

DESIGN, SYNTHESIS AND CHARACTERIZATION OF Cu(II) INORGANIC-
ORGANIC HYBRID COORDINATION POLYMERS BASED ON β -
CYANODIKETONATES AND TELECHELIC NITROGENOUS SPACERS

by

Carter Martin Silvernail

A DISSERTATION

Presented to the Faculty of

The Graduate College at the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Doctor of Philosophy

Major: Chemistry

Under the Supervision of Professor John Belot

May, 2005

UMI Number: 3176803

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI[®]

UMI Microform 3176803

Copyright 2005 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

DISSERTATION TITLE

Design, Syntheses and Characterization of Cu(II) Inorganic-Organic Hybrid Coordination

Polymers Based on Beta-Cyanodiketones and Telechelic Nitrogenous Spacers

BY

Carter M. Silvernail

SUPERVISORY COMMITTEE:

Approved

Date

Signature

John A. Belot
Typed Name

Signature

Victor W. Day
Typed Name

Signature

T. Adrian George
Typed Name

Signature

Jody Redepinning
Typed Name

Signature

Stephen Ragsdale
Typed Name

Signature

4/20/05

4/20/05

4/20/05

4/20/05

4/20/05

UNIVERSITY OF
Nebraska
Lincoln

**DESIGN, SYNTHESIS AND CHARACTERIZATION OF Cu(II) INORGANIC-
ORGANIC HYBRID COORDINATION POLYMERS BASED ON β -
CYANODIKETONATES AND TELECHELIC NITROGENOUS SPACERS**

Carter M. Silvernail, Ph.D.

University of Nebraska, 2005

Adviser: John A. Belot

The design and preparation of coordination networks assembled via discrete inorganic and organic molecular components has undergone rapid expansion in the field of supramolecular chemistry over the past decade. Interest in this area is driven by fascinating structural diversity and potential applicability of metal-based molecular architectures as functional materials. Although numerous efforts have been geared toward controlling network formation through judicious choice of metal ions, spacer ligands and reaction conditions, the design of self-assembled networks based on multifunctional metal β -diketonate templates remains a relatively unexplored avenue in coordination chemistry. This dissertation focuses on the design, syntheses and characterization of multifunctional β -cyanodiketones and their utility for constructing one- and two-dimensional inorganic-organic hybrid materials from prefabricated Cu(II) β -cyanodiketonate constituents.

TABLE OF CONTENTS

	Page
List of Figures.....	iii
List of Tables.....	v
List of Schemes.....	vii
Acknowledgements.....	viii
CHAPTER 1: Introduction to Self-Assembled Coordination Networks.....	
A. Overview.....	1
B. References.....	5
CHAPTER 2: Design and Synthesis of β -Cyano- α,γ -Diketones and Their Cu(II) Complexes.....	7
A. Introduction.....	7
B. Results and Discussion.....	10
C. Conclusions.....	24
D. X-ray Crystallographic Experimental.....	25
E. Experimental.....	28
F. References.....	35
CHAPTER 3: The Intramolecular Hydrogen Bond Investigation of β -Cyanodiketones.....	39
A. Introduction.....	39
B. Results and Discussion.....	45
C. Conclusions.....	53

D. Experimental.....	54
E. References.....	54
CHAPTER 4: Synthesis and Characterization of Inorganic-Organic Hybrid Materials Using Cu(II) Homoleptic Chelates.....	58
A. Introduction.....	58
B. Results and Discussion.....	61
i. Thermogravametric Analyses (TGA) of Compounds 9-14	75
C. Conclusions.....	77
D. X-ray Crystallographic Experimental.....	78
E. Experimental.....	80
F. References.....	83
CHAPTER 5: Synthesis and Characterization of Linear, Trinuclear Cu(II) Coordination Polymers.....	86
A. Introduction.....	86
B. Results and Discussion.....	89
i. Thermogravametric Analyses (TGA) of Compounds 18 and 19	108
ii. Magnetic Properties of Compound 19	109
C. Conclusions.....	111
D. X-ray Crystallographic Experimental.....	112
E. Experimental.....	115
F. References.....	120
APPENDIX A.....	125

