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Beta-diketone and beta-ketoenamine based molecular squares

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BETA-DIKETONE AND BETA-KETOENAMINE BASED MOLECULAR SQUARES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

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Abstract

This dissertation focuses on synthesis of β-diketone and β-ketoenamine ligands for molecular polygons. Previous work with the bis(β-diketone) $m$-pbaH$_2$ showed that it can be converted to a copper molecular square, Cu$_4$(m-pba)$_4$, but its use in host-guest reactions was limited by its low solubility in most organic solvents. Accordingly, in the present work, the $m$-pbhxH$_2$ ligand, with pentyl chains replacing the methyl groups in the β-diketone moieties of $m$-pbaH$_2$, was successfully prepared beginning with 6-dodecyn. This ligand reacts with Cu$^{2+}$ to make the molecular square Cu$_4$(m-pbhx)$_4$, which is soluble in a wider range of solvents. Host-guest reactions of Cu$_4$(m-pbhx)$_4$ with a variety of guest molecules were studied. The structures of the “empty” square, [Cu$_4$(m-pbhx)$_4$(CH$_3$OH)$_2$], and its adducts with several guest molecules, were determined by single crystal X-ray analysis. In these host-guest adducts, the Cu---Cu distances range from 13.7-15.1 Å.

As part of a study of the effects of substituents on the properties of the resulting molecular squares, the 2-MeO-$m$-pbaH$_2$ ligand had been prepared previously. This dissertation reports an improved synthesis of 2-MeO-$m$-pbaH$_2$, and its larger homolog 2-MeO-$m$-pbprH$_2$ was synthesized as well. Treatment of 2-MeO-$m$-pbprH$_2$ with Cu$^{2+}$ afforded a molecular square that is soluble in chloroform and dichloromethane. Treatment of the square with guest molecules did not yield adducts, most likely because of steric interference from the internal methoxy groups.

The two ligands $m$-pbaH$_2$ and $m$-pbprH$_2$ were converted to their ketoenamine analogs $m$-pbiH$_2$ and $m$-pbpriH$_2$ through microwave-assisted synthesis. The molecular squares Cu$_4$(m-pbi)$_4$,
Cu₄(m-pbpri)₄, and Ni₄(m-pbpri)₄ were prepared from these ligands and characterized by single crystal X-ray analysis, UV-Vis spectroscopy, and cyclic voltammetry.

Two new bis(β-diketone) ligands based on triphenylamine were prepared for the first time. The new ligands were designed to make Cu(II) molecular squares that are larger (Cu---Cu ca. 21 Å) than Cu₄(m-pba)₄ and its derivatives.
Chapter 1: Introduction - Porous Metal-Organic Materials

Porous materials have continued to attract attention from researchers because of their potential applications in areas such as gas storage,\textsuperscript{1-3} catalysis,\textsuperscript{4-7} and separations.\textsuperscript{8-10} Different types of porous materials are known, including carbon nanotubes, zeolites, activated carbon, and metal-organic materials. This chapter will concentrate on supramolecular metal-organic molecules; molecules prepared by combining multidentate organic linkers with metal ions. There are three common kinds of metal-organic molecules: metal-organic frameworks (MOFs) (Figure 1.1), metal-organic polygons (metallacycles) (see Figure 1.4), and metal-organic polyhedra (MOPs) (see Figure 1.5).

\textbf{Figure 1.1} Structure of a portion of a metal-organic framework (MOF).\textsuperscript{11} This material is composed of metalloporphyrin units (one highlighted in green box) linked by dicobalt carboxylate bridging groups (one highlighted in blue box) in a 2-dimensional square grid.
MOFs are sometimes referred to as porous coordination polymers (PCPs) or 2- or 3-dimensional infinite structures. A portion of a 2-D MOF structure is shown in Figure 1.1. This structure contains dimetal carboxylate bridging groups commonly known as paddle-wheel units, $\text{M}_2(\text{COO})_4$ (M = Zn, Co) (see Figure 1.2) linked to metalloporphyrin units M(TCPP) (see Figure 1.3) resulting in a 2-D square grid network.\(^\text{11}\)

![Image of MOF structure](image)

**Figure 1.2** A Cu$_2$(O$_2$CPh)$_4$ paddle wheel-unit. Hydrogen atoms omitted for clarity.

A variety of multidentate organic linkers have been utilized in the preparation of MOFs; the most common are polycarboxylic acids such as 1,4-benzenedicarboxylic acid (BDC), 1,3,5-benzenetricarboxylic acid (BTC), and M(TCPP) (see Figure 1.3). Many 3-D MOF compounds from polycarboxylic acids\(^\text{12-14}\) and other organic linkers\(^\text{15-17}\) are known. One unique property of MOF compounds is that they have large surface areas, some exceeding 4000 m$^2$ g$^{-1}$,\(^\text{18,19}\); in comparison the highest value reported for activated carbon is 2030 m$^2$ g$^{-1}$,\(^\text{20}\) and for zeolites is 904 m$^2$ g$^{-1}$.\(^\text{21}\) As a result, metal-organic frameworks are being investigated for applications in gas storage,\(^\text{2}\) among other potential applications.
Figure 1.3 Polycarboxylic acid linkers for making MOFs.

Metal-organic polygons (metallacycles) constitute the second class of metal-organic molecules. These are discrete 2-dimensional assemblies and are represented by the molecular square in Figure 1.4. This molecular square\(^{22}\) was reported in 1990 by the Fujita group. The square was made by reaction between 4,4’-bipyridine and (en)Pd(NO\(_3\))\(_2\) (en = ethylenediamine) (Figure 1.4). The palladium centers were capped by ethylenediamine and the resulting (en)(Pd)\(^{2+}\) units after removal of nitrate groups provide the 90° “corners” of the square. Thus the corners of the square are the metal ions and the linkers are the edges. The square has an overall charge of +8 since 4,4’-bpy and ethylenediamine are neutral; this charge is balanced by the nitrate ions from the starting material. Because of the large positive charge, the square is soluble in polar solvents such as water. This square encapsulates small organic molecules such as 1,3,5-trimethoxybenzene.
Metal-organic polygons have been prepared from both linear and bent organic linkers. Stang and Olenyuk have developed a general molecular architecture library which can be used to predict the polygon that can be formed based on the geometry of the linker and the chosen metal ion.

Sometimes, the product obtained is not what is predicted on the basis of the geometry of the metal ions and linkers.

Metal-organic polyhedra (MOPs) are the third class of metal-organic molecules and they are discrete 3-D structures and the molecular octahedron in Figure 1.5 is a representative of this class of molecules. This structure was reported by the Fujita group in 1995 and was synthesized by treating the tripyridyltriazine organic linker (Figure 1.6a) with (en)Pd(NO₃)₂. The six vertices of the octahedron are occupied by palladium atoms that are capped by ethylenediamine. Reactions between carefully designed linkers with chosen metal ions have led to the realization of MOPs such as cubes, tetrahedra, octahedra, and others. Most of the organic linkers are pyridine-based although other linkers such as carboxylates and catecholates have been used as well (Figure 1.6). MOP molecules have potential applications in catalysis.

**Figure 1.4** Synthesis of the molecular square²² from (en)Pd(NO₃)₂ and bpy.
Figure 1.5 The molecular octahedron prepared by the Fujita group.\textsuperscript{24} Hydrogen atoms omitted.

![Molecular Octahedron](image)

**Figure 1.5** The molecular octahedron prepared by the Fujita group.\textsuperscript{24} Hydrogen atoms omitted.

![Organic Linkers](image)

**Figure 1.6** Organic linkers that have been used to prepare MOP molecules.
It is important to note that of all the molecular polygons known, molecular squares are the most common and have been studied most extensively. Similar to other molecular polygons, molecular squares are prepared from both linear and bent bidentate linkers; linear linkers as usual require corner capping strategy at the metal center. Also most of the squares are prepared from pyridine-based or nitrogen containing donors. Sometimes molecular squares exist in equilibrium with molecular triangles such as the square in Figure 1.7 and the molecular triangle in Figure 1.8.\textsuperscript{38}

Although most of the molecular squares are based on square planar metal centers to provide the 90° corners, octahedral metal centers have also been employed. In 1996, Hupp and co-workers reported molecular squares synthesized from pyridine derivatives such as pyrazine, 4,4’-bipyridine and 1,2-bis(4-pyridyl)ethylene and octahedral rhenium centers. Figure 1.9 shows the formation of one of the squares.\textsuperscript{39} The rhenium corner was generated from Re(CO)\textsubscript{5}Cl when two of its carbonyl ligands are displaced by the linker during its coordination to the metal.

\textbf{Figure 1.7} Molecular square prepared by the Mizuno group.\textsuperscript{38}
The coordination chemistry of β-diketone and β-ketoenamine ligands (Figure 1.10) has been studied extensively. They are chelating ligands and readily form stable mononuclear complexes. To generate molecular polygons from these ligands, multidentate β-diketones and β-ketoenamines are required.
Figure 1.10 Structures of: (a) β-diketone and (b) β-ketoenamine ligands.

Because of the chelating nature of these ligands, molecular polygons derived from them may be robust. Fewer molecular polygons have been reported from β-diketone and β-ketoenamine linkers than from pyridine-based linkers. Early reports on metal-organic polygons constructed from bis(β-diketones) and bis(β-ketoenamines) were dimers, $M_2(\text{m-XBA})_2$ and $M_2(\text{BBI})_2$ (Figures 1.11 and 1.12).40,41

Figure 1.11 Reaction of $\text{m-XBAH}_2$ with Cu$^{2+}$ afforded a molecular dimer, Cu$_2(\text{m-XBA})_2$.40

Figure 1.12 Reaction of BBIH$_2$ with Cu$^{2+}$, Ni$^{2+}$, or Pd$^{2+}$ yielded molecular dimers, $M_2(\text{BBI})_2$.41

An attempt to prepare a MOP using a different bis(β-diketone) ligand, o-phenylenebis(acetylacetone) ($o$-pbaH$_2$) (Figure 1.13), by reaction with Cu$^{2+}$, afforded a
molecular dimer instead of the expected molecular triangle. This dimer exhibits a wide range of colors in the solid state.\textsuperscript{42}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure13.png}
\caption{\textit{o}-Phenylenebis(acetylacetone), \textit{o}-pbaH\textsubscript{2}.}
\end{figure}

A molecular triangle in Figure 1.14 synthesized from the 1,1′-(1,4-phenylene)bis(butane-1,3-dione) ligand (Figure 1.15a) and Cu\textsuperscript{2+} was reported by Clegg et al.\textsuperscript{29} The first molecular square to incorporate β-diketone building block was reported by Zhang et al in 1998 (Figure 1.16),\textsuperscript{43} and it was prepared by using tetraacetylene (taeH\textsubscript{2}) (Figure 1.15b) and an octahedral Co(II) corner that was capped with di-2-pyridylamine (Figure 1.15c).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure14.png}
\caption{The β-diketonate molecular triangle prepared by Clegg et al.\textsuperscript{29}}
\end{figure}
Figure 1.15 Structures of: (a) 1,1′-(1,4′-phenylene)bis(butane-1,3-dione), (b) tetraacetylene (taeH₂) and (c) di-2-pyridylamine (dpa).

Figure 1.16 Molecular square prepared from Co²⁺, tae⁻²⁻, and dpa by Zhang et al.⁴³

To date, there are no reports on molecular polygons larger than molecular squares that are derived from β-diketones. We have been interested in porous discrete metal-organic polygons based on multidentate β-diketones.

