Structure and Synthesis of Four Supramolecular Structures Involving Cu(I) and 4,7-Phenanthroline

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Dedication

I would like to dedicate my thesis and work to my Mom and Pop. Without their constant love and support I couldn’t have reached this point. A more selfless set of parents haven’t existed in 2000 years. Every day I strive to make the best use of the gifts you have given me. I hope I make you proud.
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Abstract

Structure and Synthesis of Four Supramolecular Structures Involving Cu(I) and 4,7-Phenanthroline

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The design and synthesis of supramolecular species with discrete geometric shapes has been an area of much interest and research in recent years. Three isolated species of square shaped molecules and one infinite network of covalently bonded squares are presented. The four structures are all obtained from [Cu(MeCN)$_4$]BF$_4$ and 4,7-phenanthroline, with differences in the ratio of starting material, solvents, and set ups of these materials resulting in the differences in structure. Synthesis conditions, crystal data, comparisons, and pictures of the structures are all included.
1. Introduction

You could almost define humanity’s existence by its quest for materials. What started humanity on its current path was its’ ability to manipulate the world around it by developing new items. By sharpening wood and sculpting rock humans gained an advantage over their prey, and over thousands of years became more skilled at working rock, advancing to the point of specialized spear heads and needles.

But rock was heavy and difficult to shape, so this was replaced by an alloy of copper and tin, bronze. This new material was difficult to come by, and first only used to make decorations and trinkets. But its’ malleability compared to stone gave it a high value. Soon trade routes were established so communities with one component could trade with the other.

Bronze was used before iron, as it was easier to separate copper and tin from their ores, than it was to remove iron. The reduction potentials of the common oxides of these three metals are listed in Figure 1.1. The forges of the time could not produce enough heat for the smiths to work with iron properly; it would require an advance in bellows technology to allow work with iron to progress.

\[
\begin{align*}
\text{Sn}^{+2} + 2e^- & \rightarrow \text{Sn} \quad -0.136 \text{ E(V)} \\
\text{Cu}^{+2} + 2e^- & \rightarrow \text{Cu} \quad 0.3394 \text{ E(V)} \\
\text{Fe}^{+2} + 2e^- & \rightarrow \text{Fe} \quad -0.440 \text{ E(V)}
\end{align*}
\]

Figure 1.1: Standard reduction potentials for selected metals.

Bronze had drawbacks and was eventually replaced by a harder metal, iron. It was found by thrusting the heated iron into the ashes of the flame the material could be
improved. By repeatedly thrusting the iron into the ashes other elements where added into the material and formed the alloy steel, which was stronger than bronze and would hold an edge longer.

So important were these materials to our earliest ancestors that we have even named large swaths of our history after them, The Stone Age, Bronze Age, and Iron Age. Each of these divisions represents a technological leap forward in human civilization.

Other materials contributed to our advancement also. Pottery allowed humans to store food and drink. Textiles removed humanities reliance on simply chopping the hide off a meal and wrapping it around oneself to keep out the cold. Paper allowed for records to be kept, communication to be more exact, and with the printing press the rapid spread of ideas from one area to another. Caravans of traders traveled across thousands of miles of deserts to exotic ports for something as simple as spices. Gunpowder changed the face of the battle field, taking the power out of the hands of knights who had reigned supreme in their iron shells, and place it in the hands of the lowly grunt with a musket in hand.

So called precious materials have long driven humanity. One could argue that the first experimental chemists were ancient alchemists hunched over fuming solutions and striving to find a way to turn the common and unattractive lead, into the rare and beautiful gold. The search for silver and gold had long been motivators of countless conquerors and explorers. The new world was “discovered” by Europeans searching for a better trade route to the materials they desired. The lust for gold and silver pushed the exploration of the New World and funded its’ colonization.

In more modern times, the discovery of plastics allowed for the construction of cheap lightweight materials, and gave rise to the disposable society. Electronics and
circuits have allowed for more sophisticated tools capable of doing things and going places man could never dream of.

Even today the search for new materials, and improvements on old, is going as strong as ever.

Currently many strategies for developing new materials are under scrutiny by the scientific community. One of these is supramolecular chemistry, which focuses on forming large molecules to perform specific jobs. Thanks to the variability of the materials involved in constructing supramolecular compounds, a wide variety of applications have been realized, and will be discussed below in more detail.¹

### Supramolecular Chemistry

In 1937 K.L Wolf proposed that it was possible for groups of molecules that interacted through non-covalent means to have properties of their own different from the individual molecules from which they are constructed. Wolf’s work dealt with the interactions between acetic acid molecules that formed long repeating chains (referred to as dimers). Wolf labeled these large chains “Ubermolekules”, or supermolecules.²

I place supramolecular chemistry’s birth in the early 1960's with the work of Charles Pederson (among others) with forming large cyclic compounds. By reacting bis(2-chloroethyl) ether with 2-(o-hydroxyphenoxy)tetrahydropyran they were able to form large molecules that could coordinate exclusively to a central cation.³ These developments led to further work with larger molecules and the study of their interactions with each other.
Influenced by the work with the new crown ethers, a researcher at the University of Strasbourg named Jean-Marie Lehn took the crown ethers a step further and developed three dimensional versions. These new molecules, called cryptands, were able to completely surround the cation, and by varying the size of the ring they were afforded a degree of selectivity.4

This selectivity was improved upon by Donald Cram, who took the relatively flexible crown ethers/cryptands and increased the rigidity of the structure.5 This forced the bonding sites on the ligand into certain conformations. This (and later) work earned both Cram and Lehn the 1987 Noble Prize.
It is Lehn though, who will always be remembered as the father of supramolecular chemistry, perhaps in part because he supposedly coined the phrase and gave us the definition most commonly used. Of the topic itself Lehn said “Just as there is a field of molecular chemistry based on a covalent bond, there is the field of supramolecular chemistry, the chemistry of molecular assemblies and of the intermolecular bond.”

Lehn went on to discuss and describe the participants in these molecules, naming them donors and receptors. Lehn saw the receptors as a large molecular species (in his case the macrocyclic compounds he was studying) and donors as the smaller charged ions that would fit into the larger complex. Today this term is applied to any large molecule, not just cyclic structures.

Everything from hydrogen bonding and $\pi-\pi$ interactions to dipole forces and steric constraints contribute to the formation of structures. This gives supramolecules a degree of freedom by not being limited to one type of interaction.

