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Beta-diketone and beta-ketoenamine based molecular squares

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PREVIEW

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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

by

Jackson Kiplagat Cherutoi
B.Ed (Sc), Moi University, 1996
M.Sc., Moi University, 2002
August 2012

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PREVIEW

Abstract

This dissertation focuses on synthesis of β -diketone and β -ketoenamine ligands for molecular polygons. Previous work with the bis(β -diketone) m -pbaH₂ showed that it can be converted to a copper molecular square, Cu₄(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 -pbhxH₂ ligand, with pentyl chains replacing the methyl groups in the β -diketone moieties of m -pbaH₂, was successfully prepared beginning with 6-dodecyne. This ligand reacts with Cu²⁺ to make the molecular square Cu₄(m -pbhx)₄, which is soluble in a wider range of solvents. Host-guest reactions of Cu₄(m -pbhx)₄ with a variety of guest molecules were studied. The structures of the “empty” square, [Cu₄(m -pbhx)₄(CH₃OH)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 -pbaH₂ ligand had been prepared previously. This dissertation reports an improved synthesis of 2-MeO- m -pbaH₂, and its larger homolog 2-MeO- m -pbprH₂ was synthesized as well. Treatment of 2-MeO- m -pbprH₂ with Cu²⁺ 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 -pbaH₂ and m -pbprH₂ were converted to their ketoenamine analogs m -pbiH₂ and m -pbpriH₂ through microwave-assisted synthesis. The molecular squares Cu₄(m -pbi)₄,

$\text{Cu}_4(m\text{-pbpri})_4$, and $\text{Ni}_4(m\text{-pbpri})_4$ 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 $\text{Cu}_4(m\text{-pba})_4$ and its derivatives.

PREVIEW

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,¹⁻³ catalysis,⁴⁻⁷ and separations.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).

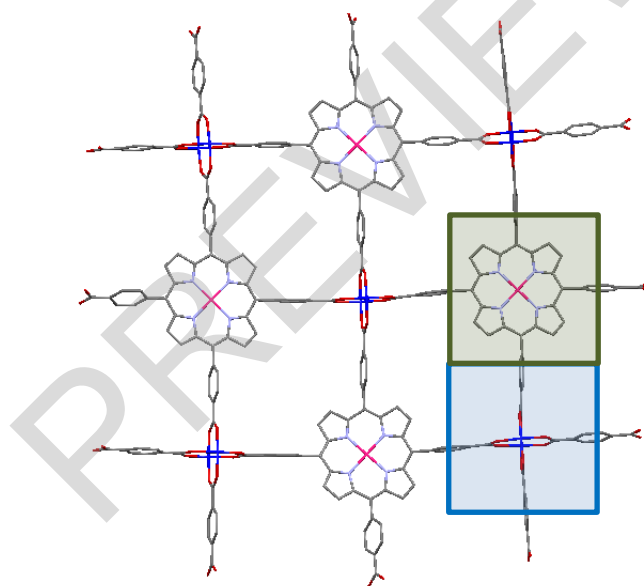


Figure 1.1 Structure of a portion of a metal-organic framework (MOF).¹¹ This material is composed of metalloporphyrin units (one highlighted in green box) linked by dicobalt carboxylate bridging groups (one highlighted in blue box) in a 2-dimensional square grid.

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, $M_2(COO)_4$ ($M = Zn, Co$) (see Figure 1.2) linked to metalloporphyrin units $M(TCPP)$ (see Figure 1.3) resulting in a 2-D square grid network.¹¹

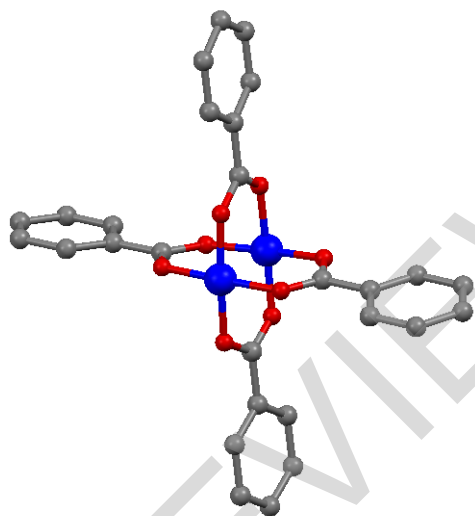


Figure 1.2 A $Cu_2(O_2CPh)_4$ paddle wheel-unit. Hydrogen atoms omitted for clarity.

