Synthesis, characterization and properties of cooper(II) beta-diketonate macrocycles

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SYNTHESIS, CHARACTERIZATION
AND PROPERTIES OF
COPPER(II) BETA-DIKETONATE MACROCYCLES

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

Sylvester Burton
B.S., Southern University, 1977
M.S., Southern University, 1986
May 2006
Foreword

ANYONE WHO HAS EVER TRIED TO PRESENT A RATHER ABSTRACT scientific subject in a popular manner knows the great difficulties of such an attempt. Either he succeeds in being intelligible by concealing the core of the problem and by offering to the reader only superficial aspects or vague allusions, thus deceiving the reader by arousing in him the deceptive illusion of comprehension; or else he gives an expert account of the problem, but in such a fashion that the untrained reader is unable to follow the exposition and becomes discouraged from reading any further.

If these two categories are omitted from today’s popular scientific literature, surprisingly little remains. But the little that is left is very valuable indeed. It is of great importance that the general public be given an opportunity to experience (consciously and intelligently) the efforts and results of scientific research. It is not sufficient that each result be taken up, elaborated, and applied by a few specialists in the field. Restricting the body of knowledge to a small group deadens the philosophical spirit of a people and leads to spiritual poverty.

Albert Einstein
Princeton, New Jersey
September 10, 1948
Acknowledgments

FOR THEIR HELP AND ADVICE IN MY MATRICULATION, I wish to thank Dr. Andrew W. Maverick, Dr. Steve Watkins, Dr. Frank Fronczek for determining all of the crystal structures presented here, and my graduate committee, of the Department of Chemistry, Louisiana State University & A&M College; Dr. Robert H. Miller, Jr. of the Department of Chemistry/College of Sciences and Dr. Mildred R. Smalley of the Department of Chemistry/Office of the Vice Chancellor for Research and Strategic Initiatives, Southern University & A&M College.

And most of all, I thank GOD.
Table of Contents

Dedication ............................................................................................................ ii
Foreword ............................................................................................................. iii
Acknowledgements ............................................................................................. iv
List of Tables ..................................................................................................... vii
List of Figures ................................................................................................... viii
List of Abbreviations ............................................................................................ xi
Abstract .............................................................................................................. xii

Chapter 1
Introduction .......................................................................................................... 1

Chapter 2
3,5-Diacetyl-2,6-Heptanedione (C$_1$BAH$_2$) and Its Metal Complexes ........... 9
  2.1 Introduction .................................................................................................... 9
  2.2 Experimental ................................................................................................ 11
  2.2.1 Materials and Equipment ...................................................................... 11
  2.2.2 Preparation of 3,5-diacetyl-2,6-heptanedione (C$_1$BAH$_2$)
      and 2-methyl-3,5,5-triacetyltetrahydropyran-2-ol ..................................... 11
  2.2.3 Attempted Preparation of C$_1$BAH$_2$ Molecular Solid ....................... 13
  2.3 Results and Discussion ............................................................................. 15

Chapter 3
$p$-Xylylenebis(acetylacetone) ($p$-XBAH$_2$) and Its Metal Complexes .......... 23
  3.1 Introduction .................................................................................................. 23
  3.2 Experimental ............................................................................................... 23
  3.2.1 Materials and Equipment ...................................................................... 23
  3.2.2 Preparation of $p$-xylylenebis(acetylacetone) ($p$-XBAH$_2$) .............. 24
  3.2.3 Attempted Preparation of Cu$_3$(p-XBA)$_3$ Molecular Solid ............... 25
  3.2.4 Structural Analysis of $p$-XBAH$_2$ ......................................................... 27
  3.3 Results and Discussion ............................................................................. 28

Chapter 4
Cu$_2$(NBA)$_2$ • [Substrate] Studies ................................................................. 30
  4.1 Introduction ................................................................................................. 30
List of Tables

Table 2.1. Melting points of 3,5-diacetyl-2,6-heptanedione tautomers ..............10

Table 2.2. $^1$H NMR shifts for 3,5-diacetyl-2,6-heptanedione ............................................11

Table 2.3. Crystal data for 3,5-diacetyl-2,6-heptanedione and 2-methyl-3,5,5-triacetyltetrahydropyran-2ol ..................................................14

Table 2.4. Elemental analysis data of Cu(C$_1$BA)$_2$ ....................................................................18

Table 3.1. Crystal data for $p$-XBAH$_2$ .................................................................................26

Table 4.1. Crystal data of Cu$_2$(NBA)$_2$ • (1,4-dithiane) ........................................33

Table 4.2. Selected bond distance comparison .................................................................34

Table 5.1. $^1$H NMR shifts of (a) XBAH$_2$, (b) XBDPrH$_2$ and (c) NBDPrH$_2$ ..........44

Table 5.2. Crystal data of Cu$_2$(NBDPr)$_2$ ...........................................................................49

Table 5.3. Tabulation of $^1$H NMR data of starting materials. .................................50
List of Figures

Figure 1.1. Acetylacetonate anion (acac)´ .................................................................2
Figure 1.2. Picture of Λ and Δ enantiomers of a M(chelate)₃ complex .................3
Figure 1.3. Trinuclear (Ni(acac)₂)₃ .........................................................................4
Figure 1.4. Face to Face porphyrin ......................................................................4
Figure 1.5. (a) Cu₂(m-XBA)₂, (b) cis-syn Cu₂(BBI)₂ ...........................................5
Figure 1.6. (a) C₁BAH₂, (b) p-XBAH₂ ..................................................................6
Figure 1.7. (a) Cu₃(p-XBA)₃ (molecular triangle) (b) Cu₆(C₁BA)₆ (molecular hexamer) .................................................................7
Figure 1.8. Oh’s Proposed 4-coordinate polymer structures .................................8
Figure 2.1. 3,5-diacetyl-2,6-heptanedione tautomers .......................................10
Figure 2.2. ORTEP diagram of 3,5-diacetyl-2,6-heptanedione (C₁BAH₂) ..........12
Figure 2.3. ORTEP diagram of 2-methyl-3,5,5-triacetyltetrahydropyran-2-ol ....13
Figure 2.4. Reaction scheme and picture of proposed Cu₆(C₁BA)₆ hexamer ....17
Figure 2.5. Di-enol form of Cu(C₁BA)₂ ................................................................18
Figure 2.6. Chemical structure drawing and molecular model of dinuclear Cu unit containing one bridging C₁BA²⁻ ligand (Δ enantiomer shown) .................................................................19
Figure 2.7. Ring-shaped hexanuclear Cu complex containing alternating Δ- and Λ- C₁BA²⁻ bridging ligands ..........................................................20
Figure 2.8. Helical hexanuclear Cu complex containing all Δ-C₁BA²⁻ bridging Ligands .................................................................................................20
Figure 2.9. SPARTAN plot of conformational energy of the bis(enol) form of C₁BAH₂ vs. central C-C-C-C torsion angle. Also shown is a ball- and-stick illustration of the molecule when this torsion angle is

viii
close to 90 deg, i.e. approximately in the highest-energy conformation required for interconversion of the two enantiomeric forms of the ligand ...........................................................................................................21

Figure 3.1. ORTEP diagram of \( p\)-XBAH\(_2\) ..........................................................24

Figure 3.2. IR Spectrum of \( p\)-XBAH\(_2\) and \( Cu_n(p\)-XBA)\(_n\)..............................26

Figure 3.3. View of \( p\)-XBAH\(_2\) along the c- axis..........................................................28

Figure 3.4. Proposed coordination polymer structures for Cu(\( p\)-XBA) .................29

Figure 4.1. Intramolecular binding of generic host by Cu(\( p\)-NBA)\(_2\) .........................31

Figure 4.2. CCDC Mercury diagram of Cu(\( p\)-NBA)\(_2\)\(^*(1,4\)-dithiane), top view.................................................................33

Figure 4.3. ORTEP diagram of Cu(\( p\)-NBA)\(_2\)\(^*(1,4\)-dithiane), side view..........................34

Figure 4.4. Crystal packing diagram of Cu(\( p\)-NBA)\(_2\)\(^*(1,4\)-dithiane), view along a, showing the packing of adjacent molecules ..........35

Figure 4.5. Comparative side views of Cu(\( p\)-NBA)\(_2\)\(^*(S)\), with \( S = 1,4\)-dithiane, dabco and 2,5-Me\(_2\)pyz.................................35

Figure 4.6. Comparative top views of Cu(\( p\)-NBA)\(_2\) \( * (S)\), with \( S = 1,4\)-dithiane, dabco and 2,5-Me\(_2\)pyz.................................36

Figure 4.7. Stick figure view of Cu(\( p\)-NBA)\(_2\) \( * (1,4\)-dithiane) showing the deviation from co-planarity of the (bis)\( \beta\)-diketonate units............37

Figure 5.1. Structure of alkylated XBA and NBA Ligands ........................................39

Figure 5.2. Structure of Cu(\( p\)-XBDPr)\(_2\) and Cu(p-NBA)\(_2\)........................................40

Figure 5.3. Structures of XBAH\(_2\), XBDPrH\(_2\) and NBDPrH\(_2\) ligands .....................44

Figure 5.4. \(^1\)H NMR spectrum of crude XBDPrH\(_2\) .............................................45

Figure 5.5. \(^1\)H NMR spectrum of crude NBDPrH\(_2\) .............................................46

Figure 5.6. ORTEP diagram of Cu(3,5-heptanedionate).........................................48

Figure 5.7. CCDC Mercury diagram of Cu(3,NBDPr)\(_2\) with view along b.................49
Figure 6.1. (Z)-3,6-diacetyloct-4-ene-2,7-dione ................................................53

Figure 6.2. Possible (bis)β-diketonate precursor compared to C1BAH₂ ............53
List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>acacH₂</td>
<td>acetylacetone</td>
</tr>
<tr>
<td>acac⁻</td>
<td>acetylacetonate anion</td>
</tr>
<tr>
<td>BBI</td>
<td>bis(β-ketoenamine)</td>
</tr>
<tr>
<td>C₁BAH₂</td>
<td>3,5-diacetyl-2,6-heptanedione</td>
</tr>
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<td>dabco</td>
<td>1,4-diaza-bicyclo[2.2.2]octane</td>
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<td>NBAH₂</td>
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Abstract

This dissertation deals with the synthesis and properties of multidentate β-diketone ligands and their transition-metal complexes.

(1) We prepared two bis(β-diketones), $C_1\text{BAH}_2$ and $p\text{-XBAH}_2$ (see sketch below), determined their crystal structures, and studied their reactions with copper(II). We envisioned that they would form macrocyclic complexes with 3-6 metal atoms. In both cases, although the initial products are soluble, as expected for the desired molecular products, we were unable to isolate well-behaved molecular solids. In the case of $C_1\text{BAH}_2$, this may be because the cyclic product requires an unusual combination of conformations of successive ligands.

(2) We studied the reactions of $\text{Cu}_2(\text{NBA})_2$ (shown below) with the heterocyclic sulfur bases 1,4-dithiane and 2,5-dihydroxy-1,4-dithiane. The reaction with 1,4-dithiane produces a 1:1 adduct with the guest molecule internally coordinated to the Cu atoms of the host. The affinity of the $\text{Cu}_2(\text{NBA})_2$ host for 1,4-dithiane is very small. The substituted derivative 2,5-dihydroxy-1,4-dithiane was also studied as a potential guest, but its solubility is not compatible with that of the $\text{Cu}_2(\text{NBA})_2$ host.
(3) We attempted to determine if extending the aliphatic chains of our NBAH$_2$ and $p$-XBAH$_2$ ligands would increase their solubility in organic solvents and afford us the versatility to extend our groups study of binuclear transition metal complex host-guest systems. We successfully synthesized Cu$_2$(NBPr)$_2$, which contains ethyl groups in place of the methyl groups of Cu$_2$(NBA)$_2$. However, the new Cu$_2$(NBPr)$_2$ host is not significantly more soluble in common organic solvents than the parent Cu$_2$(NBA)$_2$. 
Chapter 1

Introduction

Supramolecular chemistry has emerged from the studies of such covalent systems as cyclophanes, crown ethers, calixarenes and cryptands. This field has for over a decade been dominated by the study of non-covalent moieties which consist of transition metal motifs and coordination bonded assemblies.

Molecular manufacturing of advanced materials with specific properties and functions has become the major challenge that faces modern supramolecular nanotechnology. These properties and functions are determined by controlling the form, shape and distribution of each individual building block subunit and their precise placement within the supramolecule. Such intermolecular control imposes strict requirements on the nature, type and directionality of the bonding forces that operate within the entire aggregated structure. The chemical bonding of the subunits must be relatively weak, thermodynamically stable, and yet kinetically labile to allow the self arrangement of the subunits within the entire structure, thereby enabling the self-correction of possible defects. Another important requirement is the conformational rigidity of the building blocks in order to reduce entropic factors upon self-organization.

