

**Synthetic Copper-Sulfide Complexes as Models for the
Active Sites in Nitrous Oxide Reductase**

BY

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THESIS

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This dissertation is dedicated to my family and friends. Although they may not understand a majority of the text herein, their support and unyielding encouragement is disguised behind every word.

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BJJ

CONTRIBUTION OF AUTHORS

Multiple authors provided direct contributions to the published work discussed and reproduced in the ensuing chapters. The contribution of those authors will be individually credited here. The reader should note that the proceeding thesis text was originated by me, but certain experimental data interpretations are based or supplemented from the coworkers identified here. Additionally, the chapter discussions are my analysis of the research presented therein, and several were developed from the considerations within the published texts authored by Dr. Neal P. Mankad in the Department of Chemistry at the University of Illinois at Chicago (Chicago, IL). Any figures, tables and schemes not entirely constructed by me or appeared in the published manuscripts as is, will be explicitly referenced. Permission from publishers for reproduced figures or text are included in Appendices J and K. The remaining synthetic work and characterization data are my independent contributions.

CHAPTER 2

The research presented in Chapter 2 primarily correlates to the published work in reference: Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. "Assembly, Structure, and Reactivity of Cu₄S and Cu₃S Models for the Nitrous Oxide Reductase Active Site, Cu₂*" *Inorg. Chem.* **2014**, 53, 10611. Dr. Sergey V. Lindeman in the Department of Chemistry at Marquette University (Milwaukee, WI) provided the X-ray crystallographic analysis for complexes **2.2**, **2.5**, **2.4**, **2.6** and **2.7**. Dr. Neal P. Mankad in the Department of Chemistry at the University of Illinois at Chicago (Chicago, IL) authored the published text and figures therein.

CHAPTER 3

The discussion in Chapter 3 is centered around the work published in references: Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Mankad, N. P. "A Cu₄S Model for the Nitrous Oxide Reductase Active Sites Supported Only by Nitrogen Ligands" *Chem. Commun.* **2015**, 51, 11860 and Johnson, B. J.;

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Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. “A One-Hole Cu₄S Cluster with N₂O Reductase Activity: A Structural and Functional Model for Cu_Z*” *J. Am. Chem. Soc.* **2016**, *138*, 13107. In the *Chemical Communications* reference, Dr. William E. Antholine in the Department of Biophysics at Medical College of Wisconsin (Milwaukee, WI) provided the EPR analysis. Dr. Sergey V. Lindeman in the Department of Chemistry at Marquette University (Milwaukee, WI) provided the X-ray crystallographic analysis. Dr. Neal P. Mankad in the Department of Chemistry at the University of Illinois at Chicago (Chicago, IL) authored the published text and figures therein; as well as the DFT computational analysis.

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CHAPTER 5

All experimental and supporting information is included in Chapter 5 from references: Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. “Assembly, Structure, and Reactivity of Cu₄S and Cu₃S Models for the Nitrous Oxide Reductase Active Site, Cu_Z*” *Inorg. Chem.* **2014**, *53*, 10611; Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Mankad, N. P. “A Cu₄S Model for the Nitrous Oxide Reductase Active Sites Supported Only by Nitrogen Ligands” *Chem. Commun.* **2015**, *51*, 11860 and Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. “A One-Hole Cu₄S Cluster with N₂O Reductase Activity:

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A Structural and Functional Model for Cu₂*" *J. Am. Chem. Soc.* **2016**, *138*, 13107. Supporting information and figures pertaining to the EPR analysis (*Chem. Commun.* and *J. Am. Chem. Soc.*) were authored by Dr. William E. Antholine in the Department of Biophysics at Medical College of Wisconsin (Milwaukee, WI). Supporting information and figures pertaining to the X-ray crystallography analysis (*Inorg. Chem.*, *Chem. Commun.* and *J. Am. Chem. Soc.*) were authored by Dr. Sergey V. Lindeman in the Department of Chemistry at Marquette University (Milwaukee, WI). The supporting information and figures pertaining to the SQUID magnetometry analysis (*J. Am. Chem. Soc.*) were authored by Mr. Michael J. Graham in the Department of Chemistry (under the supervision of Dr. Danna E. Freedman) at Northwestern University (Evanston, IL). Supporting information for the DFT calculations, analysis and computational MO figures (*Chem. Commun.* and *J. Am. Chem. Soc.*) were authored by Dr. Neal P. Mankad in the Department of Chemistry at the University of Illinois at Chicago (Chicago, IL). Text describing the preparation of compounds, characterization spectra and tables were authored by me.

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LIST OF ABBREVIATIONS

2-dps	2,2'-Dipyridyldisulfide
Cp*	Pentamethylcyclopentadiene
CV	Cyclic voltammogram
DFT	Density functional theory
dcpm	Bis(dicyclohexylphosphino)methane
dfpma	Bis(difluorophosphino)methyl-amine
dppa	Bis(diphenylphosphino)amine
dppan	Bis(diphenylphosphino)aniline
dppe	Bis(diphenylphosphino)ethane
dppf	Bis(diphenylphosphino)ferrocene
dppipa	Bis(diphenylphosphino)isopropylamine
dppm	Bis(diphenylphosphino)methane
dppp	Bis(diphenylphosphino)propane
dtpm	Bis[bis(4-methylphenyl)phosphino]methane
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
EPR	Electron paramagnetic resonance
ESI	Electrospray ionization mass spectrometry
ET	Electron transfer
Fc	Ferrocene
Fp	Cyclopentadienyliron dicarbonyl
FT-IR	Fourier Transform Infrared
GC-MS	Gas chromatography mass spectrometry
HMDSO	Hexamethyldisiloxane
HOMO	Highest occupied molecular orbital
IPr	1,3-Bis(2,6-diisopropylphenyl)imidazole-2-ylidene
IPr*	1,3-Bis(2,6-(diphenylmethyl)-4-methylphenyl)imidazole-2-ylidene
LMCT	Ligand-to-Metal charge transfer

LIST OF ABBREIVATIONS (continued)

LUMO	Low occupied molecular orbital
MCD	Magnetic circular dichroism
Me ₂ NPY2	<i>N,N</i> -bis{2-[2-(<i>N',N'</i> -4-dimethylamino)pyridyl]ethyl} methylamine
Me ₄ chd	<i>N,N,N',N'</i> -tetramethyl-trans-1(<i>R</i>),2(<i>R</i>)-diaminocyclohexane
Me ₄ eda	<i>N,N,N',N'</i> -tetramethylethylenediamine
Me ₄ pda	<i>N,N,N',N'</i> -tetramethylpropanediamine
MeCN	Acetonitrile
N ₂ OR	Nitrous Oxide Reductase
NHC	N-heterocyclic carbene
NMR	Nuclear Magnetic Resonance
PCET	Proton-coupled electron transfer
PNP ⁻	Bis(2-diisobutylphospino-4- <i>tert</i> -butylphenyl)amide)
R ₃ TACH	<i>N</i> -alkylated <i>cis,cis</i> -1,3,5-triaminocyclohexane
R ₃ tacn	1,4,7-trialkyltriazacyclononane
RAMO	Redox-active molecular orbital
rR	Resonance Raman spectroscopy
R.T.	Retention time
RT	Room temperature
SOMO	Singly occupied molecular orbital
SQUID	Superconducting quantum interference device
TD-DFT	Time-dependent density functional theory
THF	Tetrahydrofuran
TPMA	Tris(2-pyridylmethyl)amine
TMS-Cl	Trimethylsilyl chloride
Tp ^{iPr2}	Hydrotris(3,5-diisopropylpyrazolyl)borate
TS	Transition State
XAS	X-ray absorption spectroscopy

SUMMARY

Chapter 1 introduces the critical impact of nitrous oxide as an imposing destroyer of the Earth's ozone, and as a contributor to global warming. Biological systems, however, have developed metalloenzyme active sites that prove efficient in converting gaseous nitrous oxide into temperate reaction byproducts (nitrogen and water). The enzyme responsible, nitrous oxide reductase, is presented and the specific active sites, Cu_Z^* and Cu_Z , are described according to previously published reports. Despite the current knowledge pertaining to the structural and electronic characteristics of Cu_Z^* and Cu_Z , no experimental evidence has been reported to date that unveils the two-electron reduction mechanism of nitrous oxide facilitated by either active site. Previous spectroscopic and computational efforts aimed at elucidating the chemistry occurring in the Cu_Z^* and Cu_Z active sites are highlighted, and the drawbacks of these specific approaches are discussed. Synthetic, small-molecule, model complexes as a means for investigating the reduction of nitrous oxide in the metalloenzyme active sites is presented; along with other inorganic Cu_Z^* model complexes formerly established in the literature. Synthetic strategies for accomplishing construction of biomimetic complexes related to the Cu_Z^* active site are revealed.

The research presented in Chapter 2 primarily correlates to the published work in reference Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. "Assembly, Structure, and Reactivity of Cu_4S and Cu_3S Models for the Nitrous Oxide Reductase Active Site, Cu_Z^* " *Inorg. Chem.* **2014**, 53, 10611. Within Chapter 2, use of binucleating diphosphine ligands in model synthesis is illustrated. Two novel complexes, **2.2** and **2.4**, are introduced and spectroscopically characterized to divulge similarities in their molecular properties compared to the biological active sites. Structural characteristics of the new phosphine-ligated model compounds are described based on X-ray crystallographic and NMR spectroscopy studies. The photophysical and electrochemical properties of the two model complexes are examined to establish the electronic structure present. Reactivity studies, involving **2.2** and a variety of substrates that are isoelectronic to nitrous oxide, produced four new organometallic structures; three of which are novel model-substrate adducts, as determined by X-ray crystallography.

SUMMARY (continued)

The discussion in Chapter 3 is centered around the work published in references: Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Mankad, N. P. “A Cu₄S Model for the Nitrous Oxide Reductase Active Sites Supported Only by Nitrogen Ligands” *Chem. Commun.* **2015**, 51, 11860 and Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. “A One-Hole Cu₄S Cluster with N₂O Reductase Activity: A Structural and Functional Model for Cu₂*” *J. Am. Chem. Soc.* **2016**, 138, 13107. In Chapter 3, the synthesis of two additional biomimetic complexes, **3.2** and **3.3**, is accomplished by using anionic, amidinate ligands. The structures of **3.2** and **3.3** are illustrated by X-ray crystallography and NMR spectroscopy. The rich electronic information encompassing both model complexes is discussed based on data collected by cyclic voltammetry, electronic absorption, EPR spectroscopy and DFT calculations. Model complex **3.3** was found to react with nitrous oxide and the identification of the resulting reaction products is examined. Plausible reaction mechanisms for the two-electron reduction of nitrous oxide by model **3.3** are presented.

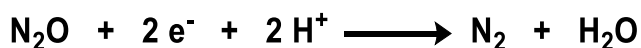
Chapter 4 provides an overview of the data collected and important findings from the model complexes studied in Chapters 2 and 3. Additionally, considerations for future studies involving model complexes of Cu₂* and Cu₂ are proposed in Chapter 4. The final chapter of this dissertation includes all supporting information, synthetic procedures and experimental spectra for all the new complexes introduced throughout this thesis

1. INTRODUCTION

1.1 Nitrous Oxide

Nitrous oxide (N₂O) is projected to be the foremost anthropogenic emission contributor to ozone depletion in the 21st century, as approximately ten million metric tons are emitted per year from agricultural fertilization, biomass/biofuel burning, fossil fuel combustion and other related industrial processes.¹ In addition, the global warming potential of N₂O is 300 times higher than that of carbon dioxide (CO₂), even though N₂O is the third most abundant greenhouse gas in the Earth's atmosphere.² The impact of nitrous oxide on both the ozone and climate are devastating and problematic; especially when considering the 120 year lifetime expected for eliminating 63% of initial emissions.³ More importantly, concentrations of N₂O are suggested to steadily increase by 0.25% annually, further dissociating current levels from atmospheric homeostasis.³ The dire statistics associating N₂O emissions to ozone erosion and climate instability have encouraged the study of efficient chemical systems that prove suitable for reducing atmospheric concentrations of N₂O.

Fortunately, the two electron reduction of nitrous oxide is thermodynamically favorable ($\Delta G^\circ = -81.3$ kcal/mol and $E^\circ = 1.35$ V) and generates nitrogen and water as the reaction byproducts (Scheme 1.1).^{1,2}



SCHEME 1.1 Reduction of nitrous oxide.

However, activation of N₂O is accompanied by a high kinetic barrier ($E_a = \sim 60$ kcal/mol) related to a spin-forbidden process; therefore, a catalyst is required to facilitate reduction.^{4,5} While transition metal-catalyzed heterogeneous^{6–10} and homogeneous^{9,11} oxidation reactions involving N₂O have been reported, both systems suffer from the fundamental shortcoming of nitrous oxide as a sufficiently coordinating ligand. The poor

σ -donating and π -accepting properties of N_2O lowers its propensity of binding to metal centers and as a result, activation becomes challenging.⁹ The transient nature of N_2O bound to transition metals has predominantly forced researchers to utilize theoretical calculations, rather than direct experimental evidence, in attempts at understanding N_2O reactivity.⁹ Identifying N_2O binding modes, subsequent activation mechanisms and driving forces behind N–O or N–N bond scission remain heavily investigated aspects that could uncover future applications of N_2O chemistry.^{9,10,12,13}

1.2 Nitrous Oxide Reductase

Luckily, nature has established an efficient way of reducing nitrous oxide by two electrons during the final step of bacterial denitrification.^{2,14,15} The process of denitrification involves the conversion of nitrate $\rightarrow$ nitrite $\rightarrow$ nitric oxide $\rightarrow$ nitrous oxide $\rightarrow$ nitrogen. Each chemical transformation is regulated by metalloenzymes and the reduction of nitrous oxide into N_2 and water, is mediated by nitrous oxide reductase (N_2OR).^{2,14,15} Two different copper sites within N_2OR facilitate the catalytic uptake, activation and reduction of N_2O . The dicopper site, Cu_A , is responsible for transferring two electrons to the catalytically active site after N_2O reduction (Figure 1.1A). The crystal structure of Cu_A in N_2OR from *Pseudomonas nautica* (2.4 Å resolution)¹⁶ and *Paracoccus denitrificans* (1.6 Å resolution)¹⁷ revealed two copper centers bridged by two separate sulfur atoms belonging to cysteine residues ($-\text{S}_\text{Cys}$). The remaining ligands attached to the copper atoms in Cu_A include histidine ($-\text{N}_\text{His}$), methionine ($-\text{S}_\text{Met}$) and tryptophan ($-\text{C}_\text{Trp}$). Located approximately 10 Å away, in an adjacent monomer, is the catalytically active site, Cu_Z^* (Figure 1.1B).^{14,15}

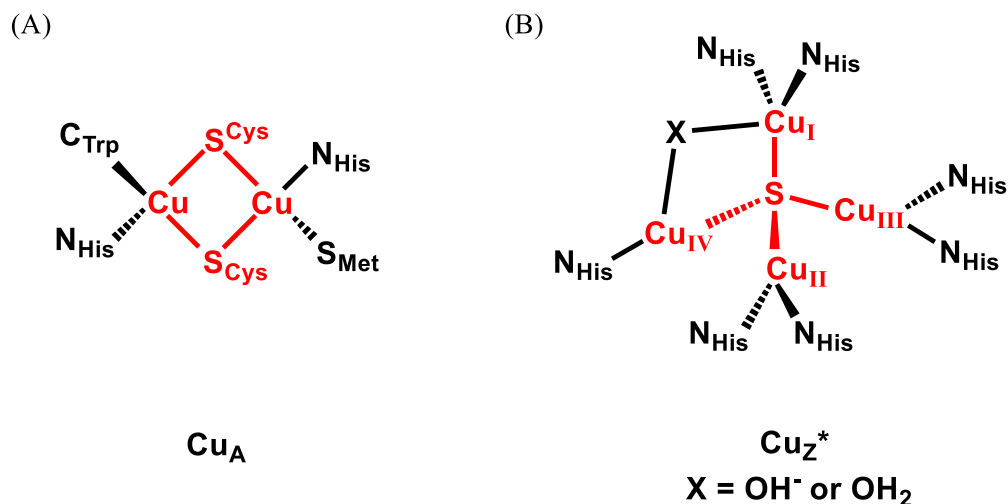


FIGURE 1.1 Core inorganic structures of (A) Cu_A ET site and (B) Cu_Z* catalytic site, located in N₂OR.

The high-resolution crystal structure of Cu_Z* (1.6 Å) in the resting state from *Pseudomonas nautica* (PnN₂OR) and *Paracoccus denitrificans* (PdN₂OR) displayed four copper atoms, all bound to a single bridging sulfide atom ($\mu_4\text{-S}^{2-}$).^{17,18} Three of the four copper centers contain two histidine (-N_{His}) ligands, while one copper atom, Cu_{IV}, possesses a single histidine residue. The structure of Cu_Z* also contains a bridging hydroxide ($\mu_2\text{-OH}^-$) or water molecule located between the tetra-coordinated Cu_I and tri-coordinated Cu_{IV}, as shown in Figure 1.1B. Recently, a crystal structure of N₂OR from *Pseudomonas stutzeri* displayed a tetracopper-*disulfide* active site (Figure 1.2); differing from the previous Cu_Z* structure because of the presence of a $\mu_2\text{-S}$ edge ligand instead of a solvent-derived molecule.¹⁹ The new active site, discovered by Einsle and coworkers, is referred to as “Cu_Z”^{15,19} and results as the major N₂OR active form when crystallized under different purification conditions than Cu_Z*.^{19,20} It was reported that samples of N₂OR generally contain a mixture of both active sites Cu_Z and Cu_Z*, and while the two different purification procedures allow for a majority of one active form to be present over the other, it is not possible to completely eliminate the alternate active site from remaining in small amounts.^{21,22} The highest quantity of Cu_Z content to be isolated, relative to remaining amounts of Cu_Z*, was reported by Solomon and coworkers to be $65 \pm 5\%$ Cu_Z to $35 \pm 5\%$ Cu_Z*.²² Alternatively, the authors were also able to isolate $96 \pm 14\%$ of the

Cu_Z^* form, with $4 \pm 14\%$ Cu_Z content remaining. It was important to isolate as much of one active form over another, in order to determine which active site proves catalytically competent for reducing N_2O , as will be discussed.

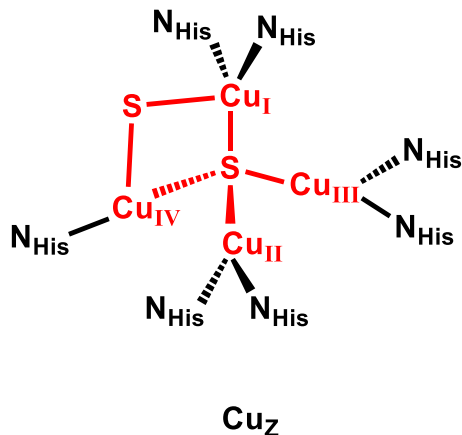


FIGURE 1.2 Core inorganic structure of the Cu_Z form in N_2OR .

Nevertheless, two different active sites exist in N_2OR : Cu_Z^* (4CuS) and Cu_Z ($4\text{Cu}_2\text{S}$). While the Cu_A electron transfer (ET) site in N_2OR has been spectroscopically characterized^{23,24} and the focus of several synthetic inorganic model studies,^{25–29} the active sites, Cu_Z^* and Cu_Z , prove more relevant to N_2O reactivity because of their direct participation. Therefore, the tetracopper enzyme centers are solely examined throughout the remainder of this dissertation.

1.2.1 Cu_Z^* and Cu_Z Reactivity with Nitrous Oxide

The resting redox state of Cu_Z^* was spectroscopically determined by Solomon and coworkers to be a mixed valent “1-hole” ($\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$) ground state.^{30–32} The electron “holes” are indicative of the number of electrons absent from a full $\text{Cu}(\text{I}) - d^{10}$ manifold; thereby signifying the presence of a formal $\text{Cu}(\text{II}) - d^9$ atom. The authors reported that upon extended incubation periods with the reductant methyl viologen, the resting 1-hole Cu_Z^* was reduced by one electron to a “fully reduced” state (4Cu^{I}); which has only been

characterized spectroscopically, and was proven to be the catalytically active redox state.³³ Solomon and coworkers reported that under steady-state assay conditions with N₂O, the specific activity of the fully reduced Cu_Z* measured $141 \pm 7 \mu\text{mol N}_2\text{O min}^{-1} \text{mg}^{-1}$.²² The prolonged exposure of the resting Cu_Z* form to a non-biological reductant (methyl viologen), that is required to generate the active fully reduced state, was measured to be significantly slower ($k_{\text{red}} = 0.07 \text{ min}^{-1}$)³³ than the determined steady-state turnover of PnN₂OR ($k_{\text{cat}} = 275 \text{ s}^{-1}$).³⁴ Therefore, it has been appreciated that the resting Cu_Z* form must not be the 1-hole species involved in the catalytic cycle;^{15,22,33} instead, a reaction intermediate, denoted as Cu_Z⁰, was observed by Moura and coworkers in 2010 using electronic absorption spectroscopy and electrochemical methods under single turnover conditions.³⁵ Very recently, Solomon and coworkers studied the Cu_Z⁰ intermediate using electron paramagnetic resonance (EPR), magnetic circular dichroism (MCD), electronic absorption and resonance Raman (rR) spectroscopies to divulge the electronic structure.³⁶ The authors characterized Cu_Z⁰ as being the active 1-hole (Cu^{II}3Cu^I) species formed during the catalytic cycle and is reduced by Cu_A in the presence of a biologically relevant reductant, sodium ascorbate, at a rate much faster ($k_{\text{red}} = 0.1 \text{ s}^{-1}$) than the 1-hole Cu_Z*. Despite sharing the same redox level as the resting state of the Cu_Z*, the Cu_Z⁰ is proposed to feature a terminal hydroxide ligand, bound to the Cu_{IV} atom, that is engaged in a hydrogen bonding interaction with a neighboring lysine residue.³⁶

The resting redox state of the Cu_Z (4Cu₂S) form was investigated using spectroscopic techniques by Solomon and coworkers, and revealed a “2-hole” configuration in the ground state (2Cu^{II}2Cu^I).²² One electron reduction of the 2-hole Cu_Z, by dithionite, produced a 1-hole Cu_Z redox state (Cu^{II}3Cu^I) and protonation of the $\mu_2\text{-S}^{2-}$ edge ligand (to $\mu_2\text{-SH}^-$) occurred during reduction, as observed spectroscopically.^{21,22} The authors concluded further reduction to a fully reduced 4Cu^I state like Cu_Z* inaccessible for the 1-hole Cu_Z, even if methyl viologen is used as the reductant.²² The authors also reported that reactivity with N₂O was achieved in the 1-hole Cu_Z redox state under steady-state assay conditions; however, the specific activity was much lower ($54 \pm 7 \mu\text{mol N}_2\text{O min}^{-1} \text{mg}^{-1}$) compared to the fully reduced Cu_Z* center.²² Furthermore, single turnover experiments with N₂O and the 1-hole Cu_Z revealed a reaction

rate that was too slow ($k_{\text{obs}} = 0.6 \text{ hr}^{-1}$) for the Cu_Z form to be considered the kinetically competent active site that accomplishes the catalytic turnover reported for the enzyme.^{22,34}

Shown in Table 1.1 are the accessible redox states of the Cu_Z^* and Cu_Z clusters, maximum specific activity and observed single turnover reaction rate constants with N_2O . Several important properties are illuminated from the data displayed in Table 1.1: (i) the Cu_Z^* achieves catalytic reduction of N_2O in the fully reduced (4Cu^{I}) state, (ii) the Cu_Z cannot access a fully reduced state and (iii) in their respective redox active states, Cu_Z^* is the more kinetically competent active site for catalytic turnovers of N_2O .

TABLE 1.1 Accessible Redox States and Specific Activity with N_2O for Cu_Z and Cu_Z^* ^a

	Cu_Z	Cu_Z^*
Resting State	2-hole, $2\text{Cu}^{\text{II}}2\text{Cu}^{\text{I}}$	1-hole, $1\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$
Dithionite Reductant	1-hole, $1\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$ ^b	1-hole, $1\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$
Methyl Viologen Reductant	1-hole, $1\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$	Fully reduced, 4Cu^{I} ^b
N_2O Specific Activity ^c	54 ± 7	141 ± 7
N_2O Single Turnover k_{obs}	0.6 hr^{-1}	200 s^{-1}

^a See reference 22.

^b Active state. ^c In $\mu\text{mol N}_2\text{O min}^{-1} \text{ mg}^{-1}$.

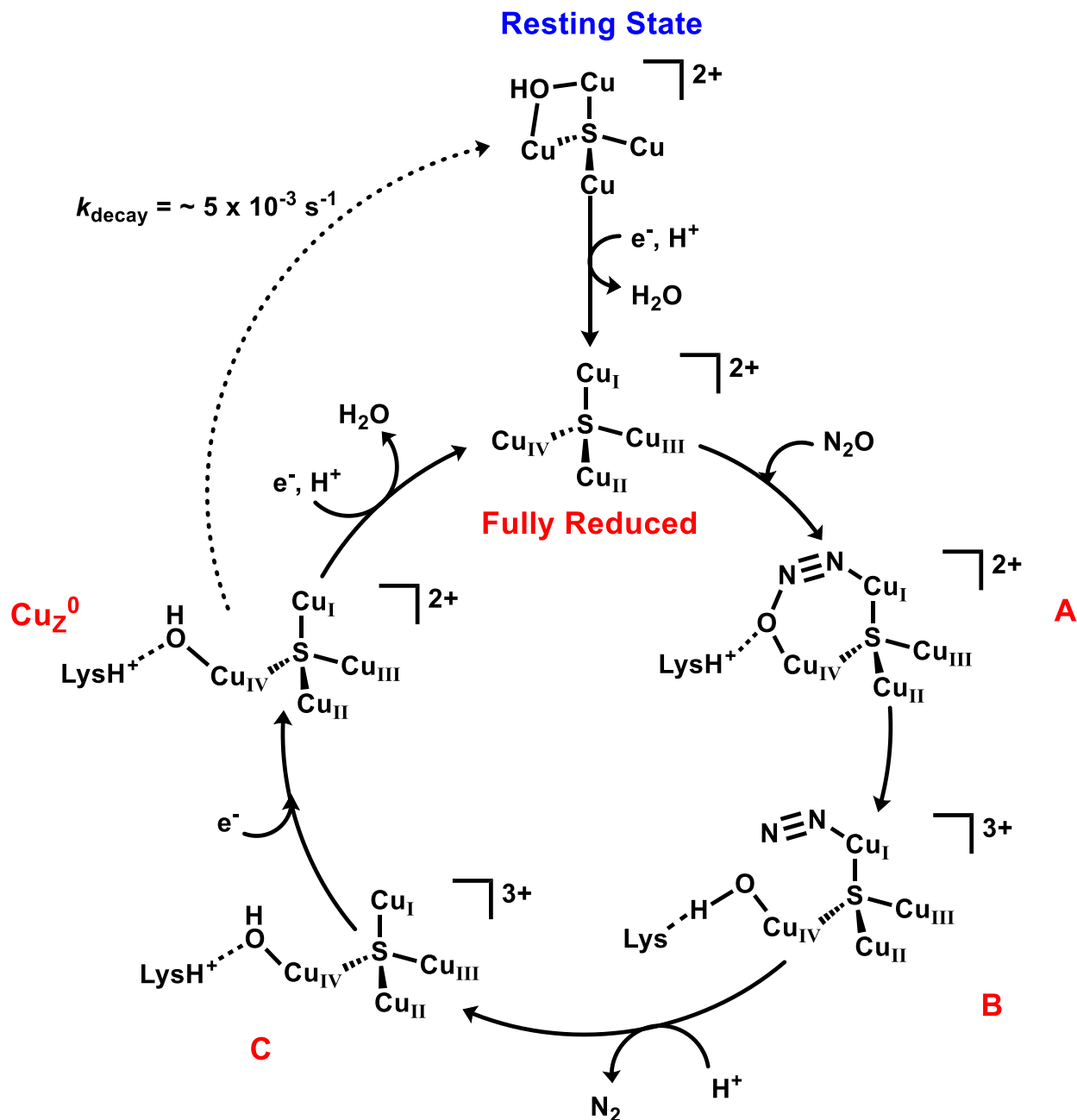
The intimate reaction dynamics at work within the active sites of N_2OR represent a prestigious example of N_2O activation by transition metal cooperativity, but remain largely unknown and elusive to researchers. To date, *no experimental evidence exists describing the N_2O binding site, the initiation of substrate activation and the reduction mechanism occurring in N_2OR .*^{2,15} Detecting important facets that contribute to the biological function of Cu_Z^* or Cu_Z will not only provide an explanation for the poorly understood reaction mechanism, but also reveal critical properties that promote multielectron and multiproton processes for the development of new catalysts, designed to activate small molecule substrates.

1.2.2 Nitrous Oxide Reductase Reactivity Investigations

Several different scientific approaches for unveiling the redox reaction regulated by Cu_Z^* and Cu_Z have been pursued.¹⁵ Spectroscopy, being one such approach, has provided exceptional information

elucidating the accessible redox states of Cu_Z^* and Cu_Z ; specifically by utilizing EPR, MCD and rR spectroscopies.^{22,30,33} Determination of the pH tolerance and protonation conditions of the respective edge ligands in both enzyme forms have previously been reported using electronic absorption, MCD, rR, EPR and X-ray absorption.^{21,31} The nature of the hydroxide ligand bound to the Cu_Z^0 intermediate and the distribution of electronic charge over the inorganic core was also recently reported according to data collected by EPR, MCD, rR and electronic absorption spectroscopy.³⁶ Specific activities, N_2O reaction rates and unique spectroscopic characteristics for Cu_Z^* and Cu_Z have also been reported utilizing this same approach method.^{21,22} However, spectroscopy becomes complicated when studying enzymatic systems like N_2OR because of the spectral overlap that results from the combination of different copper environments present (Cu_A , Cu_Z^* , Cu_Z , Cu_Z^0) within samples under certain conditions.^{22,37} Furthermore, isolating pure forms of Cu_Z^* or Cu_Z remains a challenge, as both copper sites are always present in purified samples of N_2OR , as mentioned in Section 1.2.^{15,21,22}

Computational methods have also been employed for investigating the reactivity mediated in the N_2OR active sites. In a recent report by Solomon and coworkers, density functional theory (DFT) calculations were applied to propose the N_2O reduction mechanism carried out by the fully reduced Cu_Z^* form shown in Scheme 1.2.³⁶



SCHEME 1.2 Reduction mechanism of N_2O by Cu_Z^* proposed by Solomon and coworkers supported by DFT calculations.³⁶

The authors reported that N_2O is likely coordinated to the fully reduced Cu_Z^* cluster via a hydrogen bonding interaction facilitated by neighboring amine protons on histidine and lysine residue side chains.^{17,36,38} Once coordinated to Cu_Z^* , N_2O was calculated to adopt a bent μ -1,3-N,O geometry ($\angle\text{N-N-O}$

= 135°) which substantially lowers the energy of the empty π^* orbital in N_2O and provides sufficient orbital overlap with the filled Cu d-orbitals for backbonding (intermediate A).^{15,30,33,36,38,39} Further stabilization of the bent N_2O configuration was calculated to arise from a hydrogen bonding interaction between the proton on a neighboring lysine residue and the oxygen atom, evidenced by the computed N-O bond elongation in the transition state (1.29 $\rightarrow$ 1.81 Å).³⁶ A broken symmetry singlet, consisting of α and β lowest unoccupied molecular orbitals (LUMOs), was calculated for the μ -1,3-N,O transition state and Solomon reported the α electron is transferred to N_2O via Cu_{IV} , resulting in a delocalized α LUMO over Cu_{IV} and Cu_{II} (20% and 19% character, respectively).³⁶ The N–O bond cleaves (intermediate B) and in a concerted process, proton transfer from lysine to the oxygen atom was calculated to trigger the β electron (delocalized over Cu_{IV} and oxygen during proton transfer) to be donated through the Cu_{IV} atom. Cleavage of the Cu_I –N bond, releasing N_2 , was determined to be energetically achievable (<2 kcal/mol) during the proton-coupled electron transfer (PCET) to the terminal-oxygen atom; subsequently producing a speculated 2-hole hydroxide species (intermediate C). Electron transfer from the sodium ascorbate reduced Cu_A to the 2-hole intermediate, and rapid re-protonation of the lysine residue from the solvent, was calculated to stabilize the terminal-hydroxide bound 1-hole Cu_Z^0 intermediate via a hydrogen bonding interaction with lysine. If the final electron transfer from Cu_A is perturbed to regenerate the fully reduced active state, conversion of Cu_Z^0 (kinetic product) to the inactive 1-hole Cu_Z^* resting state (thermodynamic product) occurs, as observed spectroscopically ($k_{decay} = \sim 5 \times 10^{-3} \text{ s}^{-1}$).^{35,36}

Rigorous computational analysis for the proposed reduction mechanism carried out by Cu_Z has yet to be reported.¹⁵ In the original report from Einsle and coworkers, Cu_Z was crystallized under a high pressure of N_2O and the resulting crystal structure revealed a *linear N_2O molecule* bound above the Cu_4S_2 plane, as depicted in Figure 1.3A.¹⁹ The authors hypothesized that the orientation of N_2O to Cu_Z is deliberate and results from the oxygen atom in N_2O engaging in hydrogen bonding interactions with neighboring outer-sphere residues (methionine and histidine) attached to Cu_A .^{15,19}

Alternatively, Solomon and coworkers reported a PCET to a linear N_2O molecule was exergonic (by -7.4 kcal/mol to generate N_2 and a hydroxyl radical), and speculated that the oxygen atom faces the μ_2 - SH^- edge ligand when coordinating to the 1-hole Cu_Z (Figure 1.3B); allowing for the direct hydrogen atom transfer from the μ_2 - SH^- ligand to N_2O .²¹ The second electron required for reduction then comes from the Cu_A site, due to the oxidized form of Cu_A appearing in the MCD spectrum under single turnover conditions.^{21,22} Hypothetically, rapid protonation of the resulting hydroxide molecule from a nearby solvent channel was suggested, in order to release a free H_2O molecule.²¹

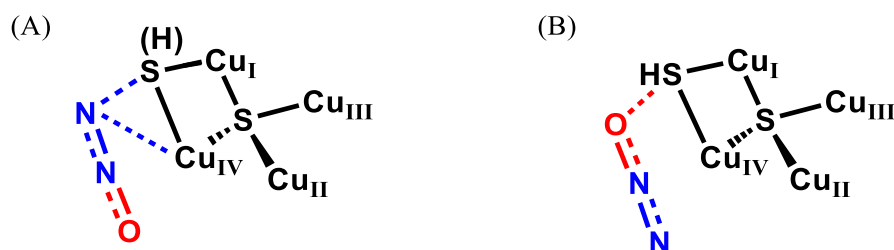


FIGURE 1.3 Inorganic core of Cu_Z and N_2O -bound in (A) crystal structure reported by Einsle and coworkers¹⁹ and (B) hypothetical binding mode for PCET proposed by Solomon and coworkers.²¹

Solomon and coworkers suggested the inability of N_2O to adopt a μ -1,3 binding mode at the edge ligand site is reflected in the decreased specific activity measured for the 1-hole Cu_Z compared to Cu_Z^* (54 ± 7 and 141 ± 7 $\mu\text{mol N}_2\text{O min}^{-1} \text{mg}^{-1}$, respectively).^{21,22}

Both approaches, spectroscopy and computational, have contributed valuable information pertaining to Cu_Z^* and Cu_Z , such as; specific activities with N_2O , potential reduction mechanisms and accessible electronic states. Both methods however, have not been able to definitively resolve some of the larger questions surrounding N_2OR chemistry. Experimental evidence revealing the N_2O binding site, substrate binding mode, activation mechanism and established reaction pathway (for either active site) are still unresolved. These, and many other questions, remain complicated questions to answer because of the difficulties related to studying a complex enzyme *in vitro*.^{15,22,37} An alternative approach for providing

additional insights for N_2OR reactivity not yet discussed, is the use of synthetic small molecule model complexes, designed to mimic the structure and biological function of the Cu_Z^* or Cu_Z active sites.

1.3 Synthetic Model Complex Approach

Utilizing synthetic inorganic complexes as a means of understanding biological active sites has been developed for a variety of other natural systems and supplemented studies examining fundamental characteristics observed in metalloenzymes.^{40,41} Investigations using biomimetic complexes that directly imitate the structure, atom connectivity, coordination environment and other related properties within specific metalloenzymes, are referred to as “structural” models.^{42–50} Inorganic complexes that accomplish relevant reactivity, substrate activation or redox transformations similar to natural active sites, are described as “functional” models.^{47,49–55}

Synthetic biomimetic systems introduce a level of control for systematically probing poorly understood behaviors or interactions observed in biomolecules. More specifically, focusing on the effects caused by ligand environments^{56,57} or conditions that permit ligand substitution reactions⁵⁸ within biological systems have been recreated by synthetic model complexes, to better understand how the active site geometry is tuned for substrate activation. Synthetic small molecule models have been used to replicate spectroscopic features inherent to certain biological systems, in order to further evaluate the properties responsible for such features.^{59–61} Perhaps most importantly, model complexes that form stable adducts with applicable substrates represent potential reaction intermediates that may not be easily isolated or characterized from the reaction taking place within a natural system. Investigations on model-substrate adducts have divulged reaction kinetics,^{62–64} bond energies,⁶⁵ electronic, structural⁶⁶ and spectroscopic characteristics,^{59,60} that better explain the nature of an intermediate formed by natural biomolecules. Studying mechanistic details utilizing biomimetic complexes established experimental methods that were eventually validated for probing in natural systems.^{58,67,68} Synthetic inorganic models have additionally been employed as a means to investigate how the biological analogue would behave in the presence of other chemical stimuli.^{51,58,69,70} In light of all the potential model compound applications, constructing mimics specifically of Cu_Z^* or Cu_Z will prove impactful to the N_2OR bioinorganic community, but also to

researchers interested in the covalent nature conserved in Cu-S moieties comprised in transition metal complexes.

Some of the fascinating redox chemistry performed by certain biological active sites has been attributed to the presence of a covalent sulfide moiety^{71–73} and in the year 2000, Helmut Beinert reported the significant impact of metal-sulfide motifs in synthetic complexes for overcoming challenging redox reactions spanning over 10 years.⁷⁴ Researchers have remained committed to investigating “transition metal sulfur” (TMS) chemistry because of the enhanced reactivity and molecular properties transpiring from incorporation of sulfide and thiolate-based ligands in transition metal complexes.⁷⁵ For example, in nickel dimer complexes bridging disulfide moieties, $(\mu\text{-}\eta^2\text{:}\eta^2\text{-S}_2)^{2-}$, have been reported as the facilitators of antiferromagnetic coupling between the two high-spin nickel(II) centers,⁷⁶ and also as participants of non-innocent redox behaviors.⁷⁷ Reports probing TMS redox^{78–80} and sulfur transfer/exchange reactions have established some of the most fundamental transformations known for transition metals.⁸¹

More related to the research discussed herein, is the examination of small molecule copper-sulfide compounds. The different structural arrangements appearing in copper-sulfide complexes^{82–87} and the fascinating reactivity patterns observed^{84,88–91} have been extensively investigated and remain an active area within the literature. The intriguing interaction between two bridging sulfur atoms in small molecule dicopper complexes has spurred debates among researchers within the literature, asserting various spectroscopic and computational evidence.^{92–95} In addition, copper-sulfide materials have become of increasing interest to areas of materials science and solid state chemistry as tunable semiconductors.^{96,97} Examination of the characteristic behaviors that dictate certain copper-sulfide cluster assemblies has also continued to be a dominate topic studied within inorganic coordination chemistry.^{82,98–100}

Collectively, several areas of scientific research would directly benefit from the synthesis, characterization and reactivity studies involving tetracopper-sulfide complexes. Primarily, the work discussed in the impending chapters will contribute to the bioinorganic community by providing structural and functional models of the active sites in N₂OR. An additional research gain will be collecting observations related to transition metal sulfur chemistry; particularly, the intimate electronic structures and

redox behaviors stemming from the covalent nature induced by sulfide ligands. The shortcomings of synthesizing specific multicopper-sulfide model complexes that previously eluded other researchers, is the fundamental challenge associated with *controlling and understanding factors that lead to desired Cu(μ -S) stoichiometries during cluster assembly and in particular, replicating a single (μ_4 -S) moiety, relevant to the structures in Cu_Z* and Cu_Z.*^{37,101}

1.4 Previously Reported Cu_Z* Model Compounds

As briefly mentioned, synthetic model complexes described as “structural” analogues of biological active sites are compounds that accomplish a high degree of similarity to features present in the active site itself.⁵⁰ Some important structural characteristics retained in model complexes include: atom economy, stereochemistry, ligation and coordination environment.^{41,50} Synthetic complexes that achieve similar reactivity as natural active sites are identified as “functional” analogues.⁴¹ These functional models are capable of transforming the same or related substrates, into the desired products by similar reaction pathways as the biological active site.⁵⁰ In general, functional models do not necessarily mimic the structural characteristics of the enzyme; nor do they have to exhibit the same reaction rate or catalytic ability as the natural system.⁵⁰

No model complexes targeting the (μ_2 -S)Cu₄(μ_4 -S) center in Cu_Z have been reported, and of the model complexes previously reported for Cu_Z*, none are both a structural *and* functional analogue. Model compounds should not only be capable of N₂O reduction, but also structurally resemble Cu_Z* and Cu_Z, so that structure-function relationships can be investigated. The synthetic complexes discussed as structural models in the forthcoming sections vary by substantial degrees in their resemblance to Cu_Z*. Nonetheless, the structural models represent impressive examples of the progress made towards creating smaller Cu_xS_y clusters, while also illuminating the variability in coordination behavior during assembly. Functional models of Cu_Z* however, are rare within the literature.^{101,102} Few examples of N₂O reduction by copper complexes occurring electrochemically¹⁰³ or mediated by Cu-ZSM-5 zeolite material^{15,104} have been reported, but only two copper-sulfur functional models to Cu_Z* are known. Both functional models will be discussed, along with the speculated N₂O reduction mechanisms proposed by the original authors.

