3), with $d_3 = 2.096(4)$, $d_2 = 1.945(4)$, and $d_1 = 1.944(4)$, both coordinated by 3 phen ligands, we see that d_3 is roughly 0.15 Å longer than d_1 or d_2 (Table 3). For Cu(1), with $d_3 = 2.040(5)$, $d_2 = 1.930(6)$,



Scheme 3. Correlation of bond lengths and angles in a three coordinate Y-shaped complex.

Table 3
Selected bond lengths and angles for compound **2**

Cu1–N1	1.927(6)	N1–Cu1–N3	153.6(3)
Cu1–N3	1.930(6)	N1–Cu1–NIA	105.2(2)
Cu1–N1A	2.040(5)	N3–Cu1–N1A	101.2(2)
Cu2–N14A	2.070(4)	N14A–Cu2–N1C	114.2(4)
Cu2–N14A#1	1.950(6)	N14A#1–Cu2–N1C	105.5(4)
Cu2–NIC	2.13(2)	N14A–Cu2–N14A#1	140.2(2)
Cu3–N2	1.891(7)	N2–Cu3–N4	157.4(3)
Cu3–N4	1.897(7)	N2–Cu3–N14C	103.7(3)
Cu3–N14C	2.251(6)	N4–Cu3–N14C	98.3(3)

and $d_1 = 1.927(6)$, and Cu(2), with $d_3 = 2.13(2)$, $d_2 = 2.070(4)$, and $d_1 = 1.950(6)$, in **2** which are both coordinated by three phenanthroline ligands, we see that d_3 is about 0.11 Å longer than d_1 or d_2 for Cu(1) and d_3 is 0.16 Å longer and 0.043 Å longer than d_1, and d_2 for Cu(2). For Cu(3), with $d_3 = 2.251(6)$, $d_2 = 1.891(7)$, and $d_1 = 1.897(7)$, which is only coordinated to three phen ligands 50% of the time d_3 is 0.35 Å longer than d_1 and d_2. In this case d_3 corresponds to the Cu(2)–N(14C) bond and is much longer than that seen for any of the other copper centers, possibly due to the disordered coordination environment about Cu(3).

3.2. Thermogravimetric analysis

1b and **2** were heated to 400 °C in N_2 (Fig. 9). For **1b**, a weight loss corresponding to the included THF solvent molecules (observed 10.0%, calculated 9.4%) occurred in the temperature range 66–142 °C. Continued weight loss consistent with the removal of PPh_3, phenanthroline, and BF_3 without any discrete steps was observed to 380 °C. Final weight percent corresponds to CuF (observed 14.06%, calculated 15.68%). The thermal decomposition of **2** occurs in three distinct steps. First, the loss of most of the included nitrobenzene solvent molecules (observed 16.36%, calculated 19.65%) in the temperature range of 54–140 °C is less than expected possibly due to loss of included solvent upon removal from the solution as the crystals become powdery when exposed to the air. Weight loss from 178 to 224 °C correlates to two phenanthroline molecules (observed 14.87%, calculated 14.68%). On further heating **2** lost weight between 256 and 373 °C corresponding to the loss of the remaining phenanthroline and BF_3; the final decomposition product is also CuF (observed 16.41%, calculated 16.47%).

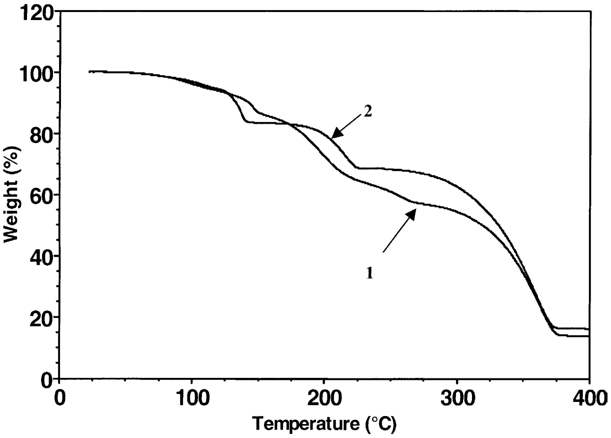


Fig. 9. Thermogravimetric analysis data for **1b** and **2**.

4. Conclusions

Two novel Cu(I)/4,7-phenanthroline coordination polymers have been synthesized and structurally characterized. The structure of **1** contains three Y-shaped trigonal Cu(I) centers linked by phenanthroline to form chains of Cu/phen triangles. The structure of **2** also contains three Y-shaped trigonal Cu(I) centers linked by phenanthroline, but in this case two disordered chains similar to those found in **1** are linked to form a complicated ladder-type network. We hypothesize that the formation of the final structures of both **1** and **2** are dominated by the ligand–ligand π–π interactions rather than metal coordination preference.

5. Supporting information available

Crystallographic data for **1a**, **1b**, and **2** have been deposited with the Cambridge Crystallographic Data Center (CDDC 190310–190312). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road Cambridge, CBZ 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.am.uk) Web at http://pubs.acs.org.

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