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 acids¹²⁻¹⁴ and other organic linkers¹⁵⁻¹⁷ are known. One unique property of MOF compounds is that they have large surface areas, some exceeding $4000 \text{ m}^2 \text{ g}^{-1}$,^{18,19}; in comparison the highest value reported for activated carbon is $2030 \text{ m}^2 \text{ g}^{-1}$,²⁰ and for zeolites is $904 \text{ m}^2 \text{ g}^{-1}$.²¹ As a result, metal-organic frameworks are being investigated for applications in gas storage,² among other potential applications.

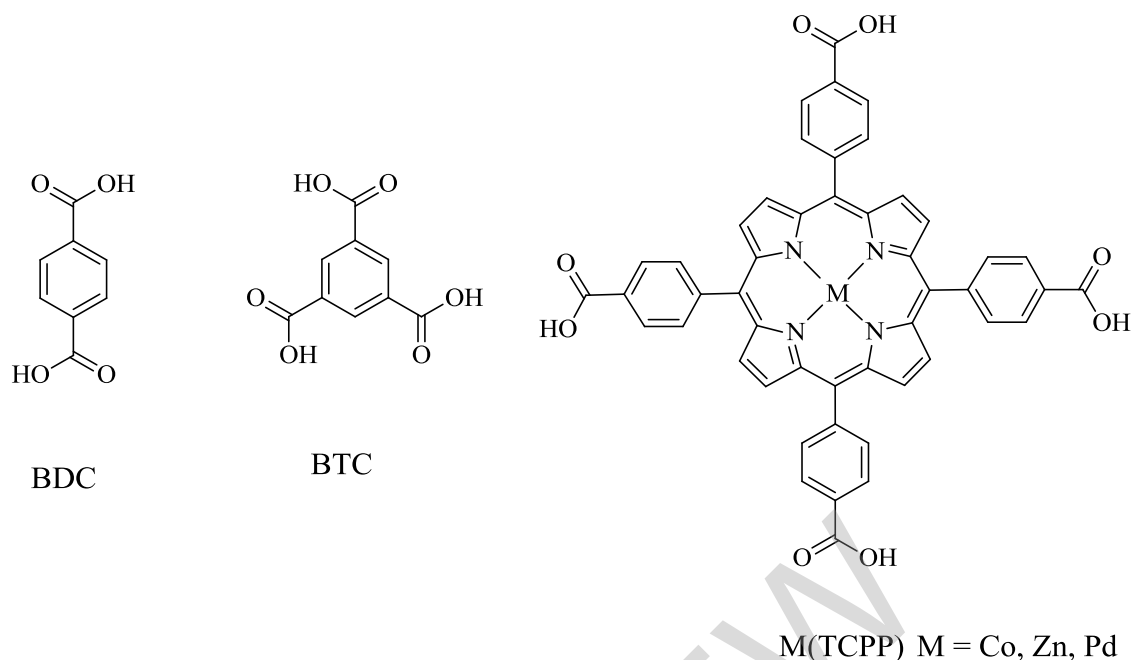


Figure 1.3 Polycarboxylic acid linkers for making MOFs.

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 square²² was reported in 1990 by the Fujita group. The square was made by reaction between 4,4'-bipyridine and (en)Pd(NO₃)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.