1.4.1 Structural Models

Within the literature, a variety of synthetic copper-sulfide complexes exist but in large cluster sizes, such as: Cu_{12}S_6 ,^{105,106} Cu_{13}S_2 ,¹⁰⁷ $\text{Cu}_{20}\text{S}_{10}$,^{106,108} $\text{Cu}_{24}\text{S}_{12}$ ¹⁰⁸ and $\text{Cu}_{50}\text{S}_{25}$.⁹⁶ While several of these copper-sulfide aggregates contain $\mu_4\text{-S}$ or $\mu_2\text{-S}$ structural motifs, the total copper-sulfide atom economy is not remotely representative of the discrete centers in Cu_Z^* or Cu_Z . Rational design of a single $\text{Cu}_4(\mu_4\text{-S})$ feature in structural models is difficult to replicate because cluster assembly has proven to be sensitive towards the supporting ligand, different copper and sulfur reagents, and the reaction conditions.^{82,101} Shown in Figure 1.4 are the inorganic cores of several small molecule copper-sulfide complexes reported within the literature. All the copper atoms represented in Figure 1.4 are reported as formally Cu(II), with the exception of a single Cu(III) atom within the $\text{Cu}^{\text{III}}\text{Cu}^{\text{II}}_2\text{S}_2$ core shown in Figure 1.4D.^{82,101} The $\text{Cu}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-S}_2)$ structure shown in Figure 1.4A displays a disulfide feature that is bound to the copper atoms “side-on” and has been synthesized and extensively characterized by Tolman et. al.^{86,90,95} and Karlin et. al.,^{88,95,109} with a variety of different bi- and tridentate ligands. Most of the side-on Cu_2S_2 model complexes, and their accompanying ligands, will be discussed in Chapter 3, but other ligands including 2,2-dipyridyldisulfide⁹⁹ and triphenylphosphine¹¹⁰ have been reported. The $\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-S}_2)$ core in Figure 1.4B reveals an “end-on” disulfide unit bridging two copper atoms when tetradentate TMPA (tris(2-pyridylmethyl)amine) serves as the supporting ligand.⁸⁵

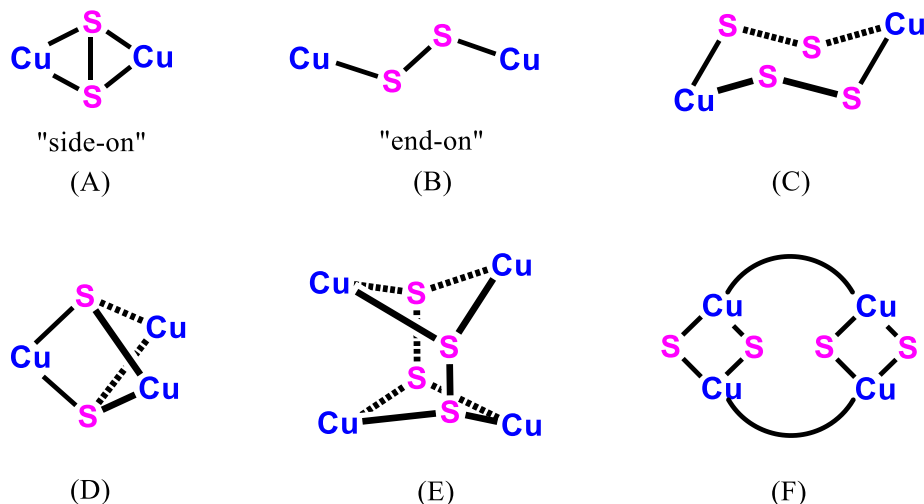


FIGURE 1.4 Inorganic cores of several Cu_xS_y complexes previously reported in the literature.

The remaining core structures in Figure 1.4 were previously reported with various organic ligands and display Cu_2S_4 (C),^{82,87} Cu_3S_2 (D)^{82,83,90} and Cu_4S_4 (E and F)^{82,100} configurations. Collectively, these structures represent the more distant “structural” models of Cu_Z^* and exhibit many intricate examples of different coordination modes formed in small molecule copper-sulfide complexes. Model compounds more closely related to the structure of Cu_Z^* are shown in Figure 1.5 and feature only one μ -sulfur entity. The monocopper-thiolate structure in Figure 1.5G has been reported in Cu(I) and Cu(II) complexes, with a N-heterocyclic carbene (NHC) ligand¹¹¹ and β -diketiminato ligand, respectively.¹¹²

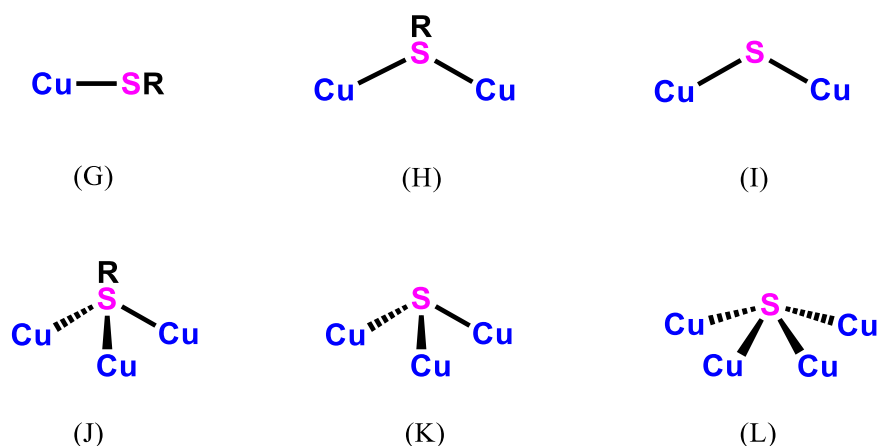


FIGURE 1.5 Inorganic cores of previously reported copper-sulfide or -thiolate complexes featuring a single μ -sulfur atom.

The dicopper(I)- and tricopper(I)-thiolate complexes (Figure 1.5H and J) were previously reported with IPr (1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) NHC ligands,¹¹¹ and dppm (bis(diphenylphosphino)methane) ligands, respectively.¹¹³ The $\text{Cu}_2(\mu_2\text{-S})$ core shown in Figure 1.5I is a beautiful synthetic accomplishment that represents the smallest copper(μ_2 -sulfide) entity reported to date, and has been isolated as 2Cu(I) atoms with two IPr* (1,3-bis(2,6-(diphenylmethyl)-4-methylphenyl)imidazole-2-ylidene) NHC ligands,¹¹⁴ and also as 2Cu(II) atoms ligated by 2-dps (2,2'-dipyridyldisulfide).¹¹⁵ The final two cores shown in Figure 1.5, K and L, are the closest structural models to Cu_Z^* because similar stoichiometry is retained and a μ -monosulfide ligand is present. Two synthetic complexes that illustrate the $\text{Cu}_3(\mu_3\text{-S})$ feature displayed in Figure 1.5K are shown as complete structures in Figure 1.6.

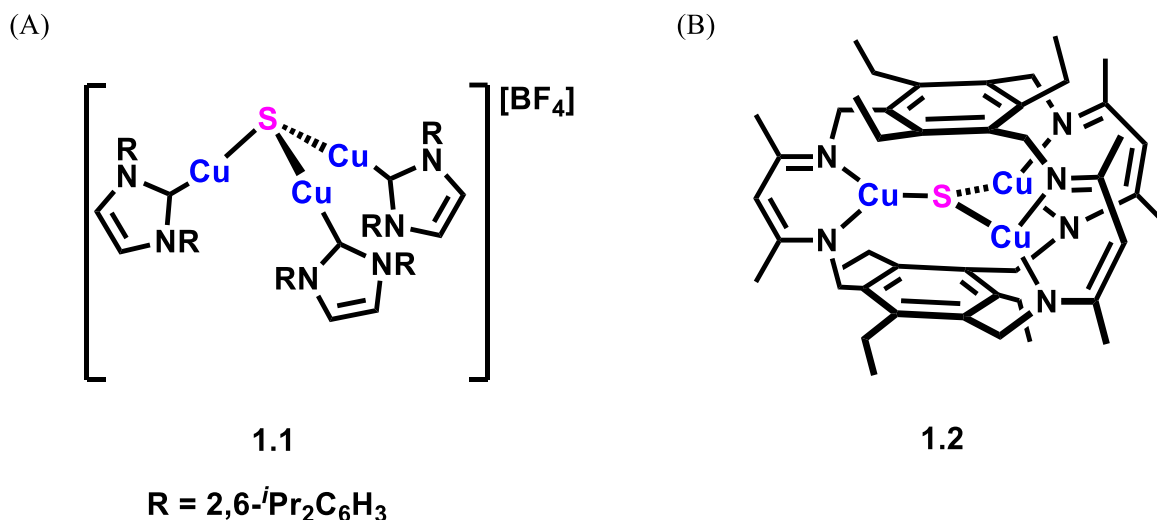
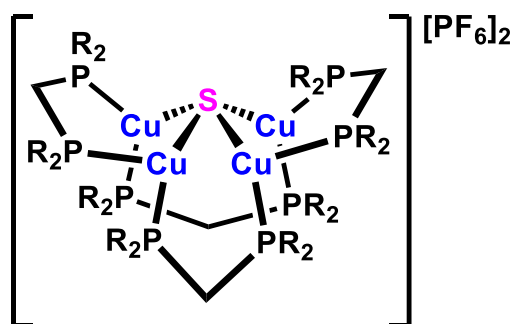


FIGURE 1.6 The $\text{Cu}_3(\mu_3\text{-S})$ complexes synthesized by (A) Hillhouse and coworkers,¹¹⁶ and (B) Murray and coworkers.¹¹⁷

Complex **1.1** (Figure 1.6A), synthesized by Hillhouse and coworkers, consists of all formal copper(I) atoms and each metal center is stabilized by a single IPr ligand.¹¹⁶ Shown in Figure 1.6B is complex **1.2**, reported by Murray and coworkers, and contains a trianionic tris(β -diketimino)cyclophane cage that is ligated to mixed valent $2\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ atoms.¹¹⁷ Murray reported that the use of a cyclophane ligand scaffold allowed for direct control over the number of copper atoms assembled and opened a coordination site for the sulfide ligand to bind as $\mu_3\text{-S}$.^{37,117} Similar reasoning from Hillhouse and coworkers was stated for accomplishing assembly of **1.1** as a tricopper-sulfide cluster due to the increased stability provided by NHC ligands to low coordinate copper atoms.^{114,116} Complexes **1.1** and **1.2** represent exceptional examples of $\text{Cu}_3(\mu_3\text{-S})$ complexes but lack the atom economy of Cu_2^* (4CuS); however, the specific structural features displayed by both tricopper complexes are relevant to discussions taking place in Chapter 2 and will be reviewed in further detail there.

Only two complexes are known that demonstrate the inorganic core shown in Figure 1.5L and completely retain the crucial $\text{Cu}_4(\mu_4\text{-S})$ characteristic applicable to the Cu_2^* and Cu_2 clusters. The two compounds only differ from one another in the substituents located on the supporting bidentate phosphine

ligands, and their structure is shown in Figure 1.7. Complexes **1.3** and **1.4** were synthesized by Yam and coworkers in 1993 and 1997 respectively, using the bis(phosphine) ligands dppm and dtpm (bis[bis(4-methylphenyl)-phosphino]methane).^{118,119} All copper atoms were characterized as formally Cu(I), and ironically, complexes **1.3** and **1.4** were studied for their photoluminescence properties^{120–122} rather than as structural models of Cu₂* because the crystal structure of the enzyme had yet to be reported.³⁷ Since then, researchers have acknowledged the similarity in structure between Cu₂* and Yam's compounds; however, no new model complexes have been constructed for exclusive biomimetic studies using the synthetic route reported by Yam and coworkers.¹⁰¹ Therefore, the new Cu₄(μ₄-S) models contributed by this dissertation author, to be discussed in upcoming chapters, were developed from a synthetic strategy that was inspired from complexes **1.3** and **1.4** reported by Yam and coworkers.



1.3: R = C₆H₅

1.4: R = 4-MeC₆H₄

FIGURE 1.7 Tetracopper-sulfide complexes synthesized by Yam and coworkers,^{118,119} responsible for the inspiration of new model complexes reported in this work.

1.4.2 Functional Models

Only two functional models of Cu₂* have been reported that contain copper-sulfur motifs and successfully reduce gaseous N₂O.³⁷ Complex **1.5** shown in Figure 1.8A, synthesized by Tolman and

colleagues in 2009, features a formal mixed valent $\text{Cu}^{\text{II}}2\text{Cu}^{\text{I}}$ arrangement and a bridging S_2^{2-} entity.¹²³ The neutral Me_3tacn (1,4,7-trimethyltriazacyclononane) ligands are tridentate, producing tetracoordinated copper atoms. Model **1.5** was synthesized from a $[(\text{Me}_3\text{tacn})\text{Cu}^{\text{I}}(\text{MeCN})]^+$ salt and Na_2S_2 at low temperature.¹²³ If warmed to room temperature, complex **1.5** was reported to degrade into the known $[(\text{Me}_3\text{tacn})_2\text{Cu}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-S}_2)]^{2+}$ compound with the disulfide bound side-on (Figure 1.4A).^{91,123}

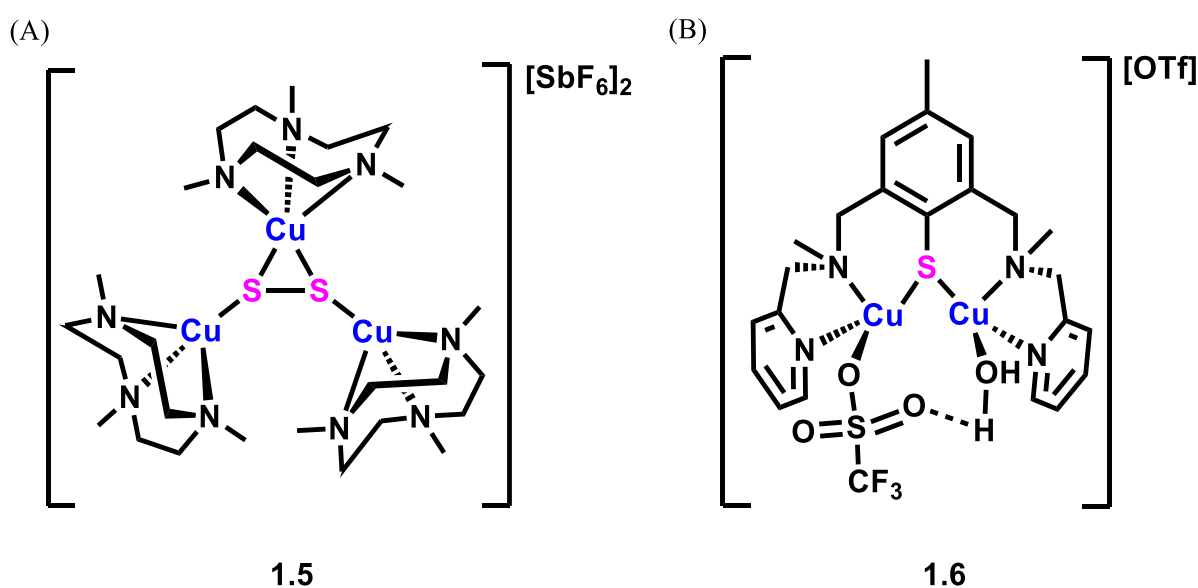
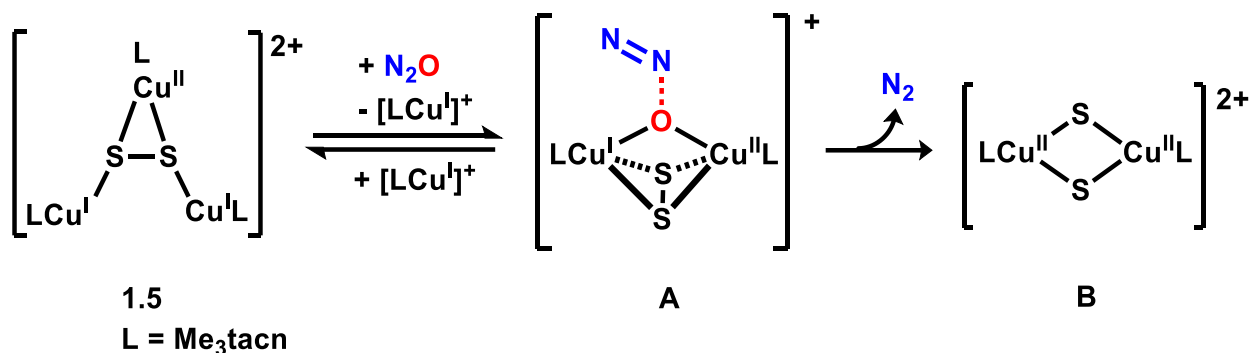


FIGURE 1.8 Functional models of Cu_2^* : (A) complex **1.5** synthesized by Tolman and colleagues,¹²³ (B) complex **1.6** reported by Torelli and coworkers.¹²⁴

The functional model shown in Figure 1.8B was reported by Torelli and coworkers in 2014, and consists of a mixed valent dicopper ($\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$) core and displays unsymmetrical ligation to individual water and triflate molecules.¹²⁴ Bridging the two copper atoms is a thiolate ligand, connected to the remaining framework of the ligand, and coordinating pendant amine and pyridine donor groups produce tetracoordinated copper atoms. Model **1.6** was synthesized from $[\text{Cu}^{\text{I}}(\text{MeCN})_4][\text{OTf}]$ and reductive cleavage of the ligand, in wet acetone.¹²⁴

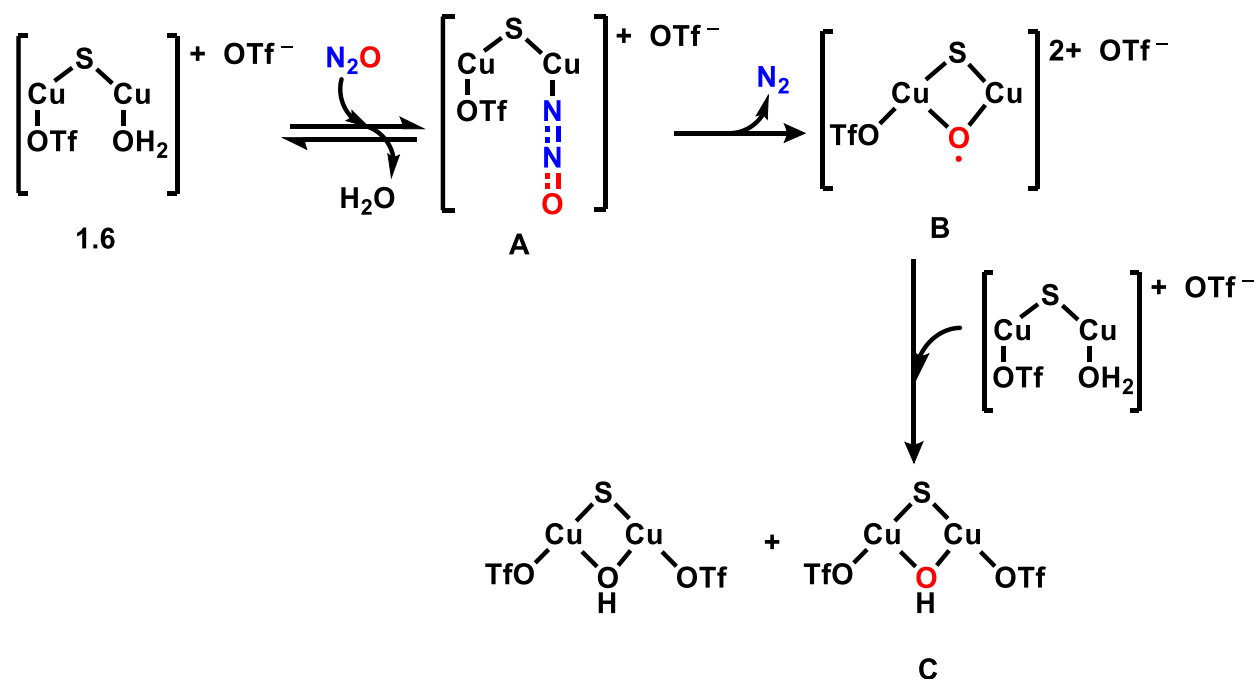
During the reaction with gaseous N_2O and complex **1.5** at $-80\text{ }^\circ\text{C}$, Tolman and coworkers reported quantitative generation of N_2 , measured by gas chromatography mass spectrometry (GC-MS) analysis.¹²³ The resulting copper species after the reaction was determined by Raman spectroscopy to be the side-on disulfide complex $[(\text{Me}_3\text{tacn})_2\text{Cu}_2\text{S}_2]^{2+}$ previously observed upon thermal degradation.¹²³ Interestingly, the authors were unable to isolate the major oxygen-containing byproduct after the reaction between **1.5** and N_2O ; however, a $\{[(\text{Me}_3\text{tacn})_2\text{Cu}_2(\text{OH})_2]\text{SbF}_6\}^+$ species was detected in the final reaction mixture by electrospray ionization (ESI) mass spectrometry as a minor oxo-byproduct. Furthermore, Tolman reported that upon addition of excess $[(\text{Me}_3\text{tacn})\text{Cu}(\text{MeCN})]^+$ salt in the presence of N_2O and **1.5**, the N_2 yield was decreased by nearly half; while in the absence of N_2O , excess $[(\text{Me}_3\text{tacn})\text{Cu}(\text{MeCN})]^+$ prohibited thermal decomposition of **1.5**. Based on these experiments, the authors suggested an equilibrium step occurs between **1.5** and two copper fragments: $[(\text{Me}_3\text{tacn})_2\text{Cu}_2\text{S}_2]^+$ and $[(\text{Me}_3\text{tacn})\text{Cu}]^+$. Although neither equilibrium fragment has been observed, Tolman speculated that the true N_2O -activating species is actually the equilibrium generated $[(\text{Me}_3\text{tacn})_2\text{Cu}_2\text{S}_2]^+$ complex (A in Scheme 1.3). This hypothesis was based on the observations from the excess $[(\text{Me}_3\text{tacn})\text{Cu}(\text{MeCN})]^+$ experiments that indicate addition of excess Cu(I) salt drives the equilibrium towards the unreactive **1.5** complex; explaining the absence of thermal degradation of **1.5** under N_2 , and the decrease in reaction yield under N_2O . DFT calculations performed by Cramer and colleagues on the reaction transition state, computed N_2O docking to the active dicopper cation via a $\mu_2\text{-O}$ bridge between the two copper atoms, shown as “A” in Scheme 1.3.



SCHEME 1.3 Reduction mechanism of N₂O by complex **1.5**, speculated by Tolman and coworkers.¹²³

The computed transition state for **1.5** and N₂O differs from the μ -N,O coordination calculated for N₂O and Cu₂^{*}, and produced a higher transition state energy ($\Delta G^\ddagger = 26.6$ kcal/mol)¹²³ compared to the energy calculated for the μ -1,3-N₂O and Cu₂^{*} transition state ($\Delta G^\ddagger = 17.7$ kcal/mol).³⁶ Lingering questions about the reaction between **1.5** and N₂O include the identity of the major oxygen-containing species, and if a two electron reduction actually took place (generating O²⁻), what species provided the second electron that allowed for stoichiometric amounts of N₂ to be produced with respect to **1.5**?

The remaining functional model **1.6**, synthesized by Torelli, was found to generate 0.4 equivalents of N₂ by GC-MS and a (μ -OH)dicopper(II) product, characterized by X-ray crystallography, per mole of **1.6** in the presence of N₂O.¹²⁴ Therefore, the authors deduced that two molecules of **1.6** are required to reduce N₂O and proposed the reduction mechanism shown in Scheme 1.4.



SCHEME 1.4 Reduction of N_2O by **1.6** proposed by Torelli and coworkers.¹²⁴

Using various spectroscopic techniques (i.e. EPR, UV-Vis, electrochemistry and nuclear magnetic resonance), Torelli and coworkers reported that the similarity in spectral features between **1.6** in the presence and absence of N_2O , suggested one copper atom binds N_2O via a ligand exchange equilibrium with the water molecule. DFT calculated models coordinating N_2O to a solitary copper atom computed a $\eta^1\text{-O}$ binding mode to be ~ 2 kcal/mol higher in energy than $\eta^1\text{-N}$ coordination, and the authors proposed the reaction adduct shown as intermediate “A” in Scheme 1.4.¹²⁴ Torelli speculated the one electron reduction of N_2O occurs intramolecularly, and generates N_2 and an unobserved bridging oxo-radical species (Scheme 1.4B).¹²⁴ A second molecule of **1.6** is proposed to act as the second sacrificial electron donor, and thereby produces equimolar amounts of the $(\mu\text{-hydroxo})\text{dicopper(II)}$ product (Scheme 1.4C) with respect to the molar amount of **1.6** initially present. An intermediate was observed during the reaction between **1.6** and N_2O by cyclic voltammetry and ^{19}F nuclear magnetic resonance spectroscopy (NMR), but an unchanged EPR spectrum led Torelli and coworkers to suggest the species to be the N_2O adduct (Scheme 1.4A) and were unable to further characterize or isolate this observed intermediate.

Models **1.5** and **1.6** share several similarities and differences concerning the suggested reaction pathways with N_2O . The functional model reported by Torelli is a mixed valent dicopper complex, similar to the suspected active species from the equilibrium step of **1.5** suggested by Tolman and coworkers. Both reactions also proposed a single atom in N_2O binds during activation. The difference in the N_2O coordinating atom ($\eta^1\text{-N}$ in **1.6** and $\mu_2\text{-O}$ in **1.5**) and the number of copper atoms participating in substrate activation are the dissimilar aspects between the Torelli and Tolman projected reaction pathways. More importantly, are the differences in the proposed N_2O reaction pathways between the functional models and Cu_Z^* . Models **1.5** and **1.6** do not feature solely Cu(I) atoms, as is the case with the active Cu_Z^* cluster; nor do the functional models provide any evidence of a $\mu\text{-1,3}$ binding mode for N_2O . Complexes **1.5** and **1.6** represent two known functional model examples to Cu_Z^* and are extraordinary accomplishments in this endeavor within biomimetic inorganic chemistry; however, additional model complexes are still imperative for sharpening the perspective on N_2O reduction carried out by the N_2OR active sites.

1.5 Attributes for Model Complexes

Important characteristics need to be considered when designing biomimetic complexes that attempt to imitate the interactions originating from observations of the N_2OR active sites. Fortuitously, Cu_Z^* and Cu_Z have more overlapping structural similarities than differences. In Section 1.2, the crystal structures of both Cu_Z^* and Cu_Z displayed four copper atoms, seven histidine residues and a single sulfur atom in the unique μ_4 -attachment.^{18,19} The crystal structures only differ by the identity of the bridging edge ligand ($\mu_2\text{-S}^{2-}$ in Cu_Z and $\mu_2\text{-OH}^-$ in Cu_Z^*). While the majority of similarities between the two active sites allows for a single model complex to be relevant to both Cu_Z^* and Cu_Z , this section will primarily focus on replicating the molecular properties in the more catalytically active Cu_Z^* form.

1.5.1 Tetracopper-sulfide Core Stoichiometry

As mentioned, the most challenging task for modeling the N_2OR active sites is reproducing the stoichiometry present in the Cu_Z or Cu_Z^* inorganic cores. The particular $\text{Cu}_4(\mu_4\text{-S})$ structure in Cu_Z^* has been argued as crucial for the activation, binding and eventual reduction of N_2O ;^{30,38,39} therefore, this feature should be retained in model complexes and any structure-function relationships can be probed further.

1.5.2 Multiple Redox States

Of equal importance for the consideration of competent model complexes for Cu_Z^* and Cu_Z is the oxidation state of the copper atoms in the $\text{Cu}_4(\mu_4\text{-S})$ core. As described in Section 1.2.1, the Cu_Z^* active site has shown maximum activity with N_2O in the fully reduced (4Cu^{I}) oxidation state.³³ Hypothetically, Cu_Z^* assumes three redox states during N_2O reduction: fully reduced, Cu_Z^0 1-hole ($\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$) and 2-hole ($2\text{Cu}^{\text{II}}2\text{Cu}^{\text{I}}$); although a 2-hole state has never been spectroscopically observed.^{15,38} Model systems for Cu_Z^* should similarly access three redox states relevant for the two electron reduction of N_2O . The Cu_Z form cannot reach a fully reduced state, but will accommodate a $\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$ active state and $2\text{Cu}^{\text{II}}2\text{Cu}^{\text{I}}$ ground state.²² Biomimetic complexes that accurately model the three redox levels relevant to Cu_Z^* also inherently model the two oxidation states achieved by Cu_Z (1-hole and 2-hole). Also of interest are the spectroscopic features displayed by model complexes across different oxidation levels, allowing for meaningful comparisons to the characteristics displayed by the enzyme in similar redox states.³⁷ Furthermore, structural rearrangements occurring across a redox series in model complexes could provide perspective on changes occurring in the N_2OR active sites in different oxidation levels. Trends across redox partners would be extremely valuable because the crystal structures reported for Cu_Z^* and Cu_Z only represent their structures in the resting state; while the redox active states, and Cu_Z^0 intermediate, have only been characterized spectroscopically.^{14,21,22}

1.5.3 Retention of $\mu_4\text{-S}^{2-}$ Geometry and N-Donor Ligands

The geometry of the $\mu_4\text{-S}^{2-}$ unit in the Cu_Z^* resting state has been described as a distorted tetrahedral^{2,38} or distorted T-shape,^{30,39} and computational model studies suggested this geometry of sulfur arises from structural constraints imposed from neighboring protein side chains.³⁸ In the absence of an outer-sphere influence on structure, model complexes could incorporate particular ligand frameworks that probe different $\mu_4\text{-S}^{2-}$ geometries and the favorable orientations of the copper atoms as a result. Furthermore, the sulfide arrangement in Cu_Z^* is reported to be the superexchange pathway that delocalizes

charge among the copper atoms during the reduction of N_2O , and facilitates the distribution of both electrons to the Cu_{IV} atom for donation in the reaction transition state.³⁶

Additionally, using N-donor ligands to mirror the histidine coordinated residues present in Cu_Z and Cu_Z^* has also been considered for model complexes reported within the literature.¹⁰¹ Perhaps more important than replicating the specific ligand donor atom, is recreating the different coordination environments among some of the copper atoms in the active sites. In reference to Cu_Z^* , variation in coordination number between tri-coordinated copper atoms (Cu_{II} , Cu_{III} and Cu_{IV} in Figure 1.1) and a single tetra-coordinated copper atom (Cu_{I}) is suggested to cause a difference in the computed distribution of electron density in the 1-hole resting state and was corroborated spectroscopically (EPR).^{15,38} Furthermore, the presence of a more “open-edge” between Cu_{I} and Cu_{IV} in Cu_Z^* is theorized to accommodate N_2O during activation.^{15,30} An open coordination site was also crucial for binding N_2O in model complex **1.6**, as reported by Torelli and coworkers; therefore, coordinatively unsaturated copper atoms could be incorporated into the design of model complexes.¹²⁴

1.5.4 Hydrogen Bonding Interactions

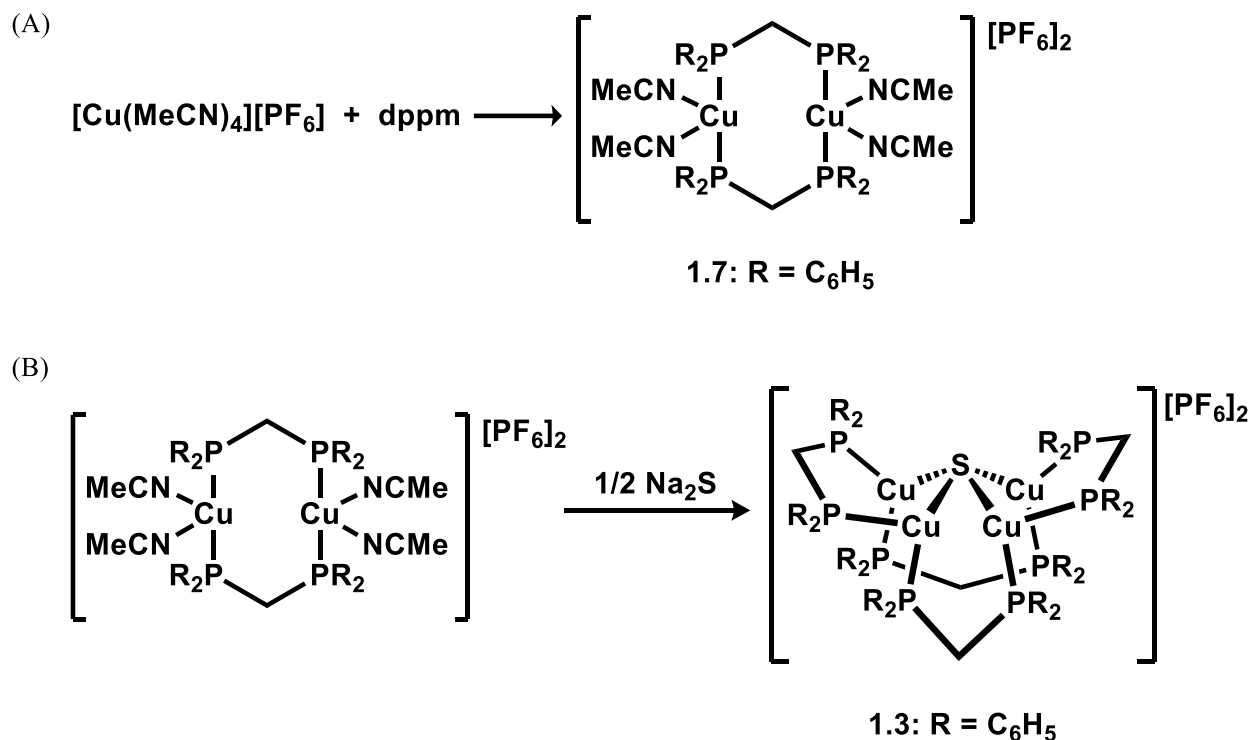
A large advantage of natural systems is the abundance of amino acid residues present throughout adjacent protein chains that readily engage in hydrogen bonding interactions.^{2,15} In the case of Cu_Z^* , the outer-sphere interactions of hydrogen atoms on histidine and lysine residues are suggested to aid in coordinating N_2O , stabilizing the bent μ -1,3-N,O geometry after activation^{17,31,38} and protonating the edge ligand that prompts the donation of the second electron during reduction.^{14,21,31,36} In addition, a hydrogen bonding network between a histidine ligand on Cu_{A} and a histidine residue on Cu_Z^* has been speculated as the electron transfer pathway.^{2,17} Incorporating hydrogen bond donor ligands on model complexes that readily engage in second-sphere interactions simulates a degree of resemblance to the natural protein environment and could introduce mechanisms for activating substrates under laboratory conditions.

All of the above-mentioned features do not represent a comprehensive list, but more the important aspects suggested to contribute to Cu_Z^* reactivity that could be integrated in model complex designs. It

may prove difficult and unbeneficial to synthesize a single model complex that appreciates all the properties discussed in this section. As previously stated, one advantage of employing synthetic models to study enzyme active sites is the ability to systematically design compounds that feature a few, but not all, of the enzyme characteristics, and study changes in the molecular behavior that occur in response to an incorporated property. These types of investigations identify entities that play vital roles in contributing to the enzyme function. One key characteristic that remains imperative to the model complexes discussed in forthcoming chapters is the $\text{Cu}_4(\mu_4\text{-S})$ core. Examination of the synthetic pathway used by Yam and coworkers for luminescent copper-sulfide clusters presented *a rational model design strategy* for overcoming the challenge of replicating the inorganic cores in the N_2OR active sites.

1.6 Model Complex Design Strategy

The tetracopper-sulfide clusters synthesized by Yam and colleagues (Figure 1.7) were solely investigated for their photophysical properties^{118–122} and the unique $\text{Cu}_4(\mu_4\text{-S})$ motif was underappreciated as an opportunity for building structural model complexes of Cu_Z^* .¹⁰¹ The synthesis of complex **1.3** is shown in Scheme 1.5. Equimolar amounts of tetrakis(acetonitrile)copper(I) hexafluorophosphate and the bis(phosphine) ligand dppm, produced the dicopper(I) precursor complex **1.7** (Scheme 1.5A), according to previously reported procedures.¹²⁵ In the synthesis engineered by Yam and coworkers, half an equivalent of sodium sulfide (Na_2S) in methanol was added to **1.7** in acetone at room temperature and resulted in the formation of complex **1.3** (Scheme 1.5B) as an *air stable* yellow solid.¹¹⁸



SCHEME 1.5 Synthesis of (A) dicopper precursor **1.7** and (B) tetracopper-sulfide complex **1.3** according to previously published procedures.^{118,125}

All of the copper atoms in **1.3** were characterized as Cu(I), which ideally resembles the oxidation level of the fully reduced Cu₂*; however, the dppm ligands stabilize **1.3** against oxidation, evidenced by the stability of the compound in open air.^{101,118} Reactions with **1.3** and N₂O, under a variety of conditions, were attempted and no reaction was observed in our hands; therefore, new model complexes were designed based on two essential aspects that appeared in the synthesis of **1.3**: (i) *use of a three-atom bridged, binucleating ligand* and (ii) *formation of a dicopper precursor complex*.

1.6.1 Binucleating Ligands Consisting of a Three-atom Bridge

In the dppm and dtppm ligands, there are only three atoms that comprise the ligand backbone: two phosphorus atoms that tether to a metal center and a single methylene group in the ligand bridgehead. Several different bidentate phosphine ligands containing more linker groups in the ligand backbone are shown in Figure 1.9A.

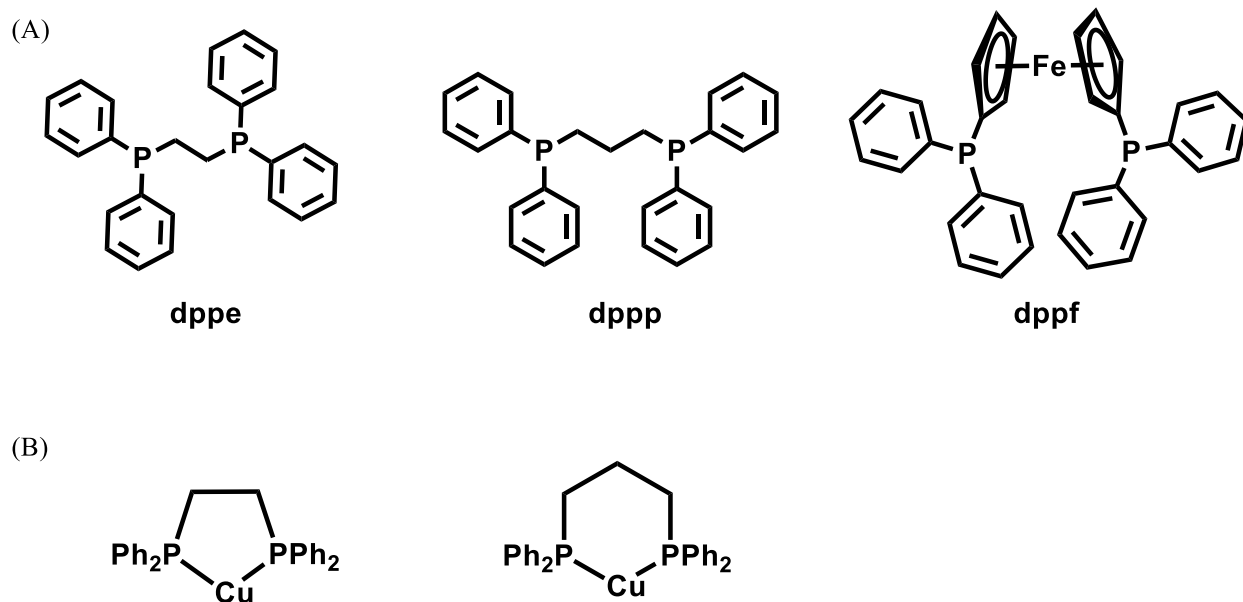


FIGURE 1.9 (A) Different bidentate phosphine ligands with extended linker chains and (B) stabilized 5- and 6-membered copper-diphosphine chelates.