LIST OF FIGURES

	Page
CHAPTER 1	
Figure 1.1. Geometric representation of linear (a), ladder (b), brick-wall (c), honeycomb (d), and diamondoid (e) coordination networks.....	4
CHAPTER 2	
Figure 2.1. Variable temperature x-ray structures of compound 1 at -1°C (a) and -45°C, -80°C, and -100°C (b).....	14
Figure 2.2. X-ray diffraction derived molecular structure of 3	18
Figure 2.3. X-ray derived structure of 6 depicting enol tautomer.....	20
Figure 4.4. Single crystal structure (a) and unit cell packing Diagram of compound 4 depicting Cu...NC intermolecular contacts (b).....	23
CHAPTER 3	
Figure 3.1. Keto (a) and enol (b) tautomers of 2,4-diketones.....	43
Figure 3.2. Illustration depicting reduced O...O separation in β -diketones as a result of backbone steric compression induced by sterically demanding exterior and β -carbon substituents.....	43
Figure 3.3. Nitromalonamide.....	44
Figure 3.4. ^1H NMR solution spectra of 1 (a) and 3 (b) depicting downfield shift of enol protons.....	47
Figure 3.5. Inelastic neutron scattering spectra of 3 (a), 3 scaled by $\sqrt{2}$ (x-axis), and 3d₁₈	50
Figure 3.6. Plot of ^2H quadrupole coupling constant (QCC) of 3d₁ (a)	

and ^1H chemical shifts (b) of 3 as a function of temperature.....	52
--	----

CHAPTER 4

Figure 4.1. Molecular structure of self-assembled coordination polymer 9 . Hydrogen atoms omitted for clarity.....	62
Figure 4.2. Crystal packing of coordination polymer 9 along unit cell c-axis.....	64
Figure 4.3. Molecular structure (a) and unit cell packing diagram along unit cell c-axis (b) depicting infinite, one-dimensional networks of 10	65
Figure 4.4. X-ray derived molecular structures of coordination polymers 11 (a) and 12 (b) Hydrogen atoms omitted for clarity.....	67
Figure 4.5. Packing diagrams of 11 (a) and 12 (b) orientated along the a-axis of the unit cell demonstrating infinite, one-dimensional networks.....	69
Figure 4.6. X-ray derived molecular structure of coordination polymer 13	70
Figure 4.7. Solid-state packing diagram of 13 along unit cell b-axis depicting CN...Cu intermolecular contacts between rectangular subunits.....	72
Figure 4.8. Solid-state molecular structure of 14 . Hydrogen atoms omitted for clarity.....	72
Figure 4.9. Overlay of self-assembled coordination networks 12 and 14 (a) and unit packing diagram (b) of 14 along unit cell axis.....	74
Figure 4.10. Thermogravimetric analyses of 9 , 11 , and 13 heated from 25-800°C at a rate of 5°C/min. under N ₂	75
Figure 4.11. Thermogravimetric analysis of 10 , 12 , and 14 heated from 25-800°C at a rate of 5°/min. under N ₂	76

CHAPTER 5

Figure 5.1. Solid state molecular structure of 15 . Methyl and methylene hydrogens omitted for clarity.....	91
Figure 5.2. X-ray crystal structure of 16 . Methyl and methylene hydrogens omitted for clarity.....	93
Figure 5.3. Single crystal x-ray structure of compound 17	94
Figure 5.4. Molecular structure (a) and packing diagram (b) along the ac diagonal plane of the unit cell depicting intermolecularly linked, infinite chains of 18 . Hydrogen atoms omitted for clarity.....	99
Figure 5.5. Trinuclear ABA asymmetric unit (a) and unit cell packing diagram (b) of 19 along c-axis depicting 1-dimensional infinite networks.....	103
Figure 5.6. Trinuclear A₁BA₂ symmetric unit (a) and unit cell packing diagram (b) of 20 depicting 1-dimensional infinite networks. Non- solvent hydrogen atoms omitted for clarity.....	106
Figure 5.7. Thermogravimetric analyses of 18 and 19 heated from 25°C-700° at a rate 0.5°C/min. under flowing N ₂ (110 sccm).....	108
Figure 5.8. Magnetization of 19 vs. temperature from 4-300K (insets indicate a highly asymmetric coercive field indicate of an exchange bias).....	110

LIST OF TABLES

CHAPTER 2

Table 2.1. Bond lengths (Å) and angles (°) for variable temperature structures 1a-e	17
Table 2.2. Bond Lengths (Å) and angles (°) for compound 3	19
Table 2.3. Bond lengths (Å) and angles (°) for 6	20
Table 2.4. Bond lengths (Å) and angles (°) for compound 7	21

CHAPTER 3

Table 3.1. ^1H NMR chemical shifts for 3-substituted-2,4-pentanediones (in CCl_4).....	48
--	----