Here for the first time we report molecular squares based on β-ketoenamine ligands. There are advantages of using β-diketone and β-ketoenamine ligands as building blocks for these molecules. The first one is that their reaction with some metal ions affords complexes with coordinatively unsaturated metal sites. This unsaturation provides room for guest molecules to
bind directly to the metal centers. The adducts formed by the reaction of the copper dimer \( \text{Cu}_2(\text{NBA})_2 \) with molecules such as pyrazine and Dabco were early demonstrations of this phenomenon (see Figure 1.17).\(^{44}\) The ability of the metal centers to bind guest molecules opens pathways for the applications of these molecules in catalysis,\(^{45,46}\) separations,\(^{47}\) host-guest chemistry,\(^{44}\) and gas storage.\(^{2,48}\)

![Figure 1.17 Molecular dimer-pyrazine adduct, [Cu$_2$(NBA)$_2$(µ-Pz)].\(^{44}\)](image)

The second advantage is that nickel(II) and palladium(II) complexes of \( \beta \)-ketoenamine ligands are diamagnetic which enables them to be studied by NMR.\(^{41,49}\)

Recently our group reported molecular squares prepared from \( \text{Cu}^{2+} \) and the bis(\( \beta \)-diketone) ligands 1 (\( m \)-phenylenebis(acetylacetone)), \( m \)-pbaH$_2$, and 2 (\( m \)-phenylenebis(dipropionyl-methane)), \( m \)-pbprH$_2$ (Figure 1.18).\(^{50}\) This square is different from the previous squares in two ways: (1) the ligands occupy the corners and the metals form the edges; and (2) the Cu metal centers are not protected and are coordinatively unsaturated, which means they can interact with guest molecules. The new squares bind 4,4’-bipyridine and \( \text{C}_6\text{H}_{60} \),\(^{50}\) 4,4’-bipyridine is coordinated through its N atoms, while \( \text{C}_6\text{H}_{60} \) is held through \( \pi-\pi \) interactions. Unfortunately, the squares are soluble only in a limited number of solvents. This limitation
prevents their use in various applications. In addition, a binding constant for the Cu square and C_{60} could not be determined because they are not soluble in the same solvents.

Figure 1.18 Reactions of bis(β-diketone) ligands 1 and 2 with Cu^{2+} afforded molecular squares.

This dissertation reports on the following topics: Syntheses of new derivatives of m-pbaH_2 (1): In chapter 2, the synthesis of the m-pbhxH_2 ligand, with pentyl chains replacing the methyl groups in the β-diketone moieties of m-pbaH_2, and the preparation of its molecular square, are described. In chapter 3 syntheses of two new ligands, 2-MeO-m-pbaH_2 and 2-MeO-m-pbprH_2 (in which a methoxy group is placed in the 2-position of the aromatic ring of m-pbaH_2), and their molecular squares are described. Chapter 4 describes the conversion of bis(β-diketones) 1 and 2 to bis(β-ketoenamines). The bis(β-ketoenamines) were treated with Cu^{2+} and Ni^{2+} which afforded molecular squares. The molecular squares have been studied by UV-VIS and by electrochemistry, and the nickel square has been studied by NMR. In an attempt to
prepare molecular squares with larger pore sizes, triphenylamine-based new bis(β-diketones) (Figure 1.19) were prepared and treated with Cu$^{2+}$. Chapter 5 discusses syntheses of these new bis(β-diketones) and their Cu$^{2+}$ complexes.

![Triphenylamine-based bis(β-diketones)](image)

**Figure 1.19** Triphenylamine-based bis(β-diketones).

### 1.1 References


(21) Chester, A. W.; Clement, P.; Han, S. US Patent 6136291A.


Chapter 2: Synthesis of a Long-Chain Bis(β-Diketone) for a More Soluble Molecular Square

2.1 Introduction

The ligands \( m \)-phenylenebis(acetylacetone), \( m \)-pba\( \text{H}_2 \) (1) and \( m \)-phenylenebis(dipropionyl-methane), \( m \)-pbpr\( \text{H}_2 \) (2) yield molecular squares with formula \( \text{Cu}_4\text{L}_4 \) (\( \text{LH}_2 = m \)-pba\( \text{H}_2 \) or \( m \)-pbpr\( \text{H}_2 \)) when treated with \( \text{Cu}^{2+} \) ions (Figure 2.1). The squares were shown to form adducts with guest molecules such as 4,4’-bipyridine and \( \text{C}_6\text{H}_{60} \).溶 Density of the two squares is limited to a small number of solvents: \( \text{Cu}_4(\text{m-pba})_4 \) (3) is only soluble in chloroform and dichloromethane, and solubility of \( \text{Cu}_4(\text{m-pbpr})_4 \) (4) is only slightly better.

\[ \text{R} = \text{CH}_3, \text{m-pba}\text{H}_2 \ (1) \]
\[ \text{R} = \text{C}_2\text{H}_5, \text{m-pbpr}\text{H}_2 \ (2) \]

**Figure 2.1** Bis(β-diketones), \( m \)-pba\( \text{H}_2 \) (1) and \( m \)-pbpr\( \text{H}_2 \) (2) react with \( \text{Cu}^{2+} \) to yield molecular squares.

This chapter reports the preparation of a bis(β-diketone) with longer alkyl groups, \( m \)-pbhx\( \text{H}_2 \) (\( m \)-phenylenebis(dihexanoylmethane), 5), as shown in Figure 2.2. I expected its copper
square, Cu₄(m-pbx)₄, to be soluble in a wider range of solvents. The more soluble molecular square will enable us to study its reactions with a variety of guest molecules.

![Chemical Structure](image)

*m-pbxH₂ (5)*

**Figure 2.2** *m*-phenylenebis(dihexanoylmethane), *m*-pbhxH₂ ligand 5.

The procedure for making 1 and 2 is well established and is achieved in two steps. First, a commercially available α-diketone (butane-2,3-dione (6) or hexane-3,4-dione (7)) is treated with trimethyl phosphite, which affords 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene²,³ (8) or 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (9)¹ respectively; both are commonly referred to as phospholenes. Then treatment of isophthalaldehyde (10) with the phospholene yields *m*-pbaH₂ (1) or *m*-pbprH₂ (2) (scheme 2.1).

To make the new ligand *m*-pbhxH₂ (5) by this method, the α-diketone dodecane-6,7-dione (12) was required as the starting material (see scheme 2.2). Then the two steps shown in scheme 2.1 above were followed: treating dodecane-6,7-dione with trimethyl phosphite to generate the phospholene 2,2,2-trimethoxy-4,5-dipentyl-1,3,2-dioxaphospholene (13), followed by treatment with isophthalaldehyde to yield the desired product. Since the starting material (dodecane-6,7-dione) is not commercially available, I had to prepare it by oxidation of 6-dodecyne (11).
Scheme 2.1 Synthesis of bis(β-diketones) 1 and 2 beginning with α-diketones.

2.2 Results and Discussion

β-Diketones are normally viewed as good ligands, binding readily to many metal ions. However, β-diketones with bulky substituents in the 1, 3, and 5 positions do not always form complexes easily. For example, referring to the illustration in Figure 2.3, ligands such as \(m\)-xbaH\(_2\) with CH\(_3\),ArCH\(_2\),CH\(_3\) substituents in the 1, 3, and 5 positions, and ligands such as \(m\)-pbH\(_2\) and \(m\)-pbprH\(_2\) with CH\(_3\),Ar,CH\(_3\) or Et,Ar,Et substituents (see Figure 2.1), form complexes easily. In addition, β-diketones with bulky substituents in the 1 and 5 positions and no substituents in the 3-positions also react with metal ions. Those ligands include dipivaloylmethane (dpmH, t-Bu,H,t-Bu) and dibenzoylmethane (dbmH, Ph,H,Ph). However, β-
diketones with bulky substituents in the 1 and 5 positions and a substituent in the 3-positions are much less likely to form metal complexes, due to steric interference between the substituents. This was observed in ligands such as $m$-xbpH$_2$ (t-Bu,ArCH$_2$-t-Bu) and $m$-xbdH$_2$ (Ph,ArCH$_2$-Ph).

![Chemical structures]

Figure 2.3 β-diketones: (a-c) generate metal complexes, (d) do not generate metal complexes.

Therefore, if we wished to increase the solubility of our molecular squares by modifying the 1 and 5 substituents in our $m$-pbaH$_2$ ligand, we could not use bulky groups like i-Pr, t-Bu, or Ph. This is because such substituent patterns (e.g. t-Bu,Ar,t-Bu) would have been highly hindered and unlikely to make metal complexes. Hence, we focused on linear alkyl groups in the 1 and 5 positions.

To choose a specific linear alkyl group, we noted that the solubility of Cu$_4$(m-pba)$_4$ ($R = CH_3$) and Cu$_4$(m-pbpr)$_4$ ($R = CH_2CH_3$) is similar. Thus, if we wished to change the solubility substantially, a significantly longer R group would probably be necessary. For this reason, we chose $R =$ pentyl (CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$) for our experiments.
Dodecane-6,7-dione (12) has been reported, and is prepared via the Grignard route;\textsuperscript{4} I tried to repeat this but found the method to be problematic. Instead, I found the NaIO\textsubscript{4} method\textsuperscript{5} and used it successfully. Briefly, treatment of 6-dodecyne (11) with NaIO\textsubscript{4} and a catalytic amount of RuO\textsubscript{2}·H\textsubscript{2}O in CCl\textsubscript{4}/CH\textsubscript{3}CN/H\textsubscript{2}O solvent mixture in 1:1:1.5 ratios yielded dodecane-6,7-dione (12) as a yellow solid (60%). \textsuperscript{1}H NMR and GC/MS of the product match those reported for the authentic compound.\textsuperscript{4} The yield (60\%) is slightly higher than that reported in the literature.\textsuperscript{4} Treatment of dodecane-6,7-dione with trimethyl phosphite afforded the desired phospholene, 2,2,2-trimethoxy-4,5-dipentyl-1,3,2-dioxaphospholene (13), which reacted with isophthalaldehyde to yield \textit{m}-pbhxH\textsubscript{2} (5), as a colorless oil after column chromatography. Synthesis of 5 starting with the oxidation of 6-dodecyne is summarized in scheme 2.2.

\textbf{Scheme 2.2} Synthesis of 5 starting with oxidation of 6-dodecyne.
When 5 was treated with Cu$^{2+}$, molecular square 14 (Figure 2.4) was isolated as a dark green solid (97%).

![Chemical structure of m-pbhxH$_2$ (5)](image)

\[ \text{m-pbhxH}_2 \rightarrow \text{[Cu(NH}_3)_4]^{2+} \rightarrow \text{[Cu}_4 \text{(m-pbhx)$_4$} \] \( R = \text{C}_5\text{H}_{11}, \text{[Cu}_4 \text{(m-pbhx)$_4$} \)

**Figure 2.4** Reaction of m-pbhxH$_2$ ligand (5) with Cu$^{2+}$ affords molecular square 14.

After obtaining square 14, the next step was to test its solubility in various solvents, in comparison with the solubility of molecular squares 3 and 4, and the results are summarized in table 2.1. The new square 14 is soluble in nine organic solvents. The increase in solubility of square 14 is attributed to the presence of the pentyl chains attached to the β-diketone moieties of 5. All three squares are insoluble in polar solvents such as methanol, acetonitrile and DMF. Other groups have used functional substituents such as alkoxy (OR, R = alkyl),$^6,^7$ and polyethyleneglycol (PEG),$^8$ in the ligands to enhance solubility of the resulting macrocycles. Macrocycles containing these substituents are often soluble in polar solvents such as water.