The more recently developed synthetic protocol, namely self-assembly, relies on critical information about the shape and properties of the target
structures being preprogrammed into each individual building block, in order to construct nanoscopic assemblies from multiple building blocks in a single step.

For many years the search for new ligands has been a prevailing goal in coordination chemistry. Through the appropriate choice of ligands, we can generally design and synthesize coordination compounds having particular specified properties. However, because of the intrinsic complexity of many of the bridging-group derivatized ligands, unexpected modes of coordination may sometimes occur, and reactions may follow undesired routes.

Beta-diketonates represent one of the oldest classes of chelating ligands, and have become one of the ligands of choice because of the recent industrial applications of several of their metal complexes. Beta-diketonates are made by methods similar to those for the alkoxides. Beta-diketonates form anions as a result of enolization and ionization after α-proton extraction by base. These beta-ketoenolate ions form very stable chelate complexes with most metal ions. The most common diketonate ionic ligand is the acetylacetonate anion (acacH)\(^-\) (Figure 1.1), where \(R = R'' = CH_3\) and \(R' = H\). The usual abbreviation for β-ketoenolate ions in general is (β-dike). Among the commonest types of diketonate complexes are those with the stoichiometries

![Figure 1.1. Acetylacetonate anion (acac)\(^-\), \(R = R'' = CH_3\) and \(R' = H\).](image-url)
M(β-dike)$_3$ and M(β-dike)$_2$ tris and bis respectively. The former have structures based on an octahedral disposition of the six oxygen atoms. These tris(chelate) molecules actually have D$_3$ symmetry and exist as enantiomers, (see Λ and Δ structures in Figure 1.2). Chiral diketonate complexes have found applications in fields such as catalysis and gas-chromatographic separations of enantiomers. Togni, for example has demonstrated that the chiral Lewis acid bis[(1R)-3-(heptafluorobutyryl)camphorato]oxovanadium(IV) can be used to promote the hetero-Diels-Alder reactions between and aldehyde and a diene of the type described by Danishefsky. Tetradiketo complexes such as M(β-dike)$_4$ on the other hand, have usually been found to be nonrigid.

Compounds with the composition M(β-dike)$_2$ are very often oligomeric, thereby allowing coordinative saturation of the metal. Thus, acetylacetonates of anhydrous Zn$^{ll}$, Ni$^{ll}$, and Mn$^{ll}$ are trinuclear (Figure 1.3) but Co(acac)$_2$ which is expected to assume a square planar or tetrahedral arrangement, actually assumes a tetrannuclear arrangement of the ligands and have bridging beta-diketonate groups. The result is a tetramer in which a pseudo-octahedral arrangement is achieved by each cobalt(II) cation. The presence of bulky substituents such as a t-butyl group on the beta-diketonate has been shown to
sterically impede oligomerization, and monomers are generally formed. These are commonly solvated by H₂O, ROH, or pyridine to give 5- or 6-coordinate complexes, such as trans-M(β-dike)₂L₁₂.¹¹

The linking of β-diketonates by specific bridges allow them to form “face-to-face” complexes similar to those of the “face-to-face” porphyrins (Figure 1.4), therefore affording the occupancy of the central cavity by small molecules. These bridged β-diketonates are commonly referred to as bis-(β-diketonates). With trivalent ions such as Ti³⁺, V³⁺, Mn³⁺, or Fe³⁺, triple-helical structures consisting of two 6-coordinate M³⁺ ions chelated by three bis-(β-diketonate) ligands can be obtained.¹¹

Our group has been interested in metal bis-(β-diketonate) complexes for years because of their host-guest chemistry¹³⁻¹⁸ and CVD applications to form
thin metal films. The goal of our group’s study of host-guest chemistry has been directed toward the use of select bis-(β-diketonates) and Schiff-base ligands to make binuclear metal-complexes and examine their suitability for host access, release and/or exchange.

In the examples discussed here, the metal atoms are either coordinatively unsaturated or contain ligands that can easily be displaced when the metallic moiety is introduced to other donors. This would allow the host to bind a variety of guest molecules,\textsuperscript{1.19} which has been shown to be the case in some of our group’s earlier work.

Therefore, the basis of our chemistry has been in the ligating ability of the acetylacetone (acacH\textsubscript{2}) moiety, which has been extensively studied over the years, primarily because of its rich coordinating ability to metal centers.\textsuperscript{1.13, 1.14, 1.20}

Cofacial binuclear transition metal complexes derived from bis-(β-diketones) and bis-(β-ketoenamine)\textsuperscript{1.13, 1.14, 1.21} ligands have also been investigated by our group (Figure 1.5). The aim of this study has been to extend the usage of bis-(β-diketones) and construct inorganic-organic hybrid molecules

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure15}
\caption{(a) Cu\textsubscript{2}(m-XBA)\textsubscript{2}, (b) cis-syn Cu\textsubscript{2}(BBI)\textsubscript{2}}
\end{figure}
which possess pores that are well defined by several types of nodes. My contribution for this phase of our group’s research has been the preparation of a series of bis-(β-diketonate) molecular solids having identical nodes which contain chemical functionalities that are spatially organized by covalent and/or noncovalent interactions during the synthetic process, thus designing sites for the recognition of small molecules. The resulting complexes were to be examined for their host binding ability to determine if these interactions could form the basis for nanoscale sensors and chemically active devices.

Accordingly, on the basis of well defined molecular angles between two bridged acetylacetonate moieties, two types of molecular complexes were envisioned for our C₁BAH₂ and p-XBAH₂ ligands (Figure 1.6). However, the formation of substrate-specific cavities while conceptually straightforward turned out to be difficult to accomplish experimentally.

The synthetic difficulties that were encountered during the preparation attempts of the trimer and hexamer molecular solids (Figure 1.7) was attributed to steric s and the tendency of these ligands to form the linear monomer coordination compounds, possessing a metal to ligand ratio of 1:2, M(L)₂ (Figure 1.8).

There are several literature references which indicate that when certain bridged beta-diketonates are treated with di- and tri-cationic transition metals
(M$^{2+}$ or M$^{3+}$), they have the tendency to form 4-coordinate linear oligomers of three (Figure 1.8) types,$^{1,22}$ (1) [(RCO)(R’CO)CH]$_2$, (2) (RCO)(R’CO)CH-Y-CH(R’CO)(RCO) and (3) (RCO)(R’CO)CH-CHR”-CH(R’CO)(RCO) with R = R’ = -CH$_3$ and Y = -(CH$_2$)$_2$- and -CH$_2$-C$_6$H$_6$-CH$_2$-. These systematic oligomeric structures were determined based on their elemental analysis.

As previously mentioned, our group in a prior study determined that Cu$_2$(NBA)$_2$ intramolecularly coordinates the nitrogen bases, dabco and pyrazine. Based on that study, I undertook the task of examining the coordinating ability of Cu$_2$(NBA)$_2$ with heterocyclic sulfur-containing bases in order to compare the relative binding strengths of Cu$_2$(NBA)$_2$ with nitrogen bases and those with sulfur bases.

However, one of the challenges discovered was that in order to enhance
the coordination, the host and the guest should be soluble in the same solvent system. This was of concern because it had been discovered that Cu$_2$(NBA)$_2$ was practically insoluble in most organic solvents. Therefore, we decided to modify our Cu$_2$(NBA)$_2$ by alkyllating the acac$^-$ moiety in an attempt to increase its solubility in organic solvents, whereby if achieved, would allow us the potential for enhancing the coordination of our guest molecules.
Chapter 2
3,5-Diacetyl-2,6 Heptanedione(C\textsubscript{1}BAH\textsubscript{2})
and Its Metal Complexes

2.1. Introduction

Since the work of Knoevenagel\textsuperscript{2.1-2.2} in the late nineteenth and early twentieth centuries, when he first reported the condensation products of 2,4-pentanedione with aldehydes, reactions of the compounds have been investigated extensively\textsuperscript{2.1-2.2,2.4-2.6}. For example Aarna et al\textsuperscript{2.7} have shown (Scheme 2.1) that with a 2:1 ratio of acacH:HCHO the product is 3,5-diacetyl-2,6-heptanedione(I) and with a 2:2 ratio of acacH\textsubscript{2}:HCHO the undesired product, 3,5,5-triacetyl-tetrahydropyran-2-ol(II) is produced.

![Scheme 2.1](image)

The IR for (I) shows two CO bands at 1735 cm\textsuperscript{-1} and 1715 cm\textsuperscript{-1}. The NMR for (I) shows chemical shifts, \(\delta = 2.2\) (Me), 2.28 2.35 (t, CH\textsubscript{2}) and 3.58, 3.66, 3.75 ppm (t,CH). We prepared the target ligand 3,5-diacetyl-heptane-2,6-dione according to the procedure introduced by Wilson\textsuperscript{2.4} who investigated the condensation reaction between formaldehyde (HCHO) and 2,4-pentanedione, (acacH\textsubscript{2}). Because of steric effects and the terminal CH\textsubscript{3}- groups, this reaction
produces the tautomeric (or enol isomeric) forms of the 1:1 condensation product 3,5-diacetyl-2,6 heptanenedione in good yield (Figure 2.1).

![Figure 2.1. 3,5-Diacetyl-2,6-heptanenedione tautomers.](image)

Conjugated intermolecular hydrogen bonding in the enol isomer causes the extent of enolization of β-diketonates and β-ketoesters to be much greater than for other carbonyl systems. It has also been shown that the more polar keto forms are stabilized by polar solvents and protic solvents of high dielectric constant, $\varepsilon$, because these have a tendency to disrupt the intermolecular hydrogen bonding that is present in the enol form. For example, at 298 K acetylacetone is 96% enolized in CCl$_4$ ($\varepsilon = 2.23$)$^{2,8}$, ~80% enolized in $p$-dioxane ($\varepsilon = 2.21$)$^{2,9,2,10}$, and only 16% enolized in water ($\varepsilon = 78.5$)$^{2,11,2,12}$ Wilson and O'Loane initially characterized this compound by melting point$^{2,4}$ (Table 2.1) and $^1$H NMR spectroscopy$^{2,5}$ (Table 2.2) respectively.

Table 2.1. Melting points of 3,5-diacetyl-2,6-heptanenedione tautomers

<table>
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<td>41.5–42.5° C</td>
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Table 2.2. $^1$H NMR shifts for 3,5-diacyl-2,6-heptanedione

<table>
<thead>
<tr>
<th>O’Loane$^{2,5}$ in CDCl$_3$</th>
<th>Experimental ppm</th>
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<tr>
<td>2.238(s)</td>
<td>2.161(s)</td>
<td>Keto -CH$_3$</td>
</tr>
<tr>
<td>2.275(t)</td>
<td>2.265(t)</td>
<td>-CH$_2$</td>
</tr>
<tr>
<td>3.700(t)</td>
<td>3.660(t)</td>
<td>-CH</td>
</tr>
<tr>
<td>not reported</td>
<td>16.891</td>
<td>Chelated OH</td>
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2.2. Experimental

2.2.1. Materials and Equipment

All compounds, reagents and solvents were spectrophotometric or reagent grade and were used as received unless otherwise specified. $^1$H NMR spectra were recorded on a Bruker 250-MHz spectrometer. UV-Visible spectra were recorded on an AVIV model 14DS UV-VIS-IR spectrophotometer. IR spectra were recorded on a Bruker Tensor-27 infrared spectrophotometer and microanalyses were performed by M-H-W Laboratories, of Phoenix, Arizona.

The molecular modeling was performed using SPARTAN (Figure 2.9) and Hyperchem version 7, and the illustrations in Figures 2.6, 2.7 and 2.8 were prepared using CCDC Mercury software.

2.2.2. Preparation of 3,5-diacyl-2,6-heptanedione (C$_1$BAH$_2$) and 2-methyl-3,5,5-triacetyltetrahydropyran-2-ol.

A mixture of 40 g (0.40 mol) 2,4-pentanedione, 15 mL. of formalin (ca. 37%) (0.20 mol) was stirred at room temperature for 5 days. At the end of the 5 day period the solvent was removed under vacuum. The residue (about 12 mL)
was diluted with an equal volume of ethyl ether and introduced to a dry ice-acetone bath which promoted crystallization of the desired product. After several repeated crystallizations in a dry ice-acetone bath, several crops of C_{1}BAH_{2} colorless crystals were obtained which eventually gave a m.p. 40.5-41°C. The final product (9.03 g, 0.0425 mole) was fully characterized by its $^1$H-NMR and IR-spectra, and X-ray crystal structure (Figure 2.2).

When the above condensation is conducted in the presence of diethylamine as catalyst, a crystalline product was observed which was later determined by X-ray diffraction to be 2-methyl-3,5,5-triacetyltetrahydropyran-2-ol.