Bidentate phosphine ligands containing longer backbone chains (i.e. dppe and dppf) were attempted for assembling tetracopper-sulfide complexes following the synthetic approach established by Yam and coworkers; however, in our hands the resulting structures incorporated multiple sulfide atoms and chelation of the bis(phosphine) ligands to a single copper atom was observed.¹²⁶ Examination of related compounds reported in the literature identified several characteristics regarding the coordination chemistry and favorable binding modes of bidentate phosphine ligands that explained the chelation observed for ligands with longer linkers in the backbone. For dppe (bis(diphenylphosphino)ethane) or dppp (bis(diphenylphosphino)propane), the ligand backbone is bridged by two and three methylene groups respectively. These extended linker groups will prefer chelation to a single metal center; thereby forming stable 5- and 6-membered rings, as shown in Figure 1.9B.^{127,128} Dissection of other literature examples concerning copper complexes with bidentate phosphine ligands demonstrated the binucleating mode as being preferred when the metal-to-ligand ratio is equivalent and three-atom bridges are used.^{125,129–132}

Conversely, when more equivalents of bidentate ligand are present, chelation is prevalent, regardless of ligand linker length.^{133–135}

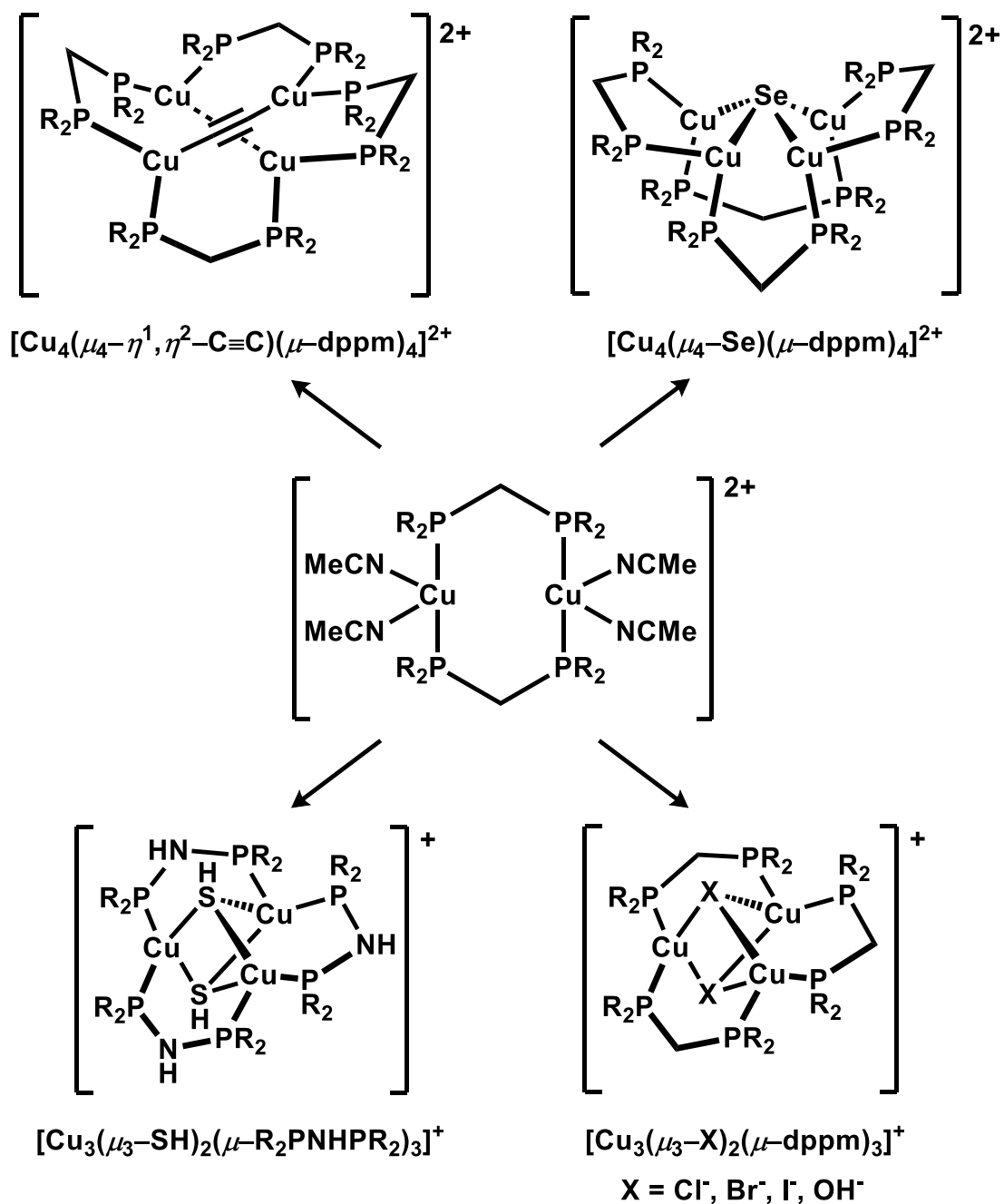
Chelation would be unfavorable when constructing models of Cu_z^* because the ligand will only control the coordination behavior of a single copper center and during cluster assembly multiple sulfur atoms will be incorporated as bridging entities between copper atoms. In fact, all the copper-sulfide cores shown in Figure 1.4 are complexed by mononucleating bi-, tri- and tetradentate ligands and all feature varied amounts of bridging sulfide atoms. Based on these observations, it was determined that mononucleating, polydentate ligands, that chelate to a single metal, do not provide adequate control over the copper-sulfide ratio during cluster assembly.

More preferential for Cu_z^* model complexes are bridging, binucleating ligand systems, where the diphosphine ligand tethers two adjacent metal centers. Evidence of using bridging, polynucleating ligands to control copper stoichiometry is not only evident in Yam's Cu_4S systems (Figure 1.7), but also manifested in complex **1.2** (Figure 1.6B) and **1.6** (Figure 1.8B). The tricopper-sulfide model **1.2**, synthesized by Murray and coworkers, uses the tris(β -diketimine)cyclophane ligand as a trinucleating cage for directly accommodating only three copper atoms and a single sulfide.¹¹⁷ The other example is the dicopper-thiolate complex **1.6**, reported by Torelli and coworkers, and features a binucleating ligand that coordinates only two copper atoms, and the thiolate group is already installed within the ligand framework.¹²⁴

This discussion has established essential components related to the rational design of tetracopper-sulfide complexes. Mononucleating ligands should be avoided in order to control the atom economy of the model compound and discourage tendencies of binding multiple sulfide moieties. Bidentate ligands are unusually apt for the construction of model complexes and, more specifically, binucleating ligands composed of a three-atom backbone show preference for bridging two metal centers.^{129,131,132} These conclusions reveal a fundamental element for the design of model complexes using bidentate ligands; *three-atom bridged, binucleating ligands are uniquely well suited for the assembly of tetracopper-sulfide complexes.*

1.6.2 Utilizing Dicopper Precursor Complexes

In Yam's synthetic route for assembling complexes **1.3** and **1.4**, a dicopper(I) precursor complex (compound **1.7**) was constructed prior to the addition of sodium sulfide (Scheme 1.5B).^{118,119} Inspection of other copper cluster assemblies within the literature revealed exceptional precedence of "self-assembly" from dinuclear starting materials. For example, Yam and coworkers also reported the synthesis of two other tetracopper clusters, shown in the top of Scheme 1.6, that feature different capping ligands (μ_4 -Se and μ_4 - η^1, η^2 -C $\equiv$ C) and assembled from the **1.7** precursor.^{120,136} Outside Yam's published work, report of a $\text{Cu}_3(\mu_3\text{-SH})_2$ complex resulted from the addition of sodium thioglycolate to a dicopper(I)-bis(phosphine) complex, shown in Scheme 1.6 bottom, left.¹³⁷ Additionally, multiple examples of halide-capped copper clusters have been reported and characterized by Samuelson and coworkers (Scheme 1.6 bottom, right) as self-assembling from a dicopper complex.¹³⁸



SCHEME 1.6 Previously reported “self-assembling” complexes from dicopper precursor compounds (R = C₆H₅).

Not only does each example in Scheme 1.6 contain binucleating ligands, as discussed in the previous section, but upon addition of an anion to the dicopper precursor, does a μ -anion preferentially form. To further test if **1.7** is necessary for producing **1.3**, a one-pot synthesis was attempted; incorporating

tetrakis(acetonitrile)copper(I) hexafluorophosphate, dppm and sodium sulfide in the appropriate molar ratios for producing **1.3**. In our hands, the resulting reaction mixture immediately produced a dark, insoluble solid (presumed copper(I) sulfide); thus, formation of a dicopper complex is required for tetracopper-sulfide construction. The synthetic mechanism that allows for the self-assembly of **1.3** from **1.7** and sodium sulfide has yet to be rationalized; unlike the extensive studies in materials science on copper-sulfide cluster assembly.^{97,139–142} In general however, Cu(I) atoms prefer to be tetracoordinated, and when in the presence of good bridging X^- or X^{2-} groups,^{129,134} a dinuclear complex becomes especially compatible for enabling the assembly of trimers or tetramers.

For all the examples shown in Scheme 1.6, and the Yam tetracopper-sulfide complexes (**1.3** and **1.4**), a dicopper precursor compound appears to be a vital component for successfully constructing copper clusters featuring μ -ligands. It is also obvious from Scheme 1.6 that all the complexes include binucleating ligands that possess a three-atom bridge. Both facets represent a synthetic strategy for building model complexes structurally relatable to the active sites in N_2OR and will be factors that are consistently incorporated into the synthesis of new model complexes discussed in the coming chapters.

1.7 Concluding Remarks

Two key research aims are frequently revisited throughout this dissertation and will be briefly clarified here, for the benefit of the reader. Not only will the ensuing investigations demonstrate considerable expansion to an underdeveloped area of Cu_Z^* and Cu_Z biomimetic studies, but also reveal the fundamental properties associated to synthetic copper-sulfide cluster chemistry. Therefore, the combined research focus has been to provide novel N_2OR model complexes; as well as, produce new examples of copper-sulfide compounds and the corresponding molecular behaviors, reactivity patterns and spectroscopic features observed. The full structural and electronic characterization, by numerous spectroscopic techniques, will unveil the intimate chemical properties and intrinsic features of copper-sulfide compounds, and supplement continuing studies within the bioinorganic or transition metal sulfur chemistry disciplines.

2. BINUCLEATING PHOSPHINE DONOR LIGANDS IN MODEL SYNTHESIS*

2.1 Background

The use of bidentate phosphine ligands coordinated to single (mononucleating) or multiple (polynucleating) transition metals have generated an abundant array of complexes studied in diverse scientific fields. Complexed to gold or silver metals, compounds have been investigated for their photophysical properties^{120,122,143}, as well as anti-tumor¹⁴⁴ and anti-cancer¹⁴⁵ agents. Bidentate phosphines are also frequently used in transition metal catalysis. Chiral diphosphines are necessary in an assortment of metal-catalyzed asymmetric transformations.^{146–148} When serving as ligands on palladium; cross-coupling^{149,150}, copolymerization¹⁵¹ and amination¹⁵² catalysis has been widely reported. Rhodium-catalyzed Michael addition¹⁵⁰ and methanol carbonylation¹⁵³ reactions occur with bidentate phosphine ligands; demonstrating the broad applicability of these ligands with transition metals for catalytic reactions.

The strategy of using bridging diphosphines in synthetic bioinorganic modeling systems is also reported within the literature for a variety of enzyme active sites. In both, structural¹⁵⁴ and functional¹⁵⁵ model systems of the iron-molybdenum cofactor in nitrogenase, a variety of different compounds were synthesized due to the different binding modes (chelation vs. bridging) intrinsic to bis(diphosphines). Synthetic analogues for iron-iron hydrogenase^{156–158} and nickel-iron hydrogenase^{46,47,52,159} use the functionality of diphosphine ligands in complex construction. A functional model for the nickel-iron hydrogenase active site reported that different bridging phosphine ligands produced a variety of geometric distortions around a nickel center and therefore, directly impacted the degree of which nickel acts as a hydride acceptor.¹⁵⁹ Influence of diphosphines on the metal coordination environment was also reported for a biomimetic complex of the nickel-iron-sulfur active site in carbon monoxide dehydrogenase.¹⁶⁰ The

* Reproduced in part with permission from Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. “Assembly, Structure, and Reactivity of Cu₄S and Cu₃S Models for the Nitrous Oxide Reductase Active Site, Cu_Z” *Inorg. Chem.* **2014**, 53, 10611. Copyright 2014 American Chemical Society.

dehydrogenase model exhibited a desired square planar nickel center when certain bidentate phosphines were ligated.

The attractiveness in using bidentate phosphine ligands for Cu_2^* model synthesis stems from: (i) the ability to change the substituents on the phosphorus atoms, and (ii) changes to the linker atom on the ligand bridgehead. Altering these two structural parameters within the ligand framework has already proven influential to the molecular electronic organization and structure-function relationship of transition metal coordination complexes reported within the literature. Differences in σ -donation and π -acceptance of diverse bidentate phosphine ligands attached to iron(II) has been derived from Mössbauer spectra,^{161–164} highlighting the electronic tunability of diphosphines to a metal center. Changes in phosphine substituents, as well as the number of alkyl groups in the linker chain, have been reported to influence different photoluminescence responses in compounds with copper(I).^{127,165} Investigations involving the steric crowding around metal centers with different bidentate phosphines have also been reported.¹⁶⁶ Furthermore, catalytic amidation reactions with copper(I) proved to be particularly sensitive to not only the phosphorus substituents, but also the type of atom in the ligand backbone.¹²⁹ Therefore, the subtle variations in diphosphine ligands can be used as a means to produce desired electronic or steric properties for bioinorganic model molecules. Despite using phosphorus donor ligands for Cu_2^* analogues instead of nitrogen based ligands more like histidine, subsequent responses in copper-sulfide molecular behavior can be detected and experimentally adjusted by purely changing the phosphine ligand used. Two specific bidentate phosphine ligands were targeted for model synthesis, dppa (bis(diphenylphosphino)amine) and dcpm (bis(dicyclohexylphosphino)methane) shown in Figure 2.1; resulting in full molecular characterization and reactivity studies involving relevant substrates.

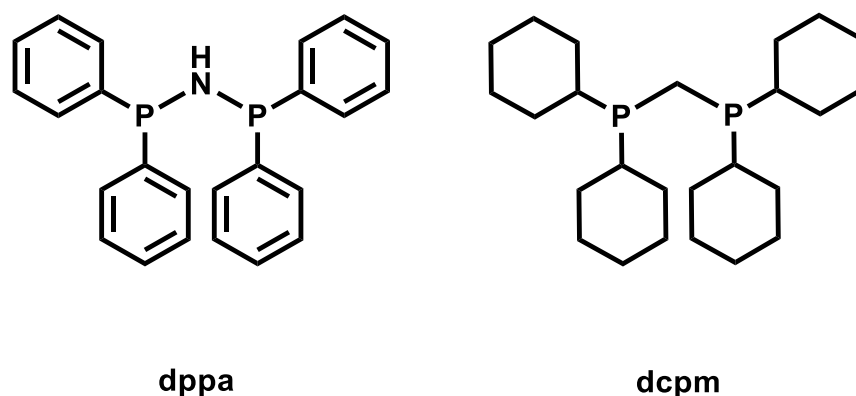


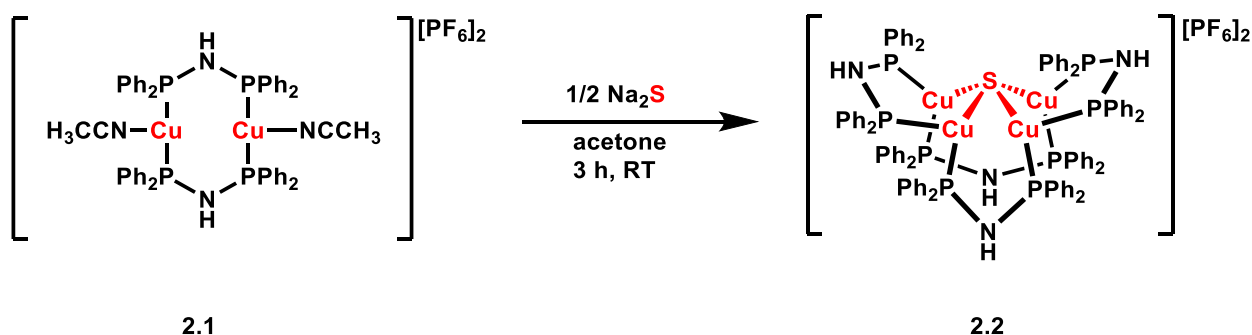
FIGURE 2.1 Bidentate phosphine ligands used for copper-sulfide complexes discussed in this chapter.

2.2 Synthesis of Compounds Using dppa Ligand

The dppa ligand features a three-atom bridge consisting of an amine as the backbone linker in between two phosphines with phenyl substituents. Primarily, reports of dppa complexed to silver(I) or copper(I), describe compound the synthesis, characterization by X-ray crystallography^{131,167,168} or photoluminescence properties.¹⁶⁹ Functionalization of the amine has also been the focus of several communications for developing new catalytic transition metal complexes.^{170,171} Beautiful work reported by Nocera and coworkers of diiridium^{172–174} and dirhodium^{173–175} catalysts activating H₂, demonstrated that the amine linker donates its lone pair to the phosphorus atoms; essentially making “PNP” ligands more electron donating than methylene bridged bis(phosphines).¹⁷⁴

Pursuit of the dppa ligand for copper-sulfide clusters was examined for two primary reasons: (i) study changes in assembly when an amine replaces the methylene backbone in dppm, (ii) observe any outer-sphere hydrogen bonding interactions of the amine proton. As previously mentioned for N₂OR, hydrogen bonding networks are hypothesized to participate in coordinating N₂O to the Cu_z* binding site and activating electron donation during reduction to generate the metastable Cu_z⁰ form (Section 1.2.2).^{17,36,38} In previously reported metal-dppa systems, hydrogen bonding occurs between the dppa amine and outer-sphere guest molecules;^{131,137} therefore suggesting a synthetic avenue for Cu_z* model studies to replicate the molecular environment related to N₂OR.

A modified synthetic route for the synthesis of the dppa ligand was used.^{176,177} Addition of an equimolar amount of tetrakis(acetonitrile)copper(I) hexafluorophosphate generated the dicopper(I) precursor complex, **2.1**, as described previously in the literature.¹⁶⁸ Two molar equivalents of **2.1** per sodium sulfide yielded complex **2.2** as a vibrant yellow solid in 71% yield (Scheme 2.1).¹⁷⁷



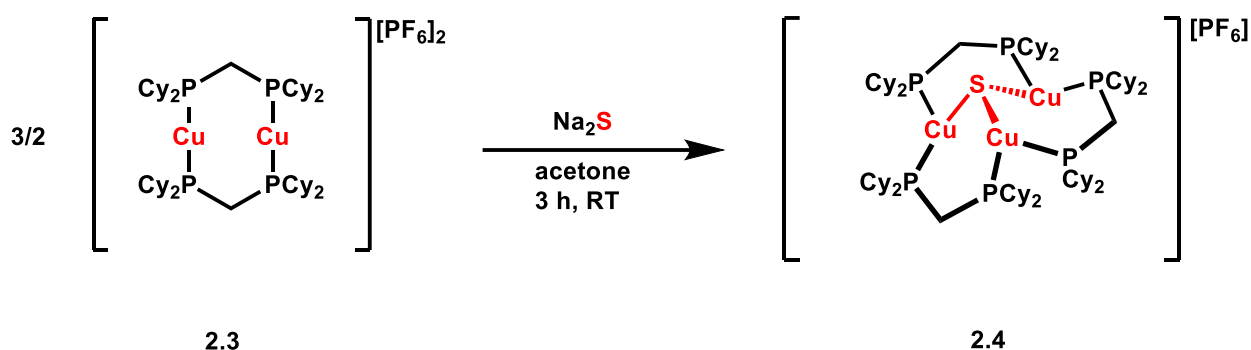
SCHEME 2.1 Synthesis of complex **2.2**.

2.3 Synthesis of Compounds Using dcpm Ligand

The dcpm ligand consists of two tertiary phosphine atoms with cyclohexyl substituents and a methylene backbone. Similar to the copper(I)-dppa systems reported in the literature, transition metals complexed with dcpm are studied extensively for their luminescent and emission properties.^{165,178,179} Interestingly, dcpm has been reported as a ligand that was screened against a variety of other bidentate phosphines investigated for an iron-iron hydrogenase model complex.¹⁸⁰ This ligand was particularly attractive for building model clusters because of the increase in electron donation to the phosphorus tether atoms by the cyclohexyl groups; in contrast to the phenyl rings in dppm and dppa ligands. Studies with this electron-rich, and very bulky, diphosphine probe the increase in electron density originating from the ligands and additional steric accommodations in copper-sulfide cluster assembly.

The dicopper(I) precursor (**2.3**) was synthesized according to reported methods.¹⁷⁹ Interestingly, when one equivalent of sodium sulfide was added to two equivalents of **2.3**, the resulting crude reaction

products yielded a large amount of unreacted **2.3**. Examination of the reaction products by single crystal X-ray diffraction revealed that the copper-sulfide containing product was a *tricopper(I)* complex, **2.4**. Reaction stoichiometry was changed to 1.5 equivalents of **2.3** per sodium sulfide and complete consumption of **2.3** was observed and the resulting pale yellow solid of **2.4** was isolated in 55% yield (Scheme 2.2).¹⁷⁷



SCHEME 2.2 Synthesis of complex **2.4**.

2.4 Structural Characterization of Complexes **2.2** and **2.4**

The crystal structures of complexes **2.2** and **2.4** are shown in Figure 2.2. The crystal structure of **2.2** (Figure 2.2A) consists of a tetracopper(I) cluster supported by four bridging dppa ligands, a μ_4 -sulfide ligand and two hexafluorophosphate counter ions. The complex has approximate C_2 symmetry (omitting the sulfide atom) through the Cu(2) and Cu(4) atoms and exhibits approximate trigonal planar geometry for all copper atoms. The inorganic core of **2.2** shows three of the four copper atoms with shorter Cu $\cdots$ Cu distances of 2.6571(7) Å (Cu(1) $\cdots$ Cu(2)) and 2.7184(4) Å (Cu(2) $\cdots$ Cu(3)) than the fourth copper atom at a farther distance of 3.1005(5) Å (Cu(4) $\cdots$ Cu(1)) and 3.5365(6) Å (Cu(4) $\cdots$ Cu(3)). This unique distortion is not reported for the dppm and dtpm analogues which feature more symmetrical tetracopper arrangements with Cu $\cdots$ Cu distances of 2.869(1) – 3.128(1) Å^{118,120} and 2.955(2) – 3.144(2) Å¹¹⁹, respectively.

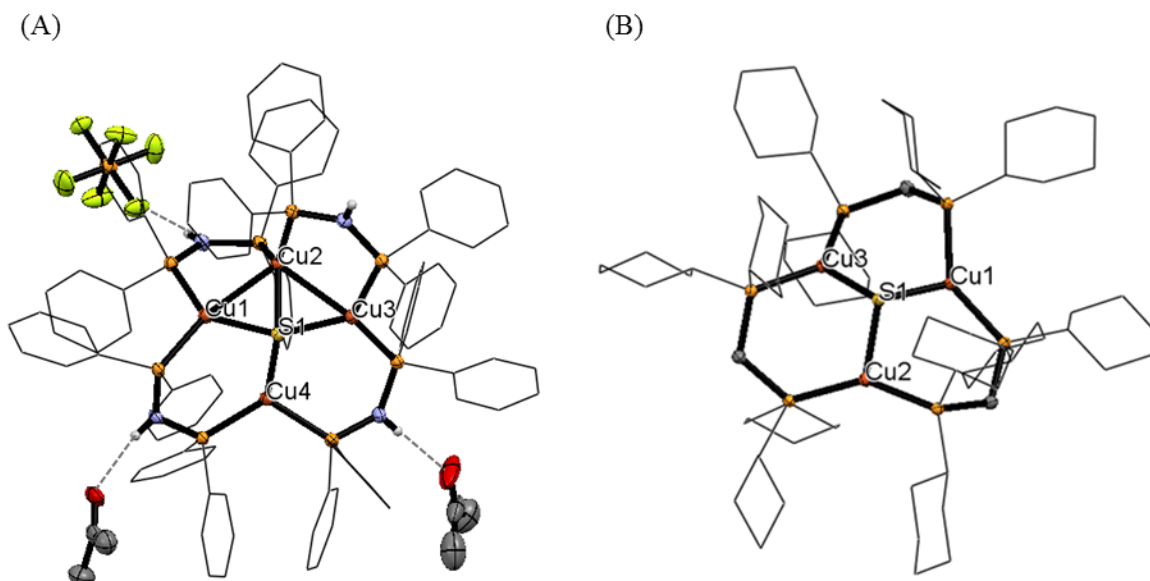


FIGURE 2.2 Crystal structures of complexes (A) **2.2** and (B) **2.4** determined by X-ray crystallography. Complexes are displayed with 50% probability ellipsoids for the core atoms and guest molecules (co-crystallized acetone and PF_6^- anion) engaged in hydrogen bonding. N-H protons are displayed in calculated positions. Substituents on the phosphine atoms are drawn as wireframe, phosphine substituent hydrogen atoms and counter ions have been omitted for clarity. Atom colors include: Cu, brown; S, yellow; P, orange; N, blue; F, green; O, red; C, gray. Reproduced with permission from Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. *Inorg. Chem.* **2014**, 53, 10611. Copyright 2014 American Chemical Society.

Closer examination of the crystal structure for **2.2** reveals that indeed, the farther Cu(4) atom attached to two dppa ligands is being drawn away from the cluster core because of the hydrogen bonding interaction occurring between two of the dppa amine protons and the recrystallization solvent (acetone). This outer-sphere hydrogen bonding interaction between the dppa amine proton and the solvent is not only evident in the solid state structure of **2.2**, but also in solution, as will be discussed in Section 2.4.3.

The crystal structure for complex **2.4** (Figure 2.2B) exhibits a tricopper(I) cluster with three bridging dcpm ligands, a μ_3 -sulfide ligand and a single hexafluorophosphate counter ion. The copper-sulfide core exhibits three-fold symmetry and each copper atom displays a distorted trigonal planar geometry. The longer Cu...Cu distances of 3.5684(3) – 3.6753(3) Å signify the demanding steric bulk imposed by the cyclohexyl substituents and that self assembly is limited to the formation of a tricopper-sulfide. Even in the presence of excess copper-dcpm (as discussed in Section 2.3) the complex will only

accommodate three copper-dcpm units around a single sulfur. An excellent visual demonstrating the effect of the dcpm ligands is represented in Figure 2.3. A space-fill model of the crystal structure for **2.4** (Figure 2.3A) is compared to the space-fill model of a different tricopper(I)-sulfide complex, **2.5**, but dppa serve as the ligands (Figure 2.3B and characterized in detail in Section 2.6). Looking down the approximate C_3 axis through the $\mu_3\text{-S}^{2-}$ atom in **2.4**, the dcpm ligands shield the sulfide which prevents more copper-dcpm units from coordinating. The same view in complex **2.5** displays the reduced shielding of the $\mu_3\text{-S}^{2-}$ when dppa is the ligand; allowing another copper-dppa unit to coordinate and presumably leads to the formation of the tetracopper(I) complex, **2.2**.

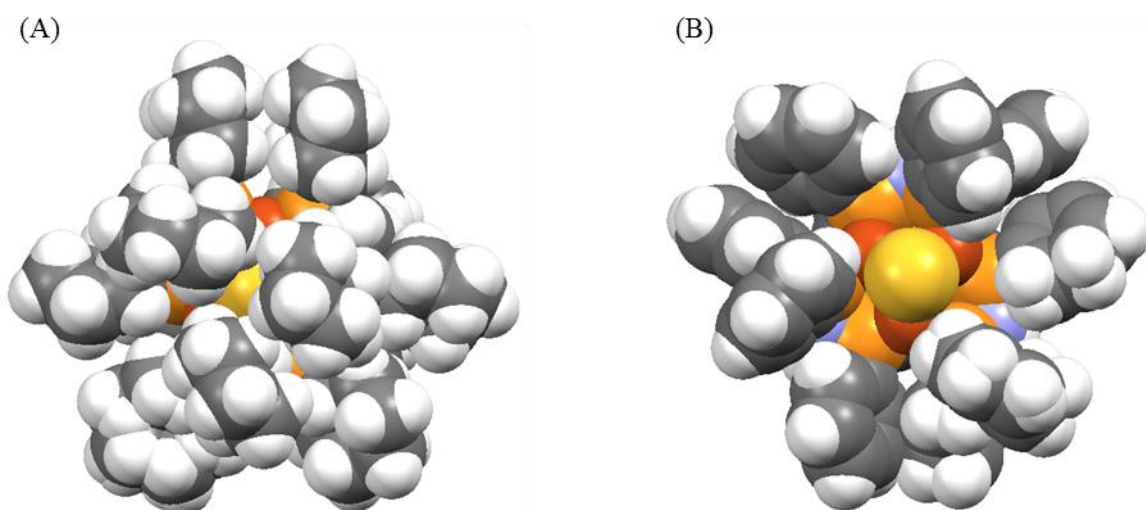


FIGURE 2.3 Space-fill models of the crystal structures for (A) **2.4** and (B) **2.5**. Only the cationic portion of both complexes is shown and both are angled to view down the sulfur (pseudo-) C_3 axis. All hydrogen atoms displayed are the calculated positions. Atom colors include: Cu, brown; S, yellow; P, orange; N, blue; C, gray; H, white. Reproduced with permission from Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. *Inorg. Chem.* **2014**, 53, 10611. Copyright 2014 American Chemical Society.

In summary, replacing the methylene backbone linker to an amine group on bidentate phosphine ligands allows for the assembly of a tetracopper(I)-sulfide cluster from a dicopper(I) precursor; with evidence of hydrogen bonding interactions between the amine proton and outer-sphere solvent molecules

(complex 2.2). Hydrogen bonding synergy in N_2OR is believed to be important to nitrous oxide reduction^{17,31,36,38} and model complexes containing the dppa ligand may provide an avenue for investigating the extent of hydrogen bonding involvement. Additionally, encumbering substituents on the phosphorus atoms leads to reduced nuclearity of copper-sulfide clusters (complex 2.4).

2.4.1 Structural Comparisons Between Tetracopper-sulfide Compounds

Reported in Table 2.1, are the $\text{Cu}\cdots\text{Cu}$ distances and $\text{Cu}-(\mu_4\text{-S})$ bond lengths for Cu_Z^* ¹⁸ and Cu_Z^{19} , both in their resting states. For comparison, 1.3¹¹⁸, 1.4¹¹⁹ and 2.2¹⁷⁷ are also reported in Table 2.1 and all tetracopper-sulfide complexes are shown in Figure 2.4.

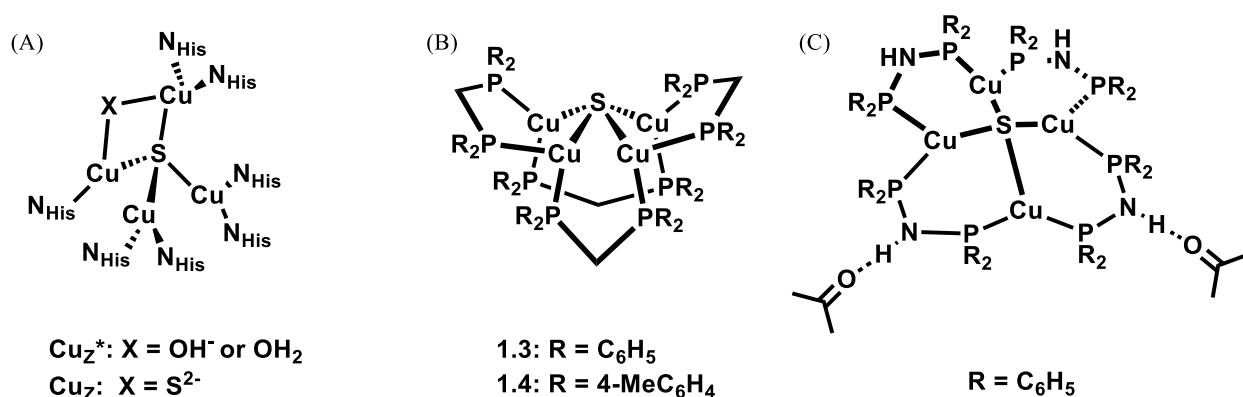


FIGURE 2.4 Core inorganic structures of tetracopper-sulfide complexes. (A) Cu_Z^* and Cu_Z . (B) Complex 1.3 and 1.4. (C) Complex 2.2.

TABLE 2.1 Comparison of Tetracopper-sulfide Structures

Structure Descriptor	Cu _Z * ^a	Cu _Z ^a	1.3 ^{bc}	1.4 ^d	2.2 ^c
Cu···Cu (Å)	2.535(3) ^e	2.830(6) ^e	2.869(2) ^e	2.955(2) ^e	2.6571(7) ^e
	2.555(6) ^e	2.842(2) ^e	2.869(2) ^e	2.955(2) ^e	2.7184(4) ^e
	3.333(2) ^e	3.379(2) ^e	3.128(1) ^e	3.144(2) ^e	3.1005(5) ^e
	3.356(5) ^e	3.405(2) ^e	3.128(1) ^e	3.144(2) ^e	3.5365(6) ^e
	2.987(9) ^f	2.954(6) ^f	4.169(2) ^f		3.9697(6) ^f
Cu-(μ ₄ -S) (Å)	4.434(2) ^f	4.597(4) ^f	4.303(1) ^f		4.2857(6) ^f
	2.094(1)	2.191(9)	2.267(1)	2.282(2)	2.2217(8)
	2.159(9)	2.224(0)	2.267(1)	2.282(2)	2.2418(7)
	2.207(6)	2.352(1)	2.269(2)	2.333(1)	2.2452(6)
	2.253(1)	2.440(0)	2.269(2)	2.333(1)	2.2619(8)
τ ₄ ^{cg}	0.66	0.71	0.59	0.50	0.64

^a See Appendix A.^b See reference 118.^c See reference 177.^d See reference 119.^e Neighboring copper atom distances.^f Cross cluster copper atom distances.^g τ₄ measurement of μ₄-sulfide atom.¹⁸¹

The shortest Cu···Cu distances (between neighboring copper atoms) belong to Cu_Z* (2.535(3) and 2.555(6) Å) and the longest Cu···Cu distances (cross cluster copper atoms) are displayed in Cu_Z (4.597(4) Å) and Cu_Z* (4.434(2) Å). The range of Cu···Cu distances for neighboring copper atoms is smallest in complex **1.4** (2.955(2) – 3.144(2) Å), which highlights its fairly symmetrical tetracopper core. The largest range of neighboring Cu···Cu distances appears in model **2.2** (2.6571(7) – 3.5365(6) Å) and more closely resembles the range of neighboring Cu···Cu distances observed in Cu_Z* (2.535(3) – 3.356(5) Å) than any of the other synthetic compounds listed in Table 2.1.

The range of neighboring Cu···Cu distances observed in **2.2** is directly resulted from the hydrogen bonding interaction between the dppa amine protons and recrystallization solvent (Figure 2.2A and Figure 2.4C). Similarly, the variety of Cu···Cu distances in Cu_Z* is perceived to occur because complex hydrogen bonding networks of neighboring protein structures forces the active site into the observed constrained orientation.³⁸ In the absence of a secondary coordination interaction (as in **1.3** and **1.4**), distortion of the copper-sulfide core is less pronounced and a more symmetrical relationship between neighboring copper

atoms is observed. A larger range of neighboring Cu $\cdots$ Cu distances (as in **2.2**) is desired when modeling Cu₂* because the binding site of nitrous oxide is hypothesized to be between two adjacent copper atoms that are ~ 3.40 Å apart.^{15,30,33,38,39} Complexes **1.3** and **1.4** do not possess any neighboring copper atoms that are more than 3.144(2) Å apart¹¹⁹; while **2.2** provides a potential binding site between two copper atoms that are 3.5365(6) Å separated. Using the dppa ligand in the construction of **2.2** generated a hydrogen bonding interaction, resulting in a range of Cu $\cdots$ Cu distances most relatable to the resting state structure of Cu₂*.

The Cu–S bond lengths for the synthetic complexes listed in Table 2.1 remain unremarkable and very similar ($\sim 2.2 - 2.3$ Å).^{118,119,177} Instead, variation of the τ_4 parameter amongst complexes in Table 2.1 is observable. The computed τ_4 value is used to describe how distorted a four-coordinate atom is from being a perfect tetrahedral, $\tau_4 = 1$, or square planar, $\tau_4 = 0$.¹⁸¹ The μ_4 -S²⁻ for all complexes in Table 2.1 can be described as having see-saw geometry resulting from intermediary τ_4 values. More notably, Cu₂* and complex **2.2** have the most similar μ_4 -S²⁻ distortion ($\tau_4 = 0.66$ and $\tau_4 = 0.64$, respectively).

Comparisons of the adjacent Cu $\cdots$ Cu distances and τ_4 parameters of the complexes in Table 2.1 resulted in **2.2** as the most structurally faithful model to the Cu₂* resting state. Structural alterations in copper-sulfide arrangement occurred because the ligand backbone amine group engaged in outer-sphere hydrogen bonding interactions.

2.4.2 Structural Comparisons of Tricopper-sulfide Compounds

A representation of Cu $\cdots$ Cu distances and Cu–S bond lengths for tricopper-(μ_3 -sulfide) complexes **2.4**¹⁷⁷, **2.5**¹⁷⁷, **1.1**¹¹⁶ and **1.2**¹¹⁷ are compared in Table 2.2. The longest Cu $\cdots$ Cu distances are observed in complex **1.2** (3.6434(5) – 3.6532(6) Å), which features a mixed valent core (formally 2Cu^{II}Cu^I) supported by the trinucleating tris(β -diketimine)cyclophane ligand that encages the copper-sulfur core (Figure 2.5C).¹¹⁷ Unsurprisingly, the shortest Cu $\cdots$ Cu distances come from complex **2.5**; where the tricopper(I)-sulfide unit is supported by three bridging dppa ligands (Figure 2.5A). The Cu $\cdots$ Cu distances in **2.5** (2.8318(7) – 2.832(1) Å) are similar to those observed in complex **2.2** (Table 2.1) because of the smaller

steric volume dppa ligands enforce when compared to the other complexes containing bulky ligands in Table 2.2.

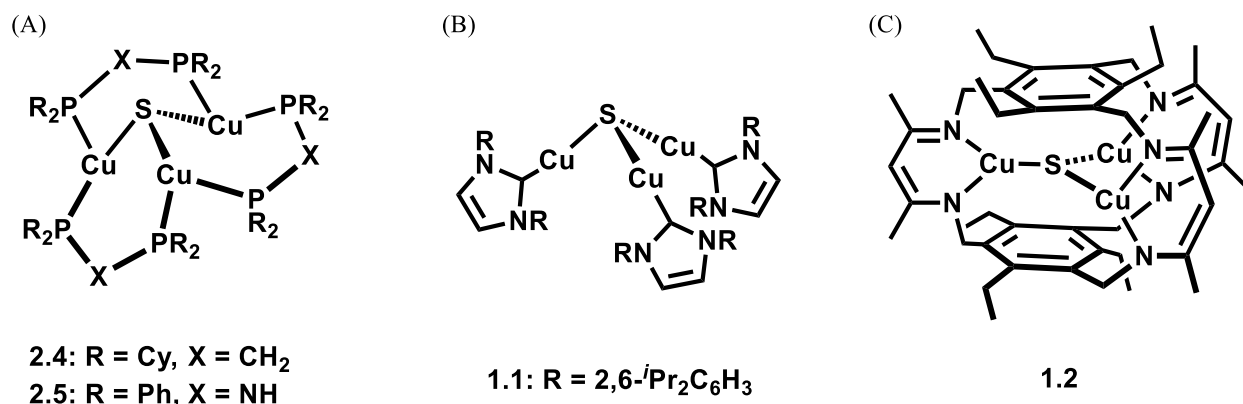


FIGURE 2.5 Core inorganic structures of tricopper-sulfide complexes. (A) 2.4 and 2.5. (B) Complex 1.1. (C) Complex 1.2.