Crystals of the new square Cu$_4$(m-pbhx)$_4$ suitable for X-ray diffraction were grown by layering its chloroform solution with methanol. Single crystal X-ray analysis revealed the square,
where two methanol are coordinated to two copper atoms and the remaining two copper atoms are uncoordinated, with the molecular formula \([\text{Cu}_4(m\text{-pbhx})_4(\text{CH}_3\text{OH})_2]\cdot 12\text{CHCl}_3\) (see Figure 2.5). For comparison, the crystal structure of square 4 is shown in Figure 2.6.

**Table 2.1** Solubility of molecular squares 3, 4 and 14 in various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Square 3 [Cu₄(m-pba)₄]</th>
<th>Square 4 [Cu₄(m-pbpr)₄]</th>
<th>square 14 [Cu₄(m-pbhx)₄]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Toluene</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>o-dichlorobenzene</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Benzene</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Methanol</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>DMF</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>
Figure 2.5 Crystal structure of the molecular square $[\text{Cu}_4(m\text{-pbhx})_4(\text{CH}_3\text{OH})_2]$ (14). Hydrogen atoms and solvent molecules have been removed for clarity.

Figure 2.6 Crystal structure of $[\text{Cu}_4(m\text{-pbpr})_4]$ (4).
Cu---Cu distances in squares 4 and 14 are shown in table 2.2.

Table 2.2 Cu---Cu distances in squares 4 and 14.

<table>
<thead>
<tr>
<th>Molecular square</th>
<th>Cu1---Cu1’ (Å)</th>
<th>Cu2---Cu2’(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>14.012</td>
<td>14.661</td>
</tr>
<tr>
<td>14</td>
<td>14.047</td>
<td>14.904</td>
</tr>
</tbody>
</table>

The crystal structure of 14 shows that the pentyl groups of the β-diketones coordinated to Cu1 and Cu1’ are bent inwards towards the cavity of the square, while those from groups coordinated to Cu2 and Cu2’ are bent away from the cavity. This probably is due to steric interaction between these groups. The Cu2---Cu2’ distance is slightly longer (14.90 Å) than in Cu1---Cu1’ (14.05 Å) due to the slight distortion at Cu2 and Cu2’ centers resulting from coordination of methanol leading to square pyramidal geometry at these centers.

2.3 Host-Guest Reactions of Square 14

Square 14 was treated with a large variety of guest molecules (see table 2.3) and the observations made can be classified into three categories: 1) In the first case, green precipitates formed which were suspected to be the unreacted square 14. These were not analyzed but were collected and used for other experiments. (2) In other cases the solutions changed color, but no product precipitated. (3) In the third case crystals formed that were analyzed by single crystal X-ray. The guests chosen were in two categories: Those that were expected to bind directly to the Cu atoms include 1,2-bis(4-pyridyl)ethylene (bpe) and polyoxometalate, $W_6O_{19}^{2-}$. The $W_6O_{19}^{2-}$ was expected to bind to the coordinatively unsaturated Cu(II) centers via the four equatorial oxygen atoms. Other guest molecules such as anthracene might bind in a π fashion.
Table 2.3 Host-guest experiments with square 14

<table>
<thead>
<tr>
<th>#</th>
<th>Complex solvent</th>
<th>Other solvent</th>
<th>Guest</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHCl₃</td>
<td>CH₃CN</td>
<td>bpe</td>
<td>Blue crystals formed after 10 days</td>
</tr>
<tr>
<td>2</td>
<td>CHCl₃</td>
<td>CH₃CH₂CN</td>
<td>bpe</td>
<td>Blue crystals formed</td>
</tr>
<tr>
<td>3</td>
<td>CHCl₃</td>
<td>CH₃CN</td>
<td>4,4’-bpy</td>
<td>Green crystals formed</td>
</tr>
<tr>
<td>4</td>
<td>CS₂</td>
<td>cyclohexane</td>
<td>anthracene</td>
<td>blue-green crystals formed</td>
</tr>
<tr>
<td>5</td>
<td>CH₂Cl₂</td>
<td>Hexanes</td>
<td>Anthracene</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>6</td>
<td>Toluene</td>
<td>Ethyl acetate</td>
<td>Anthracene</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>7</td>
<td>C₆H₅Cl</td>
<td>cyclohexane</td>
<td>Anthracene</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>8</td>
<td>C₆H₅Br</td>
<td>Ethyl acetate</td>
<td>Anthracene</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>9</td>
<td>CHCl₃</td>
<td>CH₃CN</td>
<td>2,7-dihydroxynaphthalene</td>
<td>Dark-blue solution which turned brown and deposited brown powder</td>
</tr>
<tr>
<td>10</td>
<td>CHCl₃</td>
<td>CH₃COCH₃</td>
<td>2,7-dihydroxynaphthalene</td>
<td>Same observation as 8</td>
</tr>
<tr>
<td>11</td>
<td>Toluene</td>
<td>CH₃CN</td>
<td>2,7-dihydroxynaphthalene</td>
<td>Same observation as 8</td>
</tr>
<tr>
<td>12</td>
<td>THF</td>
<td>CH₃CN</td>
<td>2,7-dihydroxynaphthalene</td>
<td>Same observation as 8</td>
</tr>
<tr>
<td>13</td>
<td>Toluene</td>
<td>MeOH</td>
<td>2-naphthol</td>
<td>Same observation as 9</td>
</tr>
<tr>
<td></td>
<td>Compound 1</td>
<td>Compound 2</td>
<td>Compound 3</td>
<td>Observation</td>
</tr>
<tr>
<td>---</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>14</td>
<td>CHCl$_3$</td>
<td>MeOH</td>
<td>2-naphthol</td>
<td>Same observation as 9</td>
</tr>
<tr>
<td>15</td>
<td>C$_6$H$_5$Cl</td>
<td>MeOH</td>
<td>Adamantanol</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>16</td>
<td>o- C$_6$H$_4$Cl$_2$</td>
<td>CH$_3$CN</td>
<td>C$_{70}$</td>
<td>Dark brown crystals</td>
</tr>
<tr>
<td>17</td>
<td>o-C$_6$H$_4$Cl$_2$</td>
<td>CH$_3$CN</td>
<td>C$_{60}$</td>
<td>Dark brown crystals</td>
</tr>
<tr>
<td>18</td>
<td>Toluene</td>
<td>Ethyl acetate</td>
<td>1,4-dinitrobenzene</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>19</td>
<td>CHCl$_3$</td>
<td>MeOH</td>
<td>1,4-dicyanobenzene</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>20</td>
<td>Toluene</td>
<td>Ethyl acetate</td>
<td>1,3-dicyanobenzene</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>21</td>
<td>CH$_2$Cl$_2$</td>
<td>CH$_3$COCH$_3$</td>
<td>Cyclohexane-1,4-dicarbonitrile</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>22</td>
<td>C$_6$H$_5$Cl</td>
<td>CH$_3$CN</td>
<td>Adamantanemethanol</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>23</td>
<td>Toluene</td>
<td>Methylcyclohexane</td>
<td>9,10-dibromoanthracene</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>24</td>
<td>CHCl$_3$</td>
<td>Ether</td>
<td>9,10-diphenylantracene</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>25</td>
<td>THF</td>
<td>CH$_3$CN</td>
<td>W$<em>6$O$</em>{19}^{2-}$</td>
<td>Blue precipitate</td>
</tr>
<tr>
<td>26</td>
<td>CHCl$_3$</td>
<td>DMSO</td>
<td>W$<em>6$O$</em>{19}^{2-}$</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>27</td>
<td>Toluene</td>
<td>CH$_3$CN</td>
<td>W$<em>6$O$</em>{19}^{2-}$</td>
<td>Green precipitate</td>
</tr>
<tr>
<td>28</td>
<td>CHCl$_3$</td>
<td>DMF</td>
<td>W$<em>6$O$</em>{19}^{2-}$</td>
<td>Blue crystals formed</td>
</tr>
<tr>
<td>29</td>
<td>CHCl$_3$</td>
<td>MeOH</td>
<td>bpa</td>
<td>Blue crystals formed</td>
</tr>
<tr>
<td>30</td>
<td>CHCl$_3$</td>
<td>MeOH</td>
<td>Cyclohexane-1,4-dicarbonitrile</td>
<td>Blue crystals formed</td>
</tr>
</tbody>
</table>
When 14 was treated with guests such as anthracene/anthracene derivatives, adamantanol or dicyanobenzenes, green precipitates formed. When solutions of 14 in different solvents were layered with 2-naphthol or 2,7-dihydroxynaphthalene in acetonitrile or methanol (colorless solutions), the solutions (all initially dark green, except for the solution in THF, which was blue) changed to dark blue within a day, then to brown and eventually brown powder precipitated after a few days. The change in color of the solutions from dark green or blue to dark blue could indicate a strong interaction between the Cu$^{2+}$ centers of the square and the OH groups of the two guests which eventually led to the decomposition of the square as indicated by deposition of brown powder. The square is blue in THF probably because THF through its oxygen atom coordinates to the Cu$^{2+}$ centers of the square changing their coordination geometry from square planar to square pyramidal or octahedral.

Green crystals that formed between the square and 4,4’-bipyridine (Number 3) were not of good quality for X-ray study. Blue-green crystals formed between 14 in carbon disulfide and anthracene in methyl cyclohexane (number 4) but did not diffract well when analyzed by single crystal X-ray. The crystals that formed in number 28 turned out to be a copper cluster, where 12 Cu-carboxylate dimer subunits (paddle-wheel units) combined to generate a Cu$_{24}$ cluster. The carboxylates in this compound are 1,3-benzenedicarboxylate, which was likely formed by oxidative cleavage of the $m$-pbhx ligands in 14. This Cu$_{24}$ cluster has been studied previously by Zaworotko and co-workers,$^{10}$ and it was not studied further here. This may suggest that DMF may not be a good solvent for layering these experiments. Analysis of the crystals in number 30 revealed the host without the guest (see Figure 2.5).

Crystals for single crystal X-ray diffraction were obtained in the following experiments: A solution of the square 14 in chloroform (dark-green) layered with 1,2-bis(4-pyridyl)ethylene
(bpe) or 1,2-bis(4-pyridyl)ethane (bpa) in methanol afforded blue block-shaped crystals. The change in color from dark-green to blue is the usual observation for Cu(β-diketonate)₂N formation.¹¹ Single crystal X-ray analysis of the crystals confirms formation of adducts, 14-bpe and 14-bpa, (15 and 16 respectively) where one bpe or bpa ligand bridges two copper atoms in the square. The two remaining copper atoms of the square have methanol co-ordinated to them from outside (Figures 2.7 and 2.8). This is different from the previously reported adduct of square 3 with 4,4'-bipyridine (17)¹ (see Figure 2.9), in which bpy molecules were also coordinated externally. Indeed, under slightly different experimental conditions, crystals of Cu₄(m-pbhx)₄(µ-bpe) were obtained with both internally and externally coordinated bpe ligands. However, these crystals were of lower quality than those of 15, and those results are not included here.

**Figure 2.7** Crystal structure of [Cu₄(m-pbhx)₄(µ-bpe)(CH₃OH)₂] (15). H atoms and solvent molecules omitted for clarity.
Figure 2.8 Crystal structure of $[\text{Cu}_4(m\text{-pbhx})_4(\mu\text{-bpa})(\text{CH}_3\text{OH})_2]$ (16). H atoms and solvent molecules omitted for clarity.