CHAPTER 4

Table 4.1. Relevant bond lengths (\AA) and angles ($^\circ$) for 9	63
Table 4.2. Bond lengths (\AA) and angles ($^\circ$) for 10	66
Table 4.3. Relevant bond lengths (\AA) and angles ($^\circ$) for 11 and 12	68
Table 4.4. Relevant bond lengths (\AA) and angles ($^\circ$) for coordination complex 13	71
Table 4.5. Bond lengths (\AA) and angles ($^\circ$) for coordination sphere of 14	73

CHAPTER 5

Table 5.1. Relevant bond lengths (\AA) and angles ($^\circ$) for 15	92
Table 5.2. Relevant bond lengths (\AA) and angles ($^\circ$) for 16	93

Table 5.3. Bond lengths (\AA) and angles ($^\circ$) for 17	96
Table 5.4. Bond lengths (\AA) and angles ($^\circ$) for compound 18	100
Table 5.5. Bond lengths (\AA) and angles ($^\circ$) for 19	104
Table 5.6. Bond lengths (\AA) and angles ($^\circ$) for 20	107

LIST OF SCHEMES

CHAPTER 2

Scheme 2.1. Syntheses of β -ketonitriles utilizing chlorosulfonyl isocyanate.....	9
Scheme 2.2. One-pot synthesis of β -diketones (1-3) utilizing chlorosulfonyl isocyanate.....	10
Scheme 2.3. NaH-induced Classien condensation to produce starting diketone for the synthesis of 2.....	10
Scheme 2.4. Synthesis of 4-thiocyanato-2,2,6,6-tetramethyl-3,5-heptanedione (5) from 4.....	11
Scheme 2.5. Synthesis of 6 via bromination of dpmH.....	12
Scheme 2.6. Syntheses of Cu(II) β -diketonates (7, 8) from β -cyanodiketones (1, 3).....	13

CHAPTER 4

Scheme 4.1. Syntheses of self-assembled coordination polymers 9-14 from Cu(II) homoleptic β -cyanodiketonates (7, 8).....	61
---	----

CHAPTER 5

Scheme 5.1. Preparation of Schiff-bases (1), Cu ²⁺ complex (2), and linear, trinuclear coordination polymers (3).....	90
Scheme 5.2. Possible mechanism of diketone cleavage to produce 17.....	95

ACKNOWLEDGEMENTS

I would like to thank Professor John Belot for his guidance and support during my graduate school education. You are an excellent scientist with perpetual knowledge. My sincere gratitude also goes out to Professor Victor Day whom I could always turn to for advice and is a true gentlemen and friend. I would also like to thank my graduate committee: Drs. Jody Redepinning, T.A. George, and Stephen Ragsdale for all of their sacrifices to help me fulfill all requirements. A special thanks to Professor Gerry Harbison and the members of his group for all of the hardwork and helpful discussions regarding the hydrogen bond studies. To the members of the Belot group, especially Dr. Steven Schuetz whom I could always turn to for valuable advice regarding my research project, alcohol consumption, and laboratory fires; you are a great friend and will always be remembered.

I would also like to acknowledge all of the staff (instrumentation personal, administrative assistances, secretaries, janitors, etc. (you know who you are). Your hard work and appreciation should never be overlooked and I thank you for everything you have done for me and the rest of the department.

I also extend my gratefulness to Ron and Carol Bergan who have always offered endless love and support concerning my education and life in general. A special thanks to my brothers, Jason and Nathan, whom I have always been able to turn to; you are the best brothers and role models anyone could ever ask for. I would like to thank Dave and

Sheila Silvernail for all of the moral, emotional, and financial support over the last 5 years. I can honestly say that I wouldn't be writing this dissertation without you. I promise to grow up and get a real job.

Finally, I would like to thank my wife, Sara. You have sacrificed everything to help me get through graduate school not to mention the last few years of our personal life. You were always there to pick me up and put a smile on my face. I could never express in words my love and appreciation for you. The first two years, although rocky at times, have been the best years of my life and I promise you many more in the future. For all you have done and mean to me I dedicate this dissertation to you.

To Sara Silvernail

Chapter 1

Introduction to Self-Assembled Coordination Networks

The design of self-assembled coordination architectures is of current and ongoing scientific investigation due to the potential applicability of these solid-state materials to many areas of science including magnetism,¹ separation science² and catalysis.³ Research pertaining to this avenue of chemistry has primarily been invested in the identification of salient chemical and physical properties that underlie the predictable construction of self-assembled networks. Unfortunately, advancements in this area have been plagued as methodologies for the design and syntheses of supramolecular networks have often yielded unexpected complexes. Given this daunting predicament, much effort has been geared toward developing reliable synthetic routes to establish systematic structure-function relationships.