TABLE 2.2 Comparison of Tricopper-sulfide Structures

Structure Descriptor	2.4 ^a	2.5 ^a	1.1 ^b	1.2 ^c
Cu···Cu (Å) ^d	3.5684(3)	2.8318(7)	3.5614(5)	3.6434(5)
	3.6227(3)	2.832(1)	3.5614(5)	3.6509(6)
	3.6753(3)	2.832(1)	3.5614(5)	3.6532(6)
Cu-(μ ₃ -S) (Å)	2.2070(4)	2.231	2.1351(5)	2.1047(9)
	2.2149(4)	2.232	2.1351(5)	2.1071(9)
	2.2320(4)	2.233	2.1351(5)	2.1088(9)
∠Cu-S-Cu (°)	107.61(2)	78.73	113.02	119.59(4)
	109.11(2)	78.74	113.02	120.10(4)
	111.78(2)	78.77	113.02	120.31(4)

^a See reference 177.

^b See reference 116.

^c See reference 117.

^d Neighboring copper atom distances.

The Cu–S bond lengths for the complexes in Table 2.2 are fairly consistent to the Cu–S bond lengths observed in Table 2.1 for the synthetic tetracopper-sulfide compounds ($\sim 2.2 - 2.3$ Å); with the exception of **1.2**. The smaller Cu–S bond lengths in **1.2** (2.1047(9) – 2.1088(9) Å) compared to all other tricopper(I)-sulfide complexes in Table 2.2 may result from the higher oxidation state of the copper atoms in **1.2** causing a shortening of the Cu–S bonds, or as the consequence of the domineering ligand scaffold.¹¹⁷ It is also interesting to note that the Cu–S bond distances for the copper(I)-only clusters reported in Tables 2.1 and 2.2 are unaffected by copper nuclearity, as well as the difference in ligand structure. Instead, the different structural features of the polydentate ligands appear to influence the *geometry* exhibited by the sulfur atom.

All tricopper-sulfide complexes in Table 2.2 and Figure 2.5 exhibit (pseudo-)C₃ symmetry through the μ_3 -S₂[−] ligand. Complexes **2.4** and **1.1** feature a distorted trigonal pyramidal geometry for the sulfur atom with $\angle\text{Cu–S–Cu}$ angles of 107.61(2) – 111.78(2)^{o177} and 113.02^{o116}, respectively. The sulfur geometry for complex **2.5** is also trigonal pyramidal but exhibits much smaller $\angle\text{Cu–S–Cu}$ angles (78.73 – 78.77^o)¹⁷⁷ than other traditional trigonal pyramidal molecules, $\sim 109^\circ$. The geometry for the μ_3 -S₂[−] in **1.2** however exhibits a classical trigonal planar arrangement with $\angle\text{Cu–S–Cu}$ bond angles of 119.59(4) – 120.31(4)^o.¹¹⁷ The difference in sulfide geometry for **1.2** compared to the other tricopper-sulfide complexes is directly resulted from the rigid structure of the tris(cyclophane) ligand enforcing a trigonal planar coordination arrangement.

Although the complexes examined in Table 2.2 exhibit a different copper-sulfide stoichiometry than the Cu_z^{*}, several conclusions pertaining to cluster assembly and structural qualities, can be inferred. Firstly, the oxidation state of the copper atoms could induce changes to Cu–S bond lengths (**1.2**). Secondly, cumbersome substituents on bidentate phosphine ligands will directly increase the resulting Cu $\cdots$ Cu distances (**2.4** vs. **2.5**). Finally, rigid or flexible ligand frameworks can be used to manipulate the geometry of the sulfide atom; exemplified by the trigonal planar (**1.2**) or trigonal pyramidal (**2.4**) coordination of the sulfur atom in model systems containing fixed vs. accommodating ligands. Understanding the factors that lead to particular cluster assemblies, reveal generalizations for building future copper-sulfide clusters that can be tailored to have desired structural properties.

2.4.3 Hydrogen Bonding Interactions in Solution for Complex 2.2

The solid state structure of model compound **2.2** exposes the outer-sphere hydrogen bonding interaction between the amine proton in two dppa ligands and the crystallization solvent (Figure 2.2A).¹⁷⁷ More interestingly, this behavior can also be observed in solution by ^{31}P NMR.

When solid **2.2** is recrystallized in acetone and analyzed by ^{31}P NMR in acetone- d_6 , a single broad peak appears at 36.6 ppm (Figure 2.6A). When the same recrystallized sample of **2.2** is then dissolved for NMR analysis in acetonitrile- d_3 , two species appear at 36.8 ppm and 36.5 ppm (Figure 2.6B). The peak at 36.5 ppm corresponds to the original acetone-coordinated amine environment and the new peak appearing at 36.8 ppm is the acetonitrile- d_3 hydrogen bonding environment resulting from displacement of the acetone molecules.

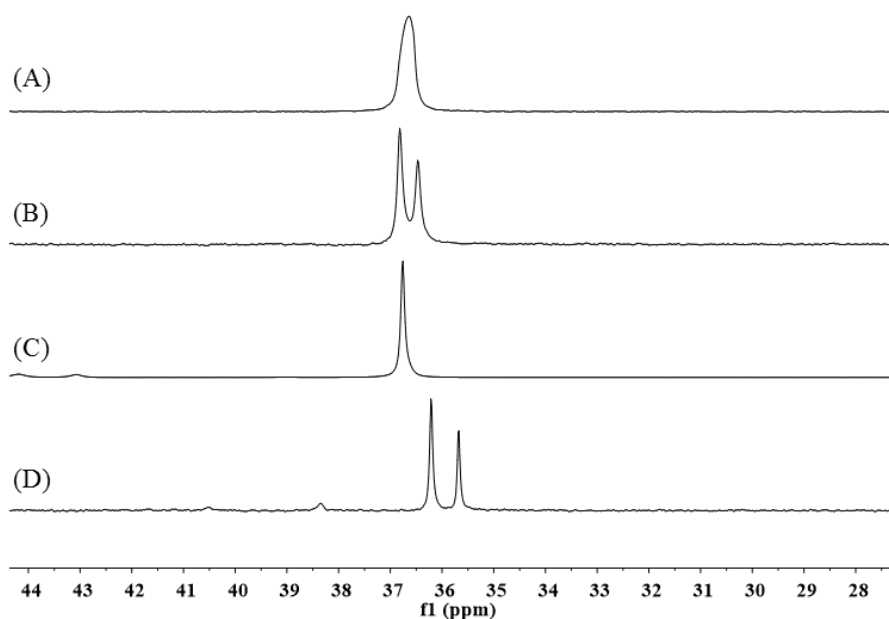


FIGURE 2.6 ^{31}P NMR spectra for hydrogen bonding interactions between **2.2** and different polar solvents. (A) Acetone recrystallized **2.2** analyzed in acetone- d_6 . (B) Acetone recrystallized **2.2** analyzed in acetonitrile- d_3 . (C) Acetonitrile recrystallized **2.2** in acetonitrile- d_3 . (D) Acetone recrystallized **2.2** in DMSO- d_6 . Reproduced with permission from Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. *Inorg. Chem.* **2014**, 53, 10611. Copyright 2014 American Chemical Society.

Additionally, if complex **2.2** is synthesized in acetonitrile, and ^{31}P NMR analysis is carried out in acetonitrile- d_3 , a single peak is revealed at 36.8 ppm; corresponding to only acetonitrile molecules interacting with the amine protons (Figure 2.6C). The ability to hydrogen bond with two solvents is again confirmed when acetone recrystallized **2.2** is analyzed in DMSO-d_6 (Figure 2.6D); producing two peaks at 36.2 ppm (acetone coordinated) and 35.7 ppm (DMSO-d_6 coordinated).

2.5 Electronic Characterization of Complexes 2.2 and 2.4

2.5.1 Photophysical Properties of 2.2 and 2.4

The photophysical properties of dicopper(I)-binucleating phosphine complexes are extensively reported within the literature.^{127,165,169,178,179} Similarly, **1.3** and **1.4** were synthesized and heavily characterized by Yam and coworkers for their luminescent properties.^{118–120,122} Unsurprisingly, complexes **2.2** and **2.4** also exhibit emission and luminescent qualities.¹⁷⁷

The emission wavelengths of complexes **2.2**, **2.4**, **1.3** and **1.4** in acetonitrile at room temperature are reported in Table 2.3 at excitation wavelength 415 nm. The bright orange complexes emit at much lower energies (618 – 704 nm) than other dicopper(I)-diphosphine complexes (400 – 560 nm).^{127,165} The highest energy emission occurred in complexes **1.3** and **1.4** (618 nm and 620 nm respectively)^{118,119}; followed by **2.4** (642 nm), and **2.2** (704 nm).¹⁷⁷

TABLE 2.3 Comparison of Photophysical Properties between Complexes **2.2**, **2.4**, **1.3** and **1.4**

Photophysical Property	2.2 ^{ab}	2.4 ^{ab}	1.3 ^{bc}	1.4 ^d
$\lambda_{\text{emission}}$ (nm) ^b	704	642	618	620
Φ^{ef}	0.067	0.0007	0.22	0.26

^a See reference 177.

^b Emission spectrum in Chapter 5, Figure 5.21.

^c From reference 118.

^d From reference 119.

^e Quantum yield measured with excitation wavelength of 415 nm in CH_3CN at RT for all compounds.

^f See Appendix B.

In Table 2.3, no apparent trend appears for emission maxima as nuclearity of the cluster is changed; evidenced by the energy transition of **2.4** falling in between emission values for the tetracopper complexes. The study of several luminescent copper(I)-halide systems with dcpm ligands have reported a trend in MeCN with decreasing energy emissions as copper(I) core content increases.¹⁷⁸ Instead, the quantum yield appears to be more sensitive to the copper nuclearity. Higher quantum yields appear inherent to the tetracopper-sulfide systems in Table 2.3 and suggest compound **2.4** may undergo an unknown non-radiative decay pathway.¹⁸² Excited state structure distortion or ligand dissociation can accelerate non-radiative processes which effectively lowers the quantum yield.^{183,184} Reports examining luminescent polynuclear copper(I) compounds propose the Cu...Cu distances as also influencing the resulting emission intensities^{178,185}; and is speculated, along with a nonradiated decay pathway, for the discrepancy in emission intensity between tetra- and tricopper complexes in Table 2.3.

2.5.2 Electrochemical Properties of **2.2** and **2.4**

Reduction of nitrous oxide requires a two e⁻ redox process to occur and therefore it was important to probe the electrochemical responses of fully reduced (all Cu^I) complexes **2.2** and **2.4**. Additionally, electrochemical studies can also provide insight into what type of ligands (S²⁻, dcpm, dppa) allow reversible or irreversible redox behaviors to occur within these particular copper(I)-sulfide clusters.

Yam and coworkers reported the redox response for **1.3** and **1.4** to be multiple irreversible oxidations in MeCN and are reported in Table 2.4.¹²⁰ It has been noted that the phosphine donation to copper(I) in **1.3** stabilizes the complex in open air and would therefore prevent the complex from forming stable oxidized species electrochemically.¹⁰¹ Complexes **2.2** and **2.4** are not air- stable and investigations of their electrochemical signatures were studied by cyclic voltammetry and are also reported in Table 2.4.¹⁷⁷

TABLE 2.4 Electrochemical Events for **2.2**, **2.4**, **1.3** and **1.4**

$E_{\text{oxidation}}$ (V) ^a	2.2 ^{bc}	2.4 ^{bd}	1.3 ^{be}	1.4 ^{be}
	-0.12 ^f	-0.35 ^f	0.27	0.29
	0.27	0.29	1.25	0.84
	0.88	0.86	1.39	1.20
	1.55	1.58		1.35

^a Redox potential versus $\text{Fc}^{+/0}$, Pt working electrode, 100mVs⁻¹ scan rate.

^b Measured in 0.1 M solution of $[\text{Bu}_4\text{N}][\text{PF}_6]$ in MeCN.

^c See CV in Chapter 5, Figure 5.11.

^d See CV in Chapter 5, Figure 5.18.

^e See reference 120.

^f Reversible redox event.

Unlike Yam's complexes, both **2.2** and **2.4** feature a reversible one e⁻ oxidation event¹⁸⁶ at -0.12 V and -0.35 V vs. $\text{Fc}^{+/0}$, respectively. Appearance of a reversible oxidation wave in **2.2** and **2.4** likely stems from the ability of the more electron donating dppe and dcpm ligands to stabilize higher oxidation states, compared to dppe and dtpe ligands. The more negative potential observed for the reversible redox couple in **2.4** suggests it is easier to oxidize, compared to **2.2**, ideally indicating the electron contribution by the dcpm ligands is greater and therefore more accommodating for the stabilization of copper(II)-containing clusters. In similar polynuclear copper(I) bis(diphenylphosphino)alkyl- or aryl-amine complexes, that feature a bridging acetylide ligand, reported by Yam and coworkers, the decreasing potential values for the oxidation couple also coincided with increasing electron donation among different phosphine ligands.¹⁸⁷ The remaining redox events displayed by **2.2** and **2.4** are irreversible oxidations and, interestingly, occur at nearly the same potentials. Some of the irreversible oxidations in **2.2** and **2.4** also appear at the same potential in the cyclic voltammogram as **1.3** ($E_{\text{oxidation}} = \sim 0.28$ V vs. $\text{Fc}^{+/0}$) and **1.4** ($E_{\text{oxidation}} = \sim 0.85$ V vs. $\text{Fc}^{+/0}$) oxidations. The similar potentials for the irreversible redox events in all the complexes cannot be ligand-based oxidations because they each have different phosphine ligands. Therefore, these events could come from the redox properties involving the copper(I)-sulfide core. The sulfide ligand cannot be excluded from participating in redox chemistry because complex **2.4** shows *four* total redox events (assuming no copper(II) to copper(III) is occurring). Attempts in synthesizing and isolating the one e⁻ oxidized species of **2.2** and **2.4** using chemical oxidants were pursued; however, they proved unsuccessful.

Although complexes **2.2** and **2.4** revealed the inability to perform two e^- reversible electrochemistry relevant to Cu_Z^* , these investigations suggest the influence of ligands (S^{2-} or diphosphine) as prominent factors for inducing specific redox behaviors. The reversible oxidation event, appearing at -0.35 V vs. $\text{Fc}^{+/0}$ in **2.4** and -0.12 V vs. $\text{Fc}^{+/0}$ in **2.2**, could be used as a spectroscopic handle to gauge the level of electron donation from different binucleating phosphine ligands. Additionally, the appearance of four redox events for **2.4** supports the non-innocent behavior of sulfur in copper-sulfide redox chemistry.^{92,94,95} Finally, the appearance of a reversible electrochemical event occurring in the more electron donating ligand systems (**2.2** and **2.4**), may take place due to the ability of the electron rich ligands in stabilizing copper-sulfide compounds in higher oxidation states.

2.6 Reactivity of 2.2 with Relevant Substrates

2.6.1 Reactivity Between 2.2 and Nitrous Oxide, Azide, Nitrite

The structural characteristics of **2.2**, previously discussed, make it an excellent model to the structural features appearing in the Cu_Z^* resting state. Perhaps more importantly, it is also valuable to explore if **2.2** serves as a functional model by investigating its reactivity with relevant substrates. Under a variety of conditions, **2.2** did not appear to react with gaseous N_2O compared to N_2 control experiments in our hands. Although N_2O is the most relevant substrate to study, other triatomic organic compounds such as azide and nitrite anions, were pursued. These were attractive substrates because N_3^- is isoelectronic and linear, compared to gaseous N_2O ; whereas NO_2^- is a bent triatomic ion. The difference in substrate geometry was targeted because in the active Cu_Z^* state, N_2O is hypothesized to bind in a bent $\mu\text{-}1,3\text{-N}_2\text{O}$ fashion during substrate activation.^{30,33,38,39,188} Reactions between **2.2** and linear N_3^- or bent NO_2^- were pursued to investigate possible substrate binding modes relevant to the reduction mechanism perceived in Cu_Z^* .

When **2.2** was reacted with an excess sodium azide, two products were spectroscopically observed (Scheme 2.3) and characterized by X-ray crystallography (Figure 2.7).¹⁷⁷

(A)

(B)

Complex **2.5** was the major reaction product and the crystal structure revealed a tricopper(I)-sulfide cluster with bridging dppa ligands and a hexafluorophosphate counter ion (Figure 2.7A). A large electron density peak was observed near an amine proton that could be a solvent or anion molecule engaged in hydrogen bonding, however it was too disordered to identify. The second reaction product **2.6**, displayed another

tricopper(I)-dppa complex, but instead of a bridging sulfide ligand, two $(\mu\text{-}1,1\text{-N}_3)^-$ molecules were appended above and below the tricopper plane (Figure 2.7B). Hydrogen bonding between the dppa ligands in **2.6** and the recrystallization solvent (THF) were refined in the crystal structure along with a hexafluorophosphate anion. Reactions with azidotrimethylsilane and **2.2** resulted in only **2.6** as the reaction product; allowing full characterization of the complex with pure samples.

The only other synthetic copper(I)- $(\mu\text{-}1,1\text{-N}_3)^-$ complex for structural comparison to **2.6** was synthesized by Mak and coworkers in 1997 and consisted of a dicopper(I) complex supported by two tridentate ligands, Ph_2Ppypz ($\text{Ph}_2\text{Ppypz} = (2\text{-diphenylphosphino-6-pyrazol-1-yl})\text{pyridine}$) and one bridging $(\mu\text{-}1,1\text{-N}_3)^-$ unit (Figure 2.8B).¹⁸⁹ Structural information for these complexes are compared in Table 2.5; along with the DFT calculated transition state of $[\text{Cu}_2\text{S}_2(\text{Me}_3\text{tacn})_2\text{-(N}_2\text{O)}]$ from the functional model reported by Tolman and coworkers (Section 1.4.2)¹²³ and the calculated $[\text{Cu}_2^*\text{-N}_2\text{O}]$ transition state (Figure 2.8C and Figure 2.8D respectively).^{36,38}

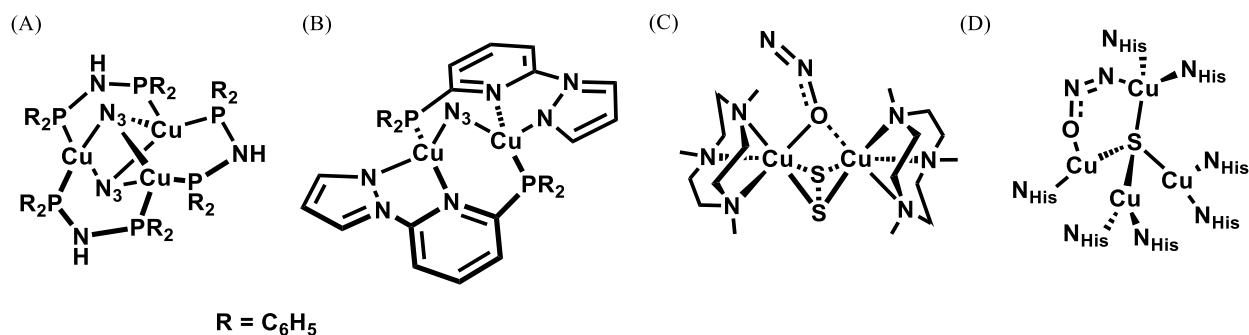


FIGURE 2.8 Core inorganic structures for complexes featuring a bridging triatomic ligand. (A) **2.6**. (B) $[\text{Cu}_2(\mu\text{-}1,1\text{-N}_3)(\text{Ph}_2\text{Ppypz})_2]^+$. (C) DFT calculated transition state structures of $[\text{Cu}_2\text{S}_2(\text{Me}_3\text{tacn})_2]^+$ and (D) Cu_2^* , with N_2O .

TABLE 2.5 Structural Parameters of Complexes Featuring a Bridging Triatomic Ligand

Parameter	2.6 ^a	[Cu ₂ (μ-1,1-N ₃)(Ph ₂ Ppypz) ₂] ^{+b}	[Cu ₂ S ₂ (Me ₃ tacn) ₂] ^{+ TS^{cd}}	[Cu ₂ *-N ₂ O] TS ^{ce}
Cu–N (Å)	2.17 ^f	2.16 ^g		1.91
Cu–O (Å)			2.175 ^g	1.55
N–N (Å)	1.108 ^{hi}	1.24(2) ^h	1.156	1.131
N–O (Å)	1.188 ^{jk}	1.15(6) ^j	1.538	1.81
∠N–N–O (°)	178.8 ^{lm}	165(1) ^l	127	115

^a See reference 177.^b See reference 189.^c DFT calculated N₂O-activated transition state.^d See reference 123.^e See references 36 and 38.^f Average Cu–N(4)/N(7) bond length, see Appendix D.^g Average Cu–(μ₂-N,O) bond length.^h N–N = (μ-N)–N_{middle} for azide.ⁱ Average (μ₃-N)–N_{middle} bond length, see Appendix D.^j N–O = N_{middle}–N_{terminal} for azide.^k Average N_{middle}–N_{terminal} bond length, see Appendix D.^l N–N–O = ∠N–N–N for azide.^m Average ∠N–N–N bond angle, see Appendix D.

The average Cu–N_{azide} bond lengths in **2.6** (2.17 Å) pair well with the reported average Cu–N_{azide} bond lengths in [Cu₂(μ-1,1-N₃)(Ph₂Ppypz)₂]⁺ (2.16 Å).¹⁸⁹ Interestingly, the (μ₃-N)–N bond lengths of the azide units in **2.6** (1.108 Å) are shorter than free azide (1.15 Å)^{190,191}; while the N_{middle}–N_{terminal} bond lengths (1.188 Å) are longer. This “short and long” substrate bond distortion is also calculated to occur for activated N₂O bound to Cu₂* in the transition state (Figure 2.8D). The calculated N–N bond becomes shorter (1.131 Å),³⁸ and the calculated N–O bond (1.81 Å)³⁶ becomes longer compared to free N₂O (1.143 Å and 1.193 Å, respectively).³⁸ Similarly, the N–O bond of [Cu₂S₂(Me₃tacn)₂-(N₂O)] in the transition state (Figure 2.8C) is calculated to also elongate (1.538 Å), but shows a slightly longer N–N bond (1.156 Å) compared to gaseous N₂O.¹²³ One reason suggested for the change in N₂O bond lengths when activated by Cu₂* is from the substantial back-bonding contributions by the copper atoms into an anti-bonding N₂O orbital; therefore, weakening the N–O bond and strengthening the N–N bond.^{38,39} It cannot be said that the observed “short and long” substrate bond behavior occurs for all triatomic molecules bound to one or several copper(I)

atoms as evidenced by the *lengthening* of the (μ_2 -N)–N bond of azide in $[\text{Cu}_2(\mu\text{-}1,1\text{-N}_3)(\text{Ph}_2\text{Ppypz})_2]^+$ and *unchanged* $\text{N}_{\text{middle}}\text{--N}_{\text{terminal}}$ length compared to free azide.

The average $\angle\text{N--N--N}$ of the azide units in complex **2.6** appear very linear, 178.8° . This is drastically different than the calculated $\angle\text{N--N--O}$ angle of 127° in $[\text{Cu}_2\text{S}_2(\text{Me}_3\text{tacn})_2\text{--}(\text{N}_2\text{O})]$ and 115° in the $[\text{Cu}_Z^*\text{--N}_2\text{O}]$ transition states. The bent geometry of N_2O in the transition state is hypothesized to cause a lowering of the π^* orbital; therefore making N_2O a better acceptor of π -backdonation from the copper atoms and facilitates the reduction mechanism.^{31,33,38,39,188} To study the reactivity of **2.2** with a bent triatomic molecule, more closely resembling N_2O in the transition state with Cu_Z^* , sodium nitrite ($\angle\text{O--N--O} = 115.7^\circ$)¹⁹² was examined. Under the same conditions as the sodium azide reaction, complex **2.2** did not react with sodium nitrite. Due to no experimental evidence of the $[\text{Cu}_Z^*\text{--N}_2\text{O}]$ transition state structure, competition experiments between different substrates (azide and nitrite) and synthetic models provide viable ways at predicting stable intermediates during the reduction of nitrous oxide.

2.6.2 Reactivity Between 2.2 and Iodide

The iodide ion is a known inhibitor of the Cu_Z^* active site in N_2OR and has been observed crystallographically.¹⁹³ The structure of iodide-bound Cu_Z^* , displays the inhibitor bridged between two neighboring copper atoms; the same two copper atoms believed to be the N_2O binding site.^{38,193} The location of iodide bound to Cu_Z^* further supports that it is occupying the same site where N_2O would coordinate.^{15,22} Therefore, iodide was an additional substrate of interest for the study of its interactions with model complex **2.2**.

When excess sodium iodide was reacted with **2.2**, two reaction products were spectroscopically observed (Scheme 2.4) and characterized by X-ray crystallography (Figure 2.9).¹⁷⁷

(A)



(B)



ORTEP diagram of the Cu₃S₁ complex. The structure shows a central Cu₃ core with three copper atoms (Cu1, Cu2, Cu3) and one sulfur atom (S1). The Cu-Cu bond lengths are approximately 2.5 Å, and the Cu-S bond length is approximately 2.3 Å. The S1 atom is coordinated to the Cu3 core. The structure is surrounded by phenyl rings, which are shown as thermal ellipsoids at the 50% probability level. The diagram is labeled (A).

ORTEP diagram of the Cu₃S₁ complex. The structure shows a central Cu₃ core with three copper atoms (Cu1, Cu2, Cu3) and one sulfur atom (S1). The Cu-Cu bond lengths are approximately 2.5 Å, and the Cu-S bond length is approximately 2.3 Å. The S1 atom is coordinated to the Cu3 core. The structure is surrounded by phenyl rings, which are shown as thermal ellipsoids at the 50% probability level. The diagram is labeled (B).

Neutral complex **2.7** was the minor reaction product and displayed a tricopper(I) complex with three bridging dppa ligands and an unusual $\mu_3\text{-S}^{2-}$ and $\mu_3\text{-I}^-$ ligated on opposite sides of the tricopper plane (Figure 2.9A). The major reaction product, **2.8**, was determined to be another tricopper(I)-dppa complex but possessed two $\mu_3\text{-I}^-$ moieties above and below the copper plane (Figure 2.9B). The crystal structure of **2.8**

also revealed one hydrogen bonding interaction between the recrystallization solvent and a dppa ligand; as well as a hexafluorophosphate counter ion.

The structural features of **2.7** and **2.8** are reported in Table 2.6 and compared to other similar tricopper(I) complexes also possessing bridging iodide motifs (Figure 2.10). The two complexes used for comparison were synthesized by Samuelson and coworkers; both feature a tricopper(I)-(μ_3 -I)₂ core (as seen in **2.8**) but contain either bridging dppm ligands¹³⁸ (Figure 2.10C), or dppan ligands (bis(diphenylphosphino)aniline)¹⁹⁴ (Figure 2.10D). The Cu···Cu distances for the complexes in Table 2.6 display the following trend: [Cu₃(μ_3 -I)₂dppan₃]⁺ < **2.7** < **2.8** < [Cu₃(μ_3 -I)₂dppm₃]⁺. The shorter Cu···Cu distances for the amino based ligand complexes compared to dppm results from the short bite angle of PNP ligands^{134,194}; causing closer copper-copper distances.

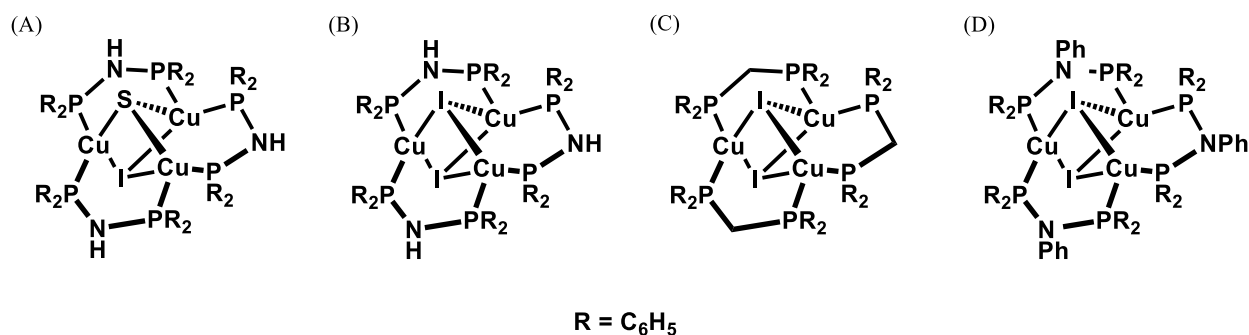


FIGURE 2.10 Inorganic core of tricopper(I) complexes featuring μ_3 -I⁻ ligand(s). (A) **2.7**. (B) **2.8**. (C) [Cu₃(μ_3 -I)₂dppm₃]⁺. (D) [Cu₃(μ_3 -I)₂dppan₃]⁺.

TABLE 2.6 Structural Parameters for Complexes Featuring (μ_3 -I) Ligand(s)

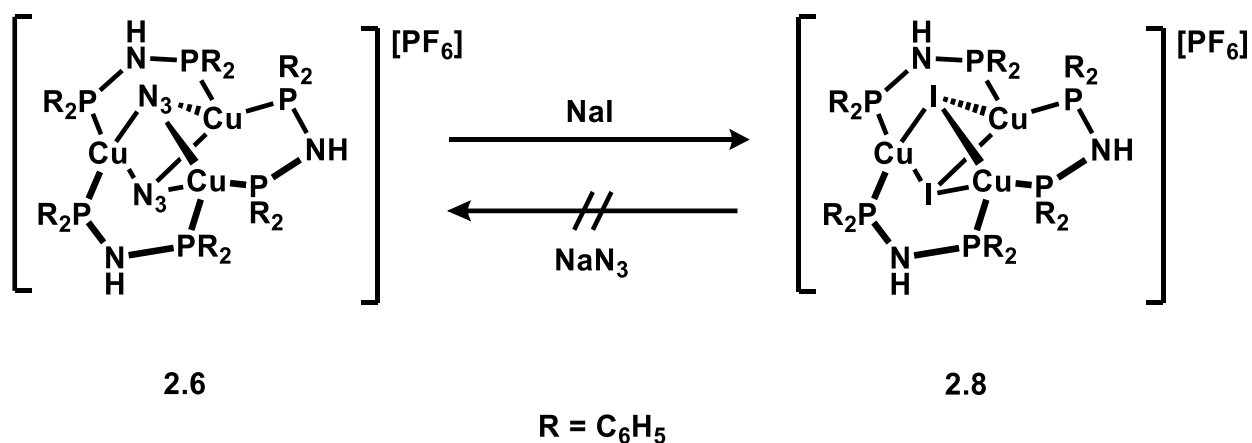
Parameter	2.7 ^a	2.8 ^a	[Cu ₃ (μ_3 -I) ₂ dppm ₃] ⁺ ^b	[Cu ₃ (μ_3 -I) ₂ dppan ₃] ⁺ ^c
Cu···Cu (Å)	2.884(7)	2.8953	3.111(3)	2.8387(13)
	2.895(6)	2.9575	3.184(5)	2.847(13)
	2.974(9)	2.9640	3.199(6)	2.8918(14)
Cu–(μ_3 -I) (Å)	2.871(3)	2.7152	2.727(5)	2.7025(11)
	2.802(5)	2.7609	2.765(5)	2.7346(11)
	2.844(5)	2.7178	2.754(2)	2.7045(11)
		2.7304	2.755(2)	2.7094(10)
		2.7551	2.766(5)	2.7071(11)
		2.7230	2.744(5)	2.7088(11)
Cu–(μ_3 -S) (Å)	2.436(4)			
	2.512(4)			
	2.579(5)			

^a See reference 177.^b See reference 138.^c See reference 194.

The Cu–(μ_3 -I) distances for **2.8**, [Cu₃(μ_3 -I)₂dppm₃]⁺ and [Cu₃(μ_3 -I)₂dppan₃]⁺ are all ~ 2.75 Å. The Cu–(μ_3 -I) bond length in **2.7** however is longer (2.871(3) – 2.844(5) Å) possibly as a result of the replusion by the closer μ_3 -S²⁻ appexed on the other side of the copper plane that is only 2.436(4) – 2.579(5) Å away from the copper atoms. The replusion of the iodide and sulfur in **2.7** also causes longer Cu–(μ_3 -S) bond lengths compared to those observed in complex **2.5** (~2.2 Å) that has only one μ_3 -S²⁻ unit. In a similar complex synthesized by Hong and coworkers in 2003, a tricopper(I) complex with bridging dppa ligands displayed two μ_3 -(SH)⁻ molecules above and below the copper plane (Scheme 1.6 bottom, left) and have similar Cu–S bond lengths to **2.7** (2.4317(16) – 2.5178(16) Å).¹³⁷

To study if the iodide in complexes **2.7** and **2.8** behave as an “inhibitor” similar to Cu_z* reactivity, several competition experiments were conducted (Section 5.1.11). First, when **2.2** was added to a 1:1 mixture of sodium azide and sodium iodide; products **2.7** and **2.8** were the only products spectroscopically observed by ³¹P NMR. Secondly, when complex **2.6** was added to sodium iodide, complex **2.8** was cleanly produced; whereas experiments under the same conditions but sodium azide was added to **2.8** (or **2.7**), no reaction occurred. These competition experiments are summarized in Scheme 2.5; confirming the ability of

complex **2.2** to behave as a functional model to Cu_2^* in the presence of iodide and demonstrated inhibition of reactivity with otherwise reactive substrates (azide).



SCHEME 2.5 Preference and inhibition of I^- binding over N_3^- . Reproduced with permission from Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. *Inorg. Chem.* **2014**, 53, 10611. Copyright 2014 American Chemical Society.

2.7 Summary and Discussion

The discussion of complexes in Chapter 2 has developed generalizations for copper(I)-sulfide cluster chemistry when binucleating phosphine ligands are used. Complex **2.2** featured desirable structural attributes relatable to Cu_2^* in the resting state and therefore, warranted further reactivity studies. Changing the methylene backbone linker in dppm to an amine (dppa) did not limit the assembly of a tetracopper(I)-sulfide complex, **2.2**, from a dicopper(I) precursor (Scheme 2.1). This evidence further supports the importance of using a three-atom bridged bidentate ligand when building tetracopper-sulfide complexes (see discussion in Section 1.6.1). The change in group on the ligand backbone did result in outer-sphere hydrogen bonding interactions, both in the solid state (Figure 2.2A) and in solution (Figure 2.6). This may be an important structural motif for model complexes because of the mentioned lysine and histidine amine protons that neighbor Cu_2^* in N_2OR that are suggested to help coordinate nitrous oxide to the active site.^{17,38}

Additionally, the proton transfer from lysine during the DFT calculated reduction mechanism in Cu_Z^* is suggested to be the key factor in stabilizing the Cu_Z^0 intermediate before regeneration of the active Cu_Z^* form (Scheme 1.2).³⁶ The hydrogen bonding exhibited in complex **2.2** was responsible for distorting the tetracopper-sulfide center, and therefore generated a wide range of $\text{Cu}\cdots\text{Cu}$ distances that are related to the $\text{Cu}\cdots\text{Cu}$ distances in the resting state of Cu_Z^* (Table 2.1). Replicating the $\text{Cu}\cdots\text{Cu}$ distances in Cu_Z^* is especially important to ensure adequate room for possible substrate binding sites. The τ_4 parameter of the sulfur atom in **2.2** also provided evidence that the secondary coordination environment influences geometric distortions about the sulfur atom. The τ_4 measurement in **2.2** was more closely related to the τ_4 parameter of the Cu_Z^* sulfur than the τ_4 of **1.3** or **1.4**, which do not possess any hydrogen bond donors. Furthermore, the extent of hydrogen bonding involving the amine proton appeared to be dependent on the model complex's molecular charge. Hydrogen bonding was evident in the crystal structures of cationic complexes **2.2**, **2.5**, **2.6** and **2.8**. The neutral complex **2.7**, did not provide any evidence of hydrogen bonding. Presumably, the lower molecular charge of **2.7** resulted in less acidic protons that do not readily engage in outer-sphere hydrogen bonding.

The reactivity studies of complex **2.2** displayed the strength of anionic substrate interactions with copper-sulfide clusters according to: $\text{I}^- > \text{N}_3^- > \text{NO}_2^-$. This study provided the only experimental evidence reported within the literature that demonstrated the strong affinity of copper-sulfide clusters to react with iodide over other ions. Furthermore, iodide was responsible for shutting off reactivity with other reactive substrates (azide); identical to the inhibitor behavior of iodide bound to Cu_Z^* .¹⁹³ Reactions with iodide and **2.2** also resulted in products where the iodide is positioned in the same location where other substrates are known to bind (**2.6** vs. **2.8**). Presumably, these observations support the argument that the iodide bound in Cu_Z^* prevents reduction of nitrous oxide because it occupies the perceived substrate docking site.^{15,22}

The substrate reactions with **2.2** also produced two reoccurring structure-alteration motifs that should be addressed. The copper containing products from the reaction between **2.2** and N_3^-/I^- featured: (i) only tricopper(I) nuclearity, and (ii) 4-coordinate copper atoms due to the addition of an extra bridging ligand (with the exception of **2.5**). Possible factors causing these two structural changes can be theorized

due to the well-reported coordination chemistry of luminescent polynuclear copper(I)-halide complexes. A tetracopper(I) complex supported by two dppipa (bis(diphenylphosphino)isopropylamine) ligands and four μ_2 -halide ligands was synthesized by Samuelson and coworkers in 2009.¹³⁴ The authors reported that upon addition of a different anion (F^- , Cl^- , Br^- , CN^- , SCN^-), the tetracopper complex broke down into a trimer consisting of three bridging dppipa ligands and two μ_3 -anions capped on opposite sides of the copper plane. The authors reported that the newly formed trimer is the preferred structure when bridging halide ligands are present.^{134,138} This exact reduction in copper nuclearity is also observed in the reaction products from **2.2** and N_3^-/I^- . Although there are several reported complexes that do feature a tetracopper(I) core with capping halides of the type $Cu_4X_4L_2$; the tetramer structure in these complexes is actually forced by the low metal to ligand ratios during synthesis.^{134,169,195–197} Hence, the tetracopper-to-tricopper behavior is encouraged due to the presence of *two* bridging halide/anion ligands and the preference to convert to a trimer. A potential solution to prevent the dismantling of tetracopper-sulfide clusters would be to generate stronger copper-ligand bonding interactions. For example, using anionic binucleating ligands would be a realistic direction to pursue for generating more tightly bound ligand to copper systems and hypothetically, prevent trimer complexes from forming.

Next, it is important to postulate why the copper atoms in **2.2** react with N_3^-/I^- and add an additional bridging anion ligand. The copper atoms in **2.2** are 3-coordinate and upon addition of excess N_3^- or I^- , all copper atoms convert to 4-coordinate by introduction of another capping anion on the opposite face of the copper plane. It has been previously reported that 4- or 2- coordinate copper atoms are more favorable than 3-coordinate.^{134,198} Indeed, the 4-coordinate copper atoms in **2.6**, **2.7** and **2.8** feature near perfect tetrahedral geometry according to their cooresponding τ_4 values: **2.6**: 0.86, **2.7**: 0.89, **2.8**: 0.93.¹⁸¹

Using a bidendate phosphine ligand with bulky substituents (dcpm) did not allow assembly of a tetracopper(I)-sulfide complex despite the ligand possessing a three-atom bridge. The steric congestion caused by the dcpm ligands in **2.4** are visually represented in the space fill model shown in Figure 2.3A and the long Cu...Cu distances reported in Table 2.2. Therefore, nuclearity of copper-sulfide clusters can be manipulated based on the steric properties of the substituents on the phosphine ligands.