Figure 2.9 Crystal structure of $[\text{Cu}_4(m\text{-pba})_4(4,4'\text{-bpy})_2]_n$ (17).¹ Hydrogen and solvent molecules have been omitted.
Table 2.4 X-ray crystallographic and structure refinement data for 14.solvate and 16.solvate

<table>
<thead>
<tr>
<th>compound</th>
<th>14.solvate</th>
<th>16.solvate</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical</td>
<td>C₁₂₈H₁₉₂Cu₄O₁₆</td>
<td>C₁₂₈H₁₉₂Cu₄O₁₆</td>
</tr>
<tr>
<td>formula</td>
<td>·2CH₃OH·12CHCl₃</td>
<td>·2CH₃OH·C₁₂H₁₂N₂·10CHCl₃</td>
</tr>
<tr>
<td>weight</td>
<td>3737.68</td>
<td>3682.98</td>
</tr>
<tr>
<td>crystal</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>system</td>
<td></td>
<td></td>
</tr>
<tr>
<td>space group</td>
<td>P₁</td>
<td>P₁</td>
</tr>
<tr>
<td>a, Å</td>
<td>18.9177(6)</td>
<td>15.0928(7)</td>
</tr>
<tr>
<td>b, Å</td>
<td>19.2984(6)</td>
<td>18.3346(8)</td>
</tr>
<tr>
<td>c, Å</td>
<td>28.0714(9)</td>
<td>19.5430(8)</td>
</tr>
<tr>
<td>α, deg</td>
<td>70.560(2)</td>
<td>63.868(2)</td>
</tr>
<tr>
<td>β, deg</td>
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<td>15469/983</td>
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<td>GOF</td>
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Table 2.5 Measured Cu---Cu and Cu-N distances (Å) in adducts 15, 16 and 17.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CuA---CuA</th>
<th>CuB---CuB</th>
<th>Cu-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 [Cu₄(m-pbhx)₄(µ-bpe)(CH₃OH)₂]</td>
<td>13.989</td>
<td>14.666</td>
<td>2.300</td>
</tr>
<tr>
<td>16 [Cu₄(m-pbhx)₄(µ-bpa)(CH₃OH)₂]</td>
<td>13.793</td>
<td>15.077</td>
<td>2.278</td>
</tr>
<tr>
<td>17 [Cu₄(m-pba)₄(4,4’-bpy)₂]ₙ</td>
<td>11.807</td>
<td>16.226</td>
<td>2.360, 2.363</td>
</tr>
</tbody>
</table>

The CuA---CuA distance in adduct 17 is shorter (11.81 Å) than in adducts 15 and 16 (13.99 and 13.79 Å) because 4,4’-bipyridine is shorter than bpe or bpa, so CuA and CuA atoms are distorted more in 17 than in 15 or 16 in order to coordinate to the nitrogen atoms of 4,4’-bpy leading to a shorter distance.

On the other hand, the CuB---CuB distances behave in the opposite way: adduct 17 has a longer distance (16.23 Å) than in adducts 15 and 16 (14.67 and 15.08 Å respectively) because of coordination of 4,4’-bpy to CuB atoms from outside of the square. The Cu-N distances in 15 (2.30 Å) and in 16 (2.278 Å) are shorter than the corresponding distances in 17 (2.360 and 2.363 Å) on account of the size of bpe and bpa guests which are longer, hence their nitrogen atoms are closer to the copper atoms.

Crystals formed when the square was treated with C₆₀ or C₇₀ were also analyzed by single crystal X-ray diffraction. The crystals of the square with C₇₀ did not diffract well, while a preliminary structure of the square with C₆₀ is shown in Figures 2.10 and 2.11 below.
Figure 2.10 Crystal structure of Cu$_4$(m-pbhx)$_4$·C$_{60}$. View perpendicular to that in Figure 2.10.

Figure 2.11 Crystal structure of Cu$_4$(m-pbhx)$_4$·C$_{60}$. View perpendicular to that in Figure 2.10.
2.3 Experimental

2.3.1 General Considerations

Sodium metaperiodate (NaIO₄) was purchased from Sigma-Aldrich, ruthenium(IV) oxide hydrate was purchased from Acros Organics, and 6-dodecyne was acquired from GFS Chemicals. Elemental analysis was performed by M-H-W Labs, Phoenix, Arizona. NMR spectra were recorded on Bruker (250 or 400 MHz) spectrometers with CDCl₃ as the solvent.

2.3.2 Synthesis of Dodecane-6,7-dione (12)

This molecule was made following the reported procedure for making other α-diketones.⁵ 6-Dodecyne (5.0 g, 30.0 mmol) was added to CCl₄/CH₃CN/H₂O (40 mL: 40 mL: 60 mL) and the mixture stirred for 10 minutes at room temperature. Into this mixture was added solid NaIO₄ (25.72 g, 120.0 mmol) and stirring continued vigorously at room temperature until the solid dissolved, giving two colorless phases. Then RuO₂·H₂O (0.088 g, 0.66 mmol) was added; immediately, the mixture turned black. Ten minutes later, the color of the mixture changed to dark green and a white solid precipitated out. As stirring continued, the mixture gradually changed to lighter green and finally to yellow. After 12 h, CH₂Cl₂ (50 mL) was added and the mixture was separated into two phases, and the organic phase was dried over Na₂SO₄, filtered and evaporated to yield a yellow solid. Column chromatography (hexane:ethyl acetate, 70:30 v/v), gave a yellow solid, 3.57 g (60%). ¹H NMR confirmed the identity of the product.⁴ ¹H NMR: δ 2.73 (t, 4H), 1.58 (q, 4H), 1.36-1.26 (m, 8H), 0.89 (t, 6H) (Figure A4).

2.3.3 Synthesis of 2,2,2-trimethoxy-4,5-dipentyl-1,3,2-dioxaphospholene (13)

Trimethyl phosphite (2.06 g, 16.64 mmol) was cooled to 0 °C (ice/water). Dodecane-6,7-dione (3.0 g, 15 mmol) dissolved in dry DCM (20 mL) was added dropwise from an addition
flask and the reaction mixture allowed to warm to room temperature under nitrogen; stirring was continued for 24 h. Completion of the reaction was indicated by the disappearance of the yellow color. The crude product was isolated as an oil by evaporation of solvent; its $^1$H NMR spectrum ($\delta$ 3.59 (d, 9H, OCH$_3$), 2.17 (t, 4H), 1.51 (q, 4H), 1.34-1.26 (m, 8H), 0.89 (t, 6H)) (Figure A5) indicated that it was sufficiently pure for use in the next step.

2.3.4 Synthesis of $m$-pbhxH$_2$ (5)

Isopthalaldehyde (0.60 g, 4.47 mmol) was dissolved in dry DCM (20 mL), followed by addition of 2,2,2-trimethoxy-4,5-dipentyl-1,3,2-dioxaphospholene (2.88 g, 8.94 mmol). The mixture was stirred at room temperature under nitrogen and monitored by $^1$H NMR. Reaction was judged to be complete when the isophthalaldehyde CHO peak (~10 ppm) had disappeared (ca. 12 h). Then methanol (30 mL) was added and the mixture refluxed for 3 h; solvent was removed to yield a light-brown oily product. Column chromatography (hexane-ethyl acetate, 70:30 v/v) yielded 5 as a colorless oil, 1.00 g (45%). $^1$H NMR: $\delta$ 16.81 (s, 2H), 7.42 (t, 1H), 7.14 (dd, 2H, $J = 7.59, 1.41$ Hz), 7.00 (s, 1H), 2.10 (t, 8H), 1.52 (q, 8H), 1.25-1.12 (m, 16H), 0.82 (t, 12H) (Figure A3).

2.3.5 Synthesis of Copper Molecular Square, Cu$_4$(m-pbhx)$_4$ (14)

CuSO$_4$·5H$_2$O (0.401 g, 1.6 mmol) was dissolved in 30 mL distilled water; ammonia solution was added in drops with stirring until a royal blue solution was formed. Into this solution was added a solution of $m$-pbhxH$_2$ (5) (0.8 g, 1.6 mmol) in DCM (40 mL) and stirring continued for 4 h; the olive green organic phase was dried over Na$_2$SO$_4$ and the solvent removed to yield a dark green solid, 0.87 g (97%). Anal. Calcd. for C$_{128}$H$_{192}$O$_{16}$Cu$_4$ (M = 2241.07): C 68.60, H 8.64; Found: C 68.42, H 8.51. Crystals for X-ray analysis were grown by layering
methanol on a chloroform solution. Anal. Calcd. for (Cu₄₃₆pbhx)₄·2CH₃OH, M = 2305.15: C 67.73, H 8.75; Found: C 68.00, H 8.64.

2.3.6 Synthesis of Adducts

a) 14-bpe (15): Square 14 (0.020 mg, 0.008 mmol) was dissolved in chloroform (2 mL); this was layered with 1,2-bis(4-pyridyl)ethylene (0.006 g, 0.03 mmol) in methanol (3 mL). The solution was left for 10 days at −20 °C, and blue block-shaped crystals had formed. Anal.Calcd. for (Cu₄₃₆pbhx)₄(µ-bpe)·2CH₃OH, M = 2606.75): C 65.89, H 8.16, N 1.07; Found: C 66.16, H 8.20, N 0.80. (b) 14-bpa (17): This adduct was prepared in the same procedure as in (a) above, except that 1,2-bis(4-pyridyl)ethane (bpa) was used in place of (bpe). After seven days, blue crystals formed. (c) Cu₄₃₆pbhx)₄·C₆₀ (18): square 14 (0.015 g, 0.006 mmol) and C₆₀ (0.005 g, 0.006 mmol) were dissolved in 1,2-dichlorobenzene (2 mL). This was carefully layered with acetonitrile (3 mL) and left at −20 °C. After 4 days dark brown crystals had formed. (d) Cu₄₃₆pbhx)₄·C₇₀ (19): The same procedure in (c) above was followed except that C₇₀ was used in place of C₆₀. After 7 days, dark brown crystals had formed.

2.4 References


Chapter 3: Synthesis of Internally Substituted \textit{m}-Phenylenebis(\textit{\(\beta\)}-Diketone) Ligands and Their Molecular Squares

3.1 Introduction

This chapter is part of the project that was begun by Jace Sandifer.\textsuperscript{1} In chapter 2, I showed that using longer alkyl chains in the \(\beta\)-diketone moieties of \textit{m}-pbhxH\textsubscript{2} (Figure 3.1) greatly improves the solubility of the resulting molecular square. We were further interested in functional substituents on the aromatic ring of \textit{m}-pbaH\textsubscript{2}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ligands.png}
\caption{Bis(\(\beta\)-diketone) ligands for making molecular squares.}
\end{figure}

Sandifer prepared 5-\textit{MeO}-\textit{m}-pbaH\textsubscript{2} (20) and 5-\textit{BuO}-\textit{m}-pbaH\textsubscript{2} (21) (see Figure 3.2) and their resulting molecular squares (see Figure 3.3) were found to be soluble in various solvents.\textsuperscript{1} He also did some preliminary studies on 2-\textit{MeO}-\textit{m}-pbaH\textsubscript{2} (22a) (Figure 3.2); I took up the project on 22a where I improved on the yields and purity of the precursors leading to 22a. In addition I prepared 2-\textit{MeO}-\textit{m}-pbprH\textsubscript{2} (22b) (Figure 3.2). Although molecular hexagons were expected from all of these ligands due to the 120° angle between their \(\beta\)-diketone moieties, only molecular squares have been isolated. We believe this is because distortions at the \(\beta\)-diketone moieties enable them to bend away from coplanarity with the metal centers. The squares may be kinetic products and not the thermodynamic ones.
Figure 3.2 Bis(β-diketone) ligands 20, 21, and 22 for molecular squares

![Figure 3.2 Bis(β-diketone) ligands 20, 21, and 22 for molecular squares](image)

Figure 3.3 Treatment of bis(β-diketones) 20 and 21 with Cu$^{2+}$ yields molecular squares 23 and 24.