A contemporary theme often exploited for the design and syntheses of extended, coordination tectons centers upon the principle of “crystal engineering”. This concept

was originally introduced to intellectually describe crystal packing principles responsible for photochemical transformations in solid-state organic molecules.⁴ Although this interpretation pertained exclusively to organic chemistry, the idea was that both physical and chemical properties of solids were inherently dependent upon the arrangement of molecular entities and the properties associated with the individual components. Since the inception of the concept of crystal engineering, there has been a continuing effort to understand and properly predict patterns accountable for formation, orientation, and connectivity in molecular systems.⁵

A more broad and diverse representation of crystal engineering was elegantly proposed by Desiraju⁶ whose description of crystal engineering assisted in bridging the gap between organic and inorganic chemistries with a particular emphasis on interactions responsible for controlling multi-component self-assembly. The general theme of this approach was self-assembled molecular networks were held together through a series of intra and intermolecular interactions to form networks. Within each discrete network, the building block (node) and connector (spacer) play a crucial role in predicting topology and geometry of the resulting network through a series of strong (i.e. covalent) interactions and weaker or secondary (i.e. hydrogen and dative) interactions. Strong interactions were predominately proposed to be most influential in determining the overall geometric shape and topology of the resulting network by coordination preference at the metal center, ligand, spacer ligating capability and component stoichiometry. However weaker or secondary interactions such as solvent effects, dative, and hydrogen

bonding, and pi-pi stacking had the potential to control and in some instances dominate structural connectivity, dimensionality and thermal stability.

While covalent type interactions in organic and inorganic chemistry have been thoroughly studied and are generally well understood,⁷ secondary forces responsible for the arrangement and stability of molecules remains nonetheless unpredictable. Consequently, the discipline of crystal engineering has since moved forward and transformed itself into a hybrid of supramolecular and materials chemistries centered on preparative methods for crystalline materials and supramolecules with desirable solid state properties.⁸ This has been extensively exemplified by numerous extended networks bearing various topologies, coordination modes, and geometries including 1-D, 2-D, and 3-D architectures (Figure 1.1).⁹⁻¹³ These networks are commonly generated from the assembly of soluble metal species with multidentate spacer ligands and preferentially “fine tuned” to control coordination number, geometry, dimensionality and thermal stability by altering the metal center and/or spacers joining the building block entities. Although these modifications are prominent factors to consider when construct functional materials, insignificant research has concentrated on alteration of the immediate metal periphery prior to network construction. In particular, the introduction of tunable, chelating ligands would be desirable to enhance thermal stability while controlling electronic and steric properties of the building block moiety.