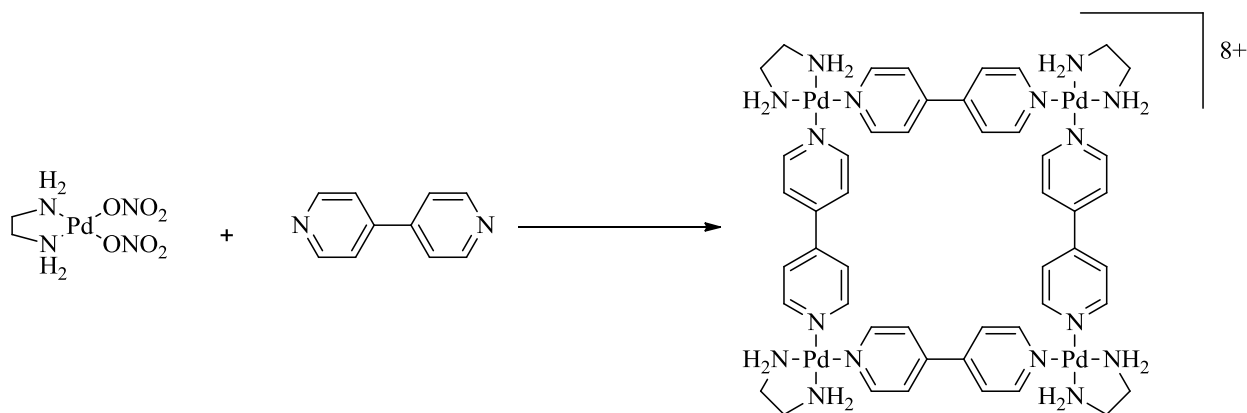


Figure 1.4 Synthesis of the molecular square²² from (en)Pd(NO₃)₂ and bpy.

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.²³ 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)₂.²⁴ 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,^{25,26} tetrahedra,²⁷⁻²⁹ octahedra,^{30,31} and others.³²⁻³⁵ 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.^{36,37}

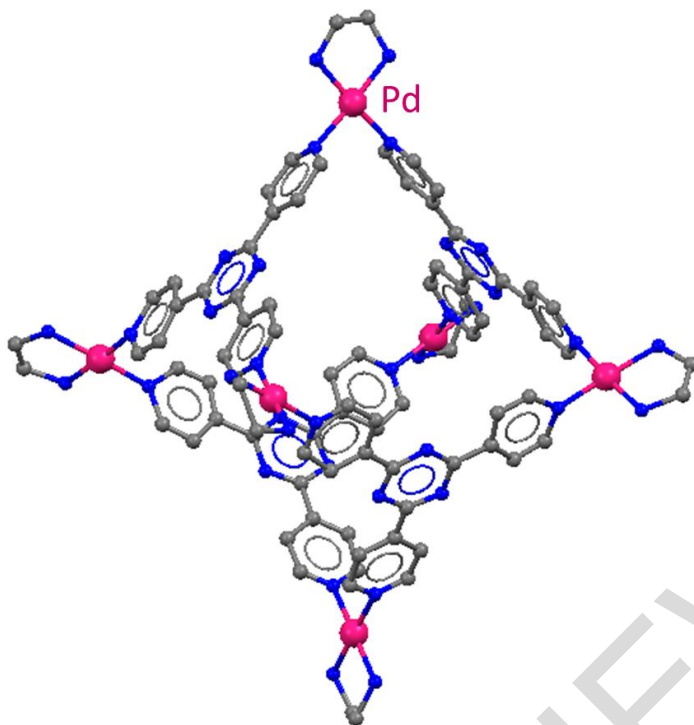


Figure 1.5 The molecular octahedron prepared by the Fujita group.²⁴ Hydrogen atoms omitted.