![Figure 3.3 Treatment of bis(β-diketones) 20 and 21 with Cu$^{2+}$ yields molecular squares 23 and 24.](image)

Adding functional groups to the 2-position of the aromatic ring of the $m$-pbaH$_2$ ligand as in 22a, b is attractive because if the substituents are large enough, they may cause steric interactions which may lead to formation of a larger macrocycle such as a molecular pentagon or a molecular hexagon. Also we wanted to study the effects of changing the chemical environment inside the squares. The Fujita group has reported a coordination cage (nanoball) whose interior is
decorated with polyethylene glycol (PEG) substituents. Here the optimized synthesis of 22a, and synthesis of 22b and their copper molecular polygons are reported.

3.2 Results and Discussion

3.2.1 Syntheses of the Ligands

These were prepared from 2-methoxyisophthalaldehyde, a compound which was prepared by Sandifer through microwave assisted synthesis. He reported a yield of 77% and its color as a yellow solid. He mentioned that the compound was not clean because there were extra peaks in its $^1$H NMR spectrum which were not expected. I prepared the 2-methoxyisophthalaldehyde using the procedure developed by Bennani et al. and obtained a yield of 97%. Sandifer avoided preparing this compound using the Bennani procedure because of the toxicity of PCC, but I think that the procedure is better than the microwave one because the yield and purity of the product is high, although PCC should be handled with care.

2-MeO-$m$-pbaH$_2$ (22a) was also prepared by Sandifer, who reported it as a yellow liquid in 10% yield, but he mentioned that the compound could have been impure as indicated by the presence of ethyl acetate peaks and extra aromatic peaks in its $^1$H NMR spectrum. I isolated 22a as a white solid after column chromatography in 45% yield. Elemental analysis agrees with the calculated values. $^1$H NMR of this compound showed well resolved peaks with the right integrations, except the aromatic region where the peaks are not individually resolved. 2-MeO-$m$-pbprH$_2$ (22b) was obtained by an analogous procedure as a colorless oil. The $^1$H NMR spectrum of 2-MeO-$m$-pbprH$_2$ (22b) showed the same behavior in the aromatic region as that of 2-MeO-$m$-pbaH$_2$ (22a).
3.2.2 Preparation of Copper Complexes

When 22a was treated with Cu$^{2+}$, complex 25a precipitated out immediately as a dark-green insoluble product. This product may have the molecular square structure shown in Figure 3.4, but I was unable to study it further due to its lack of solubility. However, when 22b was treated with Cu$^{2+}$, a dark-green CH$_2$Cl$_2$ solution was formed and molecular square 25b (Figure 3.4) was isolated as a dark green powder on evaporation of the solvent, yield (70%). The solubility of 25b was determined (see table 3.1).

![Reaction of bis(β-diketones) 22a, b with Cu$^{2+}$ yields molecular squares 25a, b.](image)

3.2.3 Solubility of Squares

Table 3.1 below shows the solubility of molecular squares 23, 24, and 25b made from ligands 20, 21, and 22b respectively. The effects of alkoxy substituents on different positions of the aromatic ring of $m$-pbaH$_2$ on solubility of the molecular squares are clearly seen. Squares 23 and 24 have alkoxy substituents on the outside since the alkoxy groups are on the 5-positions of
the aromatic rings of \( m \)-pbaH\(_2\), while square 25b is decorated on the inside as the methoxy groups are on the 2-position of the aromatic rings of the ligand.

The table shows that square 24, with the longer butoxy group, is soluble in a wider range of solvents than the methoxy analog (23). The methoxy square 23 is soluble in about the same *number* of solvents as the unsubstituted square Cu\(_4(m\)-pba)\(_4\) 3. However, the 5-methoxy groups do change the solubility of the square, making it soluble in polar solvents such as methanol. In contrast, the solubility of the molecular square does not change much when the methoxy group is on the 2-position of the aromatic ring (square 25b). The molecular square 25b was analyzed by single crystal X-ray and the structure is shown in Figure 3.5.

The Cu---Cu distance in the square 25b is 14.39 Å. The structure lies on an S\(_4\) axis in the crystal and the OCH\(_3\) groups alternate up and down. The space filling model of the square as shown in Figure 3.6 reveals the cavity to be too crowded to accommodate guest molecules.

**Table 3.1** Solubility of molecular squares 3, 23, 24, and 25b

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<th>Solvent</th>
<th>Solubility</th>
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<td><strong>Square 3</strong></td>
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<tr>
<td>Chloroform</td>
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<td>Dichloromethane</td>
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<td>o-Dichlorobenzene</td>
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<tr>
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<td>Methanol</td>
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<tr>
<td>DMF</td>
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<td>Acetonitrile</td>
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**Figure 3.5** Crystal structure of Cu₄(2-MeO-m-pbpr)₄ (25b). Hydrogen atoms have been omitted for clarity.

**Figure 3.6** Space filling model of the square 25b showing the crowding of the cavity by the internal OCH₃ groups.
**Table 3.2** X-ray crystallographic and structure refinement data for 25b.solvate.

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<th><strong>compound</strong></th>
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3.2.4 Attempted Reaction of Square 25b with Guest Molecules

When square 25b was treated with guest molecules such as 4,4’-bipyridine, 1,2-bis(4-pyridyl)ethane (bpa), and 1,2-bis(4-pyridyl)ethylene (bpe), green precipitates formed. Normally, when these guests bind to our Cu molecular squares, the color of the solution or solid changes from green to blue; thus, we believe these reactions did not yield adducts. This is most likely because of interference from the internal methoxy groups in 25b.

3.3 Experimental

3.3.1 General Considerations

2-methoxyisophthalic acid, pyridinium chlorochromate (PCC), and lithium aluminum hydride were purchased from Sigma-Aldrich. Elemental analysis was performed by M-H-W Labs, Phoenix, Arizona. 1H NMR spectra were recorded on Bruker (250 or 400 MHz) spectrometers, with CDCl3 as the solvent. The phospholenes 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene4,5 and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene6 were prepared following literature methods.

Syntheses of the precursors leading to 2-MeO-m-pbaH2 are described elsewhere.1 However I optimized the yields of the following compounds:

3.3.2 2-methoxy-1,3-benzenedimethanol

This compound was prepared following the reported procedure.1,7 Lithium aluminum hydride (0.54 g, 14.1 mmol) was suspended in dry THF (40 mL). Into this suspension was added in drops a solution of dimethyl 2-methoxyisophthalate1 (1.0 g, 4.5 mmol) in THF (20 mL) from an addition flask. Then the reaction was stirred at room temperature under N2 for 24 h. The mixture was cooled to 0 °C and an aq. solution of H2SO4 (16 mL, 1 M) was added slowly,
followed by ethyl acetate (100 mL). The organic phase was separated and washed with brine (100 mL), and dried with Na₂SO₄. On evaporation, a white solid was obtained (0.65 g, 86%).

### 3.3.3 2-methoxyisophthalaldehyde

This compound was prepared according to the procedure developed by Bennani et al. to convert 5-tert-butyl-1,3-benzenedimethanol to 5-tert-butylisophthalaldehyde.³ 2-methoxy-1,3-benzenedimethanol (0.5 g, 2.9 mmol) was dissolved in dichloromethane (30 mL) and added to a mixture of pyridinium chlorochromate (PCC) (1.92 g, 8.9 mmol) and celite (8 g) in dichloromethane (40 mL). The mixture was stirred vigorously at room temperature for 4 h, and then filtered through a short pad of silica gel. The pad was rinsed with a 1:1 mixture of dichloromethane and ethyl acetate. Solvent was removed to yield a white solid, 0.46 g (97%). ¹H NMR: δ 10.4 (s, 2H, CHO), 8.1 (d, 2H), 7.4 (t, 1H), 4.1 (s, 3H, OCH₃). Anal. Calcd. for C₉H₈O₃ (M = 164.16): C 65.85, H 4.91; Found: C 65.64, H 5.19.

### 3.3.4 2-methoxy-<i>m</i>-phenylenebis(acetylacetone), 2-MeO-<i>m</i>-pbaH₂ (22a)

2-methoxy-isophthalaldehyde (0.20 g, 1.2 mmol) and 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (0.51 g, 2.4 mmol) were dissolved in dichloromethane (5 mL) and the solution stirred at room temperature under nitrogen. The reaction mixture was monitored by ¹H NMR until the reaction was complete as indicated by the disappearance of the 2-methoxyisophthalaldehyde –CHO peak. Then methanol (30 mL) was added and the mixture refluxed for 3 h, allowed to cool to room temperature and the solvent removed. Column chromatography of the crude product (ethyl acetate-hexane, 1:4 v/v) yielded a white solid, 0.16 g (45%). The ¹H NMR of 22a is the same as what Sandifer observed.¹ Anal. Calcd. for C₁₇H₂₀O₅ (M = 304.34): C 67.09, H 6.62; Found: C 67.31, H 6.75.
3.3.5 4,4’-(2-methoxy-m-phenylenebis(3,5-heptanedione)), 2-MeO-m-pbprH₂ (22b)

This compound was prepared using the same procedure as 22a above, except that 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene was used instead. 2-methoxyisophthalaldehyde (0.20 g, 1.2 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (0.58 g, 2.4 mmol) were dissolved in dichloromethane (5 mL) and allowed to react. Column chromatography of the crude product using ethyl acetate-hexane (1:4 v/v) yielded a colorless oil, 0.13 g (30%). ¹H NMR δ: 16.9 (s, 2H), 7.10-7.18 (m, 3H, aromatic), 3.5 (s, 3H, OCH₃), 2.2 (q, 8H), 1.1 (t, 12H) (Figure A6).

3.3.6 Synthesis of Copper Molecular Squares

25a - CuSO₄·5H₂O (0.41 g, 1.6 mmol) was dissolved in distilled water (50 mL) and ammonia solution added dropwise until a royal blue solution formed. Into this solution was added 2-MeO-m-pbaH₂ (22a) (0.5 g, 1.6 mmol) in dichloromethane (40 mL). Immediately a dark green insoluble solid precipitated out.