The formation of supramolecules often relies on self-assembly. The idea of self-assembly is that when two units come together they will orientate themselves into positions that will maximize their interactions. The most significant example of this is DNA. Two long molecular chains come together in our bodies and interact at key points through hydrogen bonds. This interaction is strong enough to hold the strands together, and the interactions unique enough that exact copies are the norm.

It’s astonishing to think that these molecules are assembled not by tiny machines but simply by two molecules finding the optimal positions to interact when they come into contact with one another. While still in its infancy there are studies being done on
the way these molecules interact with one another, in hope of understanding the origins of life itself.\textsuperscript{8}

By carefully designing the molecules chemists can design structures that interact with one specific molecule or atom. The work of Pedersen with the large crown ethers and related compounds was begun to bind with specific metal ions and can be used in removing harmful ions from solutions. By optimizing such factors as size, shape, and charge of the species one can improve the selectivity of the formation mechanisms.\textsuperscript{9}

Much of the work in supramolecular chemistry has focused on coordination polymers. Coordination polymers are long chains of metal centers connected by ligands with two or more binding sites. These networks are often porous, with the structure and the pores varying depending on the materials used to synthesize the structure. The ability to rationally design molecular networks is an area of much research.\textsuperscript{2}

In addition to coordination polymers, isolated molecules with cavities formed by the structure are also being studied. Since these structures can be formed from many different starting materials it shouldn’t be surprising that there are a plethora of configurations they can assume. In 1998 Stang proposed that any polyhedron could be constructed by selecting the proper building blocks. By choosing metal centers and bidentate ligands, Stang and his group were able to duplicate a number of geometric shapes.\textsuperscript{2} For instance, by mixing palladium(II) (which typically bonds in a square planar orientation) and 4,4-bipyridine at room temperature they were able to create a molecular square with corner angles very close to 90 degrees (Figure 1.4).\textsuperscript{11} Using ligands other than 4,4-bipyridine, but with the same linear structure, they were able to produce similar squares.
Figure 1.4 A: The 4,4’-bipyridine ligand used by Stang to form square structure as seen in B. B: Square structure made by Stang et al.\textsuperscript{11}

Other structural motifs have been realized using different metals and ligands.

Researchers from the University of Windsor created a distorted hexagonal structure using 4,7-phenanthroline (Figure 1.5) and a organopalladium complex.\textsuperscript{12} Unlike 4,4’-bipyridine, 4,7-phenantholine does not have binding sites that are 180 degrees from each other. Rather the nitrogen atoms that it coordinates through are offset, forming a 60 degree angle between metal centers.
Figure 1.5  A is an organic shorthand figure of 4, 7-phenathroline. B is a stick view of the same molecule with the nitrogen atoms shown in blue, carbon in grey, and hydrogen in white.

Using Ni(II) and Zn(II) along with the ligand bptz (Figure 1.6) Dunbar et al isolated square structures using BF$_4^-$ and ClO$_4^-$ as anions, which occupied the center of their square. By increasing the size of the counter to SbF$_6^-$ used they were able to produce pentagonal structures instead.

Figure 1.6  A: The ligand bptz used by Dunbar et al in producing both squares and pentagons. B: Space fill view of Dunbars’ pentagons, inside cavity sits SbF$_6^-$. Figure 1.6 B taken from reference$^{13}$. 
Other geometrical motifs including triangles\textsuperscript{14} and rectangles\textsuperscript{15} have been discovered using different metal centers and connecting ligands.

Each of the structures discussed above exist as isolated species, with individual units not covalently bonding to any other. Infinite networks, where metal centers are connected together, are common with a wide range of shapes and motifs used. For example, using copper(I) and 4,4’-bipyridine Yaghi et al obtained extended networks of hexagons and diamonds. By changing the metal center used to cadmium(II) and nickel (II) they formed an extended grid of squares and a ladder of repeating square units.\textsuperscript{16}

The applications of supramolecular chemistry have been wide ranging. Working out of the University of Tokyo, researchers have been able to introduce an anti-tumor agent, Adriamycin (ADR), into cancerous cells by including it in a supramolecular assembly that allows it to enter the cell. The membrane that surrounds the ADR is designed to be selective as to the types of materials that are allowed to pass. By designing a micelle to include the ADR the cell allows in the structure inside, and after a change in pH the ADR is released to act on the cell.\textsuperscript{17}

Utilizing the reactivity of CO\textsubscript{2} and certain amines, Dmitry Rudkevich and Heng Xu from the University of Texas at Arlington have been able to create a supramolecular polymer that can be used to trap the gas. Using this technology the researchers hope to develop more advanced structures that could find applications in CO\textsubscript{2} sensing and removal.\textsuperscript{18}

With our current energy problems alternate sources of fuel are being studied, among them is hydrogen. Supramolecular chemistry is being used to from possible storage materials for H\textsubscript{2}. In 2003 researchers at Kyoto University were able to
completely encapsulate a hydrogen molecule using a fullerene derivative, $C_{63}NO_2SPh_2Py$, and keep it inside the cage$^{19}$.

Other applications of supramolecular chemistry range from catalysis$^{20}$, non-linear optics$^{21}$, to ion and solvent exchange$^{22}$.

**Previous Keller Group Work**

The focus of our group has been on the production of supramolecular structures. Initially the group was focused on mimicking silicate mineral structures. Many silicate structures display properties allow them to be used for solvent exchange, ion exchange, and catalysis. Although all silicates are formed by SiO$_4$ tetrahedra, the possibilities for the arrangement of the units are many.

By using copper(I), which primarily bonds four times to yield a tetrahedral structure like silicon, we attempted to mimic various silicate structures. Copper(I) had been

![Tetrahedral unit of SiO$_4^{-4}$](image)

**Figure 1.7:** Tetrahedral unit of SiO$_4$~$^{-4}$, which is the basic unit of the silicate structures. The picture on the left is an example of the structure a more common silicate, quartz.
used to make coordination polymers. Using the ligand pyrimidine, we were able to produce a structure similar to the silicate feldspar. After this success other ligands, such as 4,4’-bipyridine, 3,3’-bipryidine (similar to 4,4’ but with both nitrogens shifted over one positions on their rings), and 4,7-phenanthroline, were selected and our group has obtained a number of different structures. For example, using 3,3’-bipyridine and Cu(I) our group obtained an interpenetrated diamondoid compound, with two rings of Cu(I)-3,3’-bipyridine locked together.