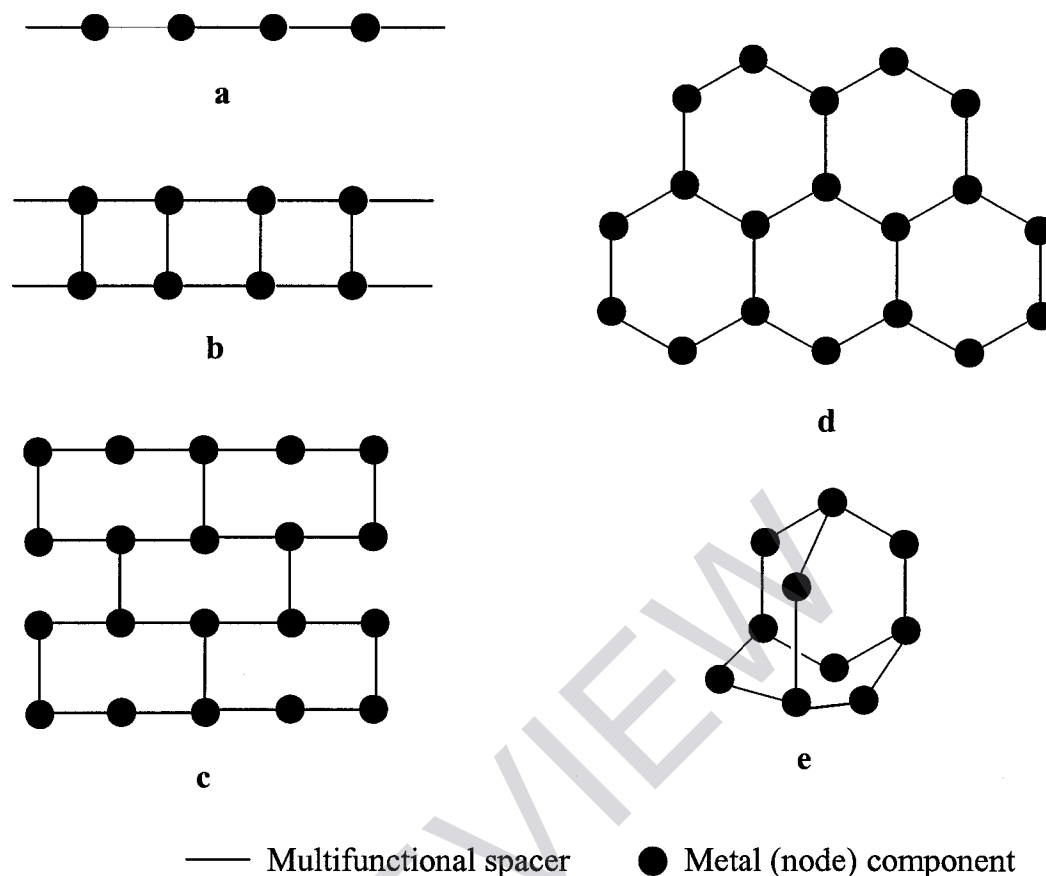


Figure 1.1. Geometric representation of linear (a), ladder (b), brick-wall (c), honeycomb (d), and diamondoid (e) coordination networks.

This dissertation will discuss the rational design, syntheses and characterization of robust inorganic supports bearing multifunctional chelate ligand frameworks in attempts to enhance thermal stability and control network dimensionality and connectivity of self-assembled coordination networks. Although a seemingly endless number of self-assembled networks have been successfully synthesized in the past, the coupling of robust (i.e. chelated), functionalized diketone and Schiff-base ligand frameworks to soluble metal ions followed by network assembly with bidentate spacers remains a relatively unexplored avenue of research. Given the low cost and tailorability of diketone

and Schiff-base frameworks, rapid and straightforward synthetic methodologies may be developed to functionalize these ligands and ultimately prepare novel coordination complexes. We believe this avenue of synthetic inorganic chemistry is inherently important to identify desirable interactions responsible for network connectivity, dimensionality, and stabilization and ultimately uncover novel functional materials for future scientific implications.

*“One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition”.*¹⁴

-J. Maddox

References

- ¹ a.) Kahn, O. *Acc. Chem. Res.* **2000**, 33, 647. b.) Ohba, M.; Ôkawa, H. *Coord. Chem. Rev.* **2000**, 198, 313.
- ² a.) Lopez, S.; Keller, S.W. *Inorg. Chem.* **1999**, 38, 1883. b.) Zaworotko, M.J. *Angew. Chem. Int. Ed.* **2000**, 39, 3052.
- ³ a.) Seo, J.S.; Whang, D.; Lee, H.; Jun, S.I.; Oh, J.; Jeon, Y.J.; Kim, K. *Nature* **2000**, 404, 982. b.) Sawaki, T.; Dewa, T.; Aoyama, Y. *J. Am. Chem. Soc.* **1998**, 120, 8539. c.) Fujita, M.; Kwon, Y.J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, 116, 1151.