25b - CuSO₄·5H₂O (0.277 g, 1.1 mmol) was dissolved in water (40 mL), and ammonia solution added dropwise until a royal blue solution was formed. Into this solution was added 2-MeO-m-pbprH₂ (22b) (0.4 g, 1.1 mmol) in DCM (40 mL) and the mixture stirred at room temperature for 4 h. The organic phase (olive green) was dried over Na₂SO₄ and the solvent removed under reduced pressure. The residue was washed with methanol and air dried to yield a dark green solid, 0.66 g (70%). Calcd. Anal. for C₅₈H₇₀₄Cu₄O₂₀: C 59.77, H 6.21: Found, C 59.64, H 6.24. Crystals suitable for X-ray analysis were grown by dissolving the complex in hot toluene and layering it with acetonitrile.
3.4 References


Chapter 4: Synthesis of Bis(β-Ketoenamine) Ligands and Their Molecular Squares

4.1 Introduction

In this chapter, two bis(β-ketoenamine) ligands and their metal molecular squares are discussed. Bis(β-ketoenamines) have the potential to generate porous metal-organic materials because they are chelating ligands like β-diketones, although they have been employed much less frequently.\(^1\) The ligands (1) and (2) (Figure 4.1), and their copper molecular squares are reported elsewhere.\(^2\) We were interested to study the squares by NMR and also by electrochemistry. Since copper molecular squares cannot be studied by NMR due to the paramagnetic nature of Cu(II), we wished to prepare molecular squares from metals such as nickel and palladium: Square-planar Ni(II) and Pd(II) complexes are nearly always diamagnetic. However, Ni(II) β-diketonates are usually octahedral and paramagnetic, and Pd(II) β-diketonates, though square-planar and diamagnetic, are often easily reduced to Pd metal. For supramolecular chemistry with Ni(II), we decided to convert our bis(β-diketones) into bis(β-ketoenamines): Both Ni(II) and Pd(II) are d\(^8\) systems and are known to react with β-ketoenamines to yield square planar diamagnetic complexes which can be studied by NMR.\(^1,3,4\) Therefore, we converted the bis(β-diketones), m-pbaH\(_2\) (1) and m-pbprH\(_2\) (2) to bis(β-ketoenamines), m-pbiH\(_2\) (26) and m-pbpriH\(_2\) (27) (see Figure 4.1), through microwave assisted synthesis (scheme 4.1). When treated with Cu\(^{2+}\), ligands 26 and 27 yield copper molecular squares; while 27 affords a nickel square on reaction with Ni\(^{2+}\). The copper and nickel molecular squares have been studied by UV-visible spectroscopy and electrochemistry; the nickel square has been studied by \(^1\)H NMR. The squares have been characterized by single crystal X-ray analysis.
Figure 4.1 Bis(β-diketones) 1 and 2, and their bis(β-ketoenamine) analogs 26 and 27.

4.2 Results and Discussion

4.2.1 Synthesis of the Ligands

The work by the Braibante group, which used a domestic microwave oven to convert β-dicarbonyl compounds to ketoenamines, motivated us to try microwave reactions. Treatment of \( m\text{-pbaH}_2 \) (1) and \( m\text{-pbprH}_2 \) (2) with ammonium acetate in toluene in microwave yielded \( m\text{-pbiH}_2 \) (26) and \( m\text{-pbpriH}_2 \) (27) in 86 and 80% respectively after column chromatography (Scheme 4.1). These reactions took 40 min to complete. Attempts to prepare a bis(β-ketoenamine) from the ligand \( m\text{-pbhxH}_2 \) (5) (see Figure 2.2 in chapter 2) did not succeed. The molecular squares from this ligand were expected to be soluble in a wider range of solvents. The nickel square in particular could enable us to study its reactions with a variety of guest molecules. Both bis(β-ketoenamine) ligands 26 and 27 were analyzed by \(^1\)H NMR and their spectra (see Appendix, Figures A7 and A9) were compared with those of their bis(β-diketone) analogs 1 and 2 (Appendix, Figures A1 and A2). The enol peak (16.64 ppm) in bis(β-diketone) 1 (Figure 1A) is replaced by two broad singlets at 10.53 ppm and 5.07 ppm, which are assigned to NH protons in ketoenamine 26 (Figure A7). . The peak at 10.53 ppm is assigned to the NH proton (a1) which is
hydrogen-bonded to the oxygen atom, while the peak at 5.07 ppm is the free NH proton \((a2)\). Methyl protons in \(1\) appear as one singlet at 1.91 ppm, while \(26\) shows two \(\text{CH}_3\) singlets. Aromatic proton peaks around 7 ppm in ketoenamine \(26\) are shifted slightly upfield compared to the diketone \(1\). Similarly, the \(^1\text{H}\) NMR spectrum of bis(\(\beta\)-ketoenamine) \(27\) (Figure A9) shows amine peaks at 10.64 ppm and 5.05 ppm. Crystal structures of \(26\) and \(27\) are shown in Figure 4.2.

\[
\text{Scheme 4.1} \text{ Conversion of bis(\(\beta\)-diketones) (1 and 2) to bis(\(\beta\)-ketoenamines) (26 and 27).}
\]

\[
\text{Figure 4.2} \text{ Crystal structures of bis(\(\beta\)-ketoenamines) \textit{m}-pbiH}_2 (26) and \textit{m}-pbpriH}_2 (27).}
\]
4.2.2 Synthesis of the Metal Squares

The two ligands were treated with Cu(NO$_3$)$_2$·3H$_2$O and Ni(NO$_3$)$_2$·3H$_2$O in DMF solution, in the presence of triethylamine as base. Reaction of the $m$-pbiH$_2$ ligand with Ni(NO$_3$)$_2$·3H$_2$O led to immediate precipitation of a brown insoluble product. This material may be the molecular square Ni$_4$($m$-pbi)$_4$; however, its low solubility made further study difficult, and I decided not to pursue it further. In contrast, no precipitates were observed when the two ligands were treated with Cu(NO$_3$)$_2$·3H$_2$O, and also when $m$-pbpriH$_2$ was treated with Ni(NO$_3$)$_2$·3H$_2$O.

(a) Cu$_4$($m$-pbi)$_4$ (28) and Cu$_4$($m$-pbpri)$_4$ (29)

Both $m$-pbiH$_2$ and $m$-pbpriH$_2$ react with Cu$^{2+}$ in DMF in the presence of Et$_3$N to yield dark green solutions which deposit dark green crystals after several days. Square 28 is insoluble, which limited further study, while 29 is soluble in both chloroform and dichloromethane.

(b) Ni$_4$($m$-pbpri)$_4$ (30)

Ligand 27 reacts with Ni$^{2+}$ in DMF in the presence of Et$_3$N to yield a red solution. The solid microcrystalline product, 30, precipitates out when acetonitrile vapor is allowed to diffuse into the red solution. Other solvents which precipitate the product are acetone and ethyl acetate, although the yields are lower than in the case of acetonitrile. Nickel square 30 is soluble in chloroform and dichloromethane solvents. The $^1$H NMR spectrum of the Ni$_4$(m-pbpir)$_4$ (30) is depicted in Figure A11. This spectrum shows that the NH peak of the ligand 27 at 10.64 ppm (Figure A9) has disappeared, as expected if nickel binds to the ligand by displacing proton a1. The free NH peak (a2) of the $m$-pbpriH$_2$ ligand 27 at 5.05 has shifted to 5.41 ppm in the nickel molecular square 30. The spectrum of the molecular square displays a single ligand environment suggesting the formation of a symmetric species such as a metallacycle.
4.2.3 UV-Vis Analysis

The UV-Vis spectra of molecular squares 29 and 30 were compared with that of the β-diketone molecular square, Cu₄(m-pba)₄ (3) (see Figure 4.3). The spectrum of the β-diketone molecular square, Cu₄(m-pba)₄ in chloroform, Figure 4.3 A shows two d-d absorption bands with maxima at 546 (ε = 177) and 670 nm (ε = 182 M⁻¹ cm⁻¹). These bands are comparable (on a per metal atom basis) to those for Cu(acac)₂ (λ = 532 (ε = 26) and 658 nm (ε = 34 M⁻¹ cm⁻¹)). Spectrum B is that of Cu₄(m-pbpr)₄ in chloroform, showing one broad band with a maximum at 593 nm (ε = 304 M⁻¹ cm⁻¹). Figure 4.3 C is the spectrum of Ni₄(m-pbpr)₄ in chloroform, also showing one broad band with a maximum at 569 nm (ε = 323 M⁻¹ cm⁻¹). We were especially interested in the UV-Vis spectrum of Cu₄(m-pbpr)₄. This is because both Cu₄(m-pba)₄ and Cu₄(m-pbpr)₄ are green, both in solution and in the solid state. Since the colors of the two compounds are very similar, the details of the electronic spectra can help to distinguish them from each other.

Figure 4.3 Room-temperature electronic absorption spectra: (A) Cu₄(m-pba)₄ (3), (B) Cu₄(m-pbpr)₄ (29), and (C) Ni₄(m-pbpr)₄ (30). All the squares were dissolved in chloroform.
4.2.4 Electrochemistry

The squares 29 and 30 were studied by electrochemistry and their cyclic voltammograms are shown in Figures 4.4 and 4.5. Cyclic voltammograms for Ni$_4$(m-pbpr)$_4$ show a partially reversible wave with $E_{1/2} = 0.70$ V (Figure 4.4). Cu$_4$(m-pbpr)$_4$ showed several waves (Figure 4.5); the best-defined one is an irreversible oxidation wave at 0.74 V. The ferrocene (Fc/Fc$^+$) reference redox couple appears at ca. 0.27 V under these conditions. These values are more anodic than those reported for the binuclear β-ketoenamine complexes Ni$_2$(BBI)$_2$ (0.26 V vs. Fc/Fc$^+$) and Cu$_2$(BBI)$_2$ (0.36 V vs. Fc/Fc$^+$). The voltammograms are also less reversible than those for M$_2$(BBI)$_2$ (for example, $i_{pc}/i_{pa} = 0.62$ and $\Delta E_p = 0.22$ V for Ni$_4$(m-pbpr)$_4$, vs. 0.81 and 0.063 V for Ni$_2$(BBI)$_2$ under similar conditions).

**Figure 4.4** Cyclic voltammogram for Ni$_4$(m-pbpr)$_4$: 1.0 x 10$^{-3}$ M in CH$_2$Cl$_2$, with 0.1 M (Bu$_4$N)PF$_6$ as the supporting electrolyte; Pt working electrode; Ag/Ag$^+$ reference electrode.
Figure 4.5 Cyclic voltammogram for Cu₄(m-pbri)₄: 1.0 x 10⁻³ M in CH₂Cl₂, with 0.1 M (Bu₄N)PF₆ as the supporting electrolyte; Pt working electrode; Ag/Ag⁺ reference electrode.

4.2.5 Structural Characterization

Crystal structures of 28, 29, and 30 are shown in Figures 4.6-4.8.

Figure 4.6 Crystal structure of (a) Cu₄(m-pbi)₄ (28), and (b) Chemdraw picture of the square.
Figure 4.7 (a) Crystal structure of Cu$_4$(m-pbpr)$_4$ (29), (b) Chemdraw picture of the square.

Figure 4.8 (a) Crystal structure of Ni$_4$(m-pbpr)$_4$ (30), (b) Chemdraw picture of the square.
The M—M (M = Cu, Ni) distances in the metal squares of 28, 29, and 30 from β-ketoenamine ligands 26 and 27 are similar to the Cu···Cu distances in the squares, Cu₄(m-pba)₄ (3) and Cu₄(m-pbpr)₄ (4),² from their β-diketone analogs 1 and 2 respectively. The distances are shown in table 4.1.

Table 4.1 M—M distances in metal squares from β-diketones 1, 2 and β-ketoamines 26, 27.

<table>
<thead>
<tr>
<th>Metal square</th>
<th>M1—M2 (Å) (M = Cu, Ni)</th>
<th>M3—M4 (Å) (M = Cu Ni)</th>
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<td>Cu₄(m-pba)₄ (3)⁡</td>
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</tr>
<tr>
<td>Cu₄(m-pbpr)₄ (4)⁡</td>
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<td>14.66</td>
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<tr>
<td>Cu₄(m-pbi)₄ (28)</td>
<td>14.22</td>
<td>14.74</td>
</tr>
<tr>
<td>Cu₄(m-pbpr)₄ (29)</td>
<td>14.59</td>
<td>14.50</td>
</tr>
<tr>
<td>Ni₄(m-pbpr)₄ (30)</td>
<td>13.89</td>
<td>14.58</td>
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4.2.6 Attempted Host-Guest Chemistry

Squares 29 and 30 were treated with guest molecules such as 4,4-bipyridine, 1,2-bis(4-pyridyl)ethylene (bpe), 1,2-bis(4-pyridyl)ethane (bpa), C₆₀ and C₇₀. The pyridine derivatives largely yielded precipitates with colors that were very similar to those of the respective “empty” β-ketoenamine squares (green for 29 and brown for 30). C₆₀ and C₇₀ with the squares afforded crystalline products, but these did not diffract well, so we were unable to determine their structures.
Table 4.2 X-ray crystallographic and structure refinement data for 28.solvate and 29.solvate.