Using copper(I) and 4, 7-phenanthroline our group has isolated a variety of unique structures by changing variables such as the counter ion, solvents used, and ratio of starting materials used. As we will see in the following chapter, using similar ratios of starting material, but varying one of the solvents used, can have a drastic effect on the structure of the resulting compound.

By mixing a 1:2 ratio of [Cu(MeCN)$_4$]BF$_4$ to 4,7-phenanthroline in a MeCN/nitrobenzene solution we have been able to isolate crystals of a linear compound of distorted trigonal planer copper (I) centers. While not common, trigonally coordinated Cu(I) is not unheard of. Each copper is bonded to two 4,7-phenanthroline ligands, which connect it to additional copper centers, and to one MeCN. Using the same ratio of starting materials, and solvents, but changing the counter ion from BF$_4^-$ to PF$_6^-$ we have been able to isolate chains of tetrahedrally coordinated copper chains. In this structure each copper is bound to two 4,7-phenanthroline molecules and two MeCN ligands. The two 4,7-phenanthrolines connect the copper to other copper centers. (Figure 1.8)
Figure 1.8: A: [Cu(4,7-Phen)(MeCN)$_2$] PF$_6$ which is a chain of tetrahedrally coordinated copper(I) metal centers. B: [Cu(4,7-Phen)(MeCN)]BF$_4$ is a chain of trigonal planer copper(I) centers.

By modifying the copper starting material to [Cu(MeCN)$_2$(PPh$_3$)$_2$]BF$_4$ and changing the ratio of starting material to 1:1.5 chains of triangle structures were obtained. Each triangle has three copper(I) centers, with two being trigonally coordinated to three 4,7-phenanthroline ligands, and the third bonding to two 4,7-phenanthroline molecules and one PPh$_3$. Each triangle is linked to two other triangles through two 4,7-phenanthroline ligands. (Figure 1.9) Simply by changing the solvent that is diffused in (from THF to diethyl ether) a separate triangle chain was obtained, using the same synthesis as above.
Figure 1.9: Two triangles formed from [Cu(MeCN)₄]BF₄, 4,7-phenanthroline, triphenylphosphine and diffusing in THF. Each triangle in the structure is linked together through a 4,7-phenanthroline to an additional triangle.

As we will see in the next section, using [Cu(MeCN)₄]BF₄ and similar solvent systems, but by varying the ratio of the copper starting material to 4,7-phenanthroline we have been able to isolate three unique square structures. The fourth can be obtained by modifying the solvent used to diffuse into the crystal system.

Squares are typically formed from two types of metal centers, square planar\textsuperscript{28-30} and from octahedral metal centers\textsuperscript{13, 14, 15, 22, 26}. These two coordination environments are more common, as the arrangement of ligands around the center should be 90 degrees. When added to a linear bidentate ligand, such as 4,4'-bipyridine, this yields direct connections that form squares.

Square structures are common among supramolecular structures, and can be formed from different metal centers and ligands. Most molecular squares have four metal centers forming the corners, but squares with non-metallic corners have been
discovered.\textsuperscript{10} At the University of Missouri-Columbia Harmata and Kahraman constructed a molecular square from two palladium metal centers and two organic ligands (Figure 1.10) designed to have a 90 degree bend between benzene rings.\textsuperscript{25} While unable to obtain crystal data on the resulting square, by using NMR they were able to determine the existence of the square.

![Ligand used to form square with two Pd centers. The ligand bends around the center ring, so that the corner of the square would sit at the oxygen.](image)

Dunbar was able to create a molecular square by linking four Ni(II) centers together with four bptz ligands.\textsuperscript{(Figure 1.11)}\textsuperscript{13} Each nickel center was bound to two bptz ligands (twice to each ligand) and to two MeCN molecules, which emanated from the corners. The square was formed by mixing [Ni(MeCN)\textsubscript{6}]BF\textsubscript{4} with bptz in methanol, than allowing toluene to diffuse in. This yielded a square with corners that fell within 4 degrees of 90, and only slightly distorted the octahedral geometry of the center Ni(II).\textsuperscript{13} The square was formed no matter what ratio of [Ni(MeCN)\textsubscript{6}]BF\textsubscript{4} was used. It should be noted that in the center of this square lies the BF\textsubscript{4}\textsuperscript{-} anion, as mentioned above by varying the anion used they were able to control the geometry of the resulting structure.
Researchers at Northwestern University were able to synthesize squares from Re(I) and 4,4’-bipyridine.\textsuperscript{26} These squares were similar to those produced by Stang (Figure 1.4 above) except that Re(I) has an octahedral coordination environment, while the Pt used by Stang was square planar. Thus the Re(I) metal centers were bonded to two additional ligands, which were CO molecules. (Figure 1.12)
Figure 1.12: Square formed from 4,4'-bipyridine and Re(I), where L is carbon monoxide.

Squares can also be produced from metal centers that have a linear coordination environment, as Rogers has shown with his silver(I) pyrimidine square. In this structure each pyrimidine sits at what we would consider the corner of the square, while it is the silver metal centers that link these ligands together and form what we would consider the edges of the square.\(^{38}\) This is in contrast to the previous squares discussed and the structures we have obtained, where the metals form what we could consider corners and ligands the edges.

What separates our structures from these is that Cu(I), which is tetrahedral having ligand-ligand angles around the center of 109.5 degrees, was used along with 4,7-phenanthroline. While the corner angles for our structures are not 90 degrees, the angles are surprisingly close, given the typical bonding angles of the metal centers used.
The square structures we have obtained are similar to another class of compounds, calix[n]arenes. Calix[n]arenes are large cyclic oligomers formed by linking a number (n) of phenol rings together. Calix[4]arene contains four phenol groups bonded together by tetrahedral carbons (–CH2-) to form a square, similar in shape and structure to our molecular squares. Depending on the orientation of the aromatic phenol groups cavities of various size and shape can be obtained, and allow for other molecules to fit in side. The orientation of the phenols as seen in Figure 1.13B resembles that of the square structures we have produced, with opposing sides perpendicular to their nearest neighbor.

Figure 1.13 Two possible configurations of the phenol groups in calyx[4]arene are for each phenol pointing in the same direction (A) or alternating pointing up and down (B).

The square structures that we have formed share a structural similarity to the silicate axinite. The arrangements of the SiO$_4^-$ molecules are such that four of the tetrahedral are linked together, alternately pointing up and down, similar also to the orientation of the phenol groups in calix[4]arene. While this arrangement is square in
nature it must also be noted that SiO$_4$ have no terminal oxides, rather each tetrahedra is connected to four others. As we will see later, in three of our structures each square exists as an independent molecule, and in only one example do the squares link up with additional units.