- ⁴ Schmidt, G.M.J. *Pure Appl. Chem.* **1971**, 27, 647.
- ⁵ a.) Evans, O.R.; Lin, W. *Acc. Chem. Res.* **2002**, 35, 511 and references therein. b.) Etter, M.C. *Acc. Chem. Res.* **1990**, 23, 120.
- ⁶ Desiraju, G.R. *J. Mol. Struct.* **2003**, 656, 5.
- ⁷ Müller-Dethlefs, K.; Hobza, P. *Chem. Rev.* **2000**, 100, 143.
- ⁸ Braga, D. *J. Chem. Soc., Dalton Trans.* **2000**, 3705.
- ⁹ a.) For examples see: Seitz, M.; Kaiser, A.; Stempfhuber, S.; Zabel, M.; Reiser, O. *J. Am. Chem. Soc.* **2004**, 126, 11426. b.) Dong, Y.-B.; Ma, J.-P.; Huang, R.-Q.; Smith, M.D.; zur Loye, H.-C. *Inorg. Chem.* **2003**, 42, 294.
- ¹⁰ a.) Blake, A.J.; Champness, N.R.; Khlobystov, A.; Lemenovskii, D.A.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 2027. b.) Losier, P.; Zaworotko, M.J. *Angew. Chem. Int. Ed.* **1996**, 35, 2779.
- ¹¹ a.) Lü, X.Q.; Jiang, J.-J.; Zhang, L.; Chen, C.-L.; Su, C.-Y.; Kang, B.-S. *Cryst. Growth Des.* **2005**, ASAP. b.) Fujita, M.; Kwon, Y.J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, 117, 7287.
- ¹² a.) Mukhopadhyay, S.; Chatterjee, P.B.; Mandal, D.; Mostafa, G.; Caneschi, A.; van Slageren, J.; Weakley, T.J.R.; Chaudhury, M. *Inorg. Chem.* **2004**, 43, 3413. b.) Dai, J.-C.; Wu, X.-T.; Fu, Z.-Y.; Cui, C.-P.; Hu, S.-M.; Du, W.-X.; Wu, L.-M.; Zhang, H.-H.; Sun, R.-Q. *Inorg. Chem.* **2002**, 41, 1391.
- ¹³ a.) Sreenivasulu, B.; Vittal, J.J. *Cryst. Growth Des.* **2003**, 3, 635. b.) Ermer, O. *J. Am. Chem. Soc.* **1988**, 110, 3747.
- ¹⁴ Maddox, J. *Nature* **1988**, 335, 201.

Chapter 2

Design and Synthesis of β -Cyano- α,γ -Diketones and Their Cu(II) Complexes

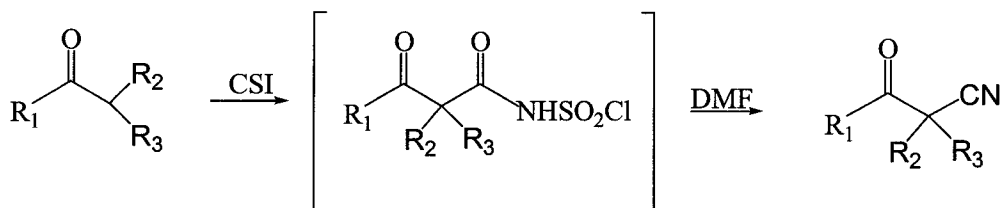
Introduction

Metal β -diketonates constitute a thoroughly studied class of inorganic compounds that have been synthesized with metals spanning the entire periodic table.¹ Interest in the complexes is a result of the rich, diverse bonding and structural characteristics of β -diketonate ligands when coupled to soluble metal ions. These ligands are advantageous for metal ion capture due to ease of tailorability and hard metal chelation through bidentate oxygen atoms providing stable six membered-chelate rings. Furthermore, parent β -diketones can be inexpensively purchased or prepared from commercial sources and are easily ligated to metal ions from various metal salts including nitrates,² chlorides,³ acetates,⁴ and sulfates.⁵ Although metal β -diketonates are conventionally synthesized and their chemistries well understood, modifications to the diketone

framework such as β -substitution would allow for the investigation of multidentate metal complexes as precursors for designing robust coordination networks.⁶

The cyanation of enolizable ketones was initially reported by Traube⁷ who demonstrated that acetylacetone reacted with cyanogen gas (i.e. C_2N_2) resulting in cyano-imido-methyl acetylacetone which was converted to 3-cyano-2,4-pentanedione by hydrolysis. Fackler expanded on this finding and synthesized pure 3-cyano-2,4-pentanedione by precipitating bis(3-cyano-2,4-pentanedionato) Cu(II) followed by a low pH work up in dilute H_2SO_4 .⁸ Although this pathway provided the coordinated 3-cyano-2,4-pentanedione ligand, cleaving the organic fragment from the metal center was impossible. Alternative synthetic routes to β -cyanodiketones were necessary to avoid multistep syntheses which required precipitation of metal β -diketonates and the use of toxic C_2N_2 . Although our primary interest in the organic compounds was their use as ligands, our curiosity in physical organic hydrogen bonding was piqued by reports of enolizable diketones from Perrin,⁹ Bertolasi,¹⁰ and Emsley.¹¹

A relevant advancement involving the desired synthesis of cyanodiketones involved Rasmussen¹² who reported that enolizable diketones could be converted to N-chlorosulfonyl- β -ketocarboxamides in the presence of an electrophilic cyanide source, chlorosulfonyl isocyanate (CSI) to afford β -ketonitriles upon hydrolysis (Scheme 2.1).