Complex **2.4** displayed a reversible oxidation event at a lower potential than the oxidation couple observed in complex **2.2**; illustrating **2.4** is easier to oxidize and preferentially stabilizes clusters in higher oxidation states due to the higher electron donation from the dcpm ligands. Furthermore, the reversible redox event in **2.2** and **2.4** could serve as a spectroscopic handle that reflects the strength of electron donation from different phosphine donors. Understanding and manipulating a model complex's electrochemical signature will provide avenues for generating complexes that feature the desired two e⁻ reversible redox property observed in Cu₂^{*}. Moreover, the cyclic voltamogram of **2.4** displayed four electrochemical events, suggesting that the sulfur atom may participate in redox chemistry; which has been well documented in other dicopper-[(μ-S)₂]ⁿ⁻ complexes.^{92,94,95}

3. CONSTRUCTION OF COPPER-SULFIDE COMPLEXES USING AMIDINATE LIGANDS^{*†}

3.1 Background

As discussed in Section 1.2, each copper atom in Cu_Z^* ¹⁸ and Cu_Z ¹⁹ possesses one or two histidine ligands; bound through a nitrogen atom within the imidazole ring. Producing structural models of Cu_Z^* or Cu_Z that utilize N-donor ligands has remained a synthetic challenge to researchers due to the sensitivity in cluster assembly based on the nitrogen ligand used, sulfur reagent, copper salt and reaction conditions.^{37,101} Published attempts in constructing several structural models containing N-donor ligands are represented in Figures 3.1 and 3.2. The complexes shown in Figure 3.1 possess inorganic cores of $[\text{Cu}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-S}_2)]^{n+}$ ($n = 0, 2$) where the sulfur is described as bound “side-on” (Figure 1.4) and both copper atoms are assigned formal oxidation states of Cu(II). Working clockwise from the top of Figure 3.1, a catalog of complexes with β -diketiminato and anilido-imine ligands, bearing varied R-substituents, have been synthesized and characterized by Tolman et. al.^{84,86} and Itoh et. al.¹⁹⁹

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† Reproduced in part with permission from Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. “A One-Hole Cu_4S Cluster with N_2O Reductase Activity: A Structural and Functional Model for Cu_Z^* ” *J. Am. Chem. Soc.* **2016**, *138*, 13107. Copyright 2016 American Chemical Society.

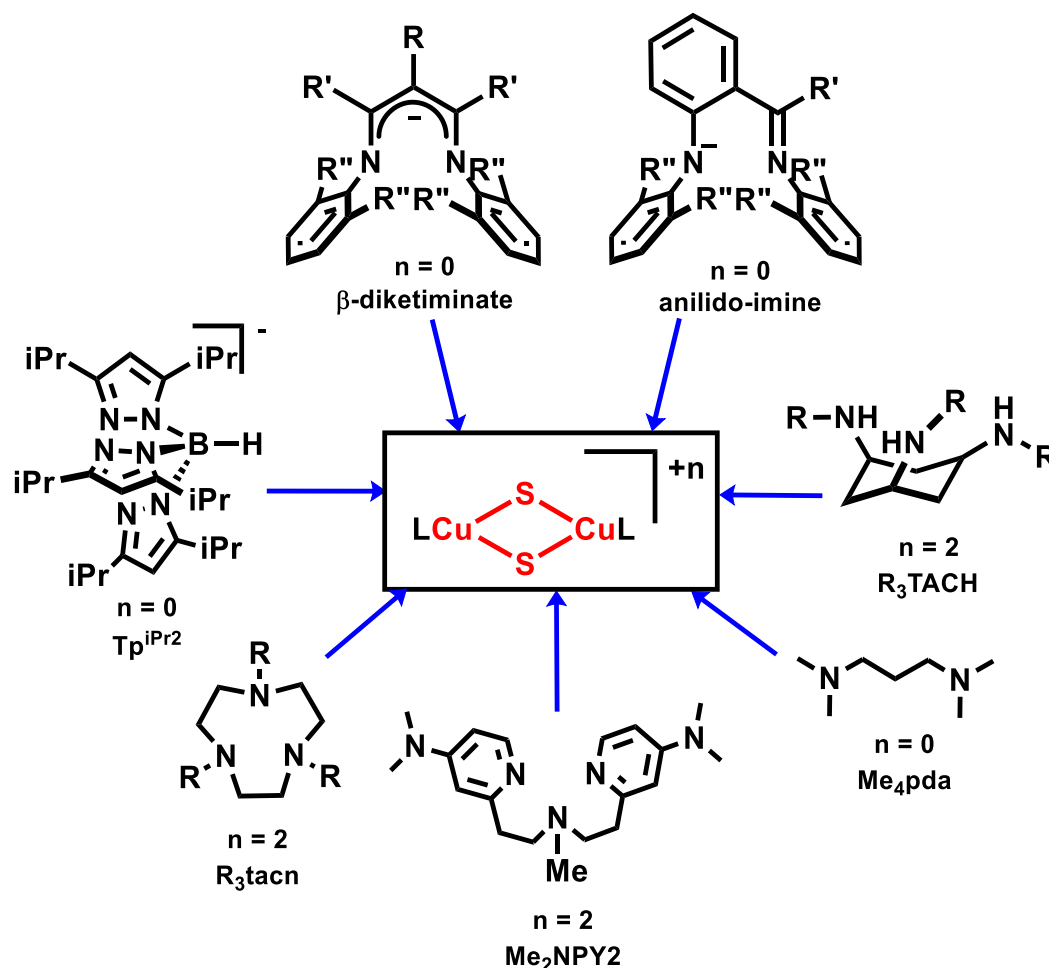


FIGURE 3.1 Selected N-donor ligands reported to produce $[Cu_2(\mu-\eta^2:\eta^2-S_2)]^{n+}$ ($n = 0, 2$) complexes.

Of the neutral ligands in Figure 3.1, R_3TACH (*N*-alkylated *cis,cis*-1,3,5-triaminocyclohexane),⁸⁹ Me_2NPY2 (*N,N*-bis{2-[2-(*N,N'*-4-dimethylamino)pyridyl]ethyl} methylamine)⁸⁸ and R_3tacn (1,4,7-trialkyltriazaclononane),^{90,91} serve as mononucleating, tridentate N-donors and produce penta-coordinated copper atoms. The remaining neutral Me_4pda (*N,N,N',N'*-tetramethylpropanediamine) coordinates as a mononucleating, bidentate ligand; generating two tetra-coordinated copper atoms that ultimately bind a triflate anion each, becoming penta-coordinated.⁹¹ The anionic Tp^{iPr_2} (hydrotris(3,5-diisopropylpyrazolyl)borate) ligand serves as a tridentate N-donor and also produces the same copper-coordination environment exhibited by the neutral ligands.^{109,200}

The bidentate ligands Me₄eda (*N,N,N',N'*-tetramethylethylenediamine) and Me₄chd (*N,N,N',N'*-tetramethyl-*trans*-1(*R*),2(*R*)-diaminocyclohexane) displayed in Figure 3.2, produce mixed valent [Cu₃(μ₂-S)₂]³⁺ complexes (2Cu^{II}Cu^I) from stoichiometric addition of a copper(I)-ligand salt and elemental sulfur.^{82,83,87,94}

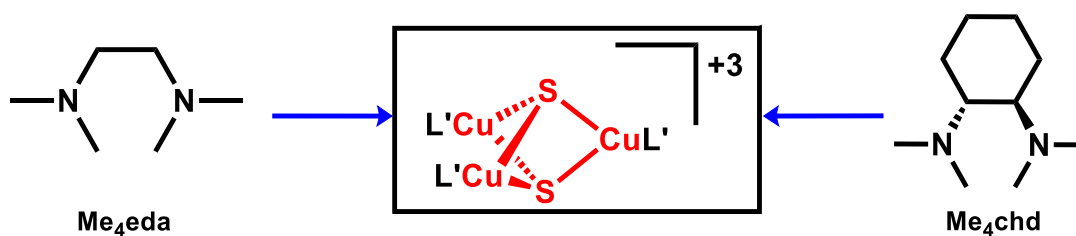


FIGURE 3.2 Selected N-donor ligands reported to produce [Cu₃(μ₃-S)₂]³⁺ complexes.

As discussed in Chapter 1, of the model complexes using nitrogen donor ligands, there have been *none reported that possess a single Cu₄(μ₄-S) feature* fundamental to Cu_z* structure. The challenging task associated with building tetracopper-sulfide compounds utilizing nitrogen ligands can truly be appreciated when surveying the extensive synthetic work shown in Figures 3.1 and 3.2. The two functional models discussed in Section 1.4.2, and displayed in Figure 3.3, establish impressive progress towards activating nitrous oxide by copper-sulfur clusters supported by N-donors, but lack the ability to provide insight pertaining to the structure-function relationship of a Cu₄S center parallel to Cu_z*.

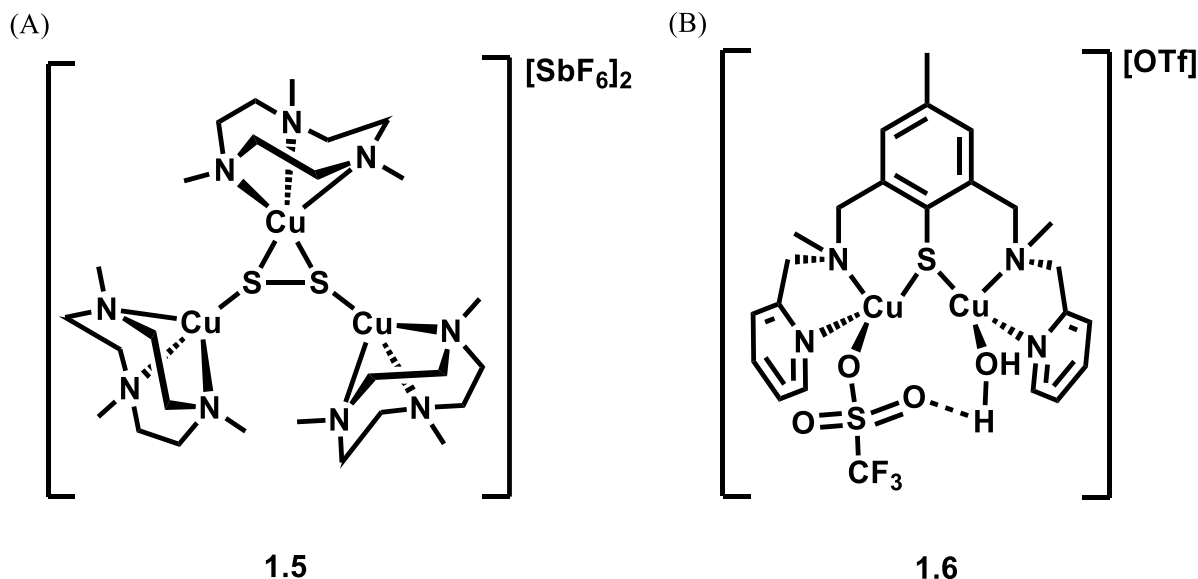
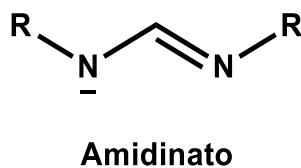


FIGURE 3.3 Functional Cu_2^+ models (A) 1.5 synthesized by Tolman and coworkers¹²³ and (B) 1.6 synthesized by Torelli and coworkers.¹²⁴

The synthetic methodology of using three-atom bridged bidentate ligands and dicopper(I) precursors to assemble tetracopper-sulfide clusters was successfully validated for phosphine ligands in Chapter 2, and therefore a viable starting place for model complexes containing N-donor ligands. In addition, using an *anionic* binucleating ligand is desired to produce stronger copper-ligand bonds (discussed in Section 2.7) and as a result, model construction using amidinate ligands (NCN^-) was pursued.



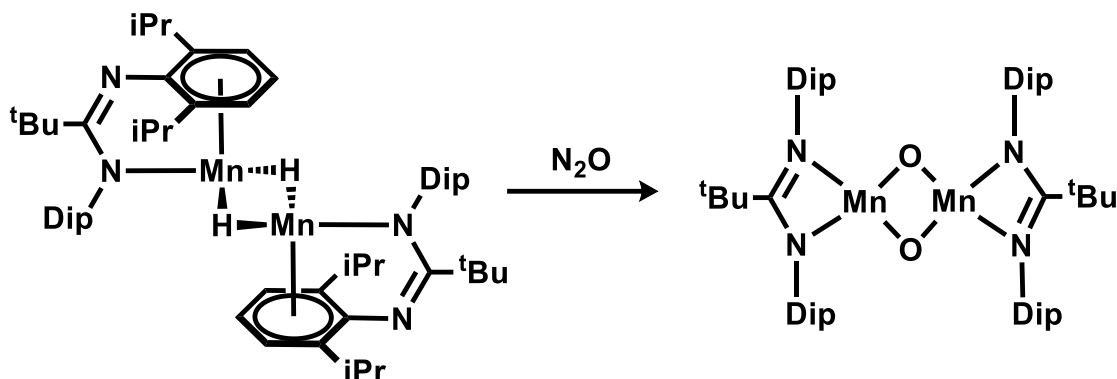
Use of amidinate ligands in transition metal compounds has produced enriched reactivity in a variety of catalysts and added stability in extremely interesting bimetallic systems.²⁰¹ Dinuclear gold(I) systems, featuring bridging amidinate ligands, successfully undergo oxidative addition of small molecules

(e.g. Cl_2 , Br_2 , I_2 , CH_3I , benzoyl peroxide) across both gold centers and generate a direct Au(II)-Au(II) metal bond due to stabilization from the NCN^- ligands.^{202,203} Reports of catalytic CO oxidation by gold particles on metal oxide supports (TiO_2 or MgO) employ gold precatalysts that utilize amidinate ligands, instead of halogens (e.g. HAuCl_4), as a means of eliminating catalytic poisoning by halogen contamination when gold is deposited on the metal oxide supports.^{204,205} In a similar fashion, use of copper(I)-amidinato precursors are preferred for atomic layer deposition (ALD) in order to produce copper metal films that are extremely pure and uniform; leading to increased conductivity and high reactivity with substrates.^{206,207} Incredibly interesting chromium and molybdenum bimetallic complexes are reported to have quintuple²⁰⁸ and quadrupole²⁰⁹ bonded metal centers when formamidinate ligands are ligated. Other studies associating amidinate ligands as useful appendages for controlling metal nuclearity in copper,^{210–213} silver²¹⁴ and gold^{215–218} clusters provide impressive dominance within the literature.

In relation to small molecule activation, dinuclear molybdenum, tungsten and titanium metal centers employing amidinate and Cp^* (Cp^* = pentamethylcyclopentadiene) ligands are reported to react with dinitrogen and produce bimetallic “end-on” ($\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2$) bridged structures.²¹⁹ The authors reported stabilization of these complexes was afforded by the use of NCN^- and Cp^* ligands, thus generating an isostructural-ligand framework for the investigation of N_2 activation across different transition metal groups. Similarly, Sita and coworkers reported tantalum,²²⁰ zirconium and hafnium²²¹ systems supported by amidinate ligands that not only bind N_2 “side-on” ($\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2$), but also allow functionalization of the N-atoms through hydrogenation and hydrosilylation reactions. Additionally, formamidinate ligands have been reported as successful analogues to β -diketiminato ligands specifically used in iron(II) compounds involved in N_2 fixation,²²² and modeled after the iron-molybdenum cofactor in nitrogenase.^{223,224}

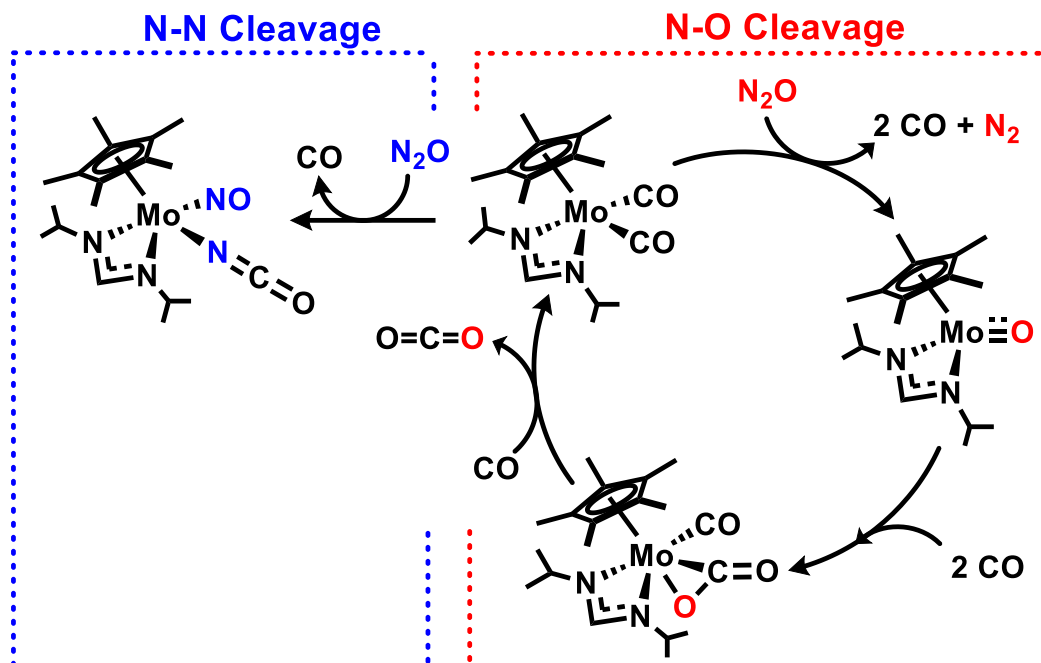
Even more encouraging, are several reports of transition metal complexes incorporating amidinate ligands that effectively react with nitrous oxide. In one particular system, a trinuclear manganese(II) complex featured chelating amidinate ligands that converted from N,N' - to N,η^3 -arene coordination on manganese in the presence of a hydride source ($\text{K}[\text{BHET}_3]$).²²⁵ The resulting amidinato-manganese(II)

hydride dimer then readily reacts with N_2O to produce a bridging (μ -oxo)-manganese(III) dimer (Scheme 3.1).



SCHEME 3.1 Reaction between amidinato-manganese(II) hydride dimer and N_2O reported by Sita and coworkers.²²⁵

In a different system, Sita and coworkers showed a molybdenum(II) complex supported by Cp^* , carbonyl and NCN^- ligands that competitively cleaves the N-N or N-O bond in nitrous oxide (Scheme 3.2).^{226,227} The authors reported that cleavage of the N-N bond was favored and resulted in the formation of a molybdenum center with nitrosyl and isocyanate appendages ($[\text{Cp}^*\{\text{NCN}\}\text{Mo}(\kappa\text{-N-NO})(\kappa\text{-N-NCO})]$). The N-O bond cleavage occurred concertedly, and generated a molybdenum(IV) terminal oxo species that was characterized crystallographically.^{226,227}



SCHEME 3.2 Competitive cleavage of N-N or N-O bond by Mo(II) complex synthesized by Sita and coworkers.²²⁷

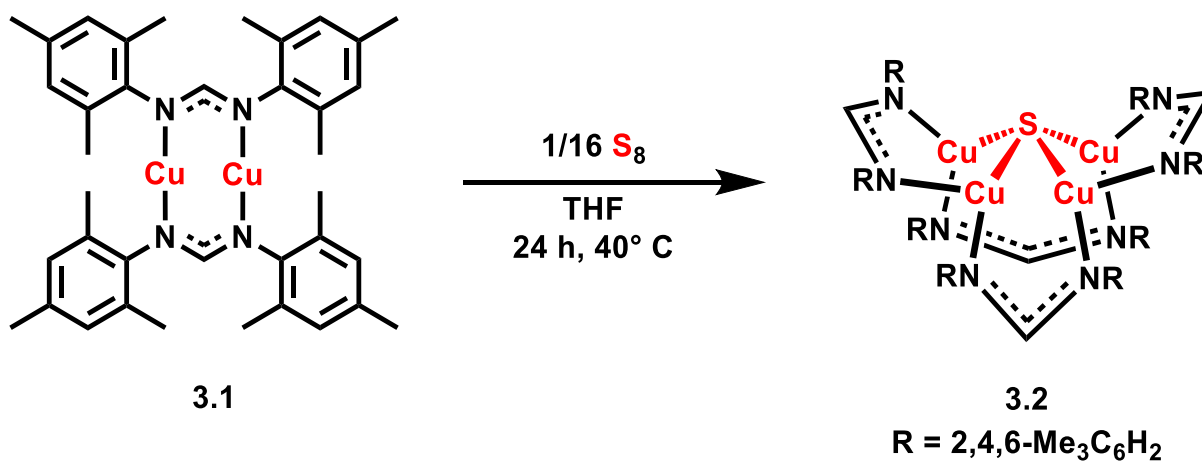
In the presence of CO however, the molybdenum(IV) oxo compound converted back to the starting molybdenum(II) complex by undergoing oxygen atom transfer to CO and subsequent release of CO₂. It was reported that once the oxo-species was recycled, it would again react with N₂O and continue to produce more of the N-N cleaved product; ultimately in 80% yield with no trace of the N-O cleaved product.²²⁷

The expansive applications of transition metal complexes supported by amidinate ligands have been highlighted and justify the utility of such ligands when performing chemical transformations. More importantly, copper-sulfide model systems comprised of N-donor ligands, similar to Cu₂⁺ ligation, proved attainable by using amidinato ligands. A full description of model synthesis, characterization and fascinating reactivity, introduce the only *structural and functional* model of Cu₂⁺ to date.

3.2 Synthesis of Compounds Using Amidinate Ligand

3.2.1 Synthesis of Model Complex 3.2

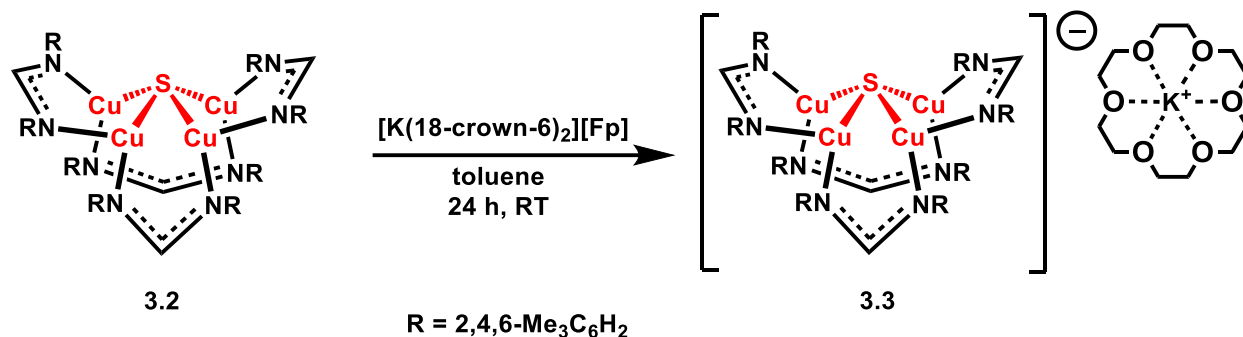
Synthesis of bis(2,4,6-trimethylphenyl)formamidine²²⁸ and the dicopper(I) precursor (**3.1**)^{213,229} have been previously reported. Upon stoichiometric addition of either elemental sulfur or triphenylantimony sulfide, the tetracopper-sulfide product **3.2**, was isolated as a dark purple solid in yields of 34% and 43% respectively (Scheme 3.3).²²⁹



SCHEME 3.3 Synthesis of complex **3.2**.

3.2.2 Synthesis of Model Complex 3.3

Electrochemical studies of complex **3.2** (detailed discussion in Section 3.4.1) revealed it could be reduced by one electron using a strong chemical reductant²³⁰ to form a new stable complex. Therefore, one equivalent of [K(18-crown-6)₂][Fp]²³¹ (Fp = cyclopentadienyliron dicarbonyl) was slowly added to a solution of **3.2** to produce the reduced complex, **3.3** in 45% yield (Scheme 3.4).²³²



SCHEME 3.4 Synthesis of complex 3.3.

3.3 Structural Characterization of Complexes 3.2 and 3.3

The solid state structures of model compounds **3.2** and **3.3** were determined by single crystal X-ray diffraction and are displayed in Figure 3.4. Both compounds feature: a tetracopper arrangement, a distorted trigonal planar geometry for all copper atoms, a single $\mu_4\text{-S}$ ligand appexed above the copper plane and four amidinate ligands bridging all copper atoms in an “up-down-up-down” pattern in relation to the Cu_4 plane. The crystal structure of **3.2** revealed two disordered Cu_4S moieties of symmetrical equivalence, similar to the shape of an octahedron (Appendix F). X-ray crystallographic analysis determined the disorder transpired from the $\mu_4\text{-S}$ ligand occupying alternating positions, either above or below the Cu_4 face, within independent molecules located in the crystalline material.²²⁹ In order to determine which of the two sets of disordered Cu_4S units pertained to more useful and accurate bond distances and angles, DFT calculations at the BVP86/LANL2TZ(f) level of theory were performed. Spin-unrestricted and symmetry-unrestricted DFT calculations for an optimized model of **3.2** (**3.2'**), that contained methyl substituents on the NCN^- ligands instead of mesityl groups, predicted short $\text{Cu}\cdots\text{Cu}$ distances of 2.45 Å and long $\text{Cu}\cdots\text{Cu}$ distances of 2.79 Å.²²⁹ These calculations were most similar to one disordered Cu_4S moiety within the crystal structure that displayed short $\text{Cu}\cdots\text{Cu}$ distances of 2.4226(6) Å and long $\text{Cu}\cdots\text{Cu}$ distances of 3.0353(6) Å. In agreement with the DFT calculated structure, one experimental Cu_4S unit was identified as containing the

most relevant structure description and is used exclusively in discussions throughout the remainder of this chapter.

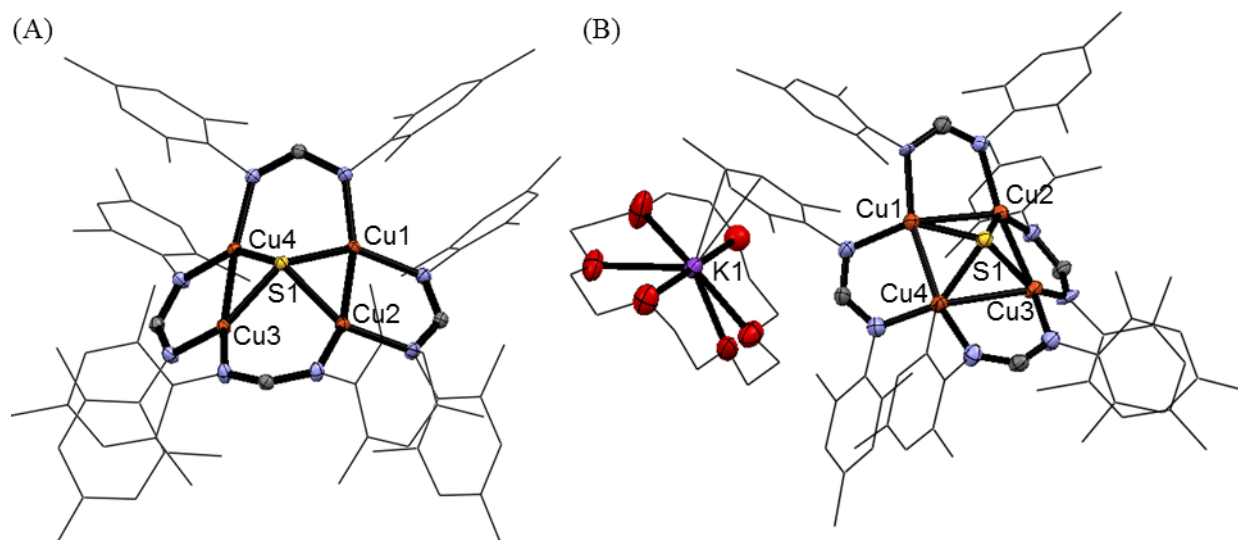


FIGURE 3.4 Crystal structures of complex (A) **3.2** showing only one disordered (μ_4 -S) unit and (B) **3.3** determined by X-ray crystallography. Reproduced from reference 229 with permission from the Royal Society of Chemistry, and reproduced with permission from Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. *J. Am. Chem. Soc.* **2016**, *138*, 13107. Copyright 2016 American Chemical Society. Complexes are displayed with 50% probability ellipsoids for the core atoms, amidinate ligands and counter ions. Substituents on amidinate nitrogen atoms are drawn as wireframe. All hydrogen atoms and co-crystallization solvents have been omitted for clarity. Atom colors include: Cu, brown; S, yellow; N, blue; O, red; C, gray.

Complex **3.2** displays C_{2v} symmetry through the S(1) atom and a highly ordered pseudo- S_4 local symmetry regarding the NCN^- scaffold. Interestingly, the excessive degree of symmetry observed in the structure of **3.2** originates from robust π -stacking between adjacent mesityl groups attached to separate NCN^- ligands. When examining complex **3.2** down the x-axis (Figure 3.5), the visual overlap of mesityl rings illustrates the intense π -stacking relationship between the amidinate ligand substituents (average mesityl $\cdots$ mesityl distance = ~ 3.36 Å).

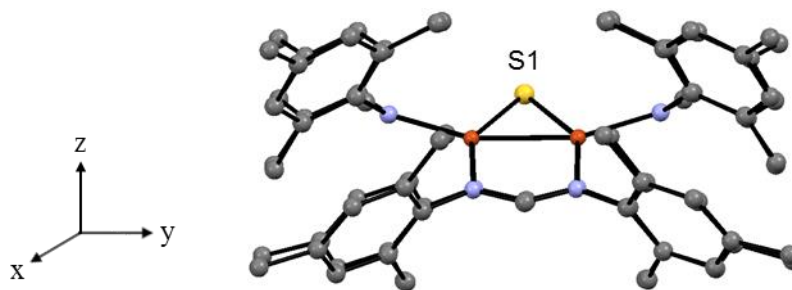


FIGURE 3.5 Ball and stick representation of complex **3.2** looking down the x-axis. Hydrogens and some of the element labels are omitted for clarity. Atom colors include: Cu, orange; S, yellow; N, blue; C, gray.

The highly symmetrical structure of **3.2** is not only evident in the solid state, but also in solution as demonstrated by ^1H NMR. At room temperature, the NMR spectrum revealed six discrete mesityl- CH_3 peaks that are related by both σ_{yz} and σ_{xz} mirror planes; highlighting the complete restriction in N- C_{aryl} bond rotation imposed by the π -stacking interaction of the neighboring mesityl substituents.

The absence of counter ions in the crystal structural of **3.2** suggested the complex is neutral and led to the assignment of a formal $2\text{Cu}^{\text{II}}2\text{Cu}^{\text{I}}$ oxidation state. Moreover, because **3.2** exhibits diamagnetism, validated by the NMR peaks appearing in the normal range, it is described as having a singlet ground state (2-hole, $S = 0$).²²⁹

In the crystal structure of **3.3** (Figure 3.4B), the counter ion $[\text{K}(18\text{-crown-6})]^+$, was found to be in close contact with the mesityl substituent of one NCN^- ligand and also with a separate mesityl ring attached to a symmetrically independent molecule of **3.3**, also within the crystal structure. The location of the counter ion encapsulated in the crown ether interrupts the π -stacking between adjacent mesityl rings and allows **3.3** to be less constrained and thus, slightly less symmetrical. The successful reduction of **3.2** by one e^- to generate **3.3**, allows for the formal oxidation state assignment to be $\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$ (1-hole, $S = 1/2$).²³²

3.3.1 Structural Comparisons Between Tetracopper-sulfide Compounds

Shown in Table 3.1, are neighboring $\text{Cu}\cdots\text{Cu}$ distances, Cu-S bond lengths and τ_4 features of tetracopper-sulfide complexes **3.2**,²²⁹ **3.3**²³² and **1.3**¹¹⁸ (Figure 3.6).

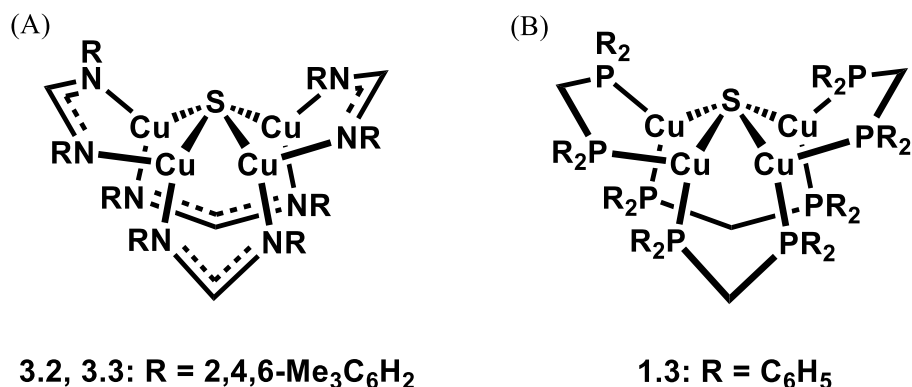


FIGURE 3.6 Core inorganic structures of tetracopper-sulfide complexes. (A) **3.2** and **3.3**. (B) Complex **1.3**.

TABLE 3.1 Comparison of Tetracopper-sulfide Structures

Structure Descriptor ^a	3.2 ^{bc}	3.3 ^c	1.3 ^d
Cu(1)···Cu(2)	2.4226(6)	2.502(1)	2.869(1)
Cu(2)···Cu(3)	3.0353(6)	2.809(1)	3.128(1)
Cu(3)···Cu(4)	2.4226(6)	2.532(1)	2.869(2)
Cu(4)···Cu(1)	3.0353(6)	2.831(1)	3.128(1)
Cu-(μ ₄ -S)	2.1790(6)	2.2144	2.268
	2.1790(6)	2.2155	2.267
	2.1812(6)	2.2178	2.268
	2.1812(6)	2.2181	2.267
τ ₄ ^{ce}	0.76	0.90	0.59

^a Bond distances are in Å.

^b See reference 229.

^c See reference 232.

^d See reference 118.

^e τ₄ measurement of μ₄-sulfide atom.¹⁸¹

Although the complexes in Figure 3.6 and Table 3.1 have different bridging ligands, important structural information based on the formal metal oxidation states can be inferred. As discussed in Section 1.2.1, the Cu₂* active site can be studied in the resting “1-hole” (Cu^{II}3Cu^I) state^{21,22,30,31} or active “fully reduced” state (4Cu^I).³³ These same electronic domains are represented in complexes **3.3** (1-hole) and **1.3** (fully reduced). Similarly, complex **3.2** represents the oxidation level characterized for the Cu₂ resting “2-hole” state (2Cu^{II}2Cu^I).^{21,22} Examination of the neighboring Cu···Cu distances in Table 3.1 for model **3.2**

compared to the Cu₂ resting state exposes much shorter distances for **3.2** (2.4226(6) – 3.0353(6) Å) than those reported for Cu₂ (2.830(6) – 3.405(2) Å).¹⁹ Instead, complex **3.2** more closely resembles the range of Cu···Cu distances observed for the resting Cu₂* state (2.535(3) – 3.356(5) Å).¹⁸ This is encouraging because hypothetically, Cu₂* accesses three different redox states during the two e⁻ reduction of N₂O (4Cu^I → Cu^{II}3Cu^I → 2Cu^{II}2Cu^I)²³² and a 2-hole Cu₂* intermediate has yet to be observed.¹⁵ In complex **3.3**, the short Cu···Cu distances (2.502(1) and 2.532(1) Å) match the short distances observed in the 1-hole resting Cu₂* structure (2.535(3) Å); but **3.3** differs greatly with respect to the long Cu···Cu distances compared to the 1-hole resting Cu₂* state (2.831(1) Å and 3.356(5) Å, respectively).

All complexes reported in Table 3.1 experience an alternating “short and long” pattern for their Cu···Cu distances. Interestingly, the short Cu···Cu distances further contract as oxidation state of the complex increases. Examination of the long Cu···Cu distances across the redox series however, display no such trend. The long Cu···Cu distances do decrease from **1.3** to **3.3**, but when moving from **3.3** to **3.2**, as shown in Figure 3.7A, the two long Cu···Cu distances in **3.3** *increase* after oxidation, as observed in **3.2**.²³²

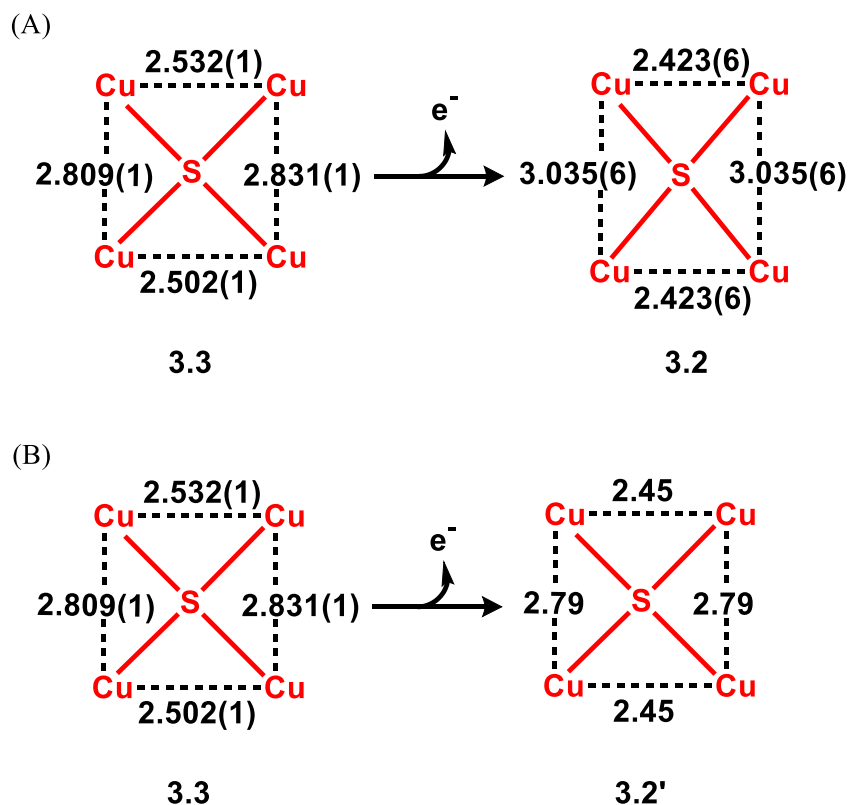


FIGURE 3.7 Change in Cu···Cu distances during oxidation of amidinate model complexes in Å. (A) Distances during the oxidation of **3.3** to **3.2**. (B) Distances during the oxidation of **3.3** to computed model **3.2'**.

The increase of two Cu···Cu distances in **3.2** may result from the robust π -stacking between neighboring mesityl rings forcing the observed Cu···Cu distances, compared to **3.3**. The π -stacking in **3.3** is disrupted by the cation ($[\text{K}(\text{18-crown-6})]^+$) that forms close contacts between mesityl rings (Figure 3.4B). Further evidence suggesting the π -stacking interaction as the cause for elongation in a pair of Cu···Cu distances comes from the computed model **3.2'**; where the mesityl rings are replaced with methyl groups and the resulting Cu···Cu distances are calculated to be 2.45 Å and 2.79 Å (Figure 3.7B).²²⁹ In the absence of π -stacking, the calculated structure of **3.2'** better follows the trend of decreasing Cu···Cu distances with increasing oxidation level suggested for the complexes in Table 3.1.

The Cu–S bond lengths also show a dependence on the oxidation level of a complex (Table 3.1). The addition of an electron across the redox series is accompanied by increasing Cu–S bond lengths: ~ 2.18

Å (**3.2**), ~ 2.20 Å (**3.3**), ~ 2.26 Å (**1.3**). However, the τ_4 parameter¹⁸¹ of the μ_4 -S ligand for the complexes in Table 3.1 does not exhibit a trend based on the formal oxidation state: $\tau_4 = 0.76$ (**3.2**), 0.90 (**3.3**) and 0.59 (**1.3**). In comparison to the structural attributes observed in the N_2OR centers, the τ_4 parameter of **3.2** best represents the sulfide distortion in its 2-hole congener, Cu_Z ($\tau_4 = 0.71$).²²⁹

In summary, the different oxidation levels observed for the model complexes listed in Table 3.1 accompanied variations detected within their individual structures. Examination of the $Cu \cdots Cu$ distances and Cu–S bond lengths of the model complexes introduced a contracting bond motif with increasing oxidation level. Speculations about the cause of this relationship will be discussed in further detail in upcoming sections. One exception was observed in a pair of $Cu \cdots Cu$ distances in **3.2** that *lengthened* after oxidation, likely due to the force of the mesityl substituents optimizing the π -stacking relationship. The sulfur geometry, exemplified by the τ_4 distortion, appears to be independent of the formal metal oxidation states; however, a see-saw geometry for the μ_4 -S ($\tau_4 = 0.71$ - 0.76) appears to be more prevalent in the 2-hole analogs (Cu_Z resting state and **3.2**).