Figure 2.2. ORTEP diagram of 3,5-diacetyl-2,6-heptanedione, (C_{1}BAH_{2}).
(Figure 2.3), the 2:2 product that Aarna, et al.\textsuperscript{2,7} and McMurry, et al.\textsuperscript{2,13} had reported when they had conducted the reaction using a basic catalyst. Comparative crystal data for 3,5-diacetyl-2,6-heptanedione and 2-methyl-3,5,5-triacetyltetrahydropyran-2-ol are listed in Table 2.3.

![Figure 2.3. ORTEP diagram of 2-methyl-3,5,5-triacetyltetrahydropyran-2-ol.](image)

**2.2.3 Attempted Preparation of C\textsubscript{1}BAH\textsubscript{2} Molecular Solid**

The molecular solid synthesis was initially conducted using Cu\textsuperscript{2+} as the metal cation. Based upon literature findings, two methods were examined in these preparative attempts with our 3,5-diacetyl-2,6-heptanedione, (C\textsubscript{1}BAH\textsubscript{2}) ligand. Initially, the molecular solid synthesis was attempted by adding a
Table 2.3. Crystal data for 3,5-diacetyl-2,6-heptanedione and 2-methyl-3,5,5-triacetyltetrahydropyran-2-ol.

<table>
<thead>
<tr>
<th>empirical formula</th>
<th>C₁₁H₁₆O₄</th>
<th>C₁₂H₁₈O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>fw (g/mol)</td>
<td>212.24</td>
<td>242.26</td>
</tr>
<tr>
<td>T (K)</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>cryst syst</td>
<td>orthorhombic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P 2 1 2 1</td>
<td>P n</td>
</tr>
<tr>
<td>a (Å)</td>
<td>7.810(2)</td>
<td>7.5981(4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.611(2)</td>
<td>8.8133(5)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>17.431(4)</td>
<td>9.1692(4)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
<td>90</td>
<td>91.260(4)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1172.27</td>
<td>613.861</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>d (calc’d) (Mg/m³)</td>
<td>1.203</td>
<td>1.311</td>
</tr>
<tr>
<td>R₁ (%)</td>
<td>4.1</td>
<td>4.6</td>
</tr>
</tbody>
</table>

chloroform solution of C₁BAH₂ to an aqueous solution consisting of a mixture of CuSO₄•5H₂O and NH₄OH (as proposed in Scheme 2.2). Specifically, a 1.299g (5.20 mmole) portion of CuSO₄•5H₂O was taken up in 10 mL of distilled water and 3 mL of NH₄OH was added to the solution. The resulting blue solution was transferred to a 125 mL separatory funnel in one portion. Afterwards, a 0.121g (0.57 mmol) portion of C₁BAH₂ was taken up in 5 mL of chloroform and introduced to the 25 mL separatory funnel. After setting for 2½ days an olive green organic layer was evident. The green organic layer was extracted over MgSO₄ and saved. Secondly, the molecular solid synthesis was attempted by dissolving a 0.198 g portion of CuCl₂•2H₂O in 2.5 mL of distilled water in a 25 mL Erlenmeyer flask. I then added dropwise over a 20 minute period, a methanol
solution (0.467 g C\textsubscript{1}BAH\textsubscript{2} in 1.0 mL) of C\textsubscript{1}baH\textsubscript{2}, which resulted in a light green solution. I then added an aqueous NaC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} (0.348 g NaC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} in 1.5 mL) component in one portion and the solution turned olive green and afforded a grayish-white precipitate. After suction filtration to collect the precipitate, I allowed the suction to continue until all the MeOH solvent had evaporated from the side armed flask leaving behind a grey and a green precipitate. The gray precipitate was insoluble in water, therefore I concluded that the grey precipitate was organic. I then treated the side arm flask with 2mL of CHCl\textsubscript{3} and separated a dark green organic layer from an apparent blue-green aqueous layer and stored it. The previously separated grey solid was taken up in 13 mL CHCl\textsubscript{3} and combined with the 2 mL CHCl\textsubscript{3} portion. The resulting mixture was dried over Na\textsubscript{2}CO\textsubscript{3} and Na\textsubscript{2}SO\textsubscript{4} and a 15 mL olive green portion was collected.

2.3. Results and Discussion

\textsuperscript{1}H NMR analysis can be used to determine the ratio of the number of different kinds of protons in a single compound. It has also been used to
determine the ratio of magnetically nonequivalent protons in the two different forms (keto and enol) of acetylacetone (Scheme 2.3). Because the keto

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{CH}_3 \\
& \quad \text{OH} & \quad \text{O} & \quad \text{H}_2 & \quad \text{a} & \quad \text{O} & \quad \text{H}_3\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{CH}_3 \\
& \quad \text{OH} & \quad \text{O} & \quad \text{H}_3\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{CH}_3
\end{align*}
\]

Scheme 2.3.

hydrogens (a) and the enol hydrogens (b and c) are magnetically nonequivalent protons, they should have different chemical shifts. According to theory there are three (3) possible isomers for 3,5-diacetyl-2,6-heptane dione (Scheme 2.4), C\textsubscript{1}BAH\textsubscript{2} (the bis-diketone, the mono-enol/mono-ketone, and the bis-enol).

Because of the 110\textdegree angle imposed on the β-diketonate groups of the C\textsubscript{1}BAH\textsubscript{2} ligand by the methylene bridge between them we believed that a six-membered hexanuclear complex similar to that shown in Scheme 2.2 and Figure 2.4 might be formed.
Because I could not produce sufficient x-ray quality crystals of the proposed Cu$_6$(C$_1$BA)$_6$ hexamer, I attempted to acquire mass spectrometer (MS) data. After numerous attempts to acquire suitable MS data failed, a sample of the olive green dendrimer looking material that had resulted from each attempt to crystallize the compound was sent out for elemental analysis by M-H-W Laboratories, Phoenix, AZ.

![Diagram of proposed Cu$_6$(C$_1$BA)$_6$ hexamer]

**Figure 2.4.** Reaction scheme and picture of proposed Cu$_6$(C$_1$BA)$_6$ hexamer

The elemental analysis did not substantiate the calculated molecular mass for the proposed hexameric structure Cu$_6$(C$_1$BA)$_6$. However, the elemental analysis does support Cu(C$_1$BA)$_2$, see Table 2.4 and Figure 2.5.

After exploring the literature and discovering the extent of work that has already been conducted with acetylacetone (our basic coordination moiety), and its coordinating behavior with numerous transition metal ions including Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$, I decided to examine the coordinating ability C$_1$BAH$_2$ with Co$^{2+}$, Ni$^{2+}$, and Zn$^{2+}$ metal ions as well, in order to ascertain whether either of
these would respectively yield one of the proposed molecular solids. As with the Cu$^{2+}$ preparation attempts, the Co$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ preparations were also attempted by both of the mentioned synthetic methods. The only products that were generated were viscous oils, which could not be characterized.

Based on the oil formations mentioned above and Oh’s$^{2,14}$ proposed polymer structures, I am led to believe that the metal and ligand do not coordinate in a cyclic fashion as we had envisioned for our molecular solids, but generally react to form polymers.

![Figure 2.5. Di-enol form of Cu(C_{1}BA)_{2}](image)

**Table 2.4. Elemental analysis data of Cu(C_{1}BA)_{2}.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Theoretical % Based on Cu$_6$(C$_1$BA)$_6$</th>
<th>Theoretical % Based on CuO$<em>4$C$</em>{22}$H$_{30}$O$_4$</th>
<th>Determined %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>47.9</td>
<td>54.37</td>
<td>a. 54.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b. 54.46</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.86</td>
<td>6.22</td>
<td>a. 6.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b. 6.34</td>
</tr>
</tbody>
</table>
Because of steric interference between methyl groups, the most stable conformation of the $C_1BA^{2-}$ ligand is twisted, as shown in Figure 2.6. This twist makes the conformation chiral, and the two possible senses of the twist can be represented as $\Delta$ and $\Lambda$. The $\Delta$ enantiomer is shown in the figure.

Assembly of a macrocyclic polynuclear complex from $C_1BA^{2-}$ requires specific conformations of the ligand. For example, the most stable ring structure for $Cu_6(C_1BA)_6$, shown in Figure 2.7, contains alternating $\Delta$ and $\Lambda$ ligands. A ring structure is much more difficult to assemble using other combinations of ligand conformations; instead, a polymer is more likely to be formed (see example in Figure 2.8). Therefore, if only a few combinations of ligand conformations are
permissible in a ring structure, with most other possible combinations leading to polymers, it is not surprising that our Cu-C\textsubscript{1}BA product behaves more like a polymeric material.

Figure 2.7. Ring-shaped hexanuclear Cu complex containing alternating Δ- and Λ- C\textsubscript{1}BA\textsuperscript{2−} bridging ligands.

Figure 2.8. Helical hexanuclear Cu polymer containing all Δ-C\textsubscript{1}BA\textsuperscript{2−} bridging ligands.
Even though only a few conformations of a Cu\(_n\)(C\(_1\)BA\(_n\) chain can lead to ring formation, rings could still form in good yield if the enantiomers of individual C\(_1\)BA units can interconvert readily. To determine whether this is possible, we modeled the enolic form of C\(_1\)BAH\(_2\) in SPARcAN\(^{2,15}\) and determined that the interconversion energy barrier between its enantiomeric forms is relatively low, \(~10.5\) kcal/mol (Figure 2.9).

![Figure 2.9: SPARcAN plot of conformational energy of the bis(enol) form of C\(_1\)BAH\(_2\) vs. central C-C-C-C torsion angle. Also shown is a ball-and stick illustration of the molecule when this torsion angle is close to 90 deg, i.e. approximately in the highest-energy conformation required for interconversion of the two enantiomeric forms of the ligand.](image-url)
Thus, interconversion of the C1BA enantiomers may be relatively rapid. However, under our conditions, the interconversion may still not be fast enough to prevent formation of polymeric products.
3.1. Introduction

In our group’s investigation of the chemistry of cofacial binuclear transition-metal complexes derived from bis(β-diketone) ligands, we have searched for new types of bis(β-diketones) to serve as linkers for our proposed molecular solids as well. Traditionally, alkylated β-diketones were prepared in a steel or glass bomb by the interaction of the sodium salt of a β-diketone and an alkyl halide. A second procedure consisted of refluxing a mixture of the sodium salt of a β-diketone with excess alkyl halide in either a high boiling solvent such as nitrobenzene or with no solvent at all. In addition we’ve searched for ways to develop novel methods for the preparation of such bis(β-diketones) as the previously known \( p \)-xylylenebis(acetylacetone) \( (p-XBAH_2) \) which we synthesized by the method devised by Martin, et al., which consisted of interacting acetylacetone and a dihalide in a \( t \)-butanolic solution of potassium \( t \)-butoxide. In a prior work by our group, we attempted to prepare the \( \text{Cu}_2(p-XBA)_2 \) dimer. However all attempts to isolate the dimer and characterize it have proved to be unsuccessful.

3.2. Experimental

3.2.1 Materials and Equipment

Chemicals and solvents were reagent or spectrophotometric grade and
were used as received. $^1$H NMR spectra were recorded on a Bruker 250-MHz spectrometer. UV-Visible spectra were run on an AVIV model 14DS UV-VIS-IR spectrophotometer. IR spectra were run on a Bruker Tensor-27 infrared spectrophotometer.

3.2.2. Preparation of $p$-Xylylenebis(acetylacetone) ($p$-XBAH$_2$)

The ligand $p$-xylylenebis(acetylacetone) ($p$-XBAH$_2$), shown in Figure 3.1, was previously prepared in our laboratory by Yeager$^{3,9}$, according to the method prescribed by Martin and Fernelius$^{3,10}$ (1959), who used it in their study as a component in the formation of organic and coordination polymers. We envisioned that this compound would act as a conformationally fixed, bridging ligand in the preparation of transition-metal coordinated molecular solid complexes. The established synthesis is shown in Scheme 3.1. The $^1$H NMR was consistent with previously reported spectrum. This compound was further

![Figure 3.1. ORTEP diagram of $p$-XBAH$_2$](image-url)
characterized by its melting point (109-110°C), IR (Figure 3.2) and x-ray structure (Figure 3.1). The x-ray crystal data for \( p\)-XBAH\(_2\) is summarized in Table 3.1.