It is these square structures and the factors that lead to their formation that will form the rest of this piece.
2. Experimental, Results, and Discussion

General Methods

All starting materials were purchased through suppliers; 4,7-phenanthroline from GFS Chemicals; and acetonitrile, nitrobenzene, diethyl ether, and tetrahydrofuran from Fisher Chemicals. THF was stored in the presence of MgSO₄ as was diethyl ether.

A typical procedure for the formation of [Cu(MeCN)₄]BF₄ was prepared by adding Cu₂O to roughly 40 mL of acetonitrile (MeCN). The solution was gently heated and HBF₄ was added to the slurry. After a few hours the solution was filtered, and the filtrate saved while the particles on the filter paper were disposed of. The filtrate was then added to 40 mL of diethyl ether, and again filtered, this time under N₂ and crystals of [Cu(MeCN)₄]BF₄ collected.³¹

Part of our work with the squares involves a technique called solvent vapor diffusion (SVD). In the production of the squares, the starting materials ([Cu(MeCN)₄]BF₄ and 4,7-phenanthroline) are first placed in a small vial and dissolved in a mixture of nitrobenzene and acetonitrile. This small vial is then placed in a larger vial containing an additional solvent (in the squares THF and diethyl ether are used) and the system is sealed.(Figure 2.1) Small amounts of the solvents evaporate and move from one vial to the other. As the outer vial solvent moves in it changes the nature of the solvent system, this change in the solvent affects the solubility of the products, changing them from soluble to insoluble.

In my literature searches I have yet to see a set naming scheme for square supramolecular structures that incorporates some convenient way of describing the structure. I created my own for the following squares. To name the structure take the
number of 4,7-phenanthroline molecules attached to Cu centers, but not involved in forming the square itself. The second number denotes the number of MeCN molecules attached to the copper atoms. Thus a square that would be named “4:4 Square” would have four terminal 4,7-phenanthroline molecules and four MeCN molecules attached to the copper corners.

Crystals of each structure were identified using polarized optical microscopy to ensure that only single crystals were chosen. Several crystals were removed from their mother liquor and placed in immersion oil, and viewed under a microscope to select crystals of suitable size. The crystals were then attached to a thin glass fiber using grease and mounted onto a Siemens SMART system equipped with a CCD area detector to collect full hemispheres of data in a cold nitrogen stream, with the exception of 3, which at room temperature showed a strong diffraction pattern and a narrow mosaic spread. With cooling the mosaic spread was broad, possibly because of an incomplete phase transition. Using the SHELXS direct method routine the structures were solved and were refined using a full least squares treatment on $F^2$. All hydrogen atoms were treated
as riders to the molecule and placed in calculated positions with respect to the carbon atoms they were attached to, bond length for C-H was set to a standard 0.93 Å.

In 1 the nitrobenzene and the uncoordinated acetonitrile were disordered and refined with isotropic thermal parameters. In 2 the diethyl ether molecule was disordered and refined with geometric constraints and isotropic thermal parameters. In 3 two of the nitrobenzene molecules were disordered and were refined with site occupancies of 0.50, and all three were refined with geometric constraints and isotropic thermal parameters. Additionally the placement of the oxygen on the THF could not be determined, and so each member of the ring was treated as a carbon and hydrogen’s omitted. One of the terminal 4,7-phanthroline ligands was partially disordered and one ring of the molecule was constrained to be hexagonal. Two BF4⁻ molecules in both 3 and 4 were disordered and were constrained to be tetrahedral and refined with isotropic thermal parameters. All other non-hydrogen atoms were refined with anisotropic thermal parameters.

\[\text{4[Cu(4,7-Phen)(MeCN)_2] \text{\bullet 4[BF}_4\text{] \text{\bullet MeCN \text{\bullet Nitrobenzene}}} \quad 1\]

[Cu(MeCN)_4]BF_4 (29.0 mg, 0.092 mmol) was placed in a 5 dram vial and dissolved by adding 0.5 mL MeCN and 3 mL of nitrobenzene. Then 4,7-phenanathroline (66.0 mg, 0.37 mmol) was added to the solution and dissolved. The small vial was placed in a larger 20 dram vial containing 3 mL diethyl ether, and sealed with a screw top. After 2-3 days yellow block like crystals of the 0:8 square, 1, were harvested from the inner vial.

By using the naming scheme I developed 1 can be identified as the 0:8 square, as it has no terminal 4,7-phenanthroline molecules and eight MeCN on the copper centers.
The synthesis of the 0:8 square stands out among the four square structures that we have obtained as produced from the lowest ratio of [Cu(MeCN)₄]BF₄ to 4,7-phenanthroline (1:4). The rest of our structures are formed from ratios almost double that amount. Like the 2 and 4 the solvent that the reaction is initially setup in is a mixture of 0.5 mL of MeCN and 3 mL of nitrobenzene, with diethyl ether set up in the outer vial.

Since the amount of 4,7-phenanthroline in the reaction is much lower than the other squares, it isn’t surprising that 1 contains few of these ligands. The only 4,7-phenanthrolines in the structure bridge between the copper centers. In contrast, the synthesis of 2, which involves almost three times the amount of 4,7-phenanthroline in the same volume of liquid, not only has 4,7-phenanthroline molecules bridging between the centers, but also two terminal ligands of this type.

Previously our group has isolated a chain of trigonally coordinated copper centers from a 1:2 ratio of [Cu(MeCN)₄]BF₄ to 4,7-phenanthroline in a nitrobenzene/MeCN solvent mixture. (Figure 1.9 above) Since 1 is formed in the same solvent conditions, but a starting material ratio of 1:4, the formation of the square must be favored by an increase in the concentration of 4,7-phenanthroline.

The square structure of 1 contains four crystallographically distinct Cu(I) centers.(Figure 2.3) While we refer to the structure as a square the angles formed by the corners are not exactly 90 degrees. Each copper is connected to another copper by a 4,7-phenanthroline molecule that is shared between the two centers. The Cu-Cu-Cu bond angles, which form what we would consider the corners of a square, vary from 88.27 to 92.20 degrees. While these angles are not exactly 90 degrees they are surprisingly close
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Figure 2.2: I with atoms shown as thermal ellipsoids with relevant crystal data.  