3.4 Electronic Characterization of Complexes **3.2** and **3.3**

3.4.1 Electrochemical Properties of **3.2**

As briefly mentioned in Section 3.2.2, the concept for synthesizing a 1-hole model complex (**3.3**) materialized after the electrochemical behavior of **3.2** was studied.²²⁹ In addition, having model complexes that can access a range of stable oxidation states is desired for understanding the two e^- reduction of nitrous oxide in N_2OR .

The CV (cyclic voltammogram) for complex **3.2** in DCM and THF is displayed in Figure 3.8. Use of DCM as the electrolyte solvent provided the appropriate solvent window to scan higher oxidizing potentials; while THF was considered appropriate for accessing more reducing potentials.

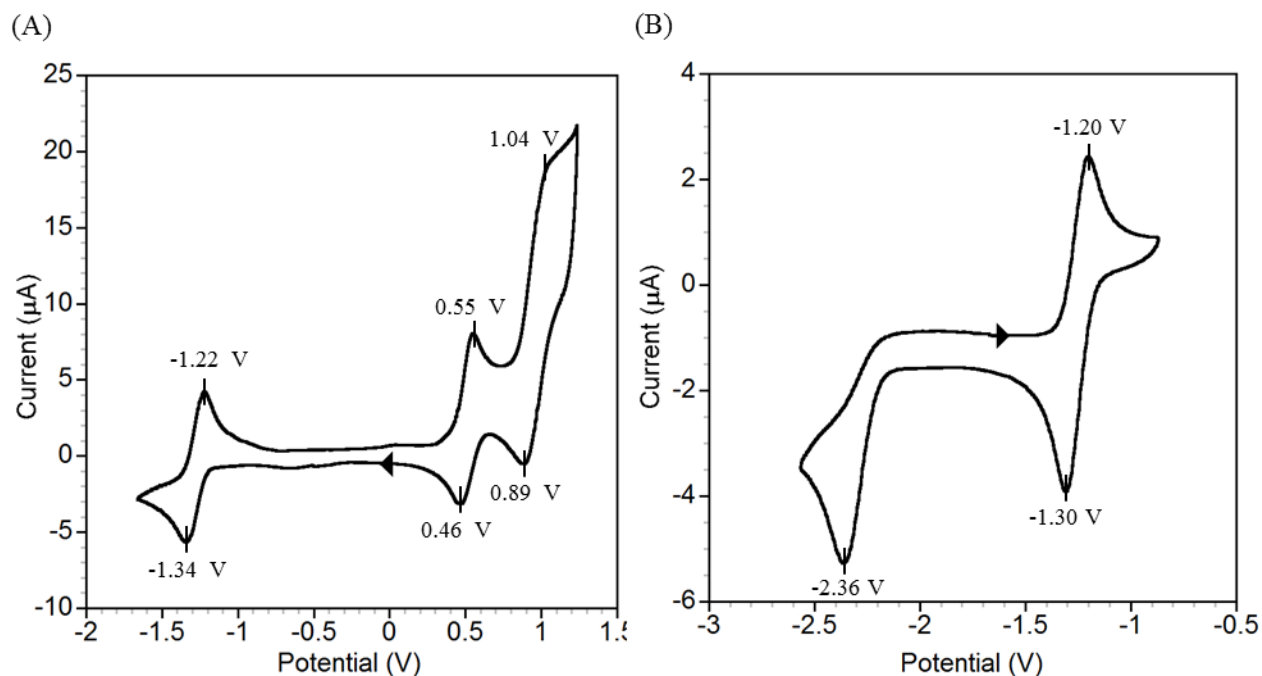


FIGURE 3.8 Cyclic voltammograms of **3.2** in 0.1 M $[\text{NBu}_4][\text{PF}_6]$ electrolyte solutions in (A) DCM and (B) THF. Recorded at 100 mV/s with platinum working electrode and Ag/AgNO_3 reference electrode. Potentials are versus $\text{Fc}^{+/0}$. Reproduced from reference 229 with permission from the Royal Society of Chemistry.

In DCM (Figure 3.8A), model **3.2** displayed one reversible redox couple at -1.28 V vs. $\text{Fc}^{+/0}$ and two quasi-reversible events at +0.51 V and approximately +0.96 V vs. $\text{Fc}^{+/0}$. When examined in THF (Figure 3.8B), the reversible couple was observed at -1.25 V vs. $\text{Fc}^{+/0}$ and an irreversible reduction wave was identified at approximately -2.36 V vs. $\text{Fc}^{+/0}$. The two quasi-reversible waves appearing at +0.51 V and +0.96 V vs. $\text{Fc}^{+/0}$ were assigned to be ligand-based oxidations due to several factors. Firstly, the electrochemical signature of the dicopper(I)-amidinate precursor (compound **3.1**) in DCM revealed the same two redox couples at +0.55 V and +0.97 V vs $\text{Fc}^{+/0}$ (Figure 5.63 in Section 5.2.10). Secondly, a similar dicopper(I) amidinate complex reported by Lee and coworkers demonstrated the same two quasi-reversible oxidation events in DCM at slightly lower potentials (+0.31 V and +0.79 V vs. $\text{Fc}^{+/0}$)²¹⁰ but still separated by ~0.45 V, as observed in the CV for compounds **3.1** and **3.2**. Additionally, Lee and coworkers performed DFT calculations on a mixed valent model ($\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$) of the dicopper-amidinate complex and examined the

Mulliken spin distribution for the redox-active molecular orbital (RAMO) and found the unpaired spin to be predominately delocalized over the two NCN^- ligands (total of 55%).²¹⁰ These reported findings, and similar characteristics within all the cyclic voltammograms, identified the NCN^- ligands as redox-active, thereby producing the oxidation couples shown in Figure 3.8A.

The reversible couple appearing at -1.25 V in THF was assigned the reduction of **3.2** by one electron and was further validated when a strong chemical reductant, such as $[\text{CpFe}(\text{CO})_2]^-$ ($E^{\circ\prime} = -1.8 \text{ V vs Fc}^{+/0}$),²³⁰ produced **3.3**. The irreversible cathodic wave appearing at -2.36 V is considered to be a two e^- reduced species (**3.2**²⁻). Generation of the doubly reduced species resulted in decreased current for the reversible couple at -1.25 V upon subsequent scans; suggesting slight decomposition to occur because of an unstable **3.2**²⁻ complex (Appendix G).

The electrochemical studies of **3.2** by cyclic voltammetry presented a rich collection of reversible redox behaviors and encouraged the synthesis of **3.3** as an exciting new model complex. In summary, (i) oxidation of **3.2** is facilitated by the NCN^- ligands, (ii) a reversible reduction of **3.2** allowed for the isolation of a 1-hole model, and (iii) two e^- reduction led to an irreversible species prone to decomposition after the onset of the second reduction. Using anionic nitrogen donor ligands assisted in allowing more active electrochemical behaviors to occur in copper-sulfide model compounds and more specifically, the use of amidinate ligands allowed for the stabilization of two redox partners with appropriate formal oxidation states to model the Cu_Z^* and Cu_Z resting states ($\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$ and $2\text{Cu}^{\text{II}}2\text{Cu}^{\text{I}}$, respectively).

3.4.2 Absorption Spectra Characteristics of **3.2** and **3.3**

Complexes **3.2** and **3.3** exhibit a truly beautiful dark purple color that manifests within the absorption spectrum. More importantly, the features arising from the visible absorption by the model complexes can be compared to the spectroscopic properties reported for the N_2OR centers. Fortunately, the absorption data has been reported for: both Cu_Z and Cu_Z^* resting states, the reduced Cu_Z active state and the $\text{Cu}_Z^0 \text{N}_2\text{O}$ reduction intermediate (introduced in Section 1.2.1).^{15,21,31,35,36} The absorbance data for models **3.2**, **3.3**²³² and relevant N_2OR sites are listed in Table 3.2.

TABLE 3.2 Absorbance Data for **3.2**, **3.3** and Related N₂OR Active Sites

	Cu _z ^{abc}	Cu _z ^{bd}	Cu _z ^{*abe}	Cu _z ^{0f}	3.2 ^g	3.3 ^g
Oxd. State ^h	2Cu ^{II} 2Cu ^I 2-hole	1Cu ^{II} 3Cu ^I 1-hole	1Cu ^{II} 3Cu ^I 1-hole	1Cu ^{II} 3Cu ^I 1-hole	2Cu ^{II} 2Cu ^I 2-hole	1Cu ^{II} 3Cu ^I 1-hole
λ_{max} (nm)	545 (635) ⁱ	685	640	671	561 (470) ⁱ	566
ϵ (M ⁻¹ cm ⁻¹)	10 000 ^j	3000	4000	2000	14 000	8600

^a Resting state.^b See reference 21.^c See reference 14.^d Fully reduced, active state.^e See reference 15.^f See reference 36.^g See reference 232.^h Formal oxidation state.ⁱ Shoulder.^j For main peak.

In general, the highest energy transitions observed for the species reported in Table 3.2 follow: Cu_z (2-hole, 545 nm)¹⁴ > **3.2** (561 nm)²²⁹ > **3.3** (566 nm)²³² > Cu_z^{*} (1-hole, 640 nm)²¹ > Cu_z⁰ (1-hole, 671 nm)³⁶ > Cu_z (1-hole, 685 nm).²¹ In all the N₂OR sites, the absorption bands are reported to be the result of ligand to metal charge transfer (LMCT) from μ_4 -S $\rightarrow$ Cu.^{15,21,35} Model complexes **3.2** and **3.3** share a high-energy CT with the Cu_z 2-hole. Apart from similar absorption energies and formal oxidation states, model **3.2** and the Cu_z 2-hole also feature the highest extinction coefficients: 14 000 M⁻¹ cm⁻¹ and 10 000 M⁻¹ cm⁻¹ respectively.^{21,229} Solomon and coworkers suggested the large intensity observed for the Cu_z 2-hole transition a result of several overlapping LMCTs; where the two most intense transitions likely come from the μ_4 -S being able to transfer charge to *two* different electron holes.²¹ This suggests the ground state of **3.2** may be a broken symmetry singlet, with α and β electron holes, producing two overlapping CTs. One could argue the two overlapping peaks responsible for the high intensity of the Cu_z 2-hole transition to possibly come from the two different sulfide ligands (μ_2 -S and μ_4 -S) concertedly participating in CT, but model **3.2** demonstrates similar absorption energy and intensity *without* a second bridging sulfide. The steep decrease in absorption intensity upon reduction of the Cu_z 2-hole to Cu_z 1-hole (ϵ = 10 000 M⁻¹ cm⁻¹ and 3000 M⁻¹ cm⁻¹, respectively) is also observed in the transition energy intensity from the 2-hole model **3.2** (14 000 M⁻¹

$^1 \text{ cm}^{-1}$) to the 1-hole **3.3** ($8600 \text{ M}^{-1} \text{ cm}^{-1}$), indicating the charge transfer to only one electron hole.²¹ Analogously, all absorption energy intensities for the 1-hole copper-sulfide centers reported in Table 3.2 fall within $\sim 4500 \text{ M}^{-1} \text{ cm}^{-1}$.^{15,36}

It is also evident among the N_2OR species that the 1-hole centers absorb at lower energies ($\sim 650 - 685 \text{ nm}$) compared to **3.3** (566 nm). Considering only the 1-hole N_2OR centers in Table 3.2, the highest energy transition follows: $640 \text{ nm Cu}_Z^* > 671 \text{ Cu}_Z^0 > 685 \text{ nm Cu}_Z$. The red-shifted energy observed for the active Cu_Z^0 intermediate compared to the resting Cu_Z^* state is proposed to occur as the result of increased electron density on the Cu_{IV} atom due to the bound terminal hydroxide molecule; differing from the $\mu_2\text{-OH}^-$ observed in the Cu_Z^* resting state.^{15,36} In a similar fashion, the difference in energy absorption between Cu_Z^* 1-hole (640 nm) and Cu_Z 1-hole (685 nm) is projected to arise from increased delocalization of electron spin on the more covalent $\mu_2\text{-SH}^-$ ligand in Cu_Z , and induces a decrease in the energy splitting.²¹ It appears that all the 1-hole N_2OR centers show sensitivity regarding the nature of the edge ligand and its presence could play a key role in lowering the transition energies to $\sim 670 \text{ nm}$ within the absorption spectra.^{21,36} Conversely, complex **3.3** has a higher energy transition, despite also having a single electron hole, and a plausible explanation could be the lack of a bridging or terminal edge ligand.

Time-dependent DFT (TD-DFT) calculations on a model of the 2-hole (**3.2'**) and 1-hole (**3.3'**) amidinate complexes were carried out, by replacing the mesityl rings with methyl groups, to further probe the CT observed experimentally.²³² Curiously, the absorption maximum of **3.2'** was calculated to occur at a higher energy ($\sim 467 \text{ nm}$) than was experimentally observed. The calculated CT intensity for **3.2'** ($\epsilon = 16000 \text{ M}^{-1} \text{ cm}^{-1}$) did prove to be consistent with the experimentally observed intensity. The TD-DFT calculations for **3.3'** proved to be spot on compared to the experimental absorption characteristics displayed by **3.3**; calculating the energy maximum at 578 nm and correctly predicting the sharp decrease in peak intensity ($\epsilon = 6000 \text{ M}^{-1} \text{ cm}^{-1}$).

The red-shift in transition energy upon reduction, that is observed for Cu_Z ($545 \text{ nm} \rightarrow 685 \text{ nm}$), was also calculated to occur for **3.2'** and **3.3'** ($467 \text{ nm} \rightarrow 578 \text{ nm}$), but the experimental data displayed a

much smaller red-shift in absorption energies (561 nm $\rightarrow$ 566 nm).²³² In another synthetic N₂OR model system, **1.2** (previously shown in Figure 1.6B and Figure 2.5C) synthesized by Murray and coworkers, an equally large energy shift is observed in the visible region of the absorption spectrum upon reduction.¹¹⁷ More specifically, the authors reported that **1.2** (formally a 2Cu^{II}Cu^I system) exhibited an energy transition at very low energy (806 nm) and upon reduction to a one electron reduced species (Cu^{II}2Cu^I), the new energy transition was *blue-shifted* to higher energy (686 nm). The absorption maxima for the **1.2** reduced species falls in the range of absorption energies displayed by all other 1-hole N₂OR centers shown in Table 3.2 (~ 650 – 685 nm). The authors were unable to obtain a crystal structure of the 1-hole **1.2** complex; therefore, any structural changes upon reduction of **1.2** cannot be definitively stated as the cause for the observed blue-shift in energy. The change in absorption energy between redox partners is observed in **1.2**, Cu₂ and calculated to occur for **3.2'** by TD-DFT. It remains curious that complexes **3.2** and **3.3** do not experience large absorption energy changes experimentally due to their different oxidation states; however, many spectroscopic similarities exist between the model complexes and the N₂OR clusters. The absorption energy and intensity of **3.2** coincides with the energy and intensity reported for the Cu₂ 2-hole center, and the decrease in absorption intensity for **3.3** matches the reported intensities of other 1-hole N₂OR centers. These spectroscopic studies between model complexes and the enzyme active sites provide additional information for interpreting the electronic structure and molecular design of uniquely constructed redox centers within enzymatic systems.

3.4.3 Electron Paramagnetic Resonance Studies of 3.3

The presence of a single electron hole in complex **3.3** leaves an unpaired electron that is susceptible to an external magnetic field and EPR spectroscopy is a valuable technique to study the electronic environment of the singly occupied molecular orbital (SOMO) within $S = \frac{1}{2}$ systems. Complex **3.2** also appeared to be EPR active and displayed a temperature dependent magnetic moment in solution studied by Evans' Method Analysis of the ¹H NMR (Section 5.2.8, Figures 5.53 and 5.54). However, rigorously purified samples of **3.2** were reexamined by EPR, in addition to magnetometry measurements (SQUID), and revealed **3.2** as being diamagnetic and the previous data suggesting paramagnetism is credited to a

mononuclear copper(II) byproduct isolated during the synthesis of **3.2** (Figure 5.70 in Section 5.2.10).²³²

Complex **3.3** was studied by X- and Q-band EPR and the subsequent spectra and data are shown in Figure 3.9 and reported in Table 3.3; along with other useful paramagnetic compounds for comparison.

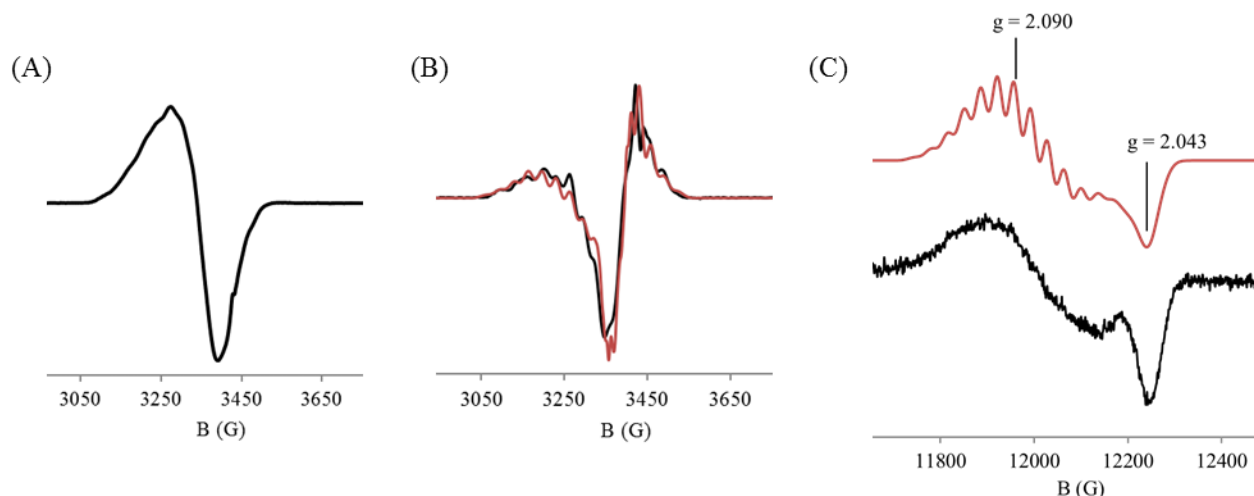


FIGURE 3.9 EPR data for **3.3** in 2-MeTHF. (A) First derivative X-band spectrum (9.632 GHz, 9.9 K). (B) Second derivative X-band experimental (black) spectrum with simulation (red) overlay. (C) First derivative Q-band experimental (black) spectrum with simulation (red) curve (34.99 GHz, 123 K). Reproduced with permission from Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. *J. Am. Chem. Soc.* **2016**, *138*, 13107. Copyright 2016 American Chemical Society.

TABLE 3.3 EPR Data for 1-hole Cu_2 , Cu_2^* and Cu_2^0 , **3.3** and **1.2**

	Cu_2^{ab}	Cu_2^{*bc}	Cu_2^0d	3.3 ^e	1.2 ^f
Oxd. State ^g	$1\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$	$1\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$	$1\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$	$1\text{Cu}^{\text{II}}3\text{Cu}^{\text{I}}$	$1\text{Cu}^{\text{II}}2\text{Cu}^{\text{I}}$
	1-hole	1-hole	1-hole	1-hole	1-hole
$g_{\parallel}$	2.152	2.160	2.177	2.043	2.095 ^h
$g_{\perp}$	2.042	2.043	~ 2.05	2.090	
$A_{\parallel}^i$	168	182, 69	125	15	97 ^h
$A_{\perp}^i$	60	75, 60		100	

^a Fully reduced, active state.

^b See reference 21.

^c Resting State.

^d See reference 36.

^e See reference 232.

^f See reference 117.

^g Formal oxidation state.

^h Isotropic signal.

ⁱ In MHz.

The X-band spectrum of **3.3** in 2-methyltetrahydrofuran at 9.9 K revealed an axial signal (Figure 3.9A), and the g values were obtained by the better resolved Q-band spectrum shown in Figure 3.9C ($g_{\perp} = 2.090$ and $g_{\parallel} = 2.043$).²³² Metal hyperfine splitting lines were observed in the high- and low-field regions of the X-band spectrum and simulated fits of the X- and Q-band determined the copper hyperfine coupling constants to be $A_{\perp} = 100$ MHz and $A_{\parallel} = 15$ MHz. The second derivative X-band spectrum revealed a 13-line splitting pattern, confirmed by the agreement in fit between simulated and experimental spectra (Figure 3.9B). The 13-line splitting pattern reveals delocalization of the electron over four equivalent copper atoms ($I_{\text{Cu}} = 3/2$).

The EPR parameters reported for the N_2OR species with $S = 1/2$ (fully reduced Cu_Z , resting Cu_Z^* and Cu_Z^0) remain fairly consistent with one another in both signature and intensity (Table 3.3).^{21,36} The signal in the X-band spectrum for Cu_Z^* was reported by Solomon and coworkers as a broad axial signal with evidence of metal hyperfine splitting.³² Accurate g values were obtained by Q-band EPR and revealed $g_{\parallel} > g_{\perp} > 2.0$, indicating the electron hole resides in an orbital with substantial metal d-character (specifically, $d_{x^2-y^2}$).³² To account for the hyperfine splitting pattern observed in the X-band, Solomon and coworkers simulated fits for the X- and Q-band spectra for two inequivalent copper atoms and reported the difference in magnitude between the two $A_{\parallel}$ values (182 and 69 MHz) a representation of the spin distribution being more localized on one of the two inequivalent copper atoms. Therefore, the best description of the unpaired electron in Cu_Z^* is reported as a semi-delocalization between a minimum of two copper atoms. The 1-hole Cu_Z was reported as having similar g and A values to Cu_Z^* (Table 3.3) but three equivalent $A_{\parallel}$ and $A_{\perp}$ values were obtained from the simulated fit of the second derivative X-band spectrum that featured the experimentally observed hyperfine splitting pattern.²¹ The nature of the unpaired spin in the 1-hole Cu_Z system is described as a delocalization over three copper atoms. Finally, the Cu_Z^0 intermediate was reported by Solomon and coworkers as sharing the same axial shape in the X-band EPR envelope as observed for Cu_Z^* , but indicated two equivalent $A_{\parallel}$ values resulted from the simulated fit of the experimental 6-line hyperfine splitting pattern observed.³⁶ Thus, the unpaired spin for the Cu_Z^0 1-hole intermediate is an equal delocalization between two copper atoms.

Inspection of the EPR data for **3.3** in comparison to the N₂OR centers shows: $g_{\perp} > g_{\parallel}$, lower g tensor values and smaller hyperfine splitting constants. The presence of a larger $g_{\perp}$ value in **3.3** suggests the SOMO (location of the unpaired electron) is not pure $d_{x^2-y^2}$, as described for Cu_Z* and Cu_Z⁰.^{32,36} The considerably small $g_{\perp}$ and $g_{\parallel}$ values for **3.3** suggests the unpaired spin is highly delocalized among the constituents that constitute the character of the SOMO.²³³ In other mixed valence copper complexes synthesized by Peters and coworkers, equally small g values ($2.0023 < g < 2.15$) were obtained in systems demonstrating a high degree of unpaired spin delocalization mediated through the auxiliary ligands.^{28,234} In the reduced **1.2** species reported by Murray and coworkers, the isotropic EPR signal also afforded a small g value ($g = 2.095$) and a 10-line splitting pattern from delocalization over three equivalent copper atoms; which is likely facilitated through the covalent μ_3 -S ligand.¹¹⁷ The 13-line splitting pattern observed for **3.3** further supports the delocalization of the unpaired spin over four copper atoms so that each metal center shares the spin distribution and electron hole equally. Low g values in cupric compounds are also inversely dependent on large energy gaps between the $d_{xy} \rightarrow d_{x^2-y^2}$ orbitals, as is the case for the low g values reported by Solomon and colleagues for the Cu_Z* and Cu_Z⁰ 1-hole forms.^{15,21,30,36} Treatment of the EPR data, to determine if the ligand field splitting (ΔE $d_{xy} \rightarrow d_{x^2-y^2}$) is responsible for low g values, is more accurate for monocupric species; as opposed to multinuclear copper $S = \frac{1}{2}$ compounds. Indeed, Cu_Z* has shown the unpaired spin to localize over mainly one copper atom so direct measurement of the Cu $d_{xy} \rightarrow$ Cu $d_{x^2-y^2}$ energy transition is applicable and considerably large ($\sim 18\,000\text{ cm}^{-1}$).^{21,30} However, in delocalized systems (such as Cu_Z 1-hole and **3.3**) the ground state is probably a combination of multiple sets of Cu d-orbitals and pinpointing the ligand field energy transition to an orbital containing pure Cu $d_{x^2-y^2}$ is subject to individual interpretation. Although a high energy transition from a combination of predominantly Cu d_{xy} orbitals to a combination of predominantly Cu $d_{x^2-y^2}$ orbitals could be the cause for the lower g values observed for **3.3**, it is more likely related to the delocalization factors; which are also attributed to the low g values reported for the Cu_Z 1-hole. Delocalization of the unpaired spin over three copper atoms and addition of a covalent μ_2 -SH⁻ edge ligand are responsible for the low g values reported for the Cu_Z 1-hole; while the $d_{xy} \rightarrow d_{x^2-y^2}$ energy transition was unidentifiable from simulations of the absorption and MCD

spectra.²¹ In a similar fashion, **3.3** displays delocalization over four copper atoms and the added covalency from the NCN^- ligands are comparable to the nature of the unpaired spin in the Cu_2 1-hole.

The smaller A values in **3.3** also indicate a high degree of delocalization⁷¹ and suggest the unpaired electron has minimal interaction with the copper atoms.^{235–237} As the electron is being delocalized, the amount of spin density on the copper atoms will directly scale with the hyperfine coupling constants. For comparison, blue copper proteins, such as plastocyanin, reveal small $A_{\parallel}$ values (189 MHz) as the result of unpaired spin primarily located on the S cysteine residue, which was verified by the large sulfur character located in the SOMO (38%) determined by S K-edge X-ray absorption spectroscopy (XAS).²³⁸ The electron transfer site in N_2OR , Cu_A is reported to show $A_{\parallel} = 132$ MHz and has 29% sulfur (cysteine residue) character in the SOMO determined XAS.^{15,73} In a different system synthesized by Tolman and coworkers, a mononuclear copper(II) thiolate complex supported by a β -diketiminato ligand, reported a higher hyperfine coupling constant, $A_{\parallel} = 332$ MHz, more consistent with typical monocupric coordination compounds.¹¹² Moreover, in Tolman's complex the copper(II) center is three coordinate (ligated by N-donor and thiolate ligands) similar to **3.3**, but the absence of additional copper atoms may limit the thiolate ligand from participating as a covalent delocalization pathway for distributing the unpaired spin; thus resulting in the higher copper hyperfine coupling constant.

In conclusion, the EPR studies of **3.3** provided valuable insight into the nature of electron density residing in the SOMO. The lower g and A parameters obtained from the X- and Q-band simulations indicated a system that allows a high degree of spin distribution over all four copper atoms equally.²³² Furthermore, the delocalization is likely facilitated by the μ_4 -S ligand and a large amount of sulfide character within the SOMO is proposed. These conclusions help identify two potential resonance systems for the inorganic core in **3.3**: $(4\text{Cu}^{1.25}\text{S}^{2-})$ or $(4\text{Cu}^{\text{I}}\text{S}^-)$.²³² Consideration of one resonance form being more accurate than the other required a deeper investigation within the electronic structure of **3.3** and anticipated a certain degree of resemblance to the electronic structure in the redox partner **3.2**; therefore, DFT calculations were pursued.

3.4.4 Density Functional Theory Calculations for **3.2** and **3.3**

As mentioned in Section 3.4.2, two computational models, **3.2'** and **3.3'**, were optimized in the ground state at the B3LYP/LANL2TZ9(f) level of theory for spin-unrestricted and symmetry-unrestricted systems and the mesityl rings on the NCN^- ligands were replaced with methyl groups.^{229,232} The computed bond lengths and bond angles of **3.2'** and **3.3'** were in agreement with the experimental data (Table 5.19 in Section 5.2.21). Because these complexes are redox partners, the LUMO in **3.2'** is the site that receives electrons during reduction and should bare resemblance to the SOMO in **3.3'**. The calculated highest occupied molecular orbital (HOMO) for **3.2'** and spin distribution plot of the SOMO for **3.3'** are shown in Figure 3.10.

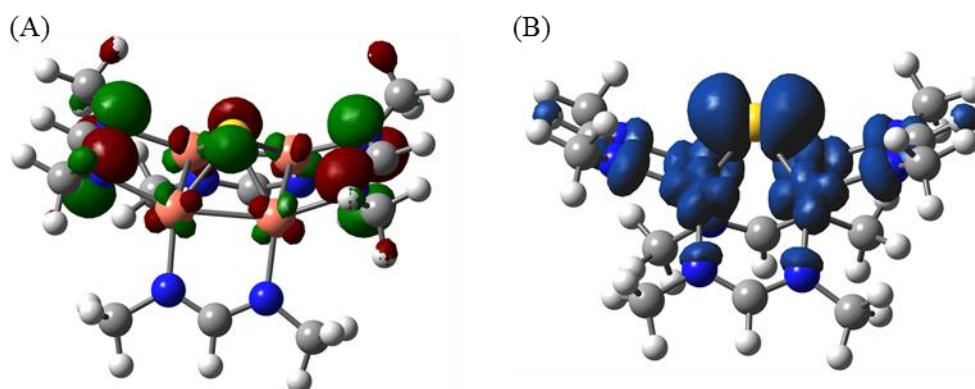


FIGURE 3.10 DFT calculated (A) HOMO for **3.2'** (0.04 isovalue) and (B) Mulliken spin density plot of **3.3'** (0.001 isovalue). Figure 3.10A reproduced from reference 229 with permission from the Royal Society of Chemistry. Figure 3.10B reproduced with permission from Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. *J. Am. Chem. Soc.* **2016**, *138*, 13107. Copyright 2016 American Chemical Society.

The ground state of **3.2'** is best described as a closed-shell singlet, as opposed to a singlet arising from antiferromagnetic coupling between two $\text{Cu}^{1.5}\text{Cu}^{1.5}$ units. Consideration for a closed-shell singlet in **3.2'** was based on the following calculation observations: (i) optimized structures for the two $\text{Cu}^{1.5}$ entities calculated α and β molecular orbitals that were degenerate and identical²²⁹ and (ii) the broken symmetry

singlet was calculated to be ± 2 kcal/mol higher in energy than the closed-shell singlet.²³² Although the electronic absorption data for **3.2** did not suggest a closed-shell system, the small energy difference calculated between closed-shell and broken-symmetry singlet states indicate higher calculations are needed to accurately represent **3.2**. Thus, the current observations led to the closed-shell ground state description for **3.2** at this time.

The calculated orbital population within the HOMO and LUMO of **3.2'** and spin distribution analysis for the SOMO in **3.3'** are reported in Table 3.4. Examination of the HOMO reveals two NCN⁻ ligands as the dominating contributors to 60% of the orbital population (15% each N). Much smaller populations were calculated for the four copper atoms (16% total 3d Cu) and sulfur (7% 3p S). The spin distribution calculated for the SOMO in **3.3'** revealed substantial spin density on the sulfur (32%); more than any other atom located in the inorganic core. The spin distribution was also calculated to be delocalized equally over all four copper atoms (10% each, 40% total Cu).

These calculations suggest that the highest fully occupied molecular orbital for both redox partners is mainly ligand based (60% total NCN⁻), while the SOMO consists of mainly copper-sulfur character (72% total).^{229,232} Discussion of how these DFT calculations are reflected within the experimental data will be discussed in Section 3.5.

TABLE 3.4 DFT Calculated MO Population and Spin Density Distributions for 1-hole Cu₄S Clusters^a

	3.2' HOMO ^b	3.2' LUMO ^b	3.3' SOMO ^c	Cu _Z * ^d	Cu _Z ^d	Cu _Z ^{0e}
Cu _I	4 %	12 %	10 %	26 %	17 %	7 %
Cu _{II}	4 %	12 %	10 %	9 %	11 %	15 %
Cu _{III}	4 %	12 %	10 %	4 %	6 %	3 %
Cu _{IV}	4 %	12 %	10 %	13 %	10 %	32 %
S	7 %	21 %	32 %	31 %	34 %	21 %
NCN ⁻	30 %	6 %	6 % ^f			
NCN ⁻	30 %	6 %	6 % ^f			

^a Spin densities are estimated from Mulliken population analysis.

^b See reference 229.

^c See reference 232.

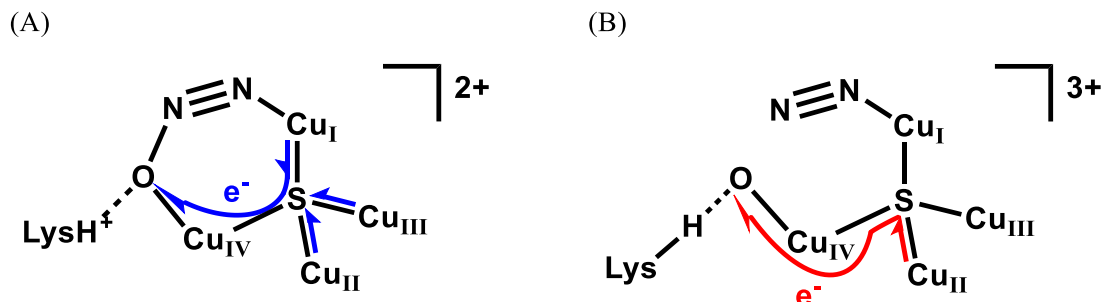
^d See reference 21.

^e See reference 36.

^f Appendix H.

DFT calculations on the spin density distribution in the 1-hole Cu_Z and Cu_Z^* , with $\mu_2\text{-SH}^-$ and $\mu_2\text{-OH}^-$ bridging ligands respectively, and the Cu_Z^0 form with a terminal hydroxide molecule on Cu_{IV} , have been reported by Solomon and coworkers, and are also represented in Table 3.4.^{21,36} The calculations on the 1-hole Cu_Z and Cu_Z^* centers displayed the highest unpaired spin density residing on the $\mu_4\text{-S}^{2-}$ ligand: Cu_Z 34% and Cu_Z^* 31%.²¹ Interestingly, the Cu_Z^0 computed model showed the highest electron density residing over Cu_{IV} (32%) instead of the $\mu_4\text{-S}^{2-}$ atom (21%).³⁶ However, Solomon suggested these calculations overestimated the terminal hydroxide ligand field on Cu_{IV} ; further evidenced by the absence of two computed copper spin densities that are equivalent, in order to parallel the EPR data observed. Similar sulfide spin density was calculated for the 1-hole **3.3'** compared to the computed values reported for 1-hole Cu_Z^* and Cu_Z sulfide centers. Specific to 1-hole copper-sulfide clusters, it could be speculated that one reason the unpaired spin resides mainly on the $\mu_4\text{-S}^{2-}$ ligand is because it is a very covalent ligand that efficiently delocalizes electron spin across multiple non-bonded metal centers.¹⁵ The remaining spin distribution in Cu_Z^* was calculated be: 26% on Cu_{I} , 9% on Cu_{II} , 4% on Cu_{III} and 13% on Cu_{IV} .²¹ These spin densities for Cu_Z^* are in agreement with the EPR data discussed in Section 3.4.3; specifically, the unpaired electron is semi-delocalized over two copper atoms, Cu_{I} and Cu_{IV} .³²

Collectively, these calculations reveal the unpaired spin in the 1-hole clusters (Cu_Z^* resting state, Cu_Z fully reduced, Cu_Z^0 and **3.3'**) resides mainly over the inorganic core; total Cu_4S spin densities of 83% (Cu_Z^*), 78% (Cu_Z), 78% (Cu_Z^0) and 72% (**3.3'**). Clearly, the electron transfer between the N_2OR centers and N_2O during reduction, occurs with large involvement from several copper atoms and the covalent $\mu_4\text{-S}^{2-}$ ligand. Indeed, DFT calculations conducted on Cu_Z^* by Solomon and coworkers led the authors to suggest the first electron donated to N_2O in the transition state is delocalized over all four copper atoms and the $\mu_4\text{-S}^{2-}$ atom acts as the superexchange pathway, as represented in Scheme 3.5A.³⁶



SCHEME 3.5 Delocalization of charge, via $\mu_4\text{-S}^{2-}$, during two electron reduction of N_2O proposed by Solomon and coworkers.³⁶

After the N–O bond is cleaved, Solomon proposed charge transferred from Cu_{II} to Cu_{IV} , via the $\mu_4\text{-S}^{2-}$ moiety, occurs concurrently with the PCET (Scheme 3.5B). Therefore, both electrons are donated through Cu_{IV} because the sulfide atom is an efficient, covalent ligand capable of delocalizing charge and the resulting 2-hole reaction intermediate contained calculated electron holes over $\text{Cu}_{\text{I}}/\text{Cu}_{\text{III}}$ and $\text{Cu}_{\text{II}}/\text{Cu}_{\text{IV}}$.³⁶ Not only do these calculations support the notion that multielectron reduction reactions require sufficient superexchange pathways, but also the *importance of having four copper atoms* arranged within the Cu_Z^* active site. More specifically, the Cu_{II} and Cu_{III} atoms are theorized to be important contributors of electron density during reduction; even though there is no direct participation in substrate activation.^{36,38} Furthermore, the presence of four copper atoms prevents protonation of the $\mu_4\text{-S}^{2-}$ ligand after the first e^- reduction, which was computed by Solomon and coworkers as favorable; thereby hindering the effectiveness of the sulfide atom for delocalizing spin across the non-bonded metal centers.^{36,38} These types of speculations present synthetic model studies with unique opportunities to independently examine the importance of each atom within a tetracopper-sulfide cluster and determine what molecular units are required for N_2O activation and reduction.

Conclusively, the DFT calculations for **3.2'** suggest the HOMO is mainly NCN^- based, and more specifically, populated by *two* NCN^- ligands; while the calculations for **3.3'** point towards a delocalized system promoted mostly by the sulfide atom. From the calculations discussed, the extensive degree of sulfur

and copper participation shown in **3.3'**, Cu_z* resting state, Cu_z⁰ and Cu_z active state, effectively identifies the redox-active components within these complexes. Moreover, the structural and spectroscopic features observed within the data during characterization of the amidinate model compounds can be rationalized based on the MO depictions provided by DFT calculations.

3.5 Interpretations of Collected Experimental and Computational Data

The collection of structural and spectroscopic data for complexes **3.2** and **3.3**, reveal intrinsic properties that manifest within the DFT calculated structures. The goal of this section is to suggest interpretations of the collected data from all characterization techniques discussed thus far and highlight the agreement between these experimental observations and the DFT calculations.

In Section 3.3 the structural information obtained by single crystal X-ray diffraction for complexes **1.3**, **3.3** and **3.2** displayed several analogies to information obtained by DFT calculations. Shown in Figure 3.11A are the average Cu–S bond lengths and average Cu···Cu distances of the rectangular sides in the Cu₄ base, for complexes **1.3**,¹¹⁸ **3.3**,²³² **3.2**.²²⁹ Moving across the redox series, it becomes apparent that as oxidation occurs, the Cu–S bonds and Cu···Cu distances decrease (exception in **3.2** results from imposed π -stacking discussed in Section 3.3.1). An explanation for the cause of these structural trends will come from a deeper examination of the MO plots calculated by DFT.

The Mulliken spin distribution calculated for complex **3.3'** (Section 3.4.4) revealed substantial sulfide and copper character in the SOMO (72% spin density on Cu₄S) and examination of the MO diagram shown in Figure 3.11B, displays the interaction between the S(p_x) and Cu(d_{xz}) orbitals to be antibonding.²³² Similarly, DFT calculations performed by Yam and coworkers on **1.3** reported a 59% Cu₄S contribution in the HOMO as partially Cu(s,p)-S bonding and Cu(d)-S antibonding.¹²¹ Therefore, as this orbital gets oxidized, the Cu–S bond lengths decrease due to the removal of electrons in a Cu-S σ^* orbital.

The SOMO of **3.3'** in Figure 3.11B also reveals that each Cu(d_{xz}) orbital experiences both a bonding and antibonding interaction with its two different neighboring Cu(d_{xz}) orbitals. These interactions likely cause the long-short-long-short pattern observed for the Cu···Cu distances reported in Table 3.1 and discussed in Section 3.3.1. Furthermore, the decrease of all Cu···Cu distances related to the increasing

oxidation level of the model complexes could result from the subtraction of electrons from an orbital containing Cu(d_{xz}) antibonding character. It is also reasonable to consider that as the Cu–S bond lengths shorten when moving to higher oxidation states, the copper atoms naturally get drawn closer together and further contribute to the decrease in Cu $\cdots$ Cu distances.