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<th>29.solvate</th>
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</thead>
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<td>C_{180}H_{104}Cu_{4}N_{8}O_{8} \cdot 4.29 CHCl_{3}</td>
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<tr>
<td>formula weight</td>
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<td>16.3334(6)</td>
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<td>85.460(3)</td>
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<td>2085.86(15)</td>
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<td>1</td>
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<td>0.1395</td>
</tr>
<tr>
<td>GOF</td>
<td>0.950</td>
<td>1.070</td>
</tr>
</tbody>
</table>
4.3 Experimental

NMR spectra were recorded on Bruker (250 or 400 MHz) spectrometers, with CDCl₃ as solvent. Elemental analysis was performed by M-H-W Laboratories, Phoenix, Arizona. Microwave reactions were performed in a CEM microwave oven. UV-Vis spectra were recorded by Bang,¹⁰ in CHCl₃ solution, using an Aviv Model 14DS spectrophotometer. Cyclic voltammograms were recorded by Dr. Hwang and Brian Imsick, using an electrochemical apparatus in the Nesterov group.

4.3.1 Microwave Assisted Synthesis of \( m\)-pbiH₂ (26) and \( m\)-pbpriH₂ (27)

\( m\)-pbiH₂ (26): \( m\)-pbaH₂ (0.50 g, 1.82 mmol) was placed in an 80 mL microwave reaction vessel with toluene (30 mL). Into this solution was added ammonium acetate (0.56 g, 7.28 mmol), and the mixture placed in the microwave oven (200 °C, 400 W, 30 m). After the reaction was complete, the solvent was removed completely by rotary evaporation to obtain a white solid which was easily purified by column chromatography (ethyl acetate-hexane, 90:10 v/v), yield 430 mg (86%) of \( m\)-pbiH₂. Crystals of \( m\)-pbiH₂ suitable for single-crystal X-ray analysis were grown from CHCl₃ by layering with hexane. \(^1\)H NMR: \( \delta \) 10.53, 5.07 (br, 4H, NH₂), 7.34 (t, 1H), 7.10 (d, 2H), 7.01 (s, 1H), 1.86 (s, 6H), 1.72 (s, 6H) (Figure A7). \(^{13}\)C NMR: \( \delta \) 196.5, 159.5, 140.7, 135.4, 130.2, 128.8, 109.9, 29.2, 22.2 (Figure A8). Anal. Calcd for C₁₆H₂₀N₂O₂ (M = 272.34): C, 70.56; H, 7.40; N, 10.29. Found: C, 70.76; H, 7.64; N, 10.47.

\( m\)-pbpriH₂ (27): Reaction of \( m\)-pbprH₂ (0.50 g, 1.5 mmol) and ammonium acetate (0.47 g, 6.0 mmol) under the same microwave conditions as reported for (26) above yielded 400 mg (80%) of \( m\)-pbpriH₂ after column chromatography (ethyl acetate/hexane, 70/30). Crystals suitable for single-crystal X-ray analysis were deposited from CHCl₃ solution by layering with
hexane over a period of 4 days. $^1$H NMR: δ 10.64, 5.05 (br, 4H, NH$_2$), 7.34 (t, 1H), 7.11 (dd, 2H, $j = 7.56$, 1.60 Hz), 7.03 (s, 1H), 2.10-1.98 (m, 8H), 1.01 (t, 6H), 0.96 (t, 6H) (Figure A9). $^{13}$C NMR: δ 200.0, 163.9, 139.9, 136.1, 130.5, 128.7, 108.8, 33.9, 27.8, 12.0, 9.2 (Figure A10). Anal. Calcd for C$_{20}$H$_{28}$N$_2$O$_2$ (M = 328.45): C, 73.14; H, 8.59; N, 8.53; Found: C, 72.91; H, 8.44; N, 8.44.

### 4.3.2 Synthesis of Copper and Nickel Squares

**Cu$_4$(m-pbi)$_4$ (28):** m-pbiH$_2$ (0.05 g, 0.18 mmol) and Et$_3$N (0.036 g, 0.36 mmol) were dissolved in DMF (30 mL) and stirred for 2 h. Into this solution was added Cu(NO$_3$)$_2$·3H$_2$O (0.044 g, 0.18 mmol) in DMF (30 mL). The resultant dark green solution was left standing for 4 days during which time dark green crystalline material precipitated. This was collected, washed with DMF and CH$_3$CN, and dried in air for 12 h to yield a dark green solid, 0.033 g (54%). Square 28 is insoluble in common solvents and so could not be recrystallized; hence, single crystal X-ray analysis was carried out on the as-synthesized crystals.

**Cu$_4$(m-pbpri)$_4$ (29):** m-pbpriH$_2$ (0.10 g, 0.30 mmol) and Et$_3$N (0.06 g, 0.60 mmol) were dissolved in DMF (50 mL) and stirred for 2 h. A solution of Cu(NO$_3$)$_2$·3H$_2$O (0.074 g, 0.30 mmol) in DMF (50 mL) was added, and the solution turned dark green. It was left standing for 5 days where dark green crystalline product precipitated. This was collected, washed with DMF and CH$_3$CN and air dried for 12 h to yield a dark green solid, 0.073 g (61%). Anal. Calcd. for C$_{80}$H$_{104}$N$_8$O$_8$Cu$_4$ (M = 1559.91): C, 61.60; H, 6.72; N, 7.18; Found: C, 61.22; H, 6.57; N, 6.98. Single crystals for X-ray analysis were prepared from CHCl$_3$ solution by layering with 2-propanol.
Ni$_4$(m-pbppri)$_4$ (30): A solution of $m$-pbpriH$_2$ (0.20 g, 0.61 mmol) and Et$_3$N (0.12 g, 1.2 mmol) in DMF (10 mL) was stirred for 2 h and treated with a solution of Ni(NO$_3$)$_2$·6H$_2$O (0.177 g, 0.61 mmol) in DMF (10 mL). A pale yellow solution was formed which turned red within a few seconds. Solvent vapor diffusion of CH$_3$CN into this DMF solution led to precipitation of a red microcrystalline product after seven days. The solid was collected, washed with DMF and CH$_3$CN, and air dried for 12 h to yield a red-brown solid, 0.11 g (47%). $^1$H NMR: δ 7.27 (t, 1H), 7.04 (dd, 2H, $J = 7.44$, 1.0 Hz), 6.88 (br s, 1H), 5.41 (s, 2H, NH), 1.90-1.71 (m, 8H), 0.9 (q, 6H), 0.82 (q, 6H) (Figure A11). Anal. Calcd. for C$_{80}$H$_{104}$N$_8$O$_8$Ni$_4$ (M = 1540.50): C 62.37; H 6.80; N 7.27: Found: C 62.15; H 6.79; N 7.23. Crystals for X-ray analysis were grown from CHCl$_3$ solution by layering with 2-propanol.

4.4 References


(10) Bang, S. *Unpublished Results*. 
Chapter 5: Triphenylamine Based Bis(β-Diketone) Ligands and Their Copper(II) Complexes

5.1 Introduction

The previous chapters report on molecular squares from \( m \)-pbaH\(_2\) derivatives. Because of the 120° angle between its β-diketone moieties, \( m \)-pbaH\(_2\) was expected to generate a molecular hexagon on reaction with square planar metal ions, and yet all of the MOPs isolated so far have been molecular squares. As part of our efforts to make larger molecular polygons, we prepared the new triphenylamine-based bis(β-diketone) ligands tpbaH\(_2\) (31) and tpbprH\(_2\) (32) (Figure 5.1). Also these ligands will have more room inside to accommodate internal functional groups.

![Figure 5.1](image)

**Figure 5.1** Structures of triphenylamine and the bis(β-diketone) ligands tpbaH\(_2\) (31) and tpbprH\(_2\) (32).

As with \( m \)-pbaH\(_2\), the 120° angle between the β-diketone moieties in these ligands should permit the formation of molecular hexagons on treatment with Cu\(^{2+}\). (In contrast to aliphatic amines, triarylamines generally exhibit trigonal planar geometry at N.) However, it is possible that ligands 31 and 32 might yield molecular squares if the experience our group had with \( m \)-pbaH\(_2\)\(^1\) is something to go by. The new ligands should yield larger pores than \( m \)-pbaH\(_2\) and its analogs, which means that the squares may be able to accommodate larger guest molecules. Here
we report syntheses of the ligands and the copper complex of 32 and its characterization by ESI-MS and microanalysis.

5.2 Results and Discussion

5.2.1 Ligands

The two compounds (31 and 32) are isolated as white solids after stirring 4,4’-diformyltriphenylamine\(^2\) (33) with 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene\(^3\) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene\(^1\) respectively (scheme 5.1) for 12 days at room temperature under N\(_2\). These reactions are quite slow and the product yields are low (17 and 14% for 31 and 32 respectively).

![Scheme 5.1 Reaction of 4,4’-diformyltriphenylamine (33) with phospholenes affords bis(β-diketones) tpbaH\(_2\) (31) and tpbprH\(_2\) (32).](image)

The formation of our previously mentioned β-diketones take shorter reaction times to complete, i.e in less than 24 h and it involves stirring the aldehydes with phospholenes at room temperature overnight, followed by refluxing the intermediate in methanol. In this particular case, the reaction does not require refluxing in methanol, but it requires more time. Prior to this
study, the thiophene-based bis(β-diketone) ligands (see scheme 5.2) had been prepared in a similar procedure in our group. This reaction took about ten days of stirring the 2,5-thiophenedicarboxaldehyde with phospholenes at room temperature and did not require refluxing in methanol, but it requires more time. The yields were also low (~20%).

**Scheme 5.2** Reaction of 2,5-thiophenedicarboxaldehyde with phospholenes yields thiophene-based bis(β-diketones).

The crystal structures of tpbaH₂ (31) and tpbprH₂ (32) are shown in Figure 5.2. In the solid state, 31 and 32 are in the enol form, which is in agreement with solution NMR data.

**Figure 5.2** Crystal structures of bis(β-diketone) ligands 31 and 32.
5.2.2 Copper Complexes

Reaction of 31 with Cu$^{2+}$ resulted in an insoluble product, while 32 afforded a dark green material (34) that is soluble in chloroform and dichloromethane. We were unable to obtain 34 in crystalline form for direct structural characterization. However, its microanalysis (C, H, N) agrees with calculated values for Cu$_n$(tpbpr)$_n$. Also we were able to analyze it by ESI-MS. Our spectrometer has a maximum $m/z$ limit of 3000, and if complex 34 is a molecular hexagon, then its molecular weight is 3354.9; this means that the parent ions Cu$_n$(tpbpr)$_n^+$, (n≥6) cannot be observed. However, smaller complexes (i.e Cu$_n$(tpbpr)$_n^+$, n < 6) would have parent ions below $m/z = 3000$ and should be observed. We saw no signal for the pentamer ($m/z ~ 2796$). In the tetramer region, signals were observed at 2234.7-2241.7 whose isotope distribution pattern matches with the theoretical distribution. This pattern is assigned to the tetramer, [M+H]$^+$, $m/z = 2237.7$ (see Figure 5.3). Additional signals are assigned to Cu$_3$(tpbpr)$_3^+$ (1675.5-1680.5) and Cu$_2$(tpbpr)$_2^+$ (1116.4 -1121.3).