*R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} * * R = \frac{\sum (|F_o| - |F_c|)^2}{\sum |F_o|^2}^{1/2}
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Figure 2.3: Bond lengths and angles with bond lengths in angstroms and angles in degrees.
given the tetrahedral geometry of the copper centers and the bent binding nature of 4,7-
phenanathroline.

While each copper center is bonded to two 4,7-phenanthroline molecules which
connect to an additional center, the bond angles between the ligands around the center are
quite different (Figure 2.3). In addition to the 4,7-phenanthrolines each Cu has two
MeCN ligands that radiate out from the inside of the square. This gives each Cu center a
distorted tetrahedral configuration with N_{phen}-Cu-N_{phen} angles being wider than the 109.5
degrees we normally associate with tetrahedral structures. This wider angle forces the
MeCN groups closer together, yielding N_{MeCN}-Cu-N_{MeCN} angle narrower than 109.5
degrees, with the exception of N14-Cu-N13, which has an angle of 113.61 degrees.

The arrangement of the MeCN ligands around the outside of the square is similar
to that in the square produced by Dunbar’s’ group, using Ni(I) and bptz (Figure 1.12).
Both of the structures contain metal centers at the corners of the square connected by the
ligand, surrounded by a fringe of MeCN ligands. The metal-metal-metal angles are also
very similar, with both structures having angles close to 90 degrees.

The 4,7-phenanthroline molecules that sit across from each other point in the
same direction, as we can see from Figure 2.4. Two edge forming 4,7-phenanthroline
molecules point up (from the view of Figure 2.4 this would be towards the viewer) and
two point down (away from the viewer). This gives the square the appearance of a box
with two flaps up and two flaps down. This is structurally similar to one of the
orientations of the calyx[4]arenas as seen in Figure 1.14B. The cavities in the 0:8 square
are not empty, as Figure 2.4 would suggest, rather they are filled by other
molecules. (Figure 2.5)
Figure 2.4: 0:8 square showing only the molecules attached to the copper centers

Figure 2.5: 1 shown in stick view and anions and solvents molecules as space fill.
Figure 2.5 shows a single 0:8 square with the counter anions and solvent molecules added in. From this view we can see that the space between the flaps now pointing towards the viewer is completely occupied with a nitrobenzene molecule, with a nitrobenzene-4,7-phenanthroline distance of about 3.467 Å. To the right of the nitrobenzene molecule there is also a lone MeCN molecule that is not attached to a center that sits off to the side. This is the only square structure that we have found that includes an acetonitrile molecule in this manner. The non-coordinating BF$_4$ anions sit off to the sides of the copper centers, with each anion sitting at least 4 Å away, with the shortest distance being 4.005 Å.

Figure 2.6: Three 0:8 squares with the 4,7-phenanthrolines $\pi$-$\pi$ stacking with nitrobenzenes shown in space fill.

The nitrobenzene that fills the cavity of this side of the square makes it impossible for the 4,7-phenanthrolines to fill this space, thus the squares interact through their edges. In Figure 2.6 three squares are shown packing together by $\pi$-$\pi$
interactions through the edge forming 4, 7-phenanthroline molecules of the square, with nitrobenzene molecules filling the spaces in each square.

Filling the gap on the other side of the molecule is an edge 4,7-phenathroline of another square, as shown in Figure 2.7. This stacking completely fills the void formed by the flaps of the molecule, with a phen-phen distance of about 3.409 Å. This distance between the π planes in the square are consistent with other examples of π-π stacking.34-36 It is not unusual to see π-π stacking in structures with aromatic rings, including supramolecular structures. In fact this type of interaction is often responsible for the packing of structures in crystals.37

Figure 2.7: Two units of 1 locking together

One of the problems faced when working with these structures in solution is the thermodynamic and kinetic factors that affect the formation of the product. It is possible that for 1, and the following structures, what we have observed is not the
thermodynamically most stable arrangement of components that could be produced. Rather our structures could be an arrangement that forms first, and the activation energy required to push the molecule to the lowest energy arrangement is too high to be overcome.

Figure 2.8 shows two possible mechanisms for the formation of the squares. While each copper is unique in its symmetry, their bonding environment is identical to that of every other copper in the square. With each copper having two acetonitriles and two 4,7-phenanthrolie ligands we can assume that the formation of the square involves one [Cu(MeCN)4]BF4 losing a MeCN (A in Figure 2.8) and gaining a 4,7-phenanthrolie in its place (B). After one copper loses an additional MeCN (forming C) Figure 2.8 shows two options. First, C can bond to another 4,7-phenanthrolie, which in turn will bond to another unit of C. The other option is that C could instead bind to a B, which would have to lose a MeCN, and connect with an additional B. (Shown on next page in Figure 2.8). This is just a proposed synthesis for 1, based on what we know of the chemistry of the starting materials and the structure of the final product. I suspect that the synthesis for 2 and 3 follows a similar route, with some obvious variations, such as the loss of additional acetonitriles and the addition of terminal 4,7-phenanthrolines.
Figure 2.8 Possible formation of 0:8 Square
4[Cr(4,7-Phen)1,5(MeCN)] • 4[BF4] • Diethyl Ether  2

[Cu(MeCN)4]BF4 (30.5 mg, 0.097 mmol) was placed in a 5 dram vial and dissolved by adding 0.5 mL MeCN and 3 mL of nitrobenzene. Then 4,7-phenanthroline (174.8 mg, 0.97 mmol) was added to the solution and sonicated until all solid was dissolved. The small vial was placed in a larger 20 dram vial containing 3 mL diethyl ether, and sealed with a screw top. In 3-4 days yellow, needle like crystals of 2 were harvested.

By the naming scheme 2 is called the 2:4 square, since it has two terminal 4,7-phenanthroline molecules and four acetonitriles around the outside of the square.

The setup to obtain the 2 is identical to the synthesis of 1, except for the substantial increase in the amount of 4,7-phenanthroline. For the 0:8 square the ratio of [Cu(MeCN)4]BF4 to 4,7-phenanthroline was 1:4, for the 2:4 square the ratio is 1:10. This pushes the limits of 4,7-phenanthrolines solubility in 0.5 mL MeCN and 3 mL of nitrobenzene, and the mixture is often slightly heated to facilitate the complete dissolution of 4,7-phenanthroline. It should also be noted that crystals of the 4:3 square ladder occasionally appear in the same vial as crystals of 2.