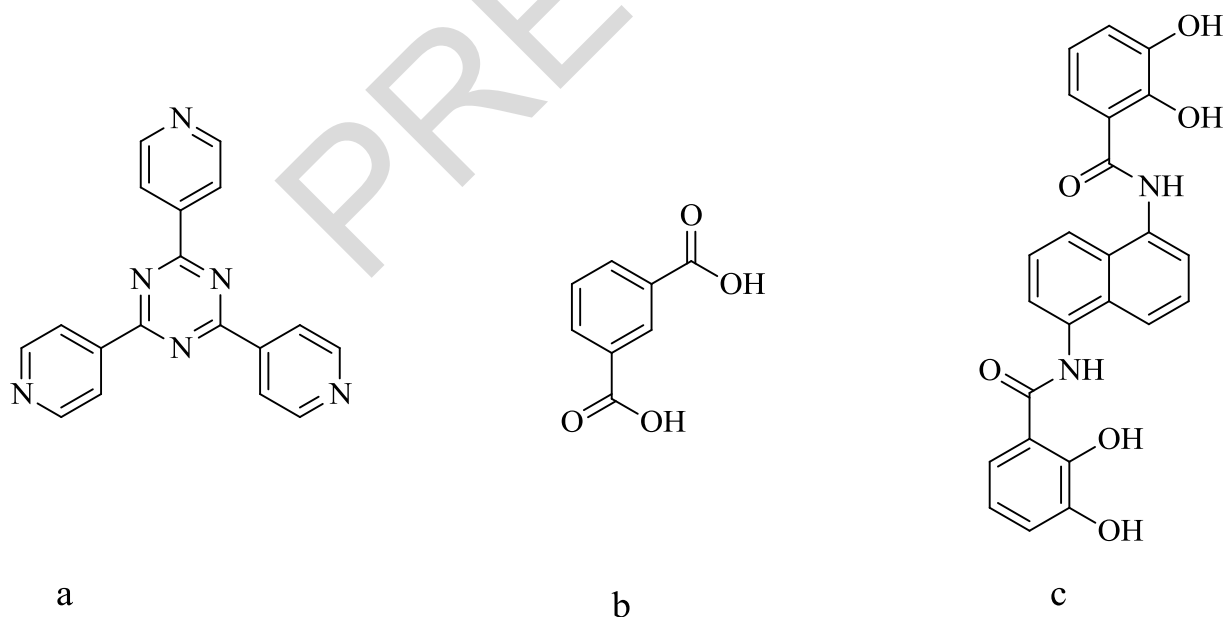


Figure 1.6 Organic linkers that have been used to prepare MOP molecules.

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 1.8.³⁸

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.³⁹ The rhenium corner was generated from $\text{Re}(\text{CO})_5\text{Cl}$ when two of its carbonyl ligands are displaced by the linker during its coordination to the metal.