### 3.2.3. Attempted Preparation of \( \text{Cu}_3(p\text{-XBA})_3 \) Molecular Solids

A 5.013 g (20.1 mmole) portion of \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) was taken up in 25 mL of distilled water and introduced to a 500 mL separatory funnel. A 35 mL portion of conc. \( \text{NH}_4\text{OH} \) was added to the funnel and the mixture was shaken until a white precipitate formed and dissolved. A 0.6065 g (2.01 mmole) portion of \( p\)-XBAH\(_2\) was taken up in 150 mL of methylene chloride (\( \text{CH}_2\text{Cl}_2 \)) and added to the mixture in the separatory funnel. After repeated agitation, the \( \text{CH}_2\text{Cl}_2 \) layer was extracted. The aqueous layer was washed with 50 mL of \( \text{CH}_2\text{Cl}_2 \) and the combined \( \text{CH}_2\text{Cl}_2 \) layers were reduced in volume at low pressure on the roto-
Table 3.1. Crystal data for $p$-XBAH$_2$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C18H22O4</td>
</tr>
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<td>fw</td>
<td>302.36</td>
</tr>
<tr>
<td>T (K)</td>
<td>100</td>
</tr>
<tr>
<td>cryst syst</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P21/c</td>
</tr>
<tr>
<td>a (Å)</td>
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<tr>
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<td>5.591(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.819(4)</td>
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<tr>
<td>α (deg)</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
<td>107.890(15)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>794.2(5)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>d (calc’d) (Mg/m$^3$)</td>
<td>1.264</td>
</tr>
<tr>
<td>R$_1$ (%)</td>
<td>4.5</td>
</tr>
</tbody>
</table>
evaporator to ~ 2 mL of a light blue-green organic solution. This solution was treated with anhydrous Na$_2$SO$_2$, filtered and allowed to air evaporate under the fume hood overnight. This yielded 0.467 g (0.421 mmole) ~63% yield of green precipitate. All attempts to grow X-ray quality crystals failed. The proposed synthetic pathway for preparing Cu$_3$(p-XBA)$_3$ is shown in Scheme 3.2.

3.2.4. Structural Analysis of p-XBAH$_2$

The p-XBAH$_2$ crystallized with two distinct molecules (Z = 2) in the unit cell. The structure was solved in the monoclinic system, in space group P2$_1$/c. Individual p-XBAH$_2$ molecules in the crystal are centrosymmetric and are oriented in a trans-type configuration. If these molecules cannot easily rotate and “trans”-type configuration is preferred, that may favor formation of polymers rather than rings. A view of p-XBAH$_2$ along the c axis is shown in Figure 3.3.

![Scheme 3.2. Proposed synthetic pathway for Cu$_3$(p-XBA)$_3$.](image)
3.3. Results and Discussion

It has been documented$^{3,8}$ that in the solid state some bis-(β-diketones) of the type [(RCO)(R’CO)-CH$_2$CHR’’ exist to an appreciable extent in the keto form. This has been evidenced by the high intensity carbonyl absorption in the 1733-1709 cm$^{-1}$ region and the relatively low intensity enol-chelate absorption near 1550 - 1600 cm$^{-1}$. Also, most of these bis-(β-diketones) have hydroxyl stretching bands near 3389.8 cm$^{-1}$. There has also been evidenced in some cases a shifting of the hydroxyl bands to where they become obscured by the C-H stretching vibration bands in the 2900 – 3000 cm$^{-1}$. This is believed to be due to enolate formation.

The IR spectra for the $p$-XBAH$_2$ ligand show two to three bands in the region 1500 -1600 cm$^{-1}$, which are characteristic of the mixed modes of vibrations.
arising due to the normal coordinates having contribution from \( \nu(C=O) \) and \( \nu(C=C) \) of the \( \beta \)-diketone groups.\(^3\)\(^,\)\(^11\) The coordination of the carbonyl groups to the Cu center is evidenced by the absence of these bands between 1550 – 1600 cm\(^{-1}\) in the Cu\(_2\)(p-XBA) complex. Shown in Figure 3.4 are the proposed coordination polymer structures for Cu(p-XBA). I believe that the product we obtained in our experiment is at the least a mixture of structures II and III in an appreciable amount, (Fig. 3.4). This assumption is based on the presence of the low intensity broad stretching band observed between 3300 cm\(^{-1}\) and 3500 cm\(^{-1}\) in the IR spectrum depicted in Figure 3.2.

Figure 3.4. Proposed coordination polymer structures for Cu(p-XBA).
Chapter 4

Cu$_2$(NBA)$_2$•[Substrate] Studies

4.1. Introduction

The use of chelating ligands in the synthesis of multimetal systems has been of both practical and fundamental interest. Numerous macrocyclic polynuclear metal complexes have been prepared in which metal atoms bind guest molecules. The complexing of two metal ions by the same macrocyclic ligand has also been the subject of a great deal of current interest. The general principle governing these structures allow for the study of (i) metal-metal interactions, (ii) insertion of substrates and their possible transformations. Furthermore, these types of structures are often found in biological systems such as metalloproteins, which often use binuclear metal centers to perform catalytic functions. Our group has been exploring the use of cofacial binuclear bis($\beta$-diketone) complexes, such as Cu$_2$(XBA)$_2$ and Cu$_2$(NBA)$_2$, for their ability to bind substrate molecules. The copper atoms bound in this manner in proteins are commonly referred to as type-3 coppers.

Our group’s prior work has focused on the development of binuclear metal complexes derived from polydentate ligands, and their previous studies have shown that our larger complex Cu$_2$(NBA)$_2$ binds substrate molecules in an intramolecular fashion, similar to those produced by several other flexible binucleating macrocycles. In light of our group’s success with binding nitrogenous bases to Cu$_2$(NBA)$_2$, I undertook the task of exploring the
chemistry associated with the binding of sulfur-containing heterocyclic bases to our Cu$_2$(NBA)$_2$ and determine if the binding associated with the sulfur analogues would be more or less than those observed for the nitrogen counterparts. I attempted to bind the sulfur bases 1,4-dithiane and 2,5-dihydroxy-1,4-dithiane with Cu$_2$(NBA)$_2$.

Figure 4.1. Intramolecular binding of generic substrate by Cu$_2$(NBA)$_2$.

4.2. Experimental

4.2.1. Materials and procedures

Our NBAH$_2$, (2,7-naphthalenediylbis(methylene)bis(acetylacetone)) ligand had previously been prepared by the general nucleophilic substitution method outlined by Martin, et. al.$^{4.7}$ Cu$_2$(XBA)$_2$ was prepared by previously published procedures,$^{4.8-4.9}$ and the 1,4-dithiane and 2,5-dihydroxy-1,4-dithiane were
obtained from the Aldrich Chemical Co. and used without further purification, unless stated otherwise.

**Preparation of Cu$_2$(NBA)$_2$ • (1,4-dithiane)**

*Dilute.* A CHCl$_3$ solution prepared from Cu$_2$(NBA)$_2$ (5.05 mM), which was initially olive-green in color, was combined with a 1,4-dithiane solution in CHCl$_3$ (40.3 mM). This mixture was filtered and then layered with acetonitrile. After 24 hours the formation of olive green Cu$_2$(NBA)$_2$ crystals was evident and there were no signs of the formation of the 1,4-dithane host guest adduct.

*More concentrated.* 1.016 M 1,4-dithane in CHCl$_3$ was prepared and combined with the initial Cu$_2$(NBA)$_2$ (5.05 mMolar) solution. After filtering and layering with acetonitrile, olive-green crystals of Cu$_2$(NBA)$_2$ were still evident after 24 hours, however, after 5 days larger olive-green crystals of Cu$_2$(NBA)$_2$ had formed along with tiny turquoise crystals of the Cu$_2$(NBA)$_2$ • (1,4-dithiane) adduct (Figures 4.2 and 4.4).

**4.2.2. X-Ray analysis of Cu$_2$(NBA)$_2$ • (1,4-dithiane)**

Diffraction data were collected at 120 K and refinement was carried out in the monoclinic space group for the unit cell ($a = 7.7580(4)$ Å, $b = 28.9810(14)$ Å, $c = 9.6400(5)$ Å, $\beta = 97.848(3)$°, MoKα source) and the structure solved in $P2_1/c$ (Figure 4.2). In this space group, the unit cell contains two complete Cu$_2$(NBA)$_2$ •(1,4-dithiane) units. The crystallographic data is summarized in Table 4.1.

Tabulated data in Table 4.2 gives a comparison of specific bond distances for Cu$_2$(NBA)$_2$(S) with S = 1,4-dithiane, dabco and 2,5-Me$_2$pyz respectively.
These data when examined next to the Cu --- Cu distance (7.349 Å) of our empty Cu$_2$(NBA)$_2$ host molecule indicate that as the size of the host molecule increases, the relative degree of skewing or puckering of the macrocyclic ring at the copper atoms increases, see Figure 4.5.

![CCDC Mercury diagram of Cu$_2$(NBA)$_2$ • (1,4-dithiane), top view.](image)

**Figure 4.2.** CCDC Mercury diagram of Cu$_2$(NBA)$_2$ • (1,4-dithiane), top view.

<table>
<thead>
<tr>
<th>Table 4.1. Crystal data for Cu$_2$(NBA)$_2$ • (1,4-dithiane).</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
</tr>
<tr>
<td>fw</td>
</tr>
<tr>
<td>$T$ (K)</td>
</tr>
<tr>
<td>cryst syst</td>
</tr>
<tr>
<td>space group</td>
</tr>
<tr>
<td>$a$ (Å)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
</tr>
</tbody>
</table>
Figure 4.3. ORTEP diagram of Cu$_2$(NBA)$_2$ • (1,4-dithiane), side view, with ellipsoids at 50% probability level.

Figure 4.5 shows that the N atoms of the 2,5-Me$_2$pyz and Dabco guests lie essentially in the same plane with the host Cu atoms, while the S atoms of the 1,4-dithiane guest do not. This is probably due to the molecular conformation (chair), and relatively larger size of the 1,4-dithiane substrate molecule.

Table 4.2. Selected bond distance comparisons.

<table>
<thead>
<tr>
<th></th>
<th>1,4-dithiane</th>
<th>2,5-Me$_2$pyz</th>
<th>Dabco</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu----Cu (Å)</td>
<td>8.130</td>
<td>7.559</td>
<td>7.399</td>
</tr>
<tr>
<td>Cu----S(N) (Å)</td>
<td>2.809</td>
<td>2.375</td>
<td>2.416</td>
</tr>
<tr>
<td>S----S (N----N)</td>
<td>3.451</td>
<td>2.808</td>
<td>2.590</td>
</tr>
</tbody>
</table>
Figure 4.4. Crystal Packing diagram of Cu$_2$(NBA)$_2$ •(1,4-dithiane), view along a, showing the packing of adjacent molecules.

Figure 4.5. Comparative side views of Cu$_2$(NBA)$_2$ •(S), with S = 1,4-dithiane, dabco and 2,5-Me$_2$pyz.

Also, Figure 4.6 shows that the naphthalene moieties are somewhat skewed and exist in parallel planes in the 1,4-dithiane and 2,5-Me$_2$pyz adducts while the dabco adduct exhibits one naphthalene ring system horizontal, while the other is angled and is not parallel or in the same plane as the other. This twisting of the naphthalene rings could be affected by solution or crystal packing effects.
Figure 4.6. Comparative top views of Cu$_2$(NBA)$_2$ • (S), with S = 1,4-dithiane, dabco and 2,5-Me$_2$pyz respectively.

We examined the Cu$_2$(NBA)$_2$ •(1,4-dithiane) host-guest molecular complex using the Cambridge Crystallographic Data Centre’s (CCDC) Mercury 1.4 software. This examination revealed that the coordinated (bis)β-diketonate units within the complex deviate from coplanarity. The dihedral angle between the resultant planes is 11.18°, Figure 4.7. This relatively large deviation is probably caused by the unusually large 1,4-dithiane guest molecule.

4.3. Results and discussion

In this study I attempted to coordinate two dithiane guest molecules, 1,4-dithiane and 2,5-dihydroxy-1,4-dithiane with our Cu$_2$(NBA)$_2$ host. After preparing the Cu$_2$(NBA)$_2$ •(1,4-dithiane) adduct, I attempted to determine its binding constant by examining its dilute methylene chloride (CH$_2$Cl$_2$) and chloroform (CHCl$_3$) solutions by UV-visible spectroscopy at room temperature.

The equilibrium constants (K) calculation was attempted by a graphical method outlined by Rose and Drago$^{4,10}$ in which Equation. 4.1 is solved simultaneously for varying concentrations of guest molecule. The spectral data for Cu$_2$(NBA)$_2$ • (1,4-dithiane) proved to be inadequate for determining sufficient
Figure 4.7. Stick figure view of Cu$_2$(NBA)$_2$ • (1,4-dithiane) showing the deviation from co-planarity of the (bis)β-diketonate units to be 11.18°.

binding constants, and we attribute this to an apparent low affinity of Cu$_2$(NBA)$_2$ for 1,4- dithiane. The spectral changes were too small, and this agrees with the premise that even with a large excess of 1,4-dithiane only a small fraction of the molecule contain guests, which is indicative that the equilibrium for the reaction is also very low.