Figure 2.10 shows that the 2:4 square contains three crystallographically different Cu(I) centers, giving the molecule a 2 fold rotation axis goes through Cu2 and Cu3. These two copper centers are very similar to the ones from the previous 0:8 structure.
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Figure 2.9: 2 with atoms shown as thermal ellipsoids with relevant crystal data.  $^*$ R = $\Sigma||F_o|| |F_c||/|F_o||$  $^\prime$ R = $\{\Sigma(||F_o|| - |F_c||)^2/|F_o||^2\}^{1/2}$
Each is bonded to two 4, 7-phenanthroline ligands which are shared with two
other Cu centers. In addition to this both of these centers are also connected to two
MeCN molecules that point away from the center of the square. This gives Cu2 and Cu3
a distorted tetrahedral configuration with Nphen-Cu-Nphen angles being wider than the
109.5 degrees we normally associate with tetrahedral structures. The NMeCN-Cu-NMeCN
angle for Cu2 is larger than the expected tetrahedral angle (116.52 degrees) while the angle for Cu3 is slightly smaller (107.97 degrees). For Cu1, which has a triagonal geometry, the square forming $N_{\text{phen}}$-Cu-$N_{\text{phen}}$ angles are 128.79 degrees, larger than the 120 degrees that we would expect. This pushes the $N_{\text{phen}}$-Cu-$N_{\text{phen}}$ angles between the square forming phen and the terminal phen to be slightly lower than 120 degrees. This distortion around the centers yields corners far from the 90 degrees that define a geometric square, with angles of roughly 99 degrees for Cu1-Cu2-Cu1/Cu1-Cu3-Cu1 and 80 degrees for Cu2-Cu1-Cu3.

As with 1, the 2:4 square has edges that alternate pointing up (facing the viewer) and down (away from the viewer), as seen in Figures 2.11 below. As with the previous structure (and the following) the structure has cavities on opposite sides of the structure. The $BF_4^-$ anions shown are those closest to the Cu centers. The closest F-Cu distance occurs between the trigonally coordinated Cu1 and the closest $BF_4^-$ at 2.566 Å.

Figure 2.11: 2 shown in space fill with $BF_4^-$ also shown in space fill.
Unlike 1, the 2:4 square has no nitrobenzene molecules filling the cavities formed by the edges. This is not left as a void though, as each cavity is filled by the edge forming 4,7-phenanthroline of a neighbor. Figure 2.12 shows how two 2:4 squares lock together, completely filling the space between the edges. The edges completely fill the space, with phen-phen distances of about 3.503 Å.

Figure 2.12: Two squares of 2 locking together, filling the cavity formed by the flaps of the neighboring square.

This fills the inner void of each structure and allows for each layer of molecules to penetrate into the layer above and below it. The next layer, by virtue of the way the
squares stack will be flipped 180 degrees and will interact with the molecule above. As shown in Figure 2.13.

![Figure 2.13: Three squares of 2 stacking on top of one another.](image)

The terminal 4,7-phenanthroline molecules of the squares form a box shape with the terminal ligands of a square that would sit diagonally from it. This can be seen in Figure 2.14, though four squares are shown to put the stacking in perspective, it is the square on the bottom left and the top right that form a square through their terminal ligands.

This space is not empty; inside each of these openings left by the interactions between the terminal ligands sit two diethyl ether molecules. This can be seen in Figure
2.14 where the squares themselves are shown in stick view, but the diethyl ether molecules shown in space fill for clarity.

Figure 2.14: Side view of trapped ether molecules between 2:4 squares

Determining the potential reactions for the formation of the individual squares is a bit trickier than with 1. While the first few steps must be the same, with Cu(MeCN)$_4$ losing a MeCN and gaining a 4,7-phenanthroline in its place, the options from here branch off in many directions. But from the synthesis conditions we can see that by increasing the amount of 4,7-phenanthroline we increase the number of 4,7-phenanthroline molecules in the molecule as compared to 1. This can be rationalized that since we are more than doubling the amount of 4,7-phenanthroline in solution it is more likely that the copper will come into contact with the ligands.
[Cu(MeCN₄)]BF₄ (40.7 mg, 0.13 mmol) was placed in a 5 dram vial and dissolved by adding 0.5 ml MeCN and 3 mL of nitrobenzene. Then 4,7-phenanthroline (166.5 mg, 0.92 mmol) was added to the solution and dissolved. The small vial was placed in a larger 20 dram vial containing 5 mL THF. After 3-4 days yellow column shaped crystals of 3 were harvested.

By my naming scheme 3 is called the 4:2 square, since it has four terminal 4,7-phenanthroline molecules and two acetonitriles around the outside of the square.

Of the squares this is the only synthesis that relies on THF as the outer vial solvent to cause crystallization. There is a tremendous difference in the vapor pressures of THF and diethyl ether. (Figure 2.15) This means that the rate at which THF evaporates from the outer vial and mixes with the solvent in the inner vial is much slower than that of ether. This gives the reactants more time to interact in the original solvent, before the introduction of the outer vial solvent. This additional time spent in the solution might account for the increase in the number of 4,7-phenanthroline ligands compared to 2. The longer the copper spend in solution the more likely it is that they will come into contact with the 4,7-phenanthroline ligands. In addition to the vapor pressure there is also a difference in the polarity of the two molecules, with THF more polar than diethyl ether. Aside from these differences in the solvents the synthesis of the 4:2 square and the 2:4 square are identical, though there is a slight difference in the ratios of starting material used.
Figure 2.15 Structures of THF and diethyl ether along with vapor pressures.

By looking at Figure 2.17, we can see that the 4:2 square contains a two fold rotation axis running through the center of the square. This gives the molecule two crystallographically unique copper centers, one that is tetrahedrally coordinated and one is coordinated to three ligands in a trigonal planer orientation. Each copper center is connected to two others through 4,7-phenanthroline molecules. In addition to the two connecting ligands the tetrahedrally coordinated Cu2 centers are also bonded to one MeCN and a terminal 4,7-phenanthroline, which is a structural feature that neither the 0:8 square or the 2:4 square have. These two centers have $N_{\text{phen}}$-Cu-$N_{\text{phen}}$ angles between the square forming ligands that are similar to tetrahedral centers in the other squares (roughly 120 degrees), but larger than we would expect form a tetrahedral geometry. The $N_{\text{MeCN}}$-Cu-$N_{\text{phen}}$ angles between the terminal ligands are also greater than the 109.5 degrees, giving the Cu2 centers a distorted tetrahedral shape.