![Figure 5.3](image)

Figure 5.3 Calculated (top) and experimental (bottom) ESI-MS spectra of parent ion ([M+H]$^+$, Cu$_4$(tpbpr)$_4$H$^+$) of 34.
Elemental analysis (C, H, N) for complex 34 agrees with calculated values for 
\( \text{Cu}_n(\text{tpbpr})_n \), \( n = 4 \). One possible geometry for \( \text{Cu}_4(\text{tpbpr})_4 \), generated by molecular modeling 
(HyperChem), is shown in Figure 5.4.

The predicted Cu---Cu distance in the model of square 34 is \( \sim 20 \text{ Å} \). Attempts to obtain 
adducts of 34 with guest molecules such as 4,4’-bipyridine, 1,2-bis(4-pyridyl)ethylene (bpe) and 
1,2-bis(4-pyridyl)ethane (bpa) did not succeed. This is probably because these guests are not 
large enough to bridge two opposite N atoms in the cavity of 34.

![Figure 5.4](image)

**Figure 5.4** A model of molecular square 34 (\( \text{Cu}_4(\text{tpbpr})_4 \)). Color coding: Carbon black, Nitrogen 
blue, Oxygen red and Copper orange. Hydrogen atoms omitted for clarity.

5.3 Experimental

5.3.1 Materials and Methods

DMF was purchased from Sigma-Aldrich and distilled once; phosphorus oxychloride and 
triphenylamine were acquired from Sigma-Aldrich and used as received. ESI-MS was performed
on an ESI-TOF instrument (Agilent-6210 TOF-LC/MS). Elemental analysis was performed by M-H-W Labs, Phoenix, Arizona. NMR spectra were recorded on a Bruker 400 MHz spectrometer with CDCl₃ as the solvent. 4,4'-Diformyltriphenylamine, 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene were prepared by literature methods.

5.3.2 Synthesis of the Ligands

a) tpbaH₂ (31): 4,4'-Diformyltriphenylamine (1.5 g, 4.9 mmol) (33) was dissolved in dichloromethane (10 mL). Into this solution was added 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (2.06 g, 9.8 mmol) and the mixture stirred under nitrogen for 12 days. This reaction was monitored by ¹H NMR where the enol peak was not observed after stirring overnight but it started appearing after 4 days and continued to get larger until no change in the peak’s size was observed after 12 days. The aldehyde –CHO resonance peak at 9.90 ppm gradually became smaller and finally disappeared during this period. The crude product was isolated by removal of solvent, and purified by column chromatography (ethyl acetate: hexane, 1:4 v/v) to yield a white solid, 0.390 g (17%), mp 185-190 °C. ¹H NMR: δ 16.67 (s, 2H, O⁻H), 7.31 (t, 3H), 7.15 (d, 2H), 7.10, 7.04 (AB, 8H, aromatic CH), 1.96 (s, 12H) (Figure A13). ¹³C NMR: δ 191.1, 146.8, 131.9, 131.0, 129.5, 125.0, 123.7, 123.6, 114.7, 24.2 (Figure A14). Anal. Calcd. for C₂₈H₂₇NO₄ (M = 441.52): C 76.17; H 6.16; N 3.17; Found: C 75.87; H 6.17; N 3.09. Crystals suitable for X-ray analysis were grown by slow evaporation of a solution in ethyl acetate-hexane.

b) tpbprH₂ (32): The same procedure for preparing 31 was followed except that 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (1.86 g, 7.8 mmol) and 4,4’-
diformyltriphenylamine (1.2 g, 3.9 mmol) were mixed together and dissolved in dichloromethane. After the reaction was complete (as judged by the disappearance of CHO aldehyde peak), the crude product was isolated by the removal of the solvent and purified by column chromatography (ethyl acetate/hexane: 1:4) to give a white solid, 0.280 g (14%), mp 135-139 °C. \(^1\)H NMR: \(\delta\) 16.72 (s, 2H, OH), 7.32 (t, 3H), 7.16 (d, 2H), 7.09, 7.03 (AB, 8H, aromatic CH), 2.21 (q, 8H), 1.07 (t, 12H) (Figure A15). \(^{13}\)C NMR: \(\delta\) 194.3, 146.8, 132.1, 130.4, 129.5, 125.2, 123.6, 123.5, 113.4, 29.9, 9.6 (Figure A16). Anal. Calcd. for C\(_{32}\)H\(_{35}\)NO\(_4\) (M = 497.62): C 77.24; H 7.09; N 2.81; Found: C 77.45; H 6.90; N 2.85. Crystals for X-ray analysis were grown by slow evaporation of a solution in ethyl acetate-hexane.

**5.3.3 Synthesis of Copper Complexes**

a) Complex 33: CuSO\(_4\)·5H\(_2\)O (0.24 g, 0.9 mmol) was dissolved in distilled water (50 mL) and ammonia solution was added in drops with stirring until a royal blue solution was formed. Into this solution was added the ligand 31 (0.3 g, 0.9 mmol) in dichloromethane (40 mL). Immediately a dark green insoluble powder precipitated out.

b) Complex 34: This complex was prepared in the same procedure as for 33 above, except that the ligand 32 was used instead. Thus, CuSO\(_4\)·5H\(_2\)O (0.10 g, 0.4 mmol) in distilled water (40 mL) was added ammonia solution in drops until a royal blue solution formed and the ligand 32 (0.20 g, 0.4 mmol) in dichloromethane (30 mL) was added. The mixture was stirred for 3 h. The dark-green organic layer was dried over Na\(_2\)SO\(_4\) and evaporated to yield a dark-green solid, 0.112 g (50%). Anal. Calcd. for C\(_{128}\)H\(_{132}\)Cu\(_4\)N\(_4\)O\(_{16}\) (M = 2236.62): C 68.74; H 5.95; N 2.50; Found: C 68.92; H 6.16; N 2.60
5.4 References


Chapter 6: Conclusions and Prospects

This dissertation focuses on synthesis of β-diketone and β-ketoenamine ligands for molecular polygons. Chapters 2-4 discuss syntheses of derivatives of \( m \)-pbaH\(_2\) and their molecular squares. Chapter 5 discusses triphenylamine based bis(β-diketones) and their copper complexes.

The new \( m \)-pbhxH\(_2\) ligand, with pentyl chains replacing the methyl groups in the β-diketone moieties of \( m \)-pbaH\(_2\), was successfully prepared beginning with 6-dodecyn. Reaction of this ligand with copper resulted in a molecular square that is soluble in a wide range of solvents. Single crystal X-ray diffraction confirmed formation of the square with molecular formula \([\text{Cu}_4(\text{m-pbhx})_4(\text{MeOH})_2]\). Host-guest reactions of the square with a variety of guest molecules were studied. In most of the cases green precipitates formed; in other cases, the color of solutions changed from dark green or blue to dark blue then to brown and eventually brown precipitates were deposited; and in a few cases crystals formed. The crystalline products were analyzed by single crystal X-ray diffraction. The squares with 1,2-bis(4-pyridyl)ethylene (bpe) and 1,2-bis(4-pyridyl)ethane (bpa) were confirmed by single crystal X-ray analysis with molecular formula \([\text{Cu}_4(\text{m-pbhx})_4(\mu-\text{bpe})(\text{MeOH})_2]\) and \([\text{Cu}_4(\text{m-pbhx})_4(\mu-\text{bpa})(\text{MeOH})_2]\) respectively. Preliminary results from the crystals formed between the square and C\(_{60}\) (dark brown) revealed a 1:1 adduct, while the square with anthracene formed blue-green crystals which did not diffract well.

The 2-MeO-\( m \)-pbaH\(_2\) ligand, with a methoxy group in the internal 2-position of its aromatic ring, was prepared previously by Jace Sandifer, though in low yield. Its synthesis has been improved by increasing yield and purity, and the closely related 2-MeO-\( m \)-pbprH\(_2\), with ethyl substituents, was synthesized as well. Treatment of 2-MeO-\( m \)-pbprH\(_2\) with copper afforded
a molecular square that is soluble in chloroform and dichloromethane. Single crystal X-ray analysis revealed the square with methoxy groups on the inside. Treatment of the square with guest molecules did not yield adducts; we attribute this to interference from the methoxy groups.

The two ligands \( m\)-pbaH_2 and \( m\)-pbprH_2 were converted to their ketoenamine analogs \( m\)-pbiH_2 and \( m\)-pbprH_2 through microwave assisted synthesis. Both bis(\( \beta \)-ketoenamines) afforded molecular squares when treated with \( \text{Cu}^{2+} \). The longer-chain \( m\)-pbpriH_2 also yielded a molecular square when treated with \( \text{Ni}^{2+} \). Single crystal X-ray analysis confirmed the formation of the squares. The two \( \text{M}_4(\text{m-pbpr})_4 \) squares were studied by UV-VIS and by electrochemistry. The nickel square is diamagnetic and was studied by NMR.

Two new bis(\( \beta \)-diketone) ligands based on triphenylamine were prepared for the first time. The ligands are formed when 4,4’-diformyltriphenylamine and phospholenes are stirred together for a long time (12 days). When treated with copper, the methyl version of the ligand yielded an insoluble product while the ethyl version yielded a copper complex that is soluble in chloroform and dichloromethane. Attempts to crystallize the complex yield yellow-green precipitates which may suggest that the complex is unstable in solution and it degrades. The soluble complex was analyzed by ESI-MS and microanalysis and the data agree with the calculated values for a molecular square and thus a molecular square is proposed for this complex.

I have explored the effects of changing alkyl substituents, coordinating atoms, and aromatic-ring substituents on the chemistry of \( m\)-pbaH_2 and its molecular squares. Further studies could be done on these molecules. For example, since 2-MeO-\( m\)-pbprH_2 afforded a molecular square; it indicates that the methoxy group does not prevent formation of the macrocycle. This
study could be extended further by introducing larger functional substituents on the 2-position of m-pbaH₂ to test the possibility of formation of larger macrocycles.
Appendix: Spectra

Figure A1 $^1$H NMR spectrum of $m$-pbaH$_2$ (1).
Figure A2 $^1$H NMR spectrum of $m$-pbprH$_2$ (2).
Figure A3 $^1$H NMR spectrum of $m$-pbhxH$_2$ (5)
Figure A4 $^1$H NMR spectrum of dodecane-6,7-dione (12).
Figure A5 $^1$H NMR spectrum of crude phospholene 13.
Figure A6 $^1$H NMR spectrum of 2-MeO-$m$-pbprH$_2$ (22b).
Figure A7 $^1$H NMR spectrum of $m$-pbiH$_2$ (26)
Figure A8 $^{13}$C NMR spectrum of $m$-pbiH$_2$ (26).
Figure A9 $^1$H NMR spectrum of $m$-pbpriH$_2$ (27).
Figure A10 $^{13}$C spectrum of $m$-pbpriH$_2$ (27).
Figure A11 $^1$H NMR spectrum of Ni$_4$(m-pbpri)$_4$ molecular square (30).
Figure A12 $^{13}$C NMR spectrum of Ni$_4$(m-pbpr)$_4$ molecular square (30).
**Figure A13** $^1$H NMR spectrum of tpbaH$_2$ (31).
Figure A14 $^{13}$C NMR spectrum of tpbaH$_2$ (31).
Figure A15 $^1$H NMR spectrum of tpbprH$_2$ (32).
Figure A16 $^{13}$C spectrum of tpbprH$_2$ (32).
Figure A17 $^1$H NMR spectrum of 4,4'-diformyltriphenylamine (33).
Vita

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