(Equation 4.1) \[ K^{-1} = \frac{[M_o][G_o]}{\Delta\varepsilon/\Delta A} - ([M_o] + [G_o]) + \Delta A/\Delta \varepsilon \]

Since the room temperature study did not allow for the successful determination of the binding constant for the Cu$_2$(NBA)$_2$ • (1,4-dithiane) adduct, I attempted to introduce 2,5-dihydroxy-1,4-dithiane into our Cu$_2$(NBA)$_2$ ligand,
hoping that the presence of the hydroxyl groups would enhance binding to the host. However, all efforts to achieve this failed due to the insolubility of the 2,5-dihydroxy1,4-dithiane guest in either CH$_2$Cl$_2$ or CHCl$_3$. 
Chapter 5

Cu₂(XBDPr)₂ and Cu₂(NBDPr)₂ Studies

5.1. Introduction

β-diketone derivatives of acetylacetone have been used commonly as extractants in the solvate extraction of metals.⁵,⁷,⁵,⁸ Formerly, Koshimura⁵,⁹ pointed out that in benzene at room temperature, the solubilities of Cu(RCOCHCOR)₂ increased substantially with increasing R, [For R = CH₃ (2.5 mM), for R = CH₂CH₃ (63 mM) and for R = CH₂CH₂CH₃ (180 mM)], and that the molar volumes for the chelates were in direct proportionality to the additional carbon atoms in the molecule.

![Figure 5.1. Structures of alkylated XBA and NBA ligands.](image)

In previous work by our research group it was determined that Cu₂(XBA)₂ and Cu₂(NBA)₂ have low solubility in CH₂Cl₂ and CHCl₃, and are almost insoluble in most other organic solvents. We undertook this segment of our work in order to examine the effect of substituents on the solubilities of our β-diketone copper chelates when the acetylacetone moiety has been alkyl-substituted. In so doing,
we undertook the synthetic challenge of preparing XBDPrH$_2$ and NBDPrH$_2$ (Figure 5.1), the alkylated derivatives of our XBAH$_2$ and NBAH$_2$ \(\beta\)-diketone ligands and their copper complexes as shown in Figure 5.2.

![Figure 5.2. Structures of \(\text{Cu}_2(\text{XBDPr})_2\) and \(\text{Cu}_2(\text{NBDPr})_2\).](image)

The reaction of alkyl halides with the enolates derived from \(\beta\)-diketones is a methodology that has been well established for forming C-C bonds. Fedorynski, et.al., showed that anhydrous sodium and potassium carbonates in the presence of catalytic amounts of tetraalkylammonium salts were strong enough bases for the generation and reaction of a variety of enolate carbanions. This methodology is usually a high yield chemoselective process. These findings had been earlier substantiated by work conducted by House, who pointed out
that the most frequently observed difficulty that arises in the alkylation of β-dicarbonyl compounds is the concurrent formation of both C-alkylated and O-alkylated products and in some cases they form products from competing Claisen condensations, β-diketone cleavage, coupling of the enol salts of the starting materials and its monoalkylation product. However, Clark\textsuperscript{5.6} later indicated that the problem of O-alkylated product formation could be minimized when hydrogen-bonding solvates were generated between tetraethylammonium fluoride and a number of β-dicarbonyl compounds. These reaction mixtures when introduced to alkyl iodides at room temperature could provide high yields of the mono-C-alkylated β-dicarbonyl products. Christoffers\textsuperscript{5.3} showed that Ar-CH$_2$-Br facile benzylation by alkyl-substituted\textsuperscript{5.4} β-diketones of the type RCCOCHR’COR”, could be mediated by nBu$_4$NF in THF-water. We have therefore, utilized a modification of Christoffers’ chemistry, to attempt to prepare the desired ligands XBDPrH$_2$ and NBDPrH$_2$ and to subsequently synthesize their copper complexes. Upon initial inspection of Christoffers’ chemistry we were led to believe that the synthesis would be straightforward and the products easily isolated.

### 5.2. Experimental

#### 5.2.1. Materials and Procedures

The starting materials were all either commercially available or prepared according to the literature procedures, unless otherwise indicated. An aqueous solution of tetra-$n$-butylammonium fluoride (75 weight % solution in water) was
purchased from Sigma-Aldrich chemical company. The 3,5-heptanedione was purchased from Acros Organics chemical company. All chemicals and solvents were spectrophotometric or reagent grade and were used as received. \textsuperscript{1}H NMR spectra were recorded on a Bruker 250-MHz spectrometer. Microanalyses were performed by M-H-W Laboratories, of Phoenix, Arizona. The X-ray diffraction and crystal structure determinations were conducted on a Nonius Kappa CCD diffractometer at approximately 100 K.

5.2.2. Preparation of 4,4′-(2,7-naphthalenediylbis(methylene))bis(dipropionyl methane) (NBDPrH\textsubscript{2}) and 4,4′-(1,3-xylenediylbis-(methylene))bis(dipropionylmethane) (XBDPrH\textsubscript{2}).

A solution of \textit{n}Bu\textsubscript{4}NF in water (75 weight % solution in water; 1.50 mL, 4.10 mmol) was added to a solution of the 3,5-heptanedione (0.56 mL, 4.10 mmol) in THF (1 mL). The mixture was stirred until homogeneous (~ 1 hour), and the aryl dibromide (a or b) (2.05 mmol) was added and this mixture was allowed to stir overnight at room temperature (Scheme 5.1). The literature cleanup and separation procedure using SiO\textsubscript{2} as a filterant proved to be inadequate for separating the reaction components and removal of inorganic reaction materials. Therefore, the THF was removed at reduced pressure and the resulting reaction mixture was taken up in minimum CH\textsubscript{2}Cl\textsubscript{2} and repeatedly washed with distilled water to remove as much of the inorganic reaction material as possible and then dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, and the CH\textsubscript{2}Cl\textsubscript{2} solvent was removed at reduced pressure. These reactions generally produced 40 – 55 % of the crude product. In an attempt to purify the products, they were
each treated with $[\text{Cu(NH}_3\text{)}_4]^2$ and then with dilute HCl in order to extract the free ligand (Figures 5.3) before taking the $^1\text{H}$ NMR spectra (Figures 5.4, 5.5, and Table 5.1).

Scheme 5.1
Figure 5.3. Structure of XBAH<sub>2</sub>, XBDPrH<sub>2</sub> and NBDPrH<sub>2</sub> ligands.

Table 5.1. <sup>1</sup>H NMR shifts of (a) XBAH<sub>2</sub>, (b) XBDPrH<sub>2</sub> and (c) NBDPrH<sub>2</sub>.

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<td>(2.2)</td>
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b. c.
Figure 5.4. $^1$H NMR spectrum of crude XBDPrH$_2$. 
Figure 5.5. $^1$H NMR spectrum of crude NBDPrH$_2$. 
5.2.3. Preparation of Cu₂(NBDPr)₂ and Attempted Preparation of Cu₂(XBDPr)₂

Cu₂(NBDPr)₂: An aqueous CuSO₄ • 5H₂O solution (0.428 molar) was treated with NH₄OH (2.0 mL) to form a transparent deep blue aqueous solution, which was subsequently combined with a CH₂Cl₂ solution of NBDPrH₂. The CuSO₄ • 5H₂O to ligand molar ratio was 2:1 respectively. A green crystalline Cu₂(NBDPr)₂ solid formed at the aqueous–organic interface during the separatory funnel extraction sequence. This crystalline solid was utilized in the x-ray structure determination. Furthermore, the organic (CH₂Cl₂) portion was extracted and dried over anhydrous Na₂SO₄. The CH₂Cl₂ solvent was removed at reduced pressure and a grey powder Cu₂(NBDPr)₂ was evident. Elemental analysis: found (calculated) for Cu₂(NBDPr)₂ • CH₂Cl₂: C, 62.21 (62.10); H, 6.10 (6.10).

Cu₂(XBDPr)₂: An aqueous CuSO₄•5H₂O solution (19.47 mmolar) was treated with NH₄OH (2.0 mL) to form a transparent deep blue aqueous solution, which was subsequently combined with a CH₂Cl₂ solution (9.74 mmolar) of crude XBDPrH₂. The CuSO₄ • 5H₂O to ligand molar ratio was 2:1 respectively. The organic (CH₂Cl₂) portion was extracted, washed repeatedly with distilled water, dried over Na₂SO₄•anhydrous, filtered and the solvent (CH₂Cl₂) was removed at reduced pressure. A mixture of blue-green and olive-green viscous to partially solid material, suspected of being both Cu(3,5-heptanedionate) and Cu₂(XBDPr)₂ (3.18 g) was evident. All attempts to generate crystalline Cu₂(XBDPr)₂ sufficient for X-ray analysis failed. However, I was able to isolate a crude crystalline
material that revealed upon X-ray analysis, the structure for Cu(3,5-heptanedionate) (Figure 5.6).

Figure 5.6. ORTEP diagram of Cu(3,5-heptanedionate).

5.2.4. Structural Analysis of Cu$_2$(NBDPr)$_2$

The elemental analysis of (Cu$_2$(NBDPr)$_2$) the gray powder (C 62.21%, H 6.10%) was in line with the calculated values when we took into account the presence of 1 trapped solvent (CH$_2$Cl$_2$) molecule. The crude X-ray structure of the Cu$_2$(NBDPr)$_2$ crystals (Figure 5.7) substantiated these findings by showing
the presence of 2 distinct molecules along with 2 trapped solvent molecules per unit cell. The crystal data is reported in Table 5.2.

Figure 5.7. CCDC Mercury diagram of Cu₂(NBDPr)₂ with view along b.

Table 5.2. Crystal Data of Cu₂(NBDPr)₂.

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5.3. Results and Discussion

The reaction sequences of the XBDPrH$_2$ and NBDPrH$_2$ were both monitored by $^1$H NMR and this revealed that the starting materials (3,5-heptanедione and tetra-n-butylammonium fluoride) concentration (Table 5.3) had diminished substantially by the end of the reaction, and further indicated that the desired ligands were present, in both the keto and enol forms, even though they were difficult to isolate. The $^1$H NMR data are impure (Table 5.1, Figures 5.4 and 5.5) of NBDPrH$_2$ and XBDPrH$_2$, but the presence of the c, d peaks along with the shifted enol peaks indicate that the desired ligands are present. Peaks a and b are not conclusive, because they could also be indicative of 3.5-heptanedione (Table 5.3).

Table 5.3. Tabulated $^1$H NMR data of starting materials.

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<th>nBu$_4$NF</th>
<th>$\alpha, \alpha'$-Br$_2$-m-Xylene</th>
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The attempts to prepare Cu$_2$(NBDPr)$_2$ and Cu$_2$(XBDPr)$_2$ crystals suitable for X-ray analysis were carried out by layering dichloromethane (CH$_2$Cl$_2$) solutions of the respective copper complexes with hexane, acetone and acetonitrile. The hexane experiments with Cu$_2$(NBDPr)$_2$ afforded crude crystals, but they were not as good as those that formed during the initial synthesis. Therefore, the crystal used in the X-ray analysis (Figure 5.7) was one of those isolated during the initial synthesis. Also, the Cu$_2$(XBDPr)$_2$ experiments to produce X-ray quality crystals failed. Furthermore, the solubility data for Cu$_2$(NBDPr)$_2$ indicate that it is less soluble in CH$_2$Cl$_2$ and CHCl$_3$ than Cu$_2$(NBA)$_2$ and insoluble in acetonitrile, benzene and THF.
Chapter 6

Summary and Conclusions

Molecular manufacturing methodologies that aim to create solid materials containing chemical functionalities that are spatially organized by covalent or noncovalent interactions may lead to materials that are useful for applications such as separations, chemical sensing, and catalysis. While these methodologies may be conceptually straightforward, they can be difficult to accomplish experimentally. Here we have reported our efforts to design coordination specific transition metal (copper) complexes that could be utilized for, (a) host-guest binding studies and (b) the formation of well defined porous molecular solids.

In our preparation of 3,5-diacetyl-2,6-heptanedione (C$_1$BAH$_2$), we utilized a modification of Knoevenagel’s 1898 condensation reaction$^{6.1}$ of acetylacetone and formalin. In so doing we were also able to isolate the crystalline form of a second alkylation product of this reaction (3,5,5-triacetyl-tetrahydropyran-2-ol) that had been prepared previously by Aarna.$^{6.2}$

The diketone groups of C$_1$BAH$_2$ (with their propensity to rotate about a central methylene bridge) orient themselves in an anti fashion and seem to be best suited for the formation of linear polymeric coordination structures. This is evidenced by its X-ray crystal structure, the copper complex’s elemental analysis and mass spectrum correlations. Therefore, this ligand was determined to be unsuitable for the preparation of our proposed cyclic molecular solids. However,
replacing the methylene bridge of C$_1$BAH$_2$ with a double bond to form (Z)-3,6-diacetyloct-4-ene-2,7-dione (Figure 6.1) could conceivably produce a more structurally rigid diketonate. This could conceptually generate a conformation for the diketo groups that would allow for the preparation of a well defined cyclic supramolecular molecular solid.