Compounds

$\text{R}_1 \neq \text{R}_2 \neq \text{R}_3 = \text{C}_6\text{H}_5, \text{CH}_3, \text{H}$	$\text{R}_1 = \text{R}_2 \neq \text{R}_3 = \text{CH}_3, \text{CH}_3, \text{H}$
$\text{R}_1 \neq \text{R}_2 \neq \text{R}_3 = \text{C}_6\text{H}_5, \text{CH}_2\text{CH}_3, \text{H}$	$\text{R}_1 \neq \text{R}_2 \neq \text{R}_3 = \text{CH}_3, \text{COCH}_3, \text{H}$
$\text{R}_1 \neq \text{R}_2 = \text{R}_3 = \text{C}_6\text{H}_5, \text{CH}_3, \text{CH}_3$	$\text{R}_1 = \text{R}_2 \neq \text{R}_3 = (\text{CH}_2)_3, (\text{CH}_2)_3, \text{H}$
$\text{R}_1 \neq \text{R}_2 \neq \text{R}_3 = \text{CH}_2\text{CH}_3, \text{CH}_3, \text{H}$	$\text{R}_1 = \text{R}_2 \neq \text{R}_3 = (\text{CH}_2)_4, (\text{CH}_2)_4, \text{H}$
$\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{CH}_3, \text{CH}_3, \text{CH}_3$	

Scheme 2.1. Syntheses of β -ketonitriles utilizing chlorosulfonyl isocyanate.

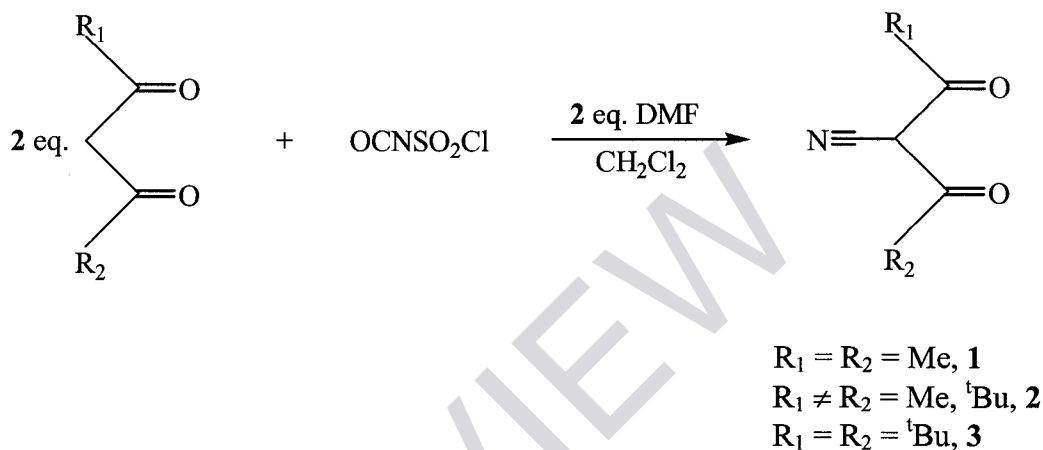
Since Rassmussen's successes utilizing chlorosulfonyl isocyanate as an electrophilic cyanide source, the cyanogenation of enolizable ketones has been achieved using various organic reagents including cyanogen halides,¹³ p-toluenesulfonyl cyanide,¹⁴ and aryl cyanates.¹⁵ However, disadvantages associated with these reagents are numerous and include toxic and unstable cyanide sources, lack of commercial availability, and multi-step syntheses to afford the target starting reagents.

This chapter focuses on the use of chlorosulfonyl isocyanate, an electrophilic cyanide source, for the functionalization of enolizable diketones and structural characteristics among various β -substituted diketones. The β -CN functionalized, ambidentate ligands will be further utilized in the preparation of two Cu(II) β -diketonate precursors and serve as supports for solid-state network assembly in the forthcoming

chapter (Chapter 4). This work provides an efficient, one-pot synthesis of β -cyanodiketones while avoiding the disadvantages associated with traditional routes.