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**Figure 2.16**: \( \text{3} \) with atoms shown as thermal ellipsoids with relevant crystal data. \( \ast \) \( R = \frac{\Sigma \vert F_o \vert - \vert F_c \vert}{\Sigma \vert F_o \vert}; \ast\ast \) \( R = \left\{ \Sigma \left( \vert F_o \vert - \vert F_c \vert \right)^2 / \Sigma \vert F_o \vert^2 \right\}^{1/2} \)
The two distorted original planer both have the two edge forming 4, 7-phenanthroline ligands. The $N_{\text{phen}}$-$Cu$-$N_{\text{phen}}$ angles between the square forming ligands is 131.57 degrees, much larger than the 120 degrees we would expect form a trigonal planer center. This forces the $N_{\text{phen}}$-$Cu$-$N_{\text{phen}}$ angles between the square forming ligands and the terminal 4, 7-phenanthroline to be narrower than what was expected.

Figure 2.17: Bond lengths and angles of 3, with bond lengths in angstroms and angles in degrees.
Much like 2 the angles of the corners that form the structure are not 90 degrees. Rather, the angles are 98.77 degrees for Cu1-Cu2-Cu1 and 80.82 degrees for the Cu2-Cu1-Cu2 corner. These angles are almost identical to those seen in 2, despite the fact that 3 has two tetrahedral centers that have a terminal 4,7-phenanthroline instead of two MeCN ligands. Apparently the addition of the larger 4,7-phenanthroline to the corners does not affect the angle of the square. (Figure 2.17)

The 4:2 square is similar in appearance to the 2:4 square with diagonal centers having similar arrangements and the edges of the square alternating pointing up and down, as is shown in Figure 2.18 below. On the other side of the molecule, the second void is filled with a 4,7-phenanthroline ligands that is not bonded to any copper.

Figure 2.18: 3 showing anions, solvent molecules, and 4,7-phenanthroline inserted in cavity. A THF molecule sits off to the side of the molecule in the crystal structure.
center. (Figure 2.19) The smallest Cu-F distance is 3.740 Å, and as with 2 this occurs between the trigonal copper center and its nearest BF$_4^-$.

As with 1 and 2 this arrangement of the edge forming ligands leaves an opening in the center of the molecule. Unlike the two previous structures, though, both of the crevices formed by the edges are filled with molecules not bonded to another structure. In 1 we saw that a nitrobenzene molecule are placed in the space between two edge ligands, and we see this repeated in the structure of 3. Figure 2.19 below shows how the nitrobenzene aligns itself in the cavity.

Figure 2.19 Side view of 3 showing nitrobenzene inserted in cavity, the nitrobenzene is shown as space fill while the square is shown in stick view.
The nitrobenzene and the 4,7-phenanthroline molecules fill both cavities with distances between the molecules and the phens that form the edges of the square being about 3.5 Å for both molecules.

Comparing 2 to 3 we see that in the 2:4 square the two terminal 4,7-phenanthroline molecules laid relatively flat, in the same plane as the Cu(I) centers. In contrast the four terminal 4,7 phenanthrolines of the 2:4 square all lie at an angle from the Cu(I) center and point in the same direction. By looking at Figure 2.20 we can see that this gives the square a cup shaped structure.

Since the cavities on both sides of the square are filled, there is no penetration of one square to another, unlike the two previous squares. Independent squares interact with their neighbors through the π-π stacking of the terminal 4,7-phenanthroline molecules, as can be seen in Figure 2.21 and Figure 2.22. The distance between the two terminal ligands of separate squares is 3.5 Å, identical to that observed between the aromatic
systems that fill the space formed by the square. The bottom square sits with the 4, 7-phenanthroline pointing up and out. The next layer of squares stacks facing down so that one set of its terminal ligands will face down and interact with one set of ligands of the square below it.

Figure 2.21: Four squares of 3. Center 4,7-phenanthrolines \( \pi \) stack on top of each other, and are shown in space fill. Despite appearances, squares do not lay in the same plane.
The formation of 3 in solution must be similar to that of 2, as they both contain two centers that share similar coordination environments. The synthesis for the two squares is similar to that of 2, with the exception of a change in the outer vial solvent, as mentioned above. The mechanism of formation for 3 remains under investigation.
4 [Cu(4,7-Phen)$_2$(MeCN)$_{75}$] • 4[BF$_4$] • 4,7-Phen • Nitrobenzene • Diethyl Ether

[Cu(MeCN)$_4$]BF$_4$ (31.5 mg, 0.10 mmol) was placed in a small test tube and dissolved by adding 0.5 ml MeCN and 3 mL of nitrobenzene. Then 4,7-phenanathroline (171.8 mg, 0.95 mmol) was added to the solution and dissolved. Using a pipette, 5 mL of diethyl ether was carefully added as to form a separate layer on top of the solution. A stopper was placed on the test tube and wrapped over with plastic to seal the system. After a week dark yellow crystals can be harvested from the inner vial.

By my naming scheme 4 is called the 4:3 square ladder, since it has four 4,7-phenathroline molecules that are not involved in forming the square itself, rather they connect each square to another. Attached to the copper centers are also three acetonitriles around the outside of the square.

The other three structures we had discussed have all been isolated species, with each square interacting with another only through π interactions. 4 is composed of repeating square units covalently linked together. Each chain, referred to here as ladder, is independent from each other, only interacting with neighboring chains through the π interactions of the connecting 4,7-phenantronlines, similar to the arrangement of 3.

With most of the structures discussed the SVD method of crystallization was used, but 4 is the exception. Rather than setting up two separate solvent systems, in this case the materials are dissolved in a nitrobenzene/MeCN mixture contained in a test tube. Then using a pipette the diethyl ether is slowly added into the test tube in such a way that the two systems do not mix. Instead two separate layers that are in contact with each other.(Figure 2.23)
Since the synthesis of the 4 is very similar to the synthesis of the 2, so it is not much a surprise that it is possible for both of these crystals to exist in the same vial. In a synthesis where the ether is allowed to enter the inner vial through vapor diffusion, 2 appear to predominate. When the ether is layered on top of the MeCN and nitrobenzene mixture 4 is more commonly found.