Collectively, these observations suggest that the HOMO in **1.3**, SOMO in **3.3** and LUMO in **3.2** represent a single RAMO that is conserved in all three redox partners and contains similar degrees of Cu–S, Cu–Cu antibonding interactions and some Cu–Cu bonding character.

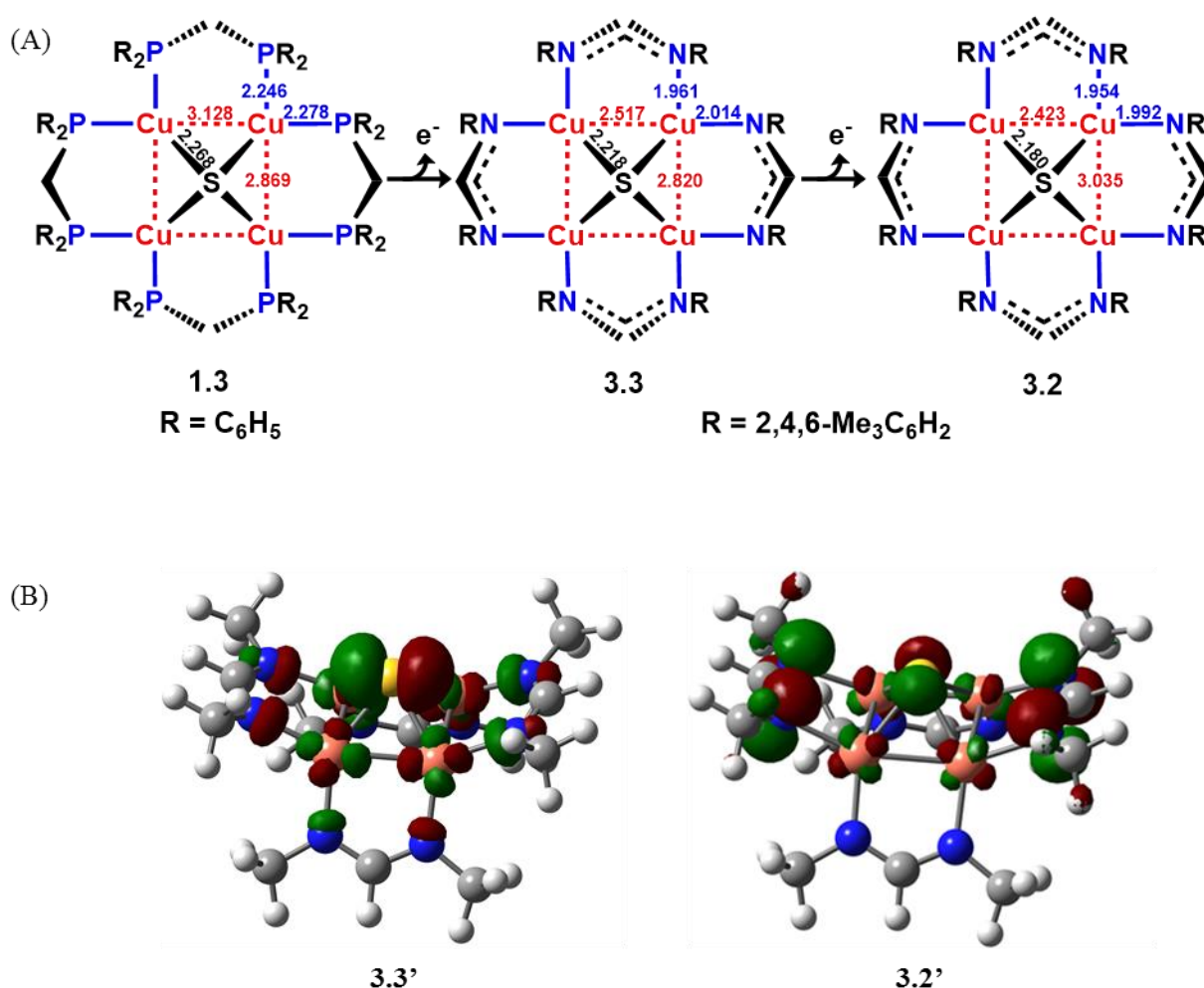


FIGURE 3.11 Structural and electronic comparisons between model complexes. (A) Average bond lengths and distances (shown in Å) for some structural features in **1.3**, **3.3** and **3.2**. (B) MO surfaces for **3.3'** (SOMO) and **3.2'** (HOMO) determined by DFT calculations, reproduced from reference 229 with permission from the Royal Society of Chemistry.

It is also obvious from Figure 3.11A that as oxidation occurs from **3.3** to **3.2**, the average Cu–N bonds also decrease. The decrease in Cu–N bond lengths upon oxidation could be the result of Cu(II) atoms being smaller than Cu(I), but more interestingly, close inspection of the average Cu–N bonds belonging to the two NCN[−] ligands “pointing up” (in relation to the Cu₄S unit) appear longer than the two NCN[−] ligands “pointing down” in both **3.3** and **3.2**. The appearance of two longer NCN[−] bonded ligands can also be explained by the orbital interactions calculated for the HOMO in **3.2'** and shown in Figure 3.11B. An antibonding interaction between the Cu(d) orbitals and two *upward facing* NCN[−] ligands cause those Cu–N bonds to lengthen, in both **3.2'** and **3.3'**. The antibonding interaction is significant enough to cause the Cu–N bond elongation observed experimentally because the HOMO in **3.2'** was calculated to have 60% NCN[−] population originating from only two amidinate ligands (Section 3.4.4). Furthermore, the electrochemical data collected for **3.2** displayed two quasi-reversible oxidations characterized as ligand-based. The HOMO of **3.2'** would be the location where oxidation takes place, thus further confirming the electrochemical oxidations are facilitated by two NCN[−] ligands that populate 60% of the oxidized orbital.²²⁹

These observations moving from **1.3** → **3.3** → **3.2** suggest: (i) structural trends across a redox series identify atoms or entities that are direct contributors to the frontier molecular orbitals, (ii) among Cu₄(μ₄-S) clusters, the four copper atoms and bridging sulfide ligand comprise the majority of character within the RAMO and (iii) a bond shortening or lengthening trend across a redox series may signify the type of interaction (bonding vs. antibonding) occurring between the contributors of the frontier MOs.

The EPR data collected for complex **3.3** provided experimental evidence, by the small *g* and *A* values (*g*_⊥ = 2.090, *g*_∥ = 2.043, *A*_⊥ = 100 MHz, *A*_∥ = 15MHz), suggesting the single electron is delocalized. Although the EPR data for **3.3** demonstrated smaller values in comparison to the EPR data of the N₂OR centers (Table 3.3), it was similar in magnitude to the values collected for the mixed valent tricopper-sulfide complex synthesized by Murray and coworkers (**1.2**).¹¹⁷ The 13-line splitting pattern of the hyperfine coupling in **3.3** advocated equivalent spin distribution across all four copper atoms, in accord with the DFT calculations (10% per Cu). In light of the EPR analysis, two resonance forms for complex **3.3** were considered: (4Cu^{1.25}S^{2−}) or (4Cu^IS[−]).²³² At this time, complex **3.3** is considered a mixed valent, highly

delocalized system ($4\text{Cu}^{1.25}\text{S}^{2-}$) as opposed to a sulfur-based radical species ($4\text{Cu}^1\text{S}^\cdot$); however, more intensive spectroscopic investigations (i.e. XAS) and higher level DFT calculations are needed to definitively describe the electronic structures in **3.3** and **3.2**; which are currently ongoing.

3.6 Reactivity of Complex **3.3** and Nitrous Oxide

Complex **3.3** was studied exclusively in the forthcoming reduction reactions with N_2O and did provide *experimental evidence as a competent functional model for Cu_Z^** .²³² In the following subsections the products of the N_2O reduction reaction with **3.3** will be characterized and potential mechanisms will be proposed.

3.6.1 Characterization of Reaction Products from Nitrous Oxide Reduction by Complex **3.3**

As shown in Scheme 3.6, reactions between **3.3** and gaseous N_2O at 1 atm, produced a variety of species that were identified but difficult to quantify.²³² Primarily, issues arose due to the products being trapped and isolated because of their different physical phases (solid, gas and liquid). Even when isolated and characterized separately, measurable yields for some of the reaction products proved inconsistent and will be briefly addressed. Therefore, at this time, the stoichiometry of the reaction between **3.3** and N_2O is unknown (shown as n in Scheme 3.6), but the following results discussed in this section are aimed to provide evidence that the reaction products are spectroscopically distinguishable and can only result from reduction of N_2O by complex **3.3**.



SCHEME 3.6 Reaction between complex **3.3** and N_2O (1 atm).

The isolation of **3.2** was carried out by exposing **3.3** to 1 atm of N_2O in DCM for 6 hours at -78° C . The low temperature is necessary for all reactions with **3.3** because control experiments have shown that in

solution, **3.3** decomposes to the dicopper precursor **3.1** rapidly at room temperature (~ 50% decomposition in 30 minutes at RT). Under N₂O, 88% yield of **3.2** was recovered (with respect to the molar amount of **3.3**) and under the same reaction conditions, but N₂ gas was used, the control yielded 30% of **3.2**, attributed to thermal decomposition after 6 hours at -78° C. With consideration of the results from the N₂ control experiment, 58% more of **3.2** resulted when **3.3** was in the presence of N₂O.

Another reaction product shown in Scheme 3.6, and perhaps one of the most important to identify, is N₂. The reaction headspace was analyzed by GC-MS after **3.3** reacted with N₂O in THF at low temperature. From the extracted ion chromatogram for species with m/z 28, integration of the resulting peak area from the reaction headspace revealed more N₂ compared to the control experiment in which identical conditions were employed but in the absence of **3.3**. In order to quantify the N₂ produced from the reaction between **3.3** and N₂O, a calibration curve was constructed with known volumes of N₂ gas in helium filled flasks; however, due to the detection sensitivity limits of the GC-MS detector, calibration curves for N₂ could not accurately or consistently be reproduced (Appendix I). Efforts in quantifying the remaining amount of N₂O present in the headspace after the reaction, proved inconsistent despite excellent calibration curves with N₂O standards (Appendix I). Although N₂ proved difficult to quantify under the reaction conditions attempted, it was necessary to use isotopically labelled nitrous oxide, ¹⁵N₂O, to provide conclusive evidence that **3.3** is capable of reducing N₂O. Shown in Table 3.5 are the headspace analysis results using ¹⁵N₂O and **3.3** in THF (Section 5.2.19).

TABLE 3.5 Integration of ¹⁵N₂ in Reaction and Blank Headspace After 6 and 48 Hours^{abc}

	¹⁵ N ₂ in Reaction Headspace	¹⁵ N ₂ in Blank Headspace
6 hours	109,835	22,868
48 hours	181,583	21,394

^a Integration of peak in the extracted ion chromatogram for m/z 30.

^b Integration values are unitless, as they represent the peak area associated to ¹⁵N₂ present.

^c See reference 232.

Integration values correspond to the peak area within the extracted ion chromatogram for species having m/z 30 ($^{15}\text{N}_2 = 30$ g/mol). A blank flask was purged to contain only $^{15}\text{N}_2\text{O}$ gas and the integration values observed in Table 3.5 for the blank correspond to the trace amounts of $^{15}\text{N}_2$ present in the original gas cylinder purchased. After 6 hours at -78°C , the reaction produced approximately 5 times more $^{15}\text{N}_2$ than was originally present (109,835). After 48 hours (to establish an equilibrium between gases dissolved in the solution and headspace) approximately 8 times the amount of $^{15}\text{N}_2$ was present in the reaction headspace compared to the blank flask (181,583 and 21,394 respectively). Gratifyingly, the headspace experiments analyzed by GC-MS confirmed the reduction of $^{15}\text{N}_2\text{O}$ by **3.3**, proving it is a functional Cu_Z^* model.

The final product to identify from the reaction between **3.3** and N_2O , was nucleophilic O^{2-} (Scheme 3.6) and trimethylsilyl chloride (TMS-Cl) was used to trap the oxygen and form hexamethyldisiloxane (HMDSO). When a slight excess of TMS-Cl (5 equivalents) was added to the resulting reaction mixture of N_2O and **3.3**, HMDSO was the major silyl-containing product, analyzed by ^1H NMR, compared to N_2 control experiments (Section 5.2.17, Figures 5.83 and 5.84). Addition of a different electrophile, such as benzoyl chloride, also proved the presence of O^{2-} by the formation of benzoic anhydride observed in the ^1H NMR spectrum (Section 5.2.18, Figure 5.86). It is speculated that K_2O is the oxide intermediate in the reaction prior to the addition of an electrophile; however, no experimental evidence has been collected to validate formation of this species. Complications in deriving percent yields of HMDSO from the TMS-Cl reactions by ^1H NMR persisted due to peak overlap between HMDSO and other silyl-containing products (potentially $\text{Si}_2(\text{Me})_6$, KOSiMe_3 , unreacted TMS-Cl and silicone grease) and other NMR solvents (benzene- d_6), used to provide better resolution between NMR peaks, did not yield consistent results. Therefore, at this stage, the TMS-Cl results provide evidence for the formation of O^{2-} from the reaction between **3.3** and N_2O .

The early stages of investigating the reaction between **3.3** and N_2O have been reported and provide spectroscopic evidence that the 1-hole model complex reduces N_2O . The oxidation of **3.3** occurs in the presence of N_2O due to the appearance and isolation of **3.2** in a 58% yield. In the presence of **3.3**, $^{15}\text{N}_2\text{O}$

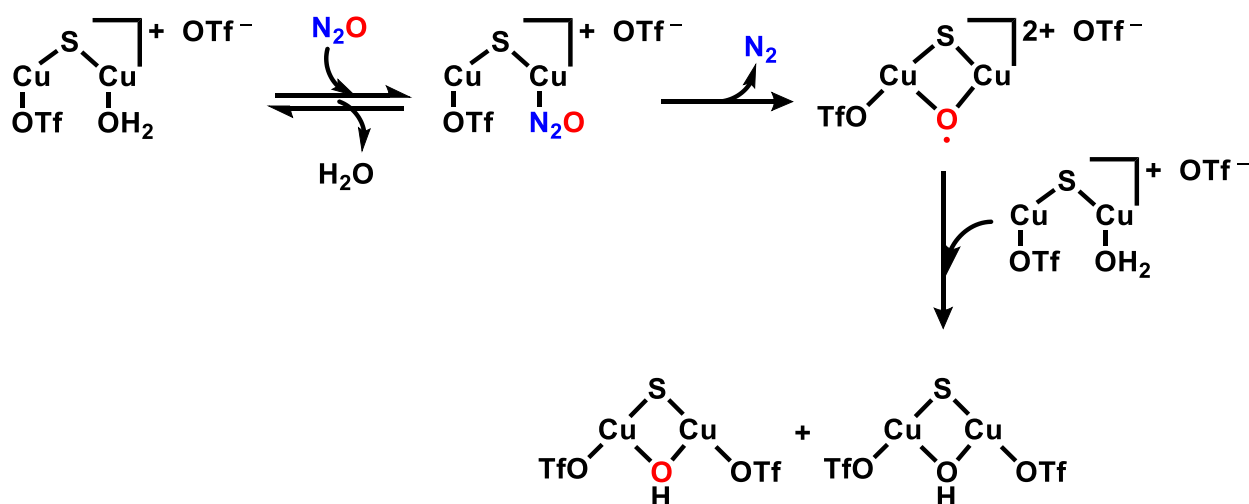
was observed to be reduced by at least one electron due to the accumulated $^{15}\text{N}_2$ observed by GC-MS and capture of the O^{2-} product (using electrophiles) suggested subsequent reduction. Detailed analyses resolving reaction stoichiometry, the reduction mechanism and kinetic parameters associated with the reduction of N_2O by **3.3** are currently ongoing. The reactivity and structural characteristics demonstrated by **3.3**, provide a functional and structural mimic to Cu_Z^* and becomes the sole tetracopper-sulfide cluster capable of N_2O activation reported to date.

3.6.2 Hypothetical Reduction Mechanisms Suggested for Complex **3.3** and Nitrous Oxide

Like Cu_Z^* , the reduction mechanism for N_2O and **3.3** requires additional experimental evidence in order to provide valuable insight relatable to the dynamics perceived for the reduction taking place in N_2OR . However, it is advantageous to speculate different reaction pathways that allow **3.3** to reduce N_2O for the benefit of elucidating potential reaction intermediates for detection or isolation, and further optimization of experimental conditions to favor one pathway perhaps, more than another. The ensuing discussion therefore, is based solely on hypothesis with literature examples to substantiate the probability of possible mechanisms for N_2O reduction by complex **3.3**. Two fundamental questions are raised when addressing potential reaction mechanisms carried out by **3.3**: (i) are two electrons provided by **3.3** per N_2O molecule and (ii) where are the possible N_2O coordination sites in **3.3**? The following proposed reduction mechanisms are aimed to provide potential resolutions to these questions and provoke future experimentation which could undoubtedly enhance the current knowledge associated to the reactivity exhibited by **3.3**.

As discussed in Section 1.2.2, when reduction occurs through the active Cu_Z^* state (4Cu^{I}), conceivably, two electrons reduce N_2O per Cu_Z^* cluster.^{15,31,33,38} In the case of the 1-hole Cu_Z , the reduction of N_2O is perceived to occur by a proton-coupled electron transfer from Cu_Z , and the second electron is donated to N_2O by the reduced Cu_A site.^{21,22} It could be possible that two molecules of **3.3** are needed to reduce nitrous oxide, more similar to the Cu_Z reduction hypothesis. Therefore, it could be reasonable to assume that N_2O coordinates to one molecule of **3.3** and after the first reduction, a second molecule of **3.3** acts as a sacrificial e^- donor, similar to the suspected role of Cu_A during the reduction mediated by the 1-

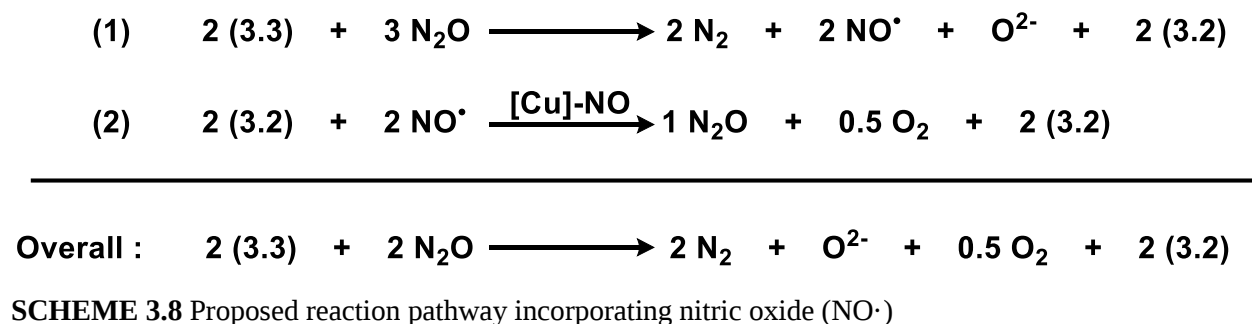
hole Cu_2 .²³² The mixed valent functional model, **1.6** (Figure 3.3B), is also proposed to go through a reaction pathway requiring two molecules to facilitate reduction (Scheme 3.7).¹²⁴



SCHEME 3.7 Reduction of N_2O by **1.6** proposed by Torelli and coworkers.¹²⁴

Torelli and colleagues suggested that after N_2O binds and is activated by one molecule of **1.6**, a second molecule is required in order to generate: (i) the neutral dicopper- $(\mu_2\text{-OH})$ complex observed in equimolar amounts as the starting material (**1.6**) and (ii) ~ 0.5 equivalents of N_2 that was experimentally quantified. If two molecules of complex **3.3** are required for N_2O reduction, it would be reasonable to assume a reaction intermediate forms after the first reduction but prior to the second, and this intermediate could be detectable using cyclic voltammetry. Conceivably, the intermediate $[\text{Cu}_4\text{S}]\text{-O}$ adduct would produce a new redox event at more oxidizing potentials within the CV; thereby allowing a second molecule of **3.3** to act as a capable reducing agent.²²⁹ Using electrochemistry to map the redox active species formed during N_2O reduction was also performed by Torelli and coworkers for **1.6**. During the reaction with N_2O , a new redox couple was observed in the CV that the authors proposed as the ligand exchange product from the equilibrium step between water and N_2O (shown as the first step in Scheme 3.7).¹²⁴

It is also important to consider the possibility of other N_xO_y intermediates forming, seemingly by the competitive cleavage of the $N-N$ bond in nitrous oxide. As discussed in Section 3.1, molybdenum(II)²²⁷ and other molybdenum(III)^{239–241} coordination compounds have been reported that cleave the $N-N$ bond in nitrous oxide and in the latter complexes, free nitric oxide ($NO\cdot$) was detected.^{240,241} Therefore another possible mechanism for N_2O reduction by **3.3** is shown in Scheme 3.8 and was proposed in unpublished work by Dr. Chia-Wei Hsu in the Mankad research group.²⁴²



All reaction equations in Scheme 3.8 are balanced with respect to the atoms and total charge, and the sum of the two pathways includes all the spectroscopically identified products. In the first reaction step, $N-O$ and $N-N$ bond cleavage occur to form N_2 and $NO\cdot$, and in the subsequent step nitric oxide reacts with **3.2** to re-generate nitrous oxide; similar to the behavior exhibited by copper nitrite reductase.^{37,243} The $[Cu]-NO$ species suggested in the second reaction step would be considered a $Cu^{II}-NO\cdot$ adduct (as opposed to Cu^I-NO^+) which has been widely reported in other copper(II)-nitric oxide complexes within the literature.^{244–247} The formation of $\frac{1}{2} O_2$ observed in the overall reaction equation has yet to be identified by GC-MS but should be detectable, along with the presence of $NO\cdot$ as an intermediate, when monitoring the reduction reaction using cyclic voltammetry²⁴⁸ and is currently under an ongoing investigation.

To suggest a substrate docking site in **3.3** that activates N_2O for reduction would be purely speculative at this point; as it also differs from the theorized μ -1,3 bridged binding mode of N_2O in Cu_2^* between the 3-coordinate Cu_I and 2-coordinate Cu_IV (Figure 3.12).^{15,30,33,38,39}

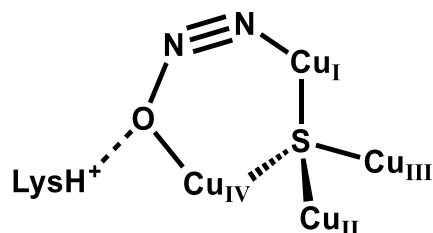


FIGURE 3.12 Bent configuration of N_2O bound to fully reduced Cu_2^* calculated in the TS.

In model complex **3.3**, all copper atoms are 3-coordinate and hypothetically, have an open coordination site for N_2O . Examination of a space fill model of the crystal structure for **3.3** down the x , y and z – axis, reveals that the NCN^- ligands saturate the space around each copper atom. The sulfide atom however, appears to have the largest surface area unencumbered by the ligand substitutes, as shown down the z – axis in Figure 3.13.

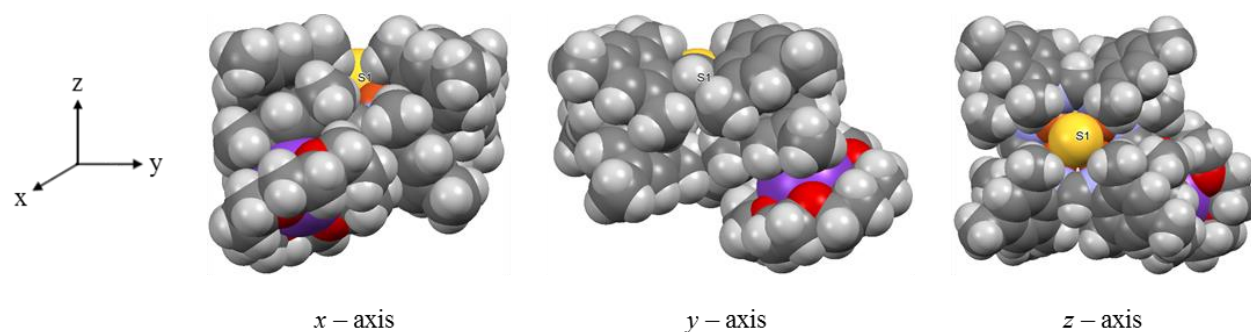


FIGURE 3.13 Space fill models of the crystal structure for **3.3** looking down x –, y – and z – axis. Hydrogens are shown in calculated positions, co-crystallization solvents and some of the element labels are omitted for clarity. Atom colors include: Cu, orange; S, yellow; N, blue; O, red; K, purple; C, gray; H, white.

It is reasonable to suggest that the sulfide atom, which also has the largest calculated unpaired spin density (32%, Table 3.4), to be the N_2O coordination site because of its physical accessibility compared to the copper atoms. DFT calculations are currently underway to determine the most energetically favorable binding mode of N_2O onto any open coordination site in **3.3**, but a simplistic predetermination of N_2O coordinating to the sulfide atom is shown in Figure 3.14. Should this binding mode and coordination site prove realistic, either through DFT calculations or spectroscopic evidence, it would be drastically different than the suggested Cu_z^* activation mechanism but perhaps comparable to the reduction proposed by Solomon and coworkers for the 1-hole Cu_z ; in that N_2O is linear when activated and reduced.^{21,22}

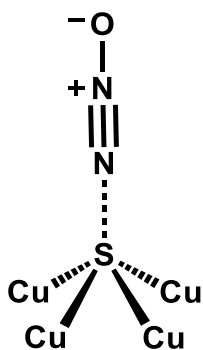


FIGURE 3.14 Hypothetical coordination of N_2O to **3.3**.

With the limited experimental information collected thus far pertaining to the N₂O reduction mechanism carried out by **3.3**, suggesting potential reduction pathways becomes more elaborate guesswork than definitive conclusions. It is equally as likely for one of the suggested mechanisms to be correct, as it is for none of them to be realistic or a different combination of other reaction pathways. What is irrefutable however, is the importance of exhausting all possible experimental and theoretical avenues in order to provide the best possible explanation for how this reduction reaction transpires through **3.3**.

3.7 Conclusion and Discussion

The combined spectroscopic data from multiple experimental techniques discussed within this chapter for **3.3** and **3.2** highlight the extensive characterization performed to better understand these sophisticated copper-sulfide systems. The crystallographic studies provided evidence that a robust π -stacking interaction between the mesityl substituents on the NCN⁻ ligands in **3.2** influences the Cu₄S center to arrange in a highly symmetrical fashion, prevalent in both the solid and solution states.

Examination of the crystal structures and DFT calculations for the fully reduced model (**1.3**), 1-hole (**3.3**) and 2-hole (**3.2**) complexes, identified a conserved RAMO; relating the HOMO of **1.3**, SOMO of **3.3** and LUMO of **3.2**. Across the redox series of model compounds, a shortening of the Cu–S bond lengths was observed (Table 3.1), resulting from the removal of Cu(d) and S(p) antibonding interactions as the RAMO gets oxidized (Figure 3.11B). In the same context, the decrease in Cu···Cu distances spanning all three model complexes upon oxidation likely results from a combination of removing the antibonding interaction between Cu(d_{xz}) orbitals present in the RAMO and the natural contraction of the spatial arrangement among the four copper atoms as the Cu–S bonds decrease simultaneously during oxidation. Alternating antibonding and bonding interactions between neighboring Cu(d_{xz}) orbitals in the RAMO explained the presence of alternating long and short Cu···Cu distances observed in the crystal structure of each model complex. The NCN⁻ ligands in **3.3** and **3.2** also exhibited shortening upon oxidation because the DFT calculated HOMO for **3.2'** (Figure 3.11B) revealed two NCN⁻ ligands as the major contributors to the orbital population, and those same two ligands are involved in an antibonding interaction with the copper atoms. Collectively, the crystallographic and DFT studies for complexes **1.3**, **3.3**, **3.3'**, **3.2** and **3.2'**

correlated the structural changes across the redox series with the intimate interactions occurring between Cu(d) and S(p) orbitals; of which, are the dominant components establishing character within the RAMO. It was also demonstrated that the type of interaction (bonding or antibonding) between atomic orbitals in the RAMO is reflected in the decreasing or increasing bond lengths among redox partners.

The ability of the amidinate model compounds to access different redox states allowed for additional spectroscopic techniques to be employed, to better understand and interpret the intrinsic electronic properties that are paramount within multimetallic systems. The electrochemical investigations of complex **3.2** revealed two quasi-reversible oxidation events, a reversible reduction couple and an irreversible reduction wave at more negative potentials (Figure 3.8). As discussed, the HOMO calculated for **3.2'** is populated by the NCN^- ligands, confirming the ligand-based assignment for the quasi-reversible oxidation events shown in the CV. The reversible reduction event led to the synthesis of model **3.3** and the irreversible reduction wave is suggested to be an unstable species because of the decreased current observed in subsequent scans (Appendix G). Although compound **3.3** still has an additional electron hole present, the inability for further reduction to a fully reduced species is probably related to the propensity exhibited by Cu_2 in reaching a maximum 1-hole oxidation level.²² Addition of a highly covalent $\mu_2\text{-SH}^-$ ligand in Cu_2 provides the increased electron density needed to stabilize higher oxidation states (2-hole Cu_2 with $\mu_2\text{-S}^{2-}$) while also preventing complete reduction to four Cu(I) atoms.²² Similarly, in **3.3**, the anionic amidinate ligands provide additional electron donation to the Cu_4S center, enabling the stabilization of the 2-hole state but precludes the two electron reduction to a fully reduced species.

Accessing a 1- and 2-hole oxidation level in the model compounds also allowed for the electronic absorption spectrum to display characteristic peaks in the visible region. Complexes **3.2** and **3.3** displayed high energy transitions (561 and 566 nm, respectively)^{229,232} near the absorption maxima reported for the Cu_2 2-hole (545 nm);^{14,21} while all other 1-hole N_2OR centers (Cu_2^* resting, Cu_2 active and Cu_2^0 states) show charge transfers $\sim 650 - 685$ nm.^{14,15,21,36} The lower energy CT for the 1-hole centers in N_2OR could be attributed to the presence of an edge ligand (SH^- or OH^-) that decreases the energy gap related to the charge transition. The absence of a bridging edge ligand in **3.3** may account for the higher transition energy

observed in the absorption spectrum. Also notable, was the intensity of the electronic absorption by the 2-hole species listed in Table 3.2, that were higher ($\epsilon_{\text{average}} = 12\,000\text{ M}^{-1}\text{ cm}^{-1}$) than the 1-hole clusters ($\epsilon_{\text{average}} = 4500\text{ M}^{-1}\text{ cm}^{-1}$). The high absorption intensity displayed by the Cu_Z 2-hole is attributed to the presence of α and β electron holes within the calculated singlet ground state.²¹ This would suggest a similar broken symmetry singlet arises in **3.2**; however, DFT calculations suggested a closed shell singlet ground state but higher level DFT calculations are currently ongoing to better model the electronic structure present in **3.2** (Section 3.4.4).²³² The TD-DFT calculations produced an absorption spectrum for **3.2'** ($\sim 467\text{ nm}$) that did not agree with the experimentally observed absorption energy (561 nm); further illuminating more detailed and intensive calculations are needed to accurately describe the ground state in **3.2**.

The presence of an electron hole in complex **3.3** also allowed for EPR measurements to be conducted, in order to probe the behavior of the unpaired spin. The low g and A values obtained from the simulated fits of the X- and Q-band spectra are proposed to originate from the extensive delocalization of the unpaired electron over four copper atoms; consistent with the 13-line splitting pattern of the hyperfine coupling to four copper atoms.²³² The high level of delocalization presumed to cause the lower EPR parameters in **3.3** is relatable to the delocalization suggested for the unpaired spin in the Cu_Z 1-hole.²¹ Solomon and coworkers reported that a more covalent edge ligand in Cu_Z ($\mu_2\text{-SH}^-$) induces increased delocalization of the unpaired electron onto the edge ligand, while the Cu_Z^* 1-hole center displays lower g and A values due to the large ligand field splitting energy ($\text{Cu } d_{xy} \rightarrow \text{Cu } d_{x^2-y^2}$).²¹ The increased delocalization in **3.3** extracted from the EPR parameters is in accord with the Mulliken spin distribution analysis calculated for **3.3'** and presented in Table 3.4. The unpaired spin was calculated to reside mainly over the $\mu_4\text{-S}$ ligand (32 %), presumably due to the inherent covalency of sulfide acting as a delocalization pathway to all four copper atoms (10% each Cu).²³² The Mulliken spin distribution calculations also revealed 72% of the unpaired electron resides over the Cu_4S core, suggesting these atoms as the likely participants in electron transfer reactions.

The two electron reduction of N_2O by **3.3** was validated by the characterization of the reaction products: **3.2**, N_2 and nucleophilic O^{2-} .²³² Complex **3.2** was isolated in 58% higher yield (with respect to

equimolar amounts of **3.3**) in the presence of N₂O compared to a N₂ control and the O²⁻ product was trapped by TMS-Cl to produce HMDSO as the major silyl-containing product when analyzed by ¹H NMR. The most critical reaction product to identify was gaseous N₂. Use of isotopically labelled ¹⁵N₂O, revealed 8 times the amount of ¹⁵N₂ was produced from the reaction between **3.3** and ¹⁵N₂O, after 48 hours, compared to the trace amount of ¹⁵N₂ present prior to the reaction when analyzed by GC-MS. The isotopically labelled N₂O experiment explicitly provides direct evidence that nitrous oxide is reduced by **3.3**. Unfortunately, the reaction products were difficult to quantify under the experimental conditions attempted and the stoichiometry of the reaction between **3.3** and N₂O is unknown at this time.

Despite the ambiguous values of *n* shown in Scheme 3.6, several reaction mechanisms are proposed to for the two e⁻ reduction of N₂O by model **3.3**. It is possible that one molecule of **3.3** binds and activates N₂O by one e⁻ and another equivalent intermolecularly acts as the second electron donor; similar to the proposed reduction mechanisms for **1.6**¹²⁴ and the 1-hole Cu₂.²¹ In the alternative suggested reaction pathway shown in Scheme 3.8, generation of a discrete nitrogen-oxide species (i.e. NO•) acts as an intermediate, producing the overall reaction equation that includes all the experimentally observed reaction products and displays a 1:1 molar ratio between **3.3** and N₂O. A reoccurring entity present in the suggested reduction mechanisms is the presence of an intermediate. Currently, no intermediates have been detected, isolated or characterized from the reaction between **3.3** and N₂O. Future experimentation utilizing additional spectroscopic techniques (cyclic voltammetry, *in situ* FT-IR spectroscopy, etc.) to monitor the reaction will undoubtedly confirm the existence, or identity, of any intermediates generated during the course of the reaction. Identifying potential reaction intermediates will illuminate more succinct reaction pathways and provide measurements to extract the kinetic parameters needed to determine formal rate laws and constants.

The abundant characteristics exhibited by the amidinate model complexes are not only of scientific value relatable to the N₂OR centers, but also for the development of utilizing the molecular behavior of inorganic coordination compounds to accomplish difficult redox-promoted transformations. In catalytic reactions, the ability to form stable, multimetallic complexes that can execute multielectron processes,

could profoundly eradicate the boundaries associated with mononuclear catalysts that are only capable of one or two electron redox reactions. Evaluation of the collected data for complexes **3.2** and **3.3**, illustrated the impactful role bridging ligands serve in mediating charge among non-bonded metallic sites and the essential cooperation between multiple metal centers that allowed for the reduction of a kinetically inert substrate, N_2O .^{2,9}

4. CONCLUSIONS AND CONTINUING RESEARCH STUDIES

4.1 Overview

Presentation of novel multinuclear copper-sulfide complex design, synthesis, characterization and reactivity discussed thus far supplements a truly underdeveloped area of N₂OR synthetic model chemistry.^{37,101} Furthermore, the compounds evaluated in Chapters 2 and 3 contribute to the fascinating copper-sulfur chemistry reported in the literature that focuses on the structural^{82,84,88,98} and electronic^{92–94} facets; as well as the evolving studies involving copper cluster assembly^{99,100,177,212,249} and reactivity patterns exhibited by copper-sulfide compounds.^{84,89} The discussion within this chapter will advocate potential research goals for future synthetic mimics to the N₂OR active sites by drawing upon several conclusions from Chapters 2 and 3. In addition, many of the revisited conclusions will naturally reveal important aspects about the intriguing molecular behavior expressed by copper-sulfide clusters.

4.2 Ligand Modifications

One of the most impactful methods for manipulating the behavior in copper-sulfide complexes is the development of optimized ligand scaffolds. Firstly, an ideal ligand would be one that allows multiple reversible redox events to occur so catalytic conditions can be evaluated, similar to those perceived in Cu₂*. The chosen bidentate phosphine and amidinate ligands provided increased electron donation (compared to dppm or dtpm) that was suggested to allow the stabilization of higher oxidation states electrochemically (Sections 2.5.2 and 3.4.1). In the case of the bridging phosphine ligated complexes, **2.2** (Figure 4.1A) and **2.4** (Figure 4.1B), one reversible oxidation was followed by three irreversible oxidations within the CV, that occurred at nearly identical redox potentials as the irreversible oxidations reported for **1.3** and **1.4**.¹²⁰

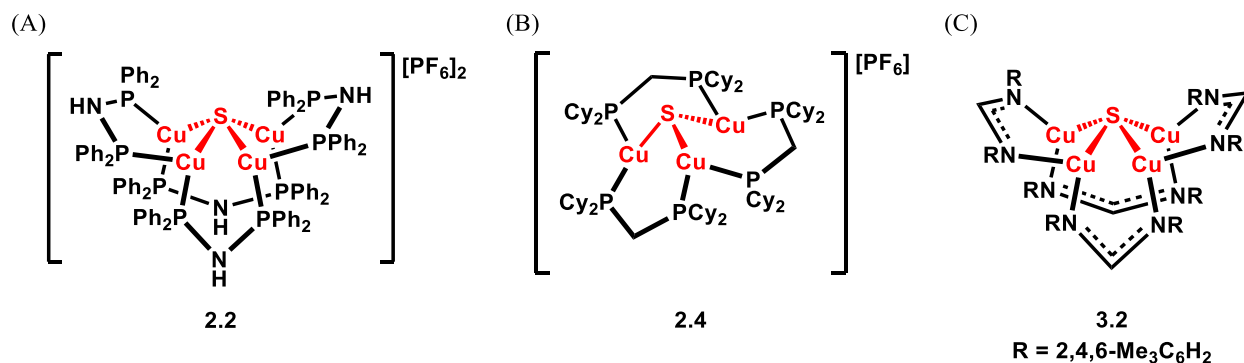


FIGURE 4.1 Tetra- and tricopper-sulfide complexes discussed in Chapters 2 and 3.

Complex 3.2 (Figure 4.1C) revealed three reversible redox events and one irreversible reduction wave in the cyclic voltammogram. The phosphine ligands provided enough electron donation to encourage formation of a 1-hole species electrochemically, but could not stabilize any higher oxidation states. The anionic amidinate ligands were capable of stabilizing 2- and 1-hole oxidation levels but prevented a “fully reduced” (4Cu^{I}) state. Ideally, a Cu_4S model system should be stabilized in three oxidation levels: 2-hole, 1-hole and fully reduced. Reversible-redox stability could come from the ligands, and in order to accommodate three different redox states the ligand substituents could be marginally adjusted to provide enough electron donation to stabilize a 2-hole state but also tolerate a fully reduced oxidation level. Suggested NCN^- ligands with more mild electron donating groups installed on the phenyl rings to tolerate a $4\text{Cu}^{\text{I}}\text{S}$ redox state are shown in Figure 4.2A.