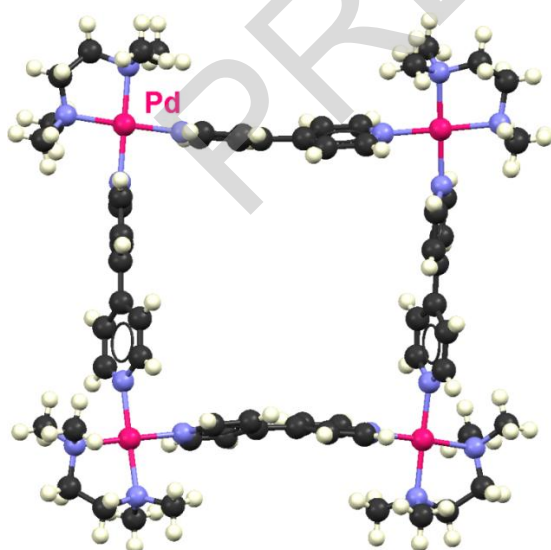


Figure 1.7 Molecular square prepared by the Mizuno group.³⁸

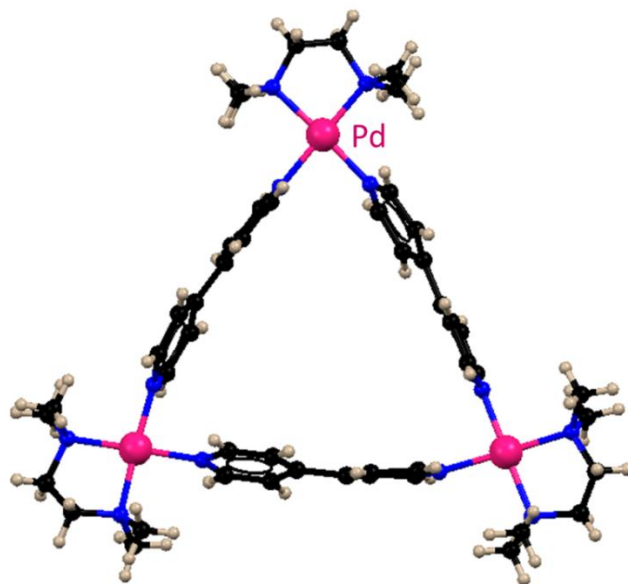


Figure 1.8 Molecular triangle prepared by the Mizuno group.³⁸

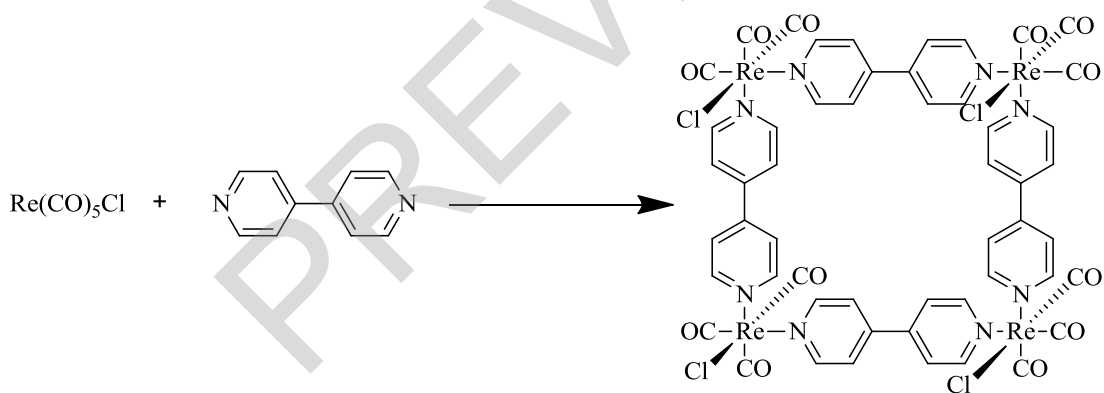


Figure 1.9 Reaction of $\text{Re}(\text{CO})_5\text{Cl}$ and bpy yielded a neutral molecular square.³⁹

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, $M_2(m\text{-XBA})_2$ and $M_2(\text{BBI})_2$ (Figures 1.11 and 1.12).^{40,41}

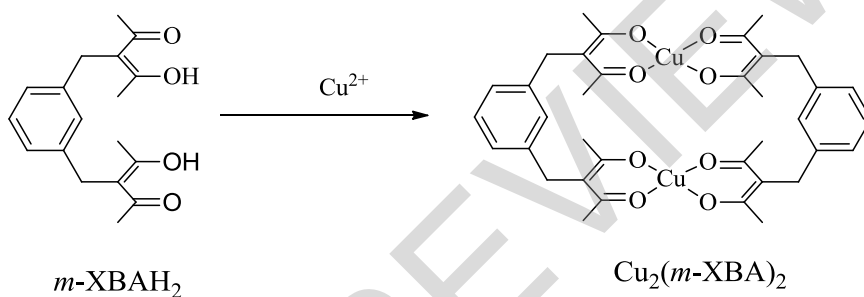


Figure 1.11 Reaction of $m\text{-XBAH}_2$ with Cu^{2+} afforded a molecular dimer, $\text{Cu}_2(m\text{-XBA})_2$.⁴⁰

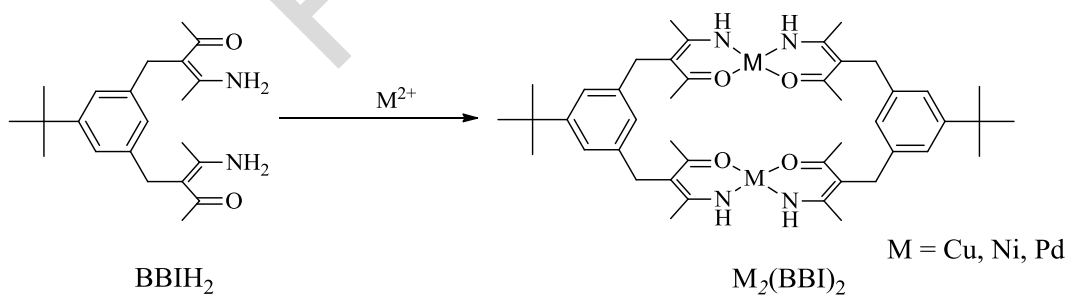


Figure 1.12 Reaction of BBIH_2 with Cu^{2+} , Ni^{2+} , or Pd^{2+} yielded molecular dimers, $M_2(\text{BBI})_2$.⁴¹