From Figure 2.25 we can see that the squares that make up the ladder have four crystallographically distinct copper centers. There are three tetrahedrally coordinated copper centers and one distorted trigonal planer center. Each copper is connected to two other copper centers through two 4,7-phenanthroline ligands. This gives each corner a different angle, with two being larger than we would expect from a square (Cu4-Cu1-Cu2 at 99.00, Cu2-Cu3-Cu4 at 99.43), and two centers that are narrower (Cu3-Cu4-Cu1 at 81.22, Cu1-Cu2-Cu3 at 79.22). These angles are very similar to those found in both 2 and 3, though both of these centers contain two tetrahedral centers and two trigonal centers while 4 had one trigonal center and three tetrahedral centers.
Figure 2.24: 4 with atoms shown as thermal ellipsoids and relevant crystal data. * R = \( \frac{\Sigma ||F_o|-|F_c||}{\Sigma |F_o|}\)  ** R = \( \{\Sigma (||F_o|-|F_c||)^2/\Sigma |F_o|^2}\}^{1/2} \)
<table>
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Figure 2.25: Bond lengths and angles of 4, with bond lengths in angstroms and angles in degrees.
The tetrahedral centers are of Cu1, Cu2, and Cu4 are each connected to two ligands that bond to additional centers that form the square, one 4,7-phenanthroline that connects to another Cu that forms the corner for a neighboring square, and one MeCN. These Cu have relatively similar \(N_{\text{phen}}-\text{Cu}-N_{\text{phen}}\) bonding angles with the corners that form the square having angles that are larger than the 109.5 degrees we would expect from a tetrahedral center, with the angles all being larger than 120 degrees. The \(N_{\text{MeCN}}-\text{Cu}-N_{\text{phen}}\) angles being pushed narrower than we would expect, with the exception of N4-Cu2-N6 which has an angle of 113.56 degrees.

The three coordinate copper center, Cu3, is bonded to three 4,7-phenanthrolines, two of which connect to other centers to form the familiar square. The other ligand connects to a tetrahedral center of a neighboring square. The \(N_{\text{phen}}-\text{Cu}-N_{\text{phen}}\) angle between the ligands that form the square 140.53, much larger than the 120 degrees that trigonal compounds normally obtain. This severely distorts the N11-Cu3-13 angle to 97.89 degrees, the narrowest angle we have seen on a trigonal copper center.

This arrangement of ligands around the copper centers forces the nitrogen atoms on the 4,7-phenanthroline ligands that do not form the square closer together, giving a N-N distance of 11.084 Å. This is closer than the N-N distance we see on the terminal 4,7-phenanthroline molecules in 3, which have a N-N distance of 12.831 Å. (Figure 2.26) This reduction in the distance is apparently enough for squares of 4 to link together to form an infinite chain, while units of 3 exist as individual squares.
Figure 2.26: A: Distance between nitrogen’s on 4 is 11.084 Å. B: Distance between nitrogen’s on 3 is 12.831 Å

Figure 2.27: One square unit of 4 with anions and nitrobenzenes shown in space fill.

As with the previous square structures, the square units that form the ladder have alternating edges that point towards the viewer and away from the viewer, seen from the perspective of Figure 2.27. Also included in this structure are two nitrobenzene molecules that sit off to the side of the square at a distance of about 3.5 Å which is
consistent with \(\pi-\pi\) stacking we have seen in previous examples. The BF\(_4^-\) ions sit around 5 Å away from the copper centers, with the closest Cu-F distance being 4.8 Å.

**Figure 2.28:** Two possible units of 4:3 square ladder.

Depending on the way the structure is viewed, the 4:3 square ladder could conceivably consist of two separate square building blocks, shown in Figure 2.28. The structure on the left, which is similar to the other squares mentioned above, has edges formed by 4,7-phenanthroline molecules alternately pointing up and down, roughly 180 degrees from each other. The smaller square, on the right, has 4,7-phenanthroline molecules that sit at 90 degree angles from another. Since all of the other structures we have described have had the 180 degree configuration, and thus look similar to the structure on the left, I will describe the units that form the ladder in this way.

These cavities are filled in a way that is reminiscent of 3. One side of the cavity formed by the edge forming 4,7-phenanthroline molecules a nitrobenzene molecule sits filling the void (bottom portion of Figure 2.29). On the other side, again very similar to 3, a lone non-bonding 4,7-phenanthroline positioned so that the nitrogen’s are aligned in such a way as that they are unable to bond to a copper center (top of Figure 2.29).
With these two molecules filling these cavities it is not possible for another unit of 4 to penetrate the square and stack with the square. This again is similar to structure 3 where the squares interacted with their neighbors through π-π stacking of the terminal ligands, with a similar plane distance of roughly 3.5 Å.

Unlike the 2:4 square and the 4:2 square there are no terminal 4,7-phenanthroline ligands extending from any copper center. Each 4,7-phenanthroline is connected to a copper center giving rise to the chain or “ladder” structure. We can see from Figure 2.30 that each of the three squares is covalently bonded to its neighbor.
Each ladder of squares engages in $\pi-\pi$ stacking through the 4,7-phenanthroline molecules that connect each square unit together. This occurs for each side of the ladder, linking each ladder to two others through $\pi-\pi$ interactions, with the distances between the terminal ligands being about 3.6 Å. This is shown in Figure 2.31, with two sets of ladders stacking.

Figure 2.30: Three square units bonded together to form ladder (shown in stick view) with nitrobenzenes and 4,7-phenanthrolines shown in space fill.

Figure 2.31: Two ladders of 4 shown stacking through 4,7-phenathroline molecules.
As 4 is an extended network, as opposed to an isolated species as the other three structures. This gives would set the formation of 4 apart from the other structures as it is still a question as to whether each square is formed first and then connects to another, or whether a square forms and then each additional copper center is added on stepwise. The formation of 4 is of interest and under investigation.
3. Concluding Remarks

We have seen four discrete square structures made from the same starting materials with slight variations in the synthesis set up. By comparing 1 to 2 and 4 we can see that by increasing the amount of 4,7-phenanthroline we have noted an increase in the number of these ligands included in the structure. This results in a change in the coordination geometry of some of the centers, and a distortion of the shape of the molecule. When the amounts of the starting materials are held constant, but a different solvent is introduced to the system or is introduced in a different manner, as is the case of 2, 3, and 4, structures with different arrangements can be obtained.

The author believes that there are many possibilities for future work with these structures. The mechanisms of formation for each and any of the squares remains in the hypothesis stage, and a greater understanding of how the squares form would lend itself to the possible rational design of related structures. As mentioned in the introduction many supramolecular species are being looked at for their use in solvent and ion exchange. By running thermogravimetric analysis on the structures we can gain a better understanding of the interactions of the molecules that fill the cavities of the squares, and how they could be replaced. In addition, by using a mixing additional ligands in the synthesis that are similar to the ones we use we can further probe the selectivity of the formation of the squares.
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Vita

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