The X-ray structure of $p$-XBAH$_2$ shows that the diketone moieties are oriented approximately trans (or anti) to each other. If the ligand has a preference for this conformation in its metal complexes, this could explain our difficulties in isolating well behaved molecular products. However, as with the C$_1$BAH$_2$ this ligand has also shown promise for being a good precursor for the formation of metal coordination polymers. Other members of the group have begun to explore other (Figure 6.2a) (bis)$\beta$-diketonates as

![Figure 6.1. (Z)-3,6-diacetyloct-4-ene-2,7-dione.](image1.png)

![Figure 6.2. Possible (bis)$\beta$-diketonate precursor compared to C1BAH$_2$.](image2.png)
possible precursors for the preparation of our envisioned molecular solids.

The room temperature study to determine binding constants of the $\text{Cu}_2(\text{NBA})_2$ complex with select heterocyclic sulfur guests proved to be unfruitful. We initiated this segment of our work by coordinating 1,4-dithiane with our $\text{Cu}_2(\text{NBA})_2$. By layering a CHCl$_3$ solution of $\text{Cu}_2(\text{NBA})_2$ and 1,4-dithiane with acetonitrile, small turquoise crystals of $\text{Cu}_2(\text{NBA})_2 \cdot (1,4\text{-dithiane})$ were obtained, which were suitable for x-ray structure determination. Additionally, attempts to incorporate 2,5-dihydroxy-1,4-dithiane into our $\text{Cu}_2(\text{NBA})_2$ ligand failed due to the insolubility of this guest in CH$_2$Cl$_2$ and CHCl$_3$.

Subsequently, all attempts to determined equilibrium binding constants for $\text{Cu}_2(\text{NBA})_2 \cdot (1,4\text{-dithiane})$ failed, and is attributed to the low affinity of $\text{Cu}_2(\text{NBA})_2$ for the heterocyclic sulfur compound. We then reviewed the low temperature binding constant calculations that had previously been determined by our group for $\text{Cu}_2(\text{NBA})_2 \cdot (\text{N})$, (where N = dabco, pyrazine, 2-Mepyz, and 2-NH$_2$pyz) and observed that a general increase in the equilibrium binding constants ($K/\text{mol}^{-1}$) occurred throughout each series as the temperature was decreased. These observations indicate that measuring low temperature visible spectra of the $\text{Cu}_2(\text{NBA})_2 \cdot (1,4\text{-dithiane})$ adduct could lead to the generation of the desired equilibrium binding constant data.

In light of the solubility characteristics that had previously been observed with $\text{Cu}_2(\text{NBA})_2$, those that were evaluated during the dithiane experiments and the other selected sulfur analogue, I decided to extend the aliphatic chains of our
betadiketone moieties by alkylating them. I had hoped that the extended aliphatic chain would increase the solubility of the Cu$_2$(NBDPr)$_2$ metal complex. However, the qualitative solubility data that I observed with ethyl groups replacing the methyls gave opposite findings from what I had anticipated. The solubility of the Cu$_2$(NBDPr)$_2$ metal complex was appreciably less in CH$_2$Cl$_2$, CHCl$_3$, acetonitrile, benzene and THF than those observed for Cu$_2$(NBA)$_2$. 
References


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3.9 Yeager, M. A.; Maverick, A. W. *unpublished work*.


5.3 Christoffers, J. Synthetic Communications, 1999, 29(1), 117-122.
# Appendix

## Crystal Data in CIF Format

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\[ \text{calc } w=1/[(s^2(Fo^2)+(0.0668P)^2+0.1309P)] \text{ where } P=(Fo^2+2Fc^2)/3 \]

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O3 0.0336(5) 0.0348(6) 0.0354(5) -0.0080(5) -0.0005(4) 0.0123(5)
O4 0.0445(7) 0.0436(6) 0.0269(5) 0.0120(4) -0.0062(5) 0.0058(6)
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C3 0.0182(5) 0.0219(5) 0.0152(4) -0.0002(4) -0.0008(4) 0.0000(4)
C4 0.0287(6) 0.0280(6) 0.0169(4) -0.0007(4) -0.0027(4) -0.0038(5)
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are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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C2 C1 H1C 109.5 . . ?
H1A C1 H1C 109.5 . . ?
H1B C1 H1C 109.5 . . ?
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O1 C2 C3 121.72(11) . . ?  
C1 C2 C3 115.90(10) . . ?  
C2 C3 C4 109.48(10) . . ?  
C2 C3 C6 112.33(10) . . ?  
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O2 C4 C3 121.09(13) . . ?  
C5 C4 C3 116.53(12) . . ?  
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C4 C5 H5B 109.5 . . ?  
H5A C5 H5B 109.5 . . ?  
C4 C5 H5C 109.5 . . ?  
H5B C5 H5C 109.5 . . ?  
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O3 C8 C9 120.65(12) . . ?  
C7 C8 C9 117.37(12) . . ?  
C8 C9 C10 108.47(10) . . ?  
C8 C9 C6 112.08(10) . . ?  
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66
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69
Refinement of $F^2$ against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on $F^2$, conventional R-factors R are based
on F, with F set to zero for negative $F^2$. The threshold expression of
$F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on $F^2$ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.

Refine $F^2$ structure factor coefficients:

- $F^2 = 1/[\sigma^2(Fo^2)+(0.0424P)^2+0.2367P]$ where $P=(Fo^2+2Fc^2)/3$

Atom sites solution:

- Primary: direct
- Secondary: difmap
- Hydrogens: geom
- Treatment: mixed
- Extinction method: none
- Extinction coefficient: ?
- Absstructure details: ?
- Flack: ?
- Number of reflections: 1796
- Number of parameters: 159
- Number of restraints: 2
- R-factor all: 0.058
- R-factor gt: 0.046
- R-factor ref: 0.106
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- Goodness of fit ref: 1.074
- Restrained S: 1.073
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Atom site: type symbol

70
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H12C H 0.5566 0.8189 0.1914 0.050 Uiso 1 1 calc R . .

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  _atom_site_aniso_U_13
  _atom_site_aniso_U_12
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O2 0.0183(8) 0.0215(9) 0.0234(8) -0.0068(7) -0.0040(7) -0.0019(7)
O3 0.0276(10) 0.0362(12) 0.0462(12) 0.0207(10) -0.0100(9) 0.0012(9)
O4 0.0340(11) 0.0405(12) 0.0267(10) -0.0064(9) -0.0020(8) 0.0043(10)
O5 0.0432(13) 0.0379(12) 0.0321(10) 0.0165(9) -0.0105(9) -0.0081(10)
C1 0.0142(10) 0.0175(12) 0.0239(12) 0.0010(9) -0.0019(9) -0.0006(9)
C2 0.0152(11) 0.0155(11) 0.0181(11) 0.0000(9) -0.0032(8) 0.0003(9)
C3 0.0177(10) 0.0150(11) 0.0200(11) 0.0019(9) -0.0021(9) -0.0010(9)
C4 0.0172(10) 0.0164(11) 0.0198(11) 0.0001(9) -0.0021(8) 0.0010(9)
C5 0.0173(10) 0.0192(12) 0.0232(11) 0.0023(9) -0.0048(9) 0.0006(10)
C6 0.0193(12) 0.0227(13) 0.0381(15) 0.0054(11) 0.0002(10) -0.0044(10)
C7 0.0194(11) 0.0163(11) 0.0311(13) -0.0007(10) -0.0089(10) -0.0029(9)
C8 0.0175(11) 0.0250(13) 0.0410(16) -0.0078(12) -0.0031(11) 0.0047(10)
C9 0.0231(12) 0.0182(12) 0.0241(12) -0.0003(9) 0.0032(9) -0.0040(10)
C10 0.0234(13) 0.0282(14) 0.0379(15) 0.0000(12) 0.0046(11) 0.0039(11)
C11 0.0238(12) 0.0165(11) 0.0239(12) 0.0023(10) 0.0013(9) 0.0014(10)
C12 0.0338(14) 0.0238(14) 0.0415(16) 0.0062(13) -0.0026(12) -0.0044(12)

_geom_special_details

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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C1 O2 H2 109.5 . . ?
O2 C1 O1 110.82(19) . . ?
O2 C1 C6 111.9(2) . . ?
O1 C1 C6 105.0(2) . . ?
O2 C1 C2 107.56(19) . . ?
O1 C1 C2 108.98(19) . . ?
C6 C1 C2 112.6(2) . . ?
C7 C2 C3 112.73(19) . . ?
C7 C2 C1 109.87(19) . . ?
C3 C2 C1 112.65(18) . . ?
C7 C2 H2A 107.1 . . ?
C3 C2 H2A 107.1 . . ?
C1 C2 H2A 107.1 . . ?
C2 C3 C4 111.76(19) . . ?
C2 C3 H3A 109.3 . . ?
C4 C3 H3A 109.3 . . ?
C2 C3 H3B 109.3 . . ?
C4 C3 H3B 109.3 . . ?
H3A C3 H3B 107.9 . . ?
C5 C4 C3 108.7(2) . . ?
C5 C4 C11 110.1(2) . . ?
C3 C4 C11 109.1(2) . . ?
C5 C4 C9 109.6(2) . . ?
C3 C4 C9 112.36(19) . . ?
C11 C4 C9 107.1(2) . . ?
O1 C5 C4 109.7(2) . . ?
O1 C5 H5A 109.7 . . ?
C4 C5 H5A 109.7 . . ?
O1 C5 H5B 109.7 . . ?
C4 C5 H5B 109.7 . . ?
H5A C5 H5B 108.2 . . ?
C1 C6 H6A 109.5 . . ?
C1 C6 H6B 109.5 . . ?
H6A C6 H6B 109.5 . . ?
C1 C6 H6C 109.5 . . ?
H6A C6 H6C 109.5 . . ?
H6B C6 H6C 109.5 . . ?
O3 C7 C8 121.2(2) . . ?
O3 C7 C2 118.8(2) . . ?
C8 C7 C2 120.0(2) . . ?
C7 C8 H8A 109.5 . . ?
C7 C8 H8B 109.5 . . ?
H8A C8 H8B 109.5 . . ?
C7 C8 H8C 109.5 . . ?
H8A C8 H8C 109.5 . . ?
H8B C8 H8C 109.5 . . ?
O4 C9 C10 121.4(2) . . ?
O4 C9 C4 122.3(2) . . ?
C10 C9 C4 116.4(2) . . ?
C9 C10 H10A 109.5 . . ?
C9 C10 H10B 109.5 . . ?
H10A C10 H10B 109.5 . . ?
C9 C10 H10C 109.5 . . ?
H10A C10 H10C 109.5 . . ?
H10B C10 H10C 109.5 . . ?
O5 C11 C12 121.7(2) . . ?
O5 C11 C4 120.3(2) . . ?
C12 C11 C4 118.0(2) . . ?
C11 C12 H12A 109.5 . . ?
C11 C12 H12B 109.5 . . ?
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H12B C12 H12C 109.5 . . ?

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O1 C1 C2 C7 -176.58(19) . . . ?
C6 C1 C2 C7 67.4(3) . . . ?
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O1 C1 C2 C3 -50.0(2) . . . ?
C6 C1 C2 C3 -166.0(2) . . . ?
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C1 C2 C3 C4 47.7(3) . . . ?
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C2 C3 C4 C11 -171.08(19) . . . . ?
C2 C3 C4 C9 70.4(3) . . . . ?
C1 O1 C5 C4 -66.7(2) . . . . ?
C3 C4 C5 O1 59.2(2) . . . . ?
C11 C4 C5 O1 178.63(19) . . . . ?
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C1 C2 C7 O3 -92.7(3) . . . . ?
C3 C2 C7 C8 -39.3(3) . . . . ?
C1 C2 C7 C8 87.2(3) . . . . ?
C5 C4 C9 O4 130.1(3) . . . . ?
C3 C4 C9 O4 9.1(3) . . . . ?
C11 C4 C9 O4 -110.6(3) . . . . ?
C5 C4 C9 C10 -50.1(3) . . . . ?
C3 C4 C9 C10 -171.0(2) . . . . ?
C11 C4 C9 C10 69.2(3) . . . . ?
C5 C4 C11 O5 7.7(3) . . . . ?
C3 C4 C11 O5 126.8(3) . . . . ?
C9 C4 C11 O5 -111.4(3) . . . . ?
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    _geom_hbond_distance_DA
    _geom_hbond_angle_DHA

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# END OF CIF
**p-xylylenebis(3-(2,4-pentanedione))**

\[(p-XBAH_2)\]

---

**_audit_creation_method**

SHELXL-97

**_chemical_name_systematic**

1,4-bis-(2,2-diacectylethyl)-benzene

**_chemical_name_common**

p-xylylenebis(3-(2,4-pentanedione))

**_chemical_melting_point**

not measured

**_chemical_compound_source**

'local laboratory'

**_chemical_formula_moiety**

'C18 H22 O4'

**_chemical_formula_sum**

'C18 H22 O4'

**_chemical_formula_weight**

302.36

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**_symmetry_space_group_name_H-M**

'P 21/c'

**_symmetry_cell_setting**

'Monoclinic'

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**_symmetry_equiv_pos_as_xyz**

'x, y, z'

'-x, y+1/2, -z+1/2'

'-x, -y, -z'

'x, -y-1/2, z-1/2'

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13.796(6)

**_cell_length_b**

5.591(2)

**_cell_length_c**

10.819(4)

**_cell_angle_alpha**

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**_cell_angle_beta**

107.890(15)

**_cell_angle_gamma**

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**_cell_volume**

794.2(5)

**_cell_formula_units_Z**

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**_cell_measurement_temperature**

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**_cell_measurement_reflns_used**

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**_cell_measurement_theta_min**

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**_cell_measurement_theta_max**

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_computing_data_reduction  'Denzo and Scalepak (Otwinowski & Minor, 1997)'

78
Refinement of $F^2$ against ALL reflections. The weighted R-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional R-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating $R$-factors(gt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger.