An attempt to prepare a MOP using a different bis(β -diketone) ligand, *o*-phenylenebis(acetylacetonate) (*o*-pbaH₂) (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.⁴²

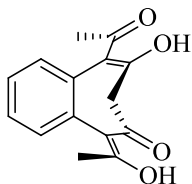


Figure 1.13 *o*-Phenylenebis(acetylacetonate), *o*-pbaH₂.

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 Cu²⁺ was reported by Clegg et al.²⁹ The first molecular square to incorporate β -diketone building block was reported by Zhang et al in 1998 (Figure 1.16),⁴³ and it was prepared by using tetraacetylthane (taeH₂) (Figure 1.15b) and an octahedral Co(II) corner that was capped with di-2-pyridylamine (Figure 1.15c).

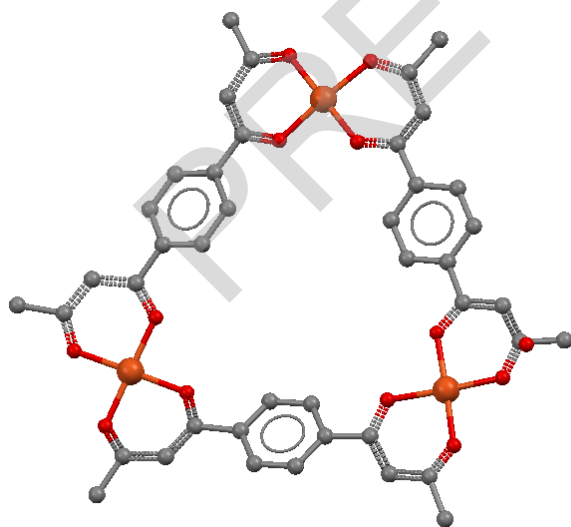


Figure 1.14 The β -diketonate molecular triangle prepared by Clegg et al.²⁹

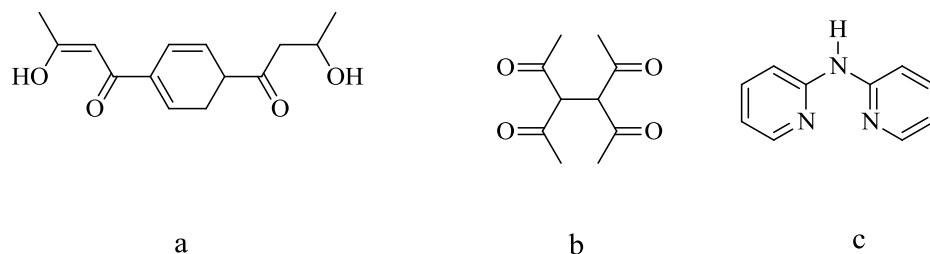


Figure 1.15 Structures of: (a) 1,1'-(1,4'-phenylene)bis(butane-1,3-dione), (b) tetraacetyethane (taeH_2) and (c) di-2-pyridylamine (dpa).

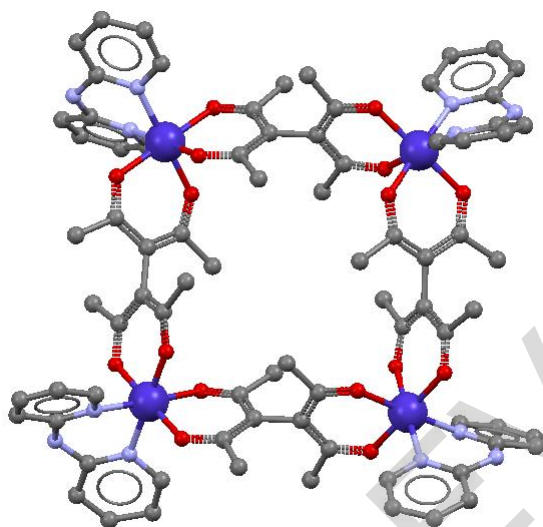


Figure 1.16 Molecular square prepared from Co^{2+} , tae^{2-} , and dpa by Zhang et al.⁴³