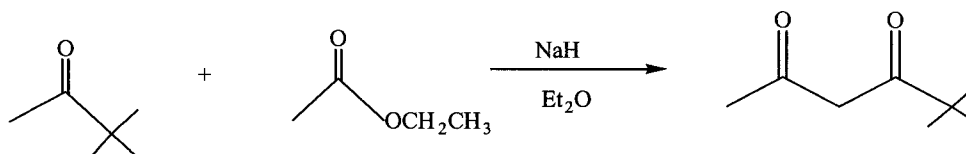
Results and Discussion

The syntheses of 3-cyano-2,4-pentanedione (**1**), 3-cyano-7,7-dimethyl-2,4-



Scheme 2.2. One-pot synthesis of β -diketones (**1-3**) utilizing chlorosulfonyl isocyanate.

hexanedione (**2**) and 4-cyano-2,2,6,6-tetramethyl-3,5-heptanedione (**3**) was accomplished utilizing an electrophilic cyanide source, chlorosulfonylisocyanate (ClSO_2NCO), dimethylformamide (DMF) and the appropriate diketone in CH_2Cl_2 (Scheme 2.2). The

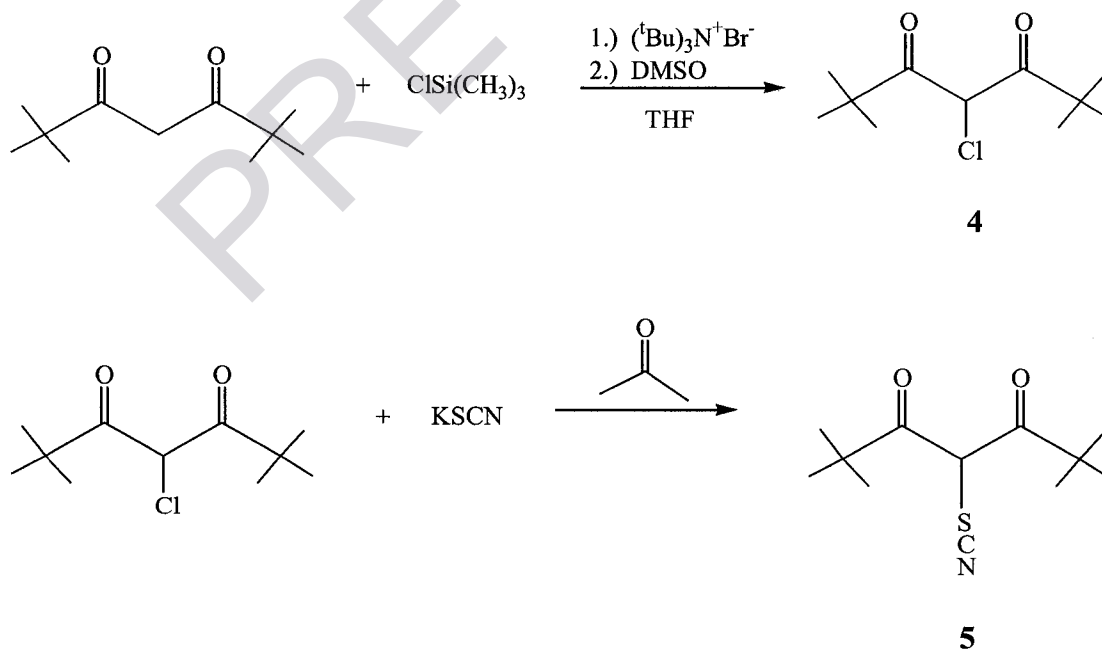


Scheme 2.3. NaH-induced Claisen condensation to produce starting diketone for the synthesis of **2**.

diketone employed for the synthesis of **2** was prepared via a NaH-induced Claisen condensation of ethylacetate and pinacolone in diethyl ether (Scheme 2.3) while those

used to prepare **1** and **3** were commercially purchased. The reaction conditions utilized for **1-3** were previously established as an effective method for introducing “electrophilic” cyanides to enolizable ketones and aldehydes.¹⁶ All diketones were distilled immediately prior to use to substantially increase product yields by presumably removing trace acid impurities from stock reagents. Acidic conditions were further confirmed to be undesirable through the observation that any diketone $-\text{CF}_3$ substitution (i.e. decreased pK_a) completely prohibited the formation of desired cyano diketones. Compounds **1-3** were isolated as colorless crystalline solids (**1**, **3**) or a colorless liquid (**2**) and storable indefinitely at temperatures $\leq 0^\circ\text{C}$.

4-Chloro-2,2,6,6-tetramethyl-3,5-heptanedione (**4**) was prepared by the bromine catalyzed chlorination of 2,2,6,6-tetramethyl-3,5-heptanedione (dpmH)¹⁷ and converted to



Scheme 2.4. Synthesis of 4-thiocyanato-2,2,6,6-tetramethyl-3,5-heptanedione (**5**) from **4**.