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Refinement of $F^2$ against ALL reflections. The weighted R-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional R-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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C7 C 0.3945(5) 0.66348(12) 0.1506(4) 0.0393(10) Uani 1 1 d . . .
H7A H 0.5020 0.6625 0.2171 0.059 Uiso 1 1 calc R . .
H7B H 0.3499 0.6951 0.1435 0.059 Uiso 1 1 calc R . .
H7C H 0.4187 0.6531 0.0585 0.059 Uiso 1 1 calc R . .
C8 C 0.2612(4) 0.63233(13) 0.2010(4) 0.0296(9) Uani 1 1 d . . .
C9 C 0.1539(4) 0.64831(12) 0.2977(4) 0.0257(9) Uani 1 1 d . . .
C10 C 0.0089(4) 0.62301(13) 0.3266(4) 0.0294(9) Uani 1 1 d . . .
C11 C -0.1178(5) 0.64297(13) 0.4144(4) 0.0398(10) Uani 1 1 d . . .
H11A H -0.2097 0.6204 0.4234 0.060 Uiso 1 1 calc R . .
H11B H -0.1695 0.6710 0.3699 0.060 Uiso 1 1 calc R . .
H11C H -0.0570 0.6505 0.5076 0.060 Uiso 1 1 calc R . .
C12 C 0.1908(4) 0.69621(12) 0.3596(4) 0.0317(9) Uani 1 1 d . .
H12A H 0.1820 0.7187 0.2817 0.038 Uiso 1 1 calc R . .
H12B H 0.0985 0.7039 0.4173 0.038 Uiso 1 1 calc R . .
C13 C 0.8278(4) 0.65323(12) 0.8151(4) 0.0282(9) Uani 1 1 d . .
C14 C 0.9166(5) 0.69515(11) 0.7956(4) 0.0317(9) Uani 1 1 d . .
H14 H 1.0252 0.7011 0.8511 0.038 Uiso 1 1 calc R . .
C15 C 0.8490(5) 0.72711(12) 0.6989(4) 0.0324(9) Uani 1 1 d . .
C16 C 0.9119 0.7547 0.6881 0.039 Uiso 1 1 calc R . .
C17 C 0.6175(4) 0.75160(12) 0.5128(4) 0.0305(9) Uani 1 1 d . .
H17 H 0.6788 0.7793 0.4998 0.037 Uiso 1 1 calc R . .
C18 C 0.4621(5) 0.74330(12) 0.4318(4) 0.0323(9) Uani 1 1 d . .
C19 C 0.4176 0.7652 0.3626 0.039 Uiso 1 1 calc R . .
C20 C 0.3664(4) 0.70273(12) 0.4493(4) 0.0288(9) Uani 1 1 d . .
C21 C 0.3729 0.6432 0.5565 0.034 Uiso 1 1 calc R . .
C22 C 0.5968(4) 0.67833(12) 0.6320(4) 0.0271(9) Uani 1 1 d . .
C23 C 0.6716(4) 0.64566(12) 0.7320(4) 0.0303(9) Uani 1 1 d . .
H22 H 0.6117 0.6175 0.7420 0.036 Uiso 1 1 calc R . .
C23 A 0.4616(5) 0.46546(13) 0.6187(4) 0.0360(10) Uani 1 1 d . .
C24 C 0.4343 0.4351 0.6577 0.043 Uiso 1 1 calc R . .
C25 C 0.4763 0.4879 0.6968 0.043 Uiso 1 1 calc R . .
C26 C 0.6918(5) 0.51949(12) 0.4876(4) 0.0369(10) Uani 1 1 d . .
H26 A H 0.7030 0.5407 0.5688 0.044 Uiso 1 1 calc R . .
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O1 0.0273(14) 0.0293(15) 0.0310(16) -0.0013(12) 0.0069(11) -0.0012(11)
O2 0.0309(15) 0.0271(15) 0.0299(16) -0.0040(13) 0.0066(12) -0.0005(11)
O3 0.0332(15) 0.0310(15) 0.0260(16) -0.0006(12) 0.0053(12) -0.0016(12)
O4 0.0316(14) 0.0269(14) 0.0281(15) -0.0017(13) 0.0008(12) 0.0012(12)
C1 0.036(2) 0.038(2) 0.034(2) -0.004(2) 0.0103(19) -0.0012(19)
C2 0.026(2) 0.036(2) 0.022(2) 0.0004(19) -0.0056(17) 0.0000(18)
C3 0.025(2) 0.033(2) 0.025(2) -0.0008(19) 0.0019(17) 0.0034(18)
C4 0.030(2) 0.034(2) 0.019(2) -0.001(2) -0.0028(16) 0.003(2)
C5 0.030(2) 0.036(2) 0.036(2) -0.001(2) 0.0068(19) 0.0006(18)
C6 0.030(2) 0.031(2) 0.026(2) -0.0024(19) 0.003(17) -0.0019(17)
C7 0.044(3) 0.034(2) 0.041(3) 0.001(2) 0.011(2) -0.0044(19)
C8 0.031(2) 0.033(2) 0.023(2) 0.0065(19) -0.0048(18) -0.0018(18)
C9 0.022(2) 0.026(2) 0.027(2) 0.0027(18) -0.0013(17) 0.0017(17)
C10 0.030(2) 0.038(2) 0.018(2) 0.0033(19) -0.0032(17) 0.0090(19)
C11 0.037(2) 0.041(2) 0.043(3) -0.002(2) 0.010(2) -0.004(2)
C12 0.032(2) 0.029(2) 0.034(2) 0.0004(19) 0.0032(18) 0.0052(17)
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C17 0.031(2) 0.027(2) 0.034(2) 0.001(2) 0.0080(19) -0.0059(18)
C18 0.036(2) 0.031(2) 0.029(2) 0.0053(19) 0.0024(19) 0.0044(19)
C19 0.030(2) 0.030(2) 0.026(2) -0.0034(19) 0.0029(18) 0.0016(18)
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C22 0.038(2) 0.024(2) 0.029(2) -0.0019(19) 0.0058(19) -0.0057(18)
C23 0.033(2) 0.043(2) 0.032(2) 0.008(2) 0.0045(18) -0.005(2)
C24 0.035(2) 0.043(2) 0.033(2) 0.001(2) 0.0058(19) -0.0076(19)

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All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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Cu1 O2 1.910(2) . ?
Cu1 O3 1.918(2) 3_666 ?
Cu1 O4 1.925(2) 3_666 ?
Cu1 S1 2.8088(10) . ?
S1 C23 1.809(4) . ?
S1 C24 1.816(4) . ?
O1 C2 1.286(4) . ?
O2 C4 1.278(4) . ?
O3 C8 1.289(4) . ?
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O4 Cu1 1.925(2) 3_666 ?
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C1 H1C 0.9800 . ?
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C3 C4 1.406(5) . ?
C3 C6 1.533(5) . ?
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C23 S1 C24 101.26(17) .
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H1A C1 H1B 109.5 .
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H1A C1 H1C 109.5 . . ?
H1B C1 H1C 109.5 . . ?
O1 C2 C3 125.1(3) . . ?
O1 C2 C1 114.7(3) . . ?
C3 C2 C1 120.2(3) . . ?
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H7A C7 H7C 109.5 . . ?
H7B C7 H7C 109.5 . . ?
O3 C8 C9 125.5(3) . . ?
O3 C8 C7 113.7(3) . . ?
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O4 C10 C9 125.4(3) . . ?
O4 C10 C11 113.5(3) . . ?
C9 C10 C11 121.1(3) . . ?
C10 C11 H11A 109.5 . . ?
C10 C11 H11B 109.5 . . ?
H11A C11 H11B 109.5 . . ?
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C22 C13 C6 123.3(3) . . ?
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O2 Cu1 S1 C23 -32.59(14) . . . . ?
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O4 Cu1 S1 C23 145.55(14) 3_666 . . . ?
O1 Cu1 S1 C24 -22.68(15) . . . . ?
O2 Cu1 S1 C24 70.59(14) . . . . ?
O3 Cu1 S1 C24 157.59(15) 3_666 . . . ?
O4 Cu1 S1 C24 -111.27(15) 3_666 . . . ?
O2 Cu1 O1 C2 1.7(3) . . . . ?
O3 Cu1 O1 C2 -84.3(11) 3_666 . . . ?
O4 Cu1 O1 C2 -174.1(3) 3_666 . . . ?
S1 Cu1 O1 C2 98.4(3) . . . . ?
O1 Cu1 O2 C4 -0.5(3) . . . . ?
O3 Cu1 O2 C4 173.8(3) 3_666 . . . ?
O4 Cu1 O2 C4 105.3(13) 3_666 . . . ?
S1 Cu1 O2 C4 -99.7(3) . . . . ?
Cu1 O1 C2 C3 -2.6(5) . . . . ?
Cu1 O1 C2 C1 176.5(2) . . . . ?
O1 C2 C3 C4 1.9(5) . . . . ?
C1 C2 C3 C4 -177.1(3) . . . . ?
O1 C2 C3 C6 -178.6(3) . . . . ?
C1 C2 C3 C6 2.4(5) . . . . ?
Cu1 O2 C4 C3 0.1(5) . . . . ?
Cu1 O2 C4 C5 -177.7(2) . . . . ?
C2 C3 C4 O2 -0.6(6) . . . . ?
C6 C3 C4 O2 179.9(3) . . . . ?
C2 C3 C4 C5 177.1(3) . . . . ?
C6 C3 C4 C5 -2.4(5) . . . . ?
C4  C3  C6  C13 -97.4(4)  . . . ?
C2  C3  C6  C13  83.1(4)  . . . ?
Cu1  O3  C8  C9 -7.1(5)  3_666 . . . ?
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O3  C8  C9  C10 -10.2(6)  . . . ?
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O3  C8  C9  C12  175.4(3)  . . . ?
C7  C8  C9  C12 -6.1(5)  . . . ?
Cu1  O4  C10  C9  14.3(5)  3_666 . . . ?
Cu1  O4  C10  C11  -167.5(2)  3_666 . . . ?
C8  C9  C10  O4  6.3(5)  . . . ?
C12  C9  C10  O4  -179.5(3)  . . . ?
C8  C9  C10  C11  -171.8(3)  . . . ?
C12  C9  C10  C11  2.4(5)  . . . ?
C10  C9  C12  C19  121.8(4)  . . . ?
C8  C9  C12  C19  -63.8(4)  . . . ?
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C3  C6  C13  C14  -138.7(3)  . . . ?
C22  C13  C14  C15  0.5(5)  . . . ?
C6  C13  C14  C15  -177.6(3)  . . . ?
C13  C14  C15  C16  0.3(5)  . . . ?
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C21  C16  C17  C18  0.9(5)  . . . ?
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C17  C18  C19  C20  -2.1(5)  . . . ?
C17  C18  C19  C12  177.8(3)  . . . ?
C9  C12  C19  C20  -43.3(5)  . . . ?
C9  C12  C19  C18  136.8(3)  . . . ?
C18  C19  C20  C21  1.9(5)  . . . ?
C12  C19  C20  C21  -178.0(3)  . . . ?
C17  C16  C21  C22  177.9(3)  . . . ?
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C17  C16  C21  C20  -1.1(5)  . . . ?
C15  C16  C21  C20  -179.5(3)  . . . ?
C19  C20  C21  C22  -179.2(3)  . . . ?
C19  C20  C21  C16  -0.3(5)  . . . ?
C14  C13  C22  C21  -1.4(5)  . . . ?
C6  C13  C22  C21  176.7(3)  . . . ?
C16  C21  C22  C13  1.4(5)  . . . ?
C20  C21  C22  C13  -179.7(3)  . . . ?
C24  S1  C23  C24  59.9(3) . . . 3_666 ?
Cu1  S1  C23  C24  164.3(2) . . . 3_666 ?
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Refinement of \(F^2\) against ALL reflections. The weighted R-factor \(wR\) and goodness of fit \(S\) are based on \(F^2\), conventional R-factors \(R\) are based on \(F\), with \(F\) set to zero for negative \(F^2\). The threshold expression of \(F^2 > 2\sigma(F^2)\) is used only for calculating \(R\)-factors(gt) etc. and is not relevant to the choice of reflections for refinement. \(R\)-factors based on \(F^2\) are statistically about twice as large as those based on \(F\), and \(R\)-factors based on ALL data will be even larger.