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}

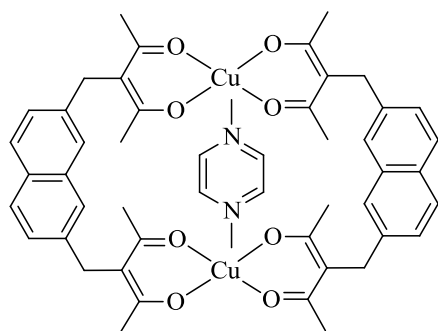


Figure 1.17 Molecular dimer- pyrazine adduct, $[\text{Cu}_2(\text{NBA})_2(\mu\text{-Pz})]$.⁴⁴

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

Recently our group reported molecular squares prepared from Cu^{2+} and the bis(β -diketone) ligands **1** (*m*-phenylenebis(acetylacetonate)), *m*-pbaH₂, and **2** (*m*-phenylenebis(dipropionyl-methane)), *m*-pbprH₂ (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 C₆₀.⁵⁰ 4,4'-bipyridine is coordinated through its N atoms, while C₆₀ is held through π - π 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 C₆₀ could not be determined because they are not soluble in the same solvents.

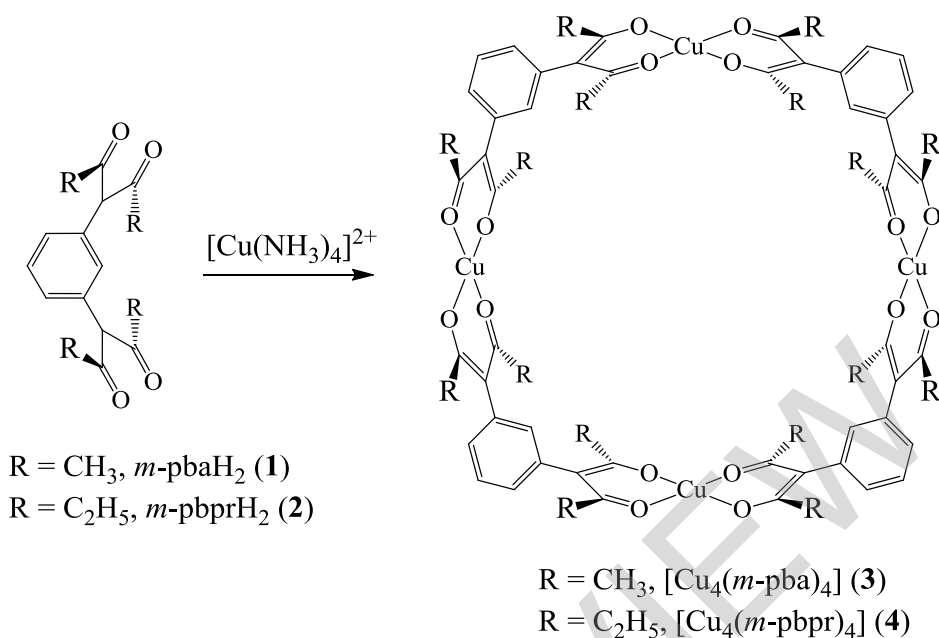


Figure 1.18 Reactions of bis(β -diketone) ligands **1** and **2** with Cu²⁺ afforded molecular squares.⁵⁰

This dissertation reports on the following topics: Syntheses of new derivatives of *m*-pbaH₂ (**1**): In chapter 2, the synthesis of the *m*-pbhxH₂ ligand, with pentyl chains replacing the methyl groups in the β -diketone moieties of *m*-pbaH₂, and the preparation of its molecular square, are described. In chapter 3 syntheses of two new ligands, 2-MeO-*m*-pbaH₂ and 2-MeO-*m*-pbprH₂ (in which a methoxy group is placed in the 2-position of the aromatic ring of *m*-pbaH₂), 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 Cu²⁺ and Ni²⁺ 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