Refinement of \(F^2\) against ALL reflections. The weighted R-factor \(wR\) and goodness of fit \(S\) are based on \(F^2\), conventional R-factors \(R\) are based on \(F\), with \(F\) set to zero for negative \(F^2\). The threshold expression of \(F^2 > 2\sigma(F^2)\) is used only for calculating \(R\)-factors(gt) etc. and is not relevant to the choice of reflections for refinement. \(R\)-factors based on \(F^2\) are statistically about twice as large as those based on \(F\), and \(R\)-factors based on ALL data will be even larger.
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H1B H 0.9686 0.5013 0.1623 0.066 Uiso 1 1 calc R . . .
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H26B H 0.3727 0.0993 -0.0461 0.072 Uiso 1 1 calc R . .
H26C H 0.2345 0.0671 -0.0337 0.072 Uiso 1 1 calc R . .
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C29 C 0.1371(18) 0.0901(16) 0.4444(9) 0.035(6) Uiso 1 1 d . . .
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C31 C 0.273(2) 0.0596(19) 0.5368(10) 0.052(7) Uiso 1 1 d . . .
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H44B H 0.2289 0.6562 0.2657 0.080 Uiso 1 1 calc R . .
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C46 C 0.330(2) 0.7158(18) 0.3660(11) 0.046(6) Uiso 1 1 d . . .
C47 C 0.343(2) 0.7188(19) 0.4301(12) 0.054(7) Uiso 1 1 d . . .
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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
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Refinement of $F^2$ against ALL reflections. The weighted R-factor $wR$ and
goodness of fit $S$ are based on $F^2$, conventional R-factors $R$ are based
on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of
$F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on $F^2$ are statistically about twice as large as those based on $F$, and R-
factors based on ALL data will be even larger.

Refinement details:

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not relevant to the choice of reflections for refinement. R-factors based
on $F^2$ are statistically about twice as large as those based on $F$, and R-
factors based on ALL data will be even larger.

- Refinement of $F^2$ against ALL reflections. The weighted R-factor $wR$ and
goodness of fit $S$ are based on $F^2$, conventional R-factors $R$ are based
on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of
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factors based on ALL data will be even larger.
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_refine_ls_shift/su_mean         0.000

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O2 O 0.8286(9) 0.9337(5) 0.0871(2) 0.0224(11) Uani 1 1 d . .
O3 O 0.2645(9) 0.1565(2) 0.5529(2) 0.0236(11) Uani 1 1 d . .
C1 C 0.5545(15) 0.6731(8) -0.0868(4) 0.0254(17) Uani 1 1 d . .
H1A H 0.4081 0.7445 -0.1185 0.030 Uiso 1 1 calc R . .
H1B H 0.4486 0.5959 -0.0622 0.030 Uiso 1 1 calc R . .
C2 C 0.6633(14) 0.7678(7) -0.0323(4) 0.0196(16) Uani 1 1 d . .
C3 C 0.5541(15) 0.7617(8) 0.0366(4) 0.0232(17) Uani 1 1 d . .
C4 C 0.6448(15) 0.8398(8) 0.0928(4) 0.0218(17) Uani 1 1 d . .
C5 C 0.5327(15) 0.8095(8) 0.1676(4) 0.0260(18) Uani 1 1 d . .
H5A H 0.3355 0.7784 0.1646 0.031 Uiso 1 1 calc R . .
H5B H 0.6738 0.7202 0.1916 0.031 Uiso 1 1 calc R . .
C6 C 0.8062(14) 0.5847(8) -0.1321(4) 0.0290(18) Uani 1 1 d . .
H6A H 0.7206 0.6259 0.1665 0.044 Uiso 1 1 calc R . .
H6B H 0.9492 0.5114 -0.1013 0.044 Uiso 1 1 calc R . .
H6C H 0.9097 0.6604 -0.1574 0.044 Uiso 1 1 calc R . .
C7 C 0.5013(17) 0.9501(9) 0.2120(4) 0.037(2) Uani 1 1 d . .
H7A H 0.4310 0.9229 0.2596 0.055 Uiso 1 1 calc R . .
H7B H 0.3563 1.0379 0.1895 0.055 Uiso 1 1 calc R . .
H7C H 0.6962 0.9808 0.2158 0.055 Uiso 1 1 calc R . .
C8 C -0.1266(15) 0.1656(8) 0.3362(4) 0.0265(18) Uani 1 1 d . .
H8A H -0.2291 0.0755 0.3341 0.032 Uiso 1 1 calc R . .
H8B H 0.0354 0.1514 0.3004 0.032 Uiso 1 1 calc R . .
C9 C 0.0190(14) 0.1547(8) 0.4087(4) 0.0216(16) Uani 1 1 d . . .
C10 C -0.1153(15) 0.2444(8) 0.4626(4) 0.0252(18) Uani 1 1 d . . .
H10 H -0.3026 0.3126 0.4522 0.030 Uiso 1 1 calc R . . .
C11 C -0.1153(15) 0.2444(8) 0.4626(4) 0.0252(18) Uani 1 1 d . . .
C12 C -0.1670(16) 0.3538(9) 0.5835(4) 0.0305(19) Uani 1 1 d . . .
H12A H -0.1410 0.4622 0.5699 0.037 Uiso 1 1 calc R . . .
H12B H -0.3835 0.3525 0.5803 0.037 Uiso 1 1 calc R . . .
C13 C -0.3504(16) 0.3138(9) 0.3133(4) 0.039(2) Uani 1 1 d . . .
H13A H -0.4294 0.3032 0.2661 0.059 Uiso 1 1 calc R . . .
H13B H -0.2511 0.4042 0.3117 0.059 Uiso 1 1 calc R . . .
H13C H -0.5156 0.3297 0.3474 0.059 Uiso 1 1 calc R . . .
C14 C -0.0651(17) 0.3123(9) 0.6601(4) 0.0350(19) Uani 1 1 d . . .
H14A H -0.1828 0.3880 0.6909 0.053 Uiso 1 1 calc R . . .
H14B H 0.1478 0.3161 0.6642 0.053 Uiso 1 1 calc R . . .
H14C H -0.0948 0.2061 0.6746 0.053 Uiso 1 1 calc R . . .

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Cu2 0.0199(7) 0.0238(8) 0.0236(8) -0.0037(6) 0.0000(5) -0.0018(5)
O1 0.016(3) 0.024(3) 0.023(3) -0.001(2) -0.0004(19) -0.005(2)
O2 0.019(3) 0.023(3) 0.027(3) -0.003(2) 0.001(2) -0.009(2)
O3 0.026(3) 0.024(3) 0.024(3) -0.003(2) -0.001(2) -0.002(2)
O4 0.019(3) 0.025(3) 0.027(3) -0.007(2) -0.003(2) -0.001(2)
C1 0.029(4) 0.023(4) 0.027(5) 0.001(3) 0.003(3) -0.012(3)
C2 0.021(4) 0.012(4) 0.023(4) 0.001(3) -0.001(3) 0.000(3)
C3 0.031(4) 0.015(4) 0.027(5) -0.003(3) 0.003(3) -0.014(3)
C4 0.023(4) 0.020(4) 0.019(4) 0.003(3) -0.002(3) 0.003(3)
C5 0.026(4) 0.029(4) 0.025(4) 0.002(4) -0.003(3) -0.008(3)
C6 0.027(4) 0.028(4) 0.032(5) -0.008(4) 0.000(3) -0.003(3)
C7 0.049(5) 0.037(5) 0.025(5) -0.002(4) 0.016(4) -0.011(4)
C8 0.024(4) 0.028(4) 0.026(5) -0.001(3) -0.003(3) -0.003(3)
C9 0.019(4) 0.018(4) 0.029(4) -0.003(3) 0.003(3) -0.004(3)
C10 0.024(4) 0.028(4) 0.020(5) 0.000(4) -0.002(3) 0.001(3)
C11 0.020(4) 0.019(4) 0.031(5) -0.002(3) 0.004(3) -0.005(3)
C12 0.029(4) 0.029(4) 0.034(5) -0.015(4) 0.004(3) -0.004(3)
C13 0.041(5) 0.041(5) 0.031(5) 0.001(4) -0.004(4) 0.036(4)
C14 0.048(5) 0.031(5) 0.022(5) 0.001(4) 0.009(4) 0.000(4)
All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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  Cu1 O2 1.918(5)  .  .
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  O1 C2 1.277(8)  .  .
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  O3 C9 1.271(7)  .  .
  O4 C11 1.276(8)  .  .
  C1 C2 1.503(9)  .  .
  C1 C6 1.534(9)  .  .
  C1 H1A 0.9900  .  .
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  C2 C3 1.389(9)  .  .
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  C4 C5 1.522(9)  .  .
  C5 C7 1.508(10)  .  .
  C5 H5A 0.9900  .  .
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  C6 H6A 0.9800  .  .
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  C7 H7A 0.9800  .  .
C7 H7B 0.9800 .
C7 H7C 0.9800 .
C8 C9 1.515(9) .
C8 C13 1.515(9) .
C8 H8A 0.9900 .
C8 H8B 0.9900 .
C9 C10 1.385(9) .
C10 C11 1.393(9) .
C10 H10 0.9500 .
C11 C12 1.527(9) .
C12 C14 1.520(10) .
C12 H12A 0.9900 .
C12 H12B 0.9900 .
C13 H13A 0.9800 .
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O1 Cu1 O1 180.000(1) 2_775 .
O3 Cu2 O3 180.0(2) . 2_656 ?
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O3 Cu2 O4 86.57(18) 2_656 ?
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C2 O1 Cu1 125.6(4) . . ?
C4 O2 Cu1 125.4(4) . . ?
C9 O3 Cu2 126.1(4) . . ?
C11 O4 Cu2 125.4(4) . . ?
C2 C1 C6 113.6(5) . . ?
C2 C1 H1A 108.9 . . ?
C6 C1 H1A 108.9 . . ?
C2 C1 H1B 108.9 . . ?
C6 C1 H1B 108.9 . . ?
H1A C1 H1B 107.7 . . ?
O1 C2 C3 124.5(6) . . ?
O1 C2 C1 116.0(6) . . ?
C3 C2 C1 119.4(6) . . ?
C2 C3 C4 125.1(6) . . ?
C2 C3 H3 117.5 . . ?
C4 C3 H3 117.5 . . ?
O2 C4 C3 124.7(6) . . ?
O2 C4 C5 115.4(6) . . ?
C3 C4 C5 119.9(6) . . ?
C7 C5 C4 113.3(6) . . ?
C7 C5 H5A 108.9 . . ?
C4 C5 H5A 108.9 . . ?
C7 C5 H5B 108.9 . . ?
C4 C5 H5B 108.9 . . ?
H5A C5 H5B 107.7 . . ?
C1 C6 H6A 109.5 . . ?
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C9 C8 H8A 107.7 . . ?
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C9 C8 H8B 107.7 . . ?
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O3 C9 C10 124.6(6) . . ?
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C10 C11 C12 119.3(6) . . ?
C14 C12 C11 114.0(6) . . ?
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H12A C12 H12B 107.6 . . ?
C8 C13 H13A 109.5 . . ?
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# END OF CIF
Vita

Sylvester Burton was born on September 25, 1954, to Arless and Francis Burton in Shreveport, Louisiana. He attended Southern University where he received his Bachelor of Science degree in chemistry in May of 1977. He pursued a career in the petroleum reservoir engineering industry from 1978 until 1983. He returned to Southern University in 1983 where he received his Master of Science degree in chemistry in December of 1986. He was formerly an Instructor of Chemistry at the University of Southwestern Louisiana from 1986 until 1992. In 1994 he returned to Southern University as an Instructor of Chemistry, and in 1997 he entered Louisiana State University and expects to receive the degree of Doctor of Philosophy in May of 2006.