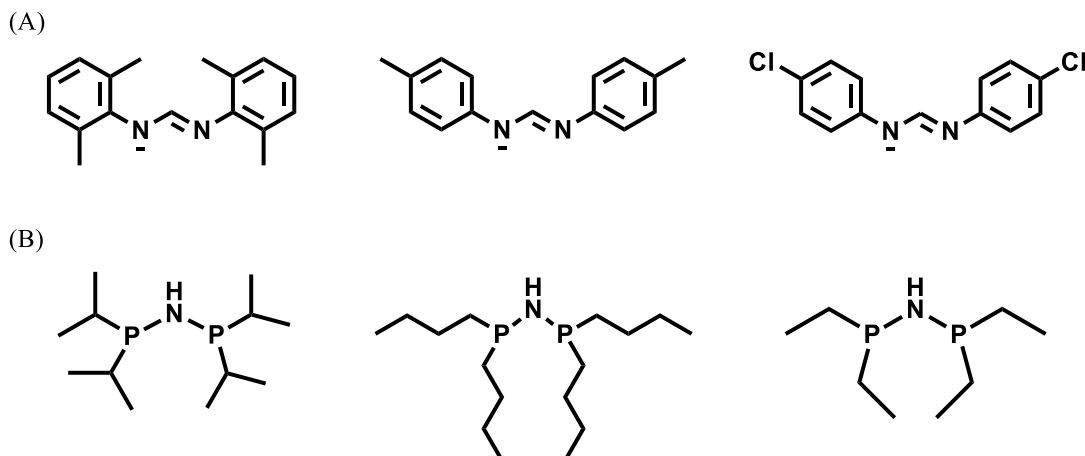


FIGURE 4.2 Suggested future bidentate amidinate and phosphine ligands.

In the phosphine ligand systems, more electron donation from the phosphorus tether atoms should allow stabilization of higher oxidation states. Several electron-rich diphosphines are shown in Figure 4.2B and all feature the amine backbone linker atom because, as discussed in Section 2.2, the amine linker donates more electron density than a methylene backbone.^{173,174} Retention of the amine group in the phosphine ligands could also induce hydrogen bonding interactions with outer-sphere guest molecules and cause longer Cu $\cdots$ Cu distances, as observed in 2.2 (Section 2.4.1).¹⁷⁷ The range of Cu $\cdots$ Cu distances in model complexes should attempt to replicate the distances in Cu $_2^*$ at the proposed N $_2$ O docking site (~ 3.40 Å).^{15,30,33,39} The phosphorus substituents shown in Figure 4.2B were chosen because they donate similar electron density as cyclohexane, but exhibit smaller cone angles to potentially allow arrangement of a tetracopper cluster.²⁵⁰

If simple substituent modifications on the amidinate and bis(phosphine) ligands do not allow tetracopper-sulfide assembly or three stabilized redox states, other bridging ligands observed in systems with three accessible oxidation levels should be pursued. It may even prove advantageous to construct a polydentate ligand containing both P- and N-donor atoms. In one particular dicopper system, reported by Peters and coworkers, a tridentate PNP $^-$ ligand (PNP $^-$ = bis(2-diisobutylphosphino-4-*tert*-butylphenyl)amide) allowed stabilization of 2Cu I , Cu II Cu I and 2Cu II redox states (Figure 4.3).²⁷

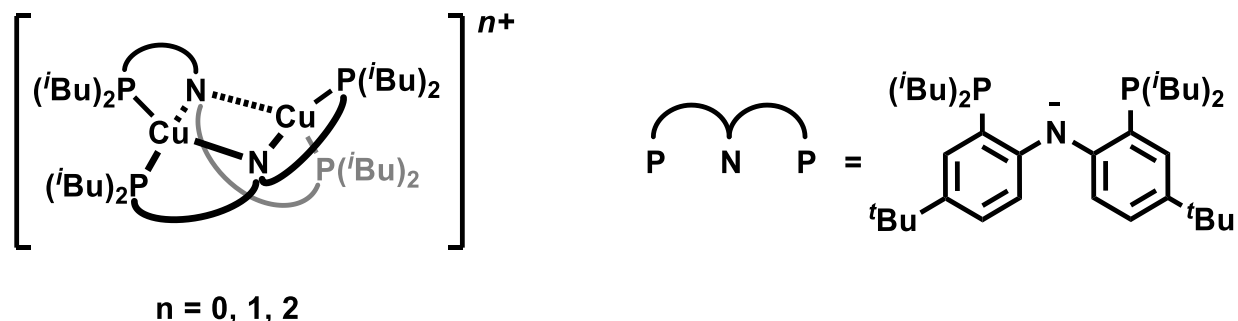


FIGURE 4.3 Dicopper-PNP redox partners synthesized by Peters and coworkers.²⁷

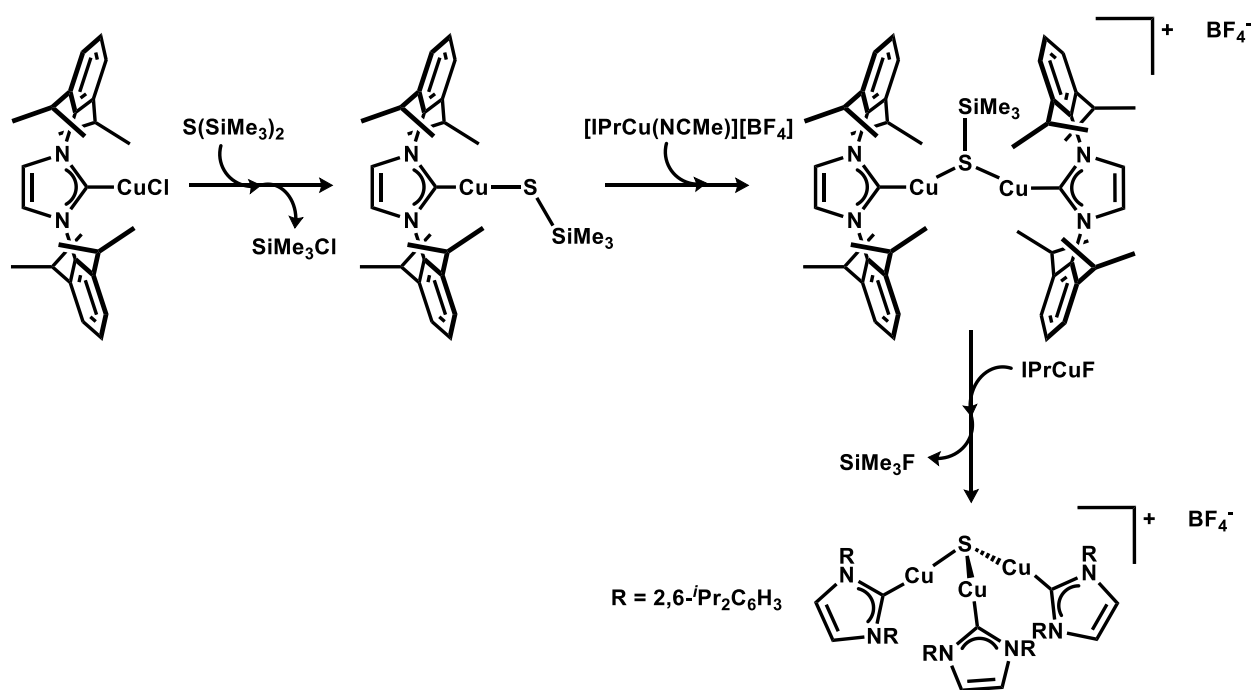
Although, the PNP^- does not exhibit the three-atom bridge denticity presumed to aid in the assembly of tetracopper-sulfide clusters from dicopper precursors (discussed in Section 1.6), stabilization of copper across all oxidation levels is afforded in the complexes developed by Peters and colleagues.

Several key conclusions highlighting the particular effect of different ligands in 2.2, 2.4, 3.2 and 3.3 revealed: (i) three-atom bridged phosphine and amidinate ligands readily form multinuclear $\text{Cu}(\mu\text{-S})$ compounds, (ii) bulky substituents on the ligand donor atom alternatively form tricopper-sulfide species, (iii) electronic donation of the ligand to the copper-sulfide center enables reversible redox behaviors and (iv) hydrogen bonding and π -stacking interactions involving the ligands could produce longer $\text{Cu}\cdots\text{Cu}$ distances. Optimizing the molecular properties in bidentate ligands or using polydentate ligands that incorporate different donor atoms, may prove extremely beneficial in producing future model compounds with desired multielectron transfer capabilities.

4.3 Alternative Methods for Generating Tetracopper-sulfide Complexes

Different synthetic mechanisms for assembling future Cu_4S molecules are needed in order to eliminate the boundaries associated with the synthetic approach used for the model complexes discussed in Chapters 2 and 3. More specifically, limiting binucleating ligands to only three-atom bridges and exclusively forming dicopper precursor complexes, narrows the survey of new ligands dramatically. Additionally, discovering new synthetic methods could also produce revelations about the unpredictable coordination behavior of $\text{Cu}(\mu\text{-S})$ clusters during assembly. One different synthetic pathway has already

been reported by Hillhouse and coworkers for the tricopper(I)-NHC supported complex, **1.1**, introduced in Section 1.4.1.¹¹⁶ As shown in Scheme 4.1, the authors assembled **1.1** by attaching single $[\text{Cu}(\text{IPr})]^+$ moieties to the sulfide atom individually. Hillhouse and coworkers suggested the ability of the NHC ligand to stabilize metals in low coordination numbers, and the added steric bulk on the NHC ligand prevents higher Cu_xS_y nuclearities from forming. In addition to the stabilization of copper provided by the NHC ligand, use of trimethylsilyl sulfide, as opposed to sodium sulfide or elemental sulfur, appears equally as essential to the step-wise addition of $[\text{Cu}(\text{IPr})]^+$ units on the sulfide atom. Using correct stoichiometric amounts of trimethylsilyl sulfide and $[\text{Cu}(\text{IPr})]^+$ salts appears to permit replacement of one SiMe_3 group on the sulfur atom at a time, making the entire synthetic mechanism very controlled in the absence of binucleating ligands. The step-wise strategy used by Hillhouse and coworkers is a beautifully simplistic route for generating $\text{Cu}(\mu\text{-S})$ compounds when the ligand demonstrates stabilization of low coordinate copper, and the sulfide reagent possesses groups for facile displacement (i.e. SiMe_3).¹¹⁴

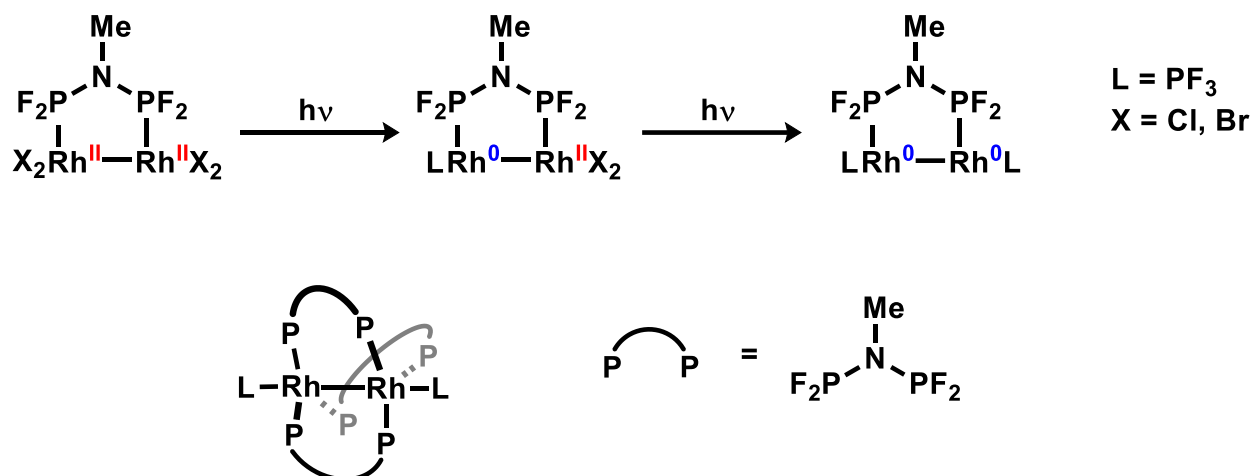


SCHEME 4.1 Synthetic mechanism for **1.1** reported by Hillhouse and coworkers.¹¹⁶

Exploring different synthetic pathways for assembling tetracopper-sulfide models will not only generate an influx of relevant Cu_Z^* (or Cu_Z) models to study, but also illuminate patterns concerning the coordination behavior of multicopper-sulfide molecules, and then cluster assembly can be predicted.

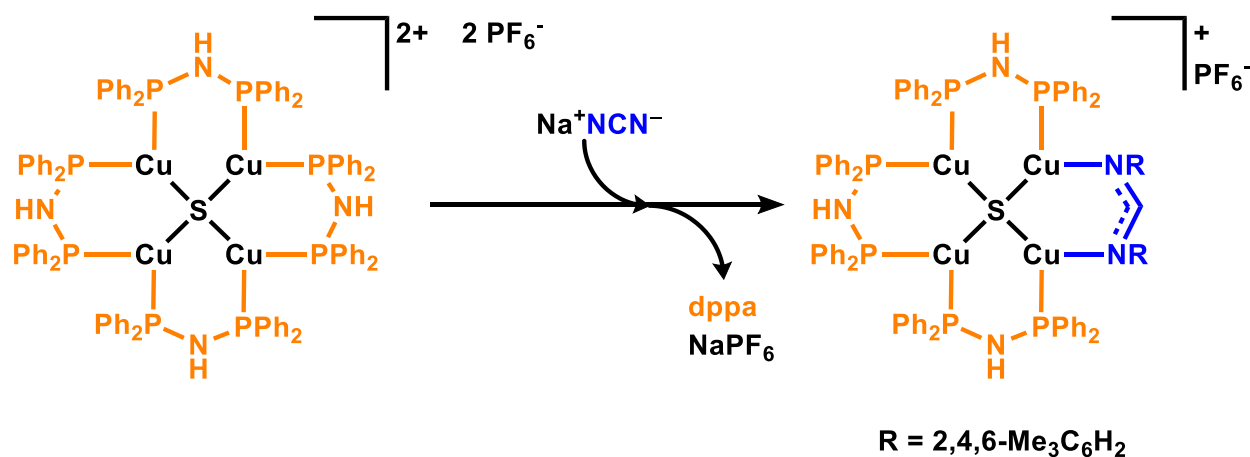
4.4 Valence Trapped Tetracopper-sulfide Systems

The spectroscopic and theoretical data collected for the 1-hole Cu_Z^0 and Cu_Z^* indicate the unpaired electron interacts over two copper atoms in the Cu_4 center in a delocalized and semi-delocalized fashion respectively (calculated spin densities of $\text{Cu}_Z^0 = 15\% \text{ Cu}_{\text{II}}$ and $32\% \text{ Cu}_{\text{IV}}$; $\text{Cu}_Z^* = 26\% \text{ Cu}_{\text{I}}$ and $13\% \text{ Cu}_{\text{IV}}$).^{21,36} The $\mu_4\text{-S}^{2-}$ ligand is the covalent delocalization pathway responsible for distributing the unpaired spin across both copper atoms in the 1-hole Cu_Z^0 and Cu_Z^* forms.^{15,36} Conversely, in the 1-hole model **3.3**, the spectroscopic and theoretical calculations suggest equal delocalization of spin density across all four copper atoms (10% each Cu).²³² The difference in distribution of the unpaired electron between the mixed valent 1-hole model, Cu_Z^0 and Cu_Z^* could be an interesting property to investigate and determine if delocalization over a specific number of copper atoms is important to N_2O activation or reduction. It may be very useful to design model complexes where the electron spin is more localized on two copper atoms, as in a valence trapped system. The complete delocalization observed in **3.3** is probably promoted by the $\mu_4\text{-S}^{2-}$ unit and the NCN^- ligands; which have proven to be redox active and covalent charge carriers (Sections 3.4.1 and 3.5). The $\mu_4\text{-S}^{2-}$ covalency is required in order to equilibrate charge across non-bonded copper atoms; however, the model compounds can be manipulated to direct the unpaired spin to only two copper atoms by exchanging one bidentate ligand for a more covalent one. Remarkable valence trapped systems have been reported by Nocera and coworkers for dirhodium^{175,251–254} and diiridium^{255,256} complexes by using a three-atom bridged phosphine ligand, dfpma (bis(difluorophosphino)methyl-amine), shown in Scheme 4.2.



SCHEME 4.2 Dirhodium dimers stabilized in three redox states by dfpma ligand.

The incredible photoredox properties of the dfpma ligand allows electron donation to the “electron-deficient” metal (M^{2+}) by withdrawing electron density from the “electron-rich” metal (M^0) and therefore stabilizes two-electron mixed valent dimers.^{173,174} The role administered by the dfpma ligand with second and third row transition metals provides an exceptional example for the influence of a ligand in directing electron density across two metal centers. In the case of the tetracopper-sulfide complex **2.2**, it may be reasonable to exchange one dppa ligand with a single NCN^- , as shown in Scheme 4.3.



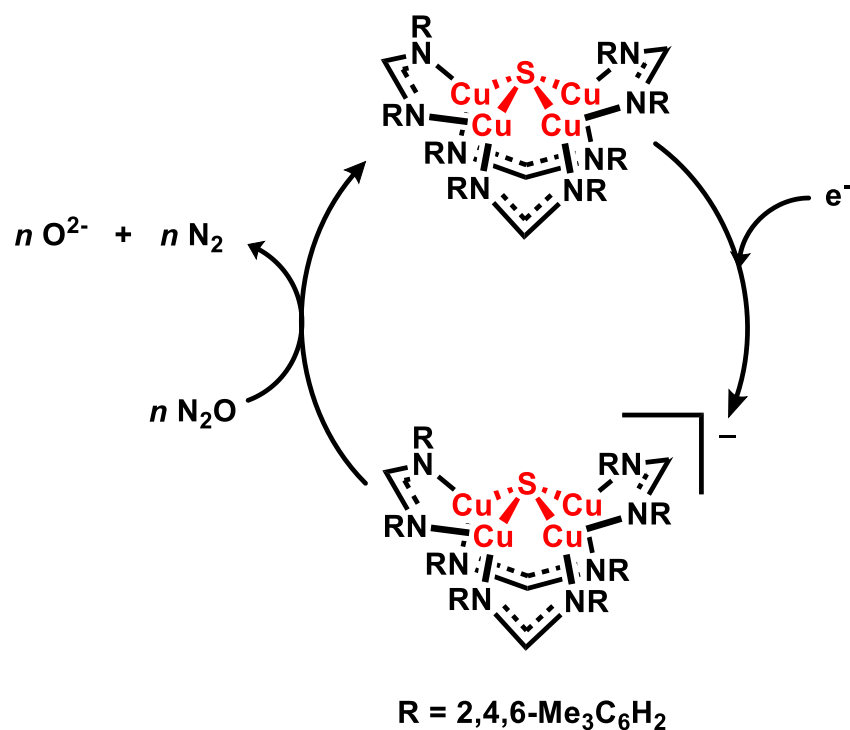
SCHEME 4.3 Proposed reaction scheme for generating a “valence trapped” Cu_4S complex.

If one phosphine ligand can be displaced, the resulting mixed ligand species will have two copper(I) atoms with only phosphorus ligands, and two copper atoms with mixed N- and P- donors. Ideally, the phosphine ligands will stifle the propensity of at least two copper atoms from participating in electron transfer and remain inert towards promoting the delocalization of charge. The single NCN^- ligand would “activate” the remaining two copper(I) atoms for redox chemistry; partially because of the efficient delocalization afforded by the NCN^- ligand after oxidation to the pair of copper atoms now sharing an electron hole.²¹⁰

Developing a tetracopper-sulfide complex that localizes unpaired spin to one or two copper atoms, would mimic the nature of the unpaired spin observed in the resting Cu_2^* site and the Cu_2^0 reaction intermediate.^{30,32,36,38} Furthermore, “spin-controlled” systems are also of interest to researchers studying single-molecule magnets²⁵⁷ and intermolecular electronic coupling in multimetallic complexes.^{258,259} Future electron-localized Cu_4S model compounds could contribute to the “spin-controlled” systems mentioned, by establishing control over the electronic structure and delocalization mechanisms across multiple metal centers.

4.5 Catalytic Conditions for Nitrous Oxide Reduction

Attempts to make the reaction between **3.3** and N_2O catalytic were pursued and deemed unsuccessful in our hands. In the presence of N_2O , **3.3** and 5 – 10 equivalents of a strong reducing agent, such as $[\text{CpFe}(\text{CO})_2]^-$ ($E^\circ = -1.8 \text{ V vs Fc}^{+/0}$),²³⁰ were reacted at low temperature and the N_2 released in the reaction headspace was measured by GC-MS. It was determined that a simultaneous reaction between $[\text{CpFe}(\text{CO})_2]^-$ and N_2O occurred, and this reaction was faster than the reaction between **3.3** and N_2O . Other bimetallic systems have also reported a reaction occurring between $[\text{CpFe}(\text{CO})_2]^-$ and N_2O .²⁶⁰ Use of a different reducing agent, like $\text{Co}(\text{Cp}^*)_2$ ($E^\circ = -1.94 \text{ V vs Fc}^{+/0}$),²³⁰ under the same catalytic conditions, did not increase the amount of N_2 ; even though $\text{Co}(\text{Cp}^*)_2$ was confirmed competent for reducing **3.2** to **3.3**. Under the conditions attempted, the reaction between **3.3** and N_2O did not appear to be catalytic; however, studies are currently underway for developing an *electrocatalytic* system. A simplistic catalytic cycle for the reaction between **3.3** and N_2O is shown in Scheme 4.4.



SCHEME 4.4 Proposed catalytic reduction of N_2O by 3.3.

Ideally, the redox reversibility displayed by the stable 1- and 2-hole amidinate complexes should be capable of catalytic turnover with N_2O electrochemically. Several synthetic hydrogenase functional models have been reported in the literature that are efficient electrocatalysts.^{158,159,261} Additionally, extensive and thorough reports on the relevant parameters and methods associated with studying electrocatalytic systems have been established.^{262–264}

4.6 Final Remarks

The intriguing characterization and reactivity discussed for the tetracopper-sulfide model complexes has been equally challenging and rewarding. These particular model complexes of the N_2OR active sites are remarkably intricate and synthetically beautiful from an inorganic coordination chemistry standpoint. They also translate the sophistication apparent in enzymatic systems that have developed cultured, sustainable and efficient biological catalysts, in order to overcome the barrier associated with activating specific small molecules. Most importantly, the model compounds discussed herein, provided

the only example of a structural and functional mimic to the Cu₂ active site reported to date.* Additionally, the tetracopper-sulfide complexes demonstrated unique structural proclivities associated to compounds featuring a μ -sulfide moiety, and displayed intense spectroscopic properties due to an advanced electronic structure. These complexes have proven to be critical contributions to the underdeveloped area of synthetic N₂OR model chemistry, and further support the scientific approach of designing practical multimetallic systems that accomplish innovative chemical transformations.

5. EXPERIMENTAL

5.1 Supporting Information for Binucleating Phosphine Donor Ligands in Model Synthesis

Reproduced with permission from Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. "Assembly, Structure, and Reactivity of Cu₄S and Cu₃S Models for the Nitrous Oxide Reductase Active Site, Cu_z*" *Inorg. Chem.* **2014**, 53, 10611. Copyright 2014 American Chemical Society.

5.1.1 General Considerations

Unless otherwise specified, all reactions and manipulations were performed under purified N₂ in a glovebox or using standard Schlenk line techniques. Glassware was oven-dried prior to use. Acetone and methanol were degassed with N₂, dried over K₂CO₃, and then distilled and stored over activated 3-Å molecular sieves. Other reaction solvents (diethyl ether, toluene, tetrahydrofuran, dichloromethane, pentane, acetonitrile) were sparged with argon and dried using a Glass Contour Solvent System built by Pure Process Technology, LLC. Unless otherwise specified, all chemicals were purchased from commercial sources and used without further purification.

5.1.2 Physical Measurements

NMR spectra were recorded at ambient temperatures using Bruker Avance DPX-400 or Bruker Avance DRX-500 MHz spectrometers. ¹H NMR chemical shifts were referenced to residual solvent peaks. ³¹P NMR chemical shifts were referenced to external H₃PO₄ (δ = 0). The following data acquisition parameters were used for quantitative ³¹P NMR spectroscopy: single pulse, 8.00 μs; power level, -3.00 dB; frequency offset of 3rd nucleus, -748516.887 ppm; recycle delay, 10 s; number of scans, 128. A calculation of signal to noise for ³¹P NMR using these parameters was 0.8%. FT-IR spectra were recorded on solid samples in a glovebox using a Bruker ALPHA spectrometer fitted with a diamond-ATR detection unit. Elemental analyses were performed by the Midwest Microlab, LLC in Indianapolis, IN. Deuterated solvents were degassed by repeated freeze-pump-thaw cycles and then stored over 3-Å molecular sieves. UV-Vis absorbance spectra were taken at room temperature using a Cary 300 Bio UV-Visible Spectrophotometer. Fluorescence emission spectra were taken at room temperature using a customized Fluorolog (HORIBA Jobin Yvon) modular spectrofluorometer. Luminescence quantum yields were determined based on

Equation (1), where A is the measured absorbance at the excitation wavelength and I is the integrated emission intensity when samples were excited at 415 nm. A 7.10×10^{-4} M solution of compound **1.3** ($\Phi=0.22$, excitation wavelength = 415 nm) in MeCN was used as the standard reference solution for the calculation in Equation (1).^{118,120,122} Samples for emission measurements were prepared as solutions of compounds **2.2** and **2.4**, in MeCN, at concentrations of 5.66×10^{-4} M and 3.14×10^{-3} M respectively.

$$\phi_{\text{sample}} = \phi_{\text{reference}} \frac{A_{\text{reference}}}{A_{\text{sample}}} \frac{I_{\text{sample}}}{I_{\text{reference}}} \quad (1)$$

Electrochemical data was measured at room temperature using a WaveNow USB Potentiostat from Pine Research Instrumentation. In a classic three-electrode system, a platinum working electrode, platinum counter electrode and a Ag/AgNO₃ (0.01 M AgNO₃/0.1M Bu₄NPF₆ in MeCN) reference electrode was used. Compounds **2.2** and **2.4** were dissolved in a 0.1 M solution of Bu₄NPF₆ in MeCN at 1.88×10^{-3} M concentration. Electrochemical measurements were referenced to a 1.88×10^{-3} M solution of FeCp₂⁺⁰ in same MeCN electrolyte solution.

5.1.3 X-ray Crystallography

X-ray crystallography data were collected at the X-ray Structural Laboratory at Marquette University (Milwaukee, WI) for complexes **2.2**, **2.5**, **2.4**, **2.6**, and **2.7**. The X-ray single-crystal diffraction data were collected at 100 K with an Oxford Diffraction SuperNova kappa-diffractometer equipped with dual microfocus Cu/Mo X-ray sources, X-ray mirror optics, Atlas CCD detector and low-temperature Cryojet device. The data were processed with CrysAlisPro program package (Oxford Diffraction Ltd., 2010) typically using a numerical Gaussian absorption correction (based on the real shape of the crystal) followed by an empirical multi-scan correction using SCALE3 ABSPACK routine. The structures were solved using SHELXS program and refined with SHELXL program²⁶⁵ within Olex2 crystallographic package.²⁶⁶ All computations were performed on an Intel PC computer under Windows 7 OS. X-ray crystallography data were collected at the University of Illinois at Chicago for complex **6**. The X-ray single-crystal diffraction data were collected at 200 K with a Bruker SMART X2S benchtop diffractometer fitted

with an Oxford Cryostreams Desktop Cooler. The structure was solved using SHELXS and refined with SHELXL.²⁶⁵

Most of the structures contain certain degree of disorder which was detected in difference Fourier syntheses of electron density and was taken care of using capabilities of SHELX package. In most cases, hydrogen atoms were localized in difference syntheses of electron density but were refined using appropriate geometric restrictions on the corresponding bond lengths and bond angles within a riding/rotating model (torsion angles of Me hydrogens were optimized to better fit the residual electron density). The particular non-standard details of structure solution and refinement are as indicated in the figure captions included as Supporting Information.

5.1.4 Preparation of Bis(diphenylphosphino)amine (dppa)

A literature procedure was adapted for isolation of dppa.¹⁷⁶ Toluene (30 mL), chlorodiphenylphosphine (3.30 mL, 18.4 mmol), and hexamethyldisilazane (1.92 mL, 9.23 mmol) were added sequentially to a 100-mL 3-neck round bottom flask inside a glovebox. Upon addition of the hexamethyldisilazane, a white precipitate began to form. The three necks were then equipped with a glass stopper, a reflux condenser fitted with a vacuum adaptor and flow regulator, and a vacuum adaptor with flow regulator, respectively. Once assembled and internally sealed, the flask was removed from the glovebox and connected to a Schlenk line and refluxed at 125°C for 3 h. During the reflux, the solution appeared to turn pale yellow with no precipitate present. After reflux, the solution was cooled to room temperature and the reflux condenser was exchanged for a glass stopper. Volatiles were then removed by vacuum evaporation (evaporation removes not only the toluene but also the byproduct Me₃SiCl). The remaining solid after evaporation was white. While the flask was under vacuum, it was pumped back into the glovebox. The solid was then washed with diethyl ether (2 x 10 mL) and dried. Yield of dppa: 2.292 g, 64%. NMR spectroscopy of the isolated product matches that of material purchased from a commercial vendor (Strem). ¹H NMR (500 MHz, CD₃CN): δ 4.33 (s, 1H, N-H), 7.33-7.38 (m, 20H, phenyls). ³¹P{¹H} NMR (500 MHz, CD₃CN): δ 41.6 (s).

5.1.5 Preparation of Dicopper Precursor Complexes 2.1 and 2.3

Reported literature procedures for **2.1**¹⁶⁸ and **2.3**¹⁷⁹ were used with the following modifications. In our hands, the reported procedure produced $[(\mu_2\text{-dppa})_2\text{Cu}_2(\text{MeCN})_2][\text{PF}_6]_2$ with only two coordinated acetonitrile molecules rather than four, which was confirmed by ^1H NMR integration in $\text{DMSO-}d_6$. The molecular weight for $[(\mu_2\text{-dppa})_2\text{Cu}_2(\text{MeCN})_2][\text{PF}_6]_2$ (1269.78 g/mol) was then used for all subsequent stoichiometric calculations. In the preparation of **2.3**, CH_2Cl_2 was used as the reaction solvent.

5.1.6 Preparation of 2.2

Complex **2.1** (1.00 g, 0.787 mmol) was added to a flask charged with acetone (30 mL) and a magnetic stir bar. In a separate vessel, Na_2S (0.0307 g, 0.393 mmol) was stirred in methanol (10 mL) until completely dissolved. The methanol solution of Na_2S was then added to the **2.1** solution dropwise, with stirring, at room temperature. Once all the Na_2S solution had been added, the resulting deep orange reaction mixture was stirred at room temperature for 3 h. The volume was reduced to 20 mL by vacuum evaporation, and then the solution was pipette-filtered through Celite to remove NaPF_6 . The filtered solution was then completely evaporated and re-constituted in acetone (4 mL). Diethyl ether (approximately 10-12 mL) was slowly added, causing a bright yellow precipitate to form. The yellow precipitate was collected by vacuum filtration and dried under vacuum. Yield of **2.2**: 0.593 g, 71%. Orange crystals may be obtained by dissolving yellow **2.2** in a minimum amount in acetone and allowing diethyl ether vapors to diffuse in through a pin sized hole. ^1H NMR (500 MHz, acetone- d_6): δ 2.08 (s, coordinated acetone), 6.06 (s, N-H), 7.12-7.39 (m, 80H, phenyls). Note: Integration values for the N-H and coordinated solvent resonances were consistently lower than expected, possibly due to exchange processes with free solvent. $^{31}\text{P}\{^1\text{H}\}$ NMR (500 MHz, acetone- d_6): δ 36.6 (s, dppa), -145.8 (sept., $J = 707.5$ Hz, PF_6^-). FT-IR (cm^{-1}): 3297 (N-H), 3052, 1481, 1434, 1098, 832, 734, 688, 555, 521, 481. Anal. calcd. for $\text{C}_{96}\text{H}_{84}\text{Cu}_4\text{F}_{12}\text{N}_4\text{P}_{10}\text{S}$: C, 54.57; H, 3.97; N, 2.64. Found: C, 54.44; H, 4.08; N, 2.75. Note: The sample submitted for elemental analysis was dissolved in tetrahydrofuran and then evaporated by vacuum three times to remove coordinated acetone molecules. Such treatment was also used to prepare samples of **2.2** for further reactivity studies described below.

5.1.7 Preparation of 2.4

Complex **2.3** (1.00 g, 0.810 mmol) was dissolved acetone (30 mL) while stirring with a magnetic stir bar. In a separate vessel, Na₂S (0.042 g, 0.54 mmol) was stirred in methanol (7.5 mL) until completely dissolved. The Na₂S solution was then added dropwise at room temperature to the **2.3** solution. Once the entire solution of Na₂S had been added, the resulting deep amber reaction mixture was stirred at room temperature for 3 h. The solution was vacuum evaporated to approximately 5 mL and then pipette-filtered through Celite to remove NaPF₆. The resulting solution was then completely evaporated, and recrystallization was conducted using the same vapor diffusion method described for complex **2.2**. Yield of **2.4**: 0.472 g, 55%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.12-1.40 (m, 60H, cyclohexyl), 1.62-1.98 (m, 72H, cyclohexyl). ³¹P{¹H} NMR (500 MHz, acetone-*d*₆): δ -6.0 (s, dcpm), -146.8 (sept., *J* = 707.7 Hz, PF₆⁻). FT-IR (cm⁻¹): 2920, 2846, 1444, 834, 754, 556, 513. Anal. calcd. for C₇₅H₁₃₈Cu₃F₆P₇S: C, 56.23; H, 8.73; N, 0.00. Found: C, 56.24; H, 8.47; N, 0.00.

5.1.8 Reaction Between 2.2 and Sodium Azide

A solution of **2.2** (0.013 g, 0.0061 mmol) was prepared in THF (1 mL). In a separate vessel, NaN₃ (0.0039 g, 0.060 mmol) was dissolved in MeOH (1 mL). The NaN₃ solution was then added dropwise to the solution of **2.2** at room temperature with stirring. No immediate color change was observed. The solution appeared cloudy during initial drops of NaN₃ but was then completely clear once all the NaN₃ had been added. Stirring was continued at room temperature for 16 h, during which time the reaction mixture became a darker orange color. The solution was then evaporated to dryness under vacuum, reconstituted in CD₂Cl₂, and then pipette-filtering through Celite to remove NaPF₆ and unreacted NaN₃. The column of Celite in the pipette was washed with a small amount of CD₂Cl₂ to capture as much product as possible. To the sample, a solution of tri(*o*-tolyl)phosphine (200 μL of a 0.030 M solution in CD₂Cl₂, 0.0060 mmol) was added as a ³¹P NMR internal standard. Yields based on quantitative ³¹P NMR: **2.5**, 51%; **2.6**, 19%; unreacted **2.2**, 8%. Crystals of **2.5** and **2.6** were obtained by vapor diffusion of diethyl ether into a THF solution of the crude mixture in the same manner as for complex **2.2**. ¹H NMR (400 MHz, CD₂Cl₂): δ 1.81 (m, 1.1 H, coordinated THF), 2.37 (s, 8.8 H, *o*-CH₃ in tri(*o*-tolyl)phosphine), 3.54 (s, 0.71 H, N-H of **2.6**), 3.64 (s,

integral not determined due to peak overlap, N-H of **2.5**), 3.66 (m, integral not determined due to peak overlap, coordinated THF), 6.69-7.37 (m, 60 H, phenyls). $^{31}\text{P}\{^1\text{H}\}$ NMR (400 MHz, CD_2Cl_2): δ 40.3 (s, dppa of **2.6**), 38.6 (s, unknown), 36.7 (s, unreacted **2.2**), 35.4 (s, dppa of **2.5**), -31.83 (s, tri(*o*-tolyl)phosphine), -146.09 (sept., $J = 710.4$ Hz, PF_6^-).

5.1.9 Preparation of **2.6** from Azidotrimethylsilane

To a solution of **2.2** (0.090 g, 0.042 mmol) in THF (3 mL) was added N_3SiMe_3 (56 μL , 0.42 mmol). No immediate color change or precipitate was observed. Stirring was continued at room temperature for 16 h, during which time the reaction color changed to dark red. The mixture was evaporated to dryness under vacuum. The red-brown residue was then reconstituted in THF (1 mL), and diethyl ether (1 mL) was added dropwise until a precipitate began to form. The tan precipitate was collected by vacuum filtration, washed diethyl ether (2 x 3 mL), and then dissolved in CH_2Cl_2 (2 mL) and pipette-filtered through Celite. The solution was then evaporated to dryness under vacuum. Crystals were obtained by vapor diffusion of diethyl ether into a THF solution in the same manner as described for complex **2.2**. Yield of **2.6**: 0.0453 g, 68%. ^1H NMR (400 MHz, CD_2Cl_2): δ 3.61 (s, 3H, N-H), 7.09-7.33 (m, 63H, phenyls). $^{31}\text{P}\{^1\text{H}\}$ NMR (400 MHz, CD_2Cl_2): δ 40.30 (s, dppa), -146.12 (sept., $J = 710.3$ Hz, PF_6^-). FT-IR (cm^{-1}): 3274 (N-H), 3052, 2920, 2851, 2046 (N_3), 1481, 1434, 1303, 1099, 909, 833, 734, 691, 522, 481. Anal. Calcd. For $\text{C}_{72}\text{H}_{63}\text{Cu}_3\text{F}_6\text{N}_9\text{P}_7$: C, 54.88; H, 4.03; N, 8.00. Found: C, 54.57; H, 4.07; N, 7.80.

5.1.10 Reaction Between **2.2** and Sodium Iodide

A solution of **2.2** (0.046 g, 0.0217 mmol) was prepared in THF (2 mL). In a separate vessel, NaI (0.0325 g, 0.218 mmol) was dissolved in MeOH (1 mL). The NaI solution was then added dropwise to the solution of **2.2** at room temperature with stirring. No immediate color change or precipitate was observed. Solution continued to stir at room temperature for 16 h, during which time the reaction mixture became a darker orange color. after 16 hours and was completely evaporated by vacuum. The solution was then evaporated to dryness under vacuum, reconstituted in CD_2Cl_2 , and then pipette-filtering through Celite to remove NaPF_6 and unreacted NaI. The column of Celite in the pipette was washed with a small amount of CD_2Cl_2 to capture as much product as possible. To the sample, a solution of tri(*o*-tolyl)phosphine (200 μL

of a 0.216 M solution in CD_2Cl_2 , 0.0216 mmol) was added as a ^{31}P NMR internal standard. Yields based on quantitative ^{31}P NMR: **2.8**, 75%; **2.7**: 13%. Crystals of **2.7** and **2.8** were obtained by a vapor diffusion of diethyl ether into a THF solution of the crude mixture in the same manner as for complex **2.2**. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.81 (m, 2.1 H, coordinated THF), 2.37 (s, 8.9 H, *o*- CH_3 in tri(*o*-tolyl)phosphine), 3.65 (m, 2.1 H, coordinated THF), 3.85 (s, 0.38 H, N-H of **2.7**), 3.87 (s, 1.2 H, N-H of **2.8**), 7.08-7.30 (m, 54.3 H, phenyls). $^{31}\text{P}\{^1\text{H}\}$ NMR (400 MHz, CD_2Cl_2): δ 33.9 (s, dppa of **2.7**), 29.7 (s, dppa of **2.8**), -31.8 (s, tri(*o*-tolyl)phosphine), -146.1 (sept., $J = 710.5$ Hz, PF_6^-). Spectroscopic characterization was verified by toluene precipitation followed by washing of the solid with diethyl ether. The combined soluble fractions were predominantly **2.7**, while the solid fraction was predominantly **2.8**. Characterization of **2.8**: ^1H NMR (400 MHz, CD_2Cl_2): δ 1.81 (m, 2H, coordinated THF), 3.56 (s, 3H, N-H), 3.66 (m, 2H, coordinated THF), 7.08-7.30 (m, 60H, phenyls). $^{31}\text{P}\{^1\text{H}\}$ NMR (400 MHz, CD_2Cl_2): δ 29.6 (s, dppa), -146.1 (sept., $J = 710.3$ Hz, PF_6^-). FT-IR (cm^{-1}): 3281 (N-H), 3051, 2921, 2852, 2120, 1481, 1433, 1099, 927, 836, 734, 691, 523, 481.

5.1.11 Competition Reaction Between Sodium Iodide/Sodium Azide and 2.2

A solution of **2.2** (0.015 g, 0.0071 mmol) in THF (approximately 1 mL) was vacuum evaporated extensively to remove any coordinated acetone molecules. Once **2.2** appeared free of acetone by ^1H NMR, it was dissolved again in 1 mL of THF. In a separate vessel, NaI (0.0053 g, 0.035 mmol) was dissolved in approximately 1 mL of MeOH. Solution of NaI was then added to NaN_3 (0.0023 g, 0.035 mmol) and added to **2.2** dropwise, at room temperature with stirring. Solution continued stirring overnight at room temperature and the resulting color was a darker orange with no obvious precipitate. Solution was completed evaporated by vacuum.

5.1.12 Experimental Spectra and Relevant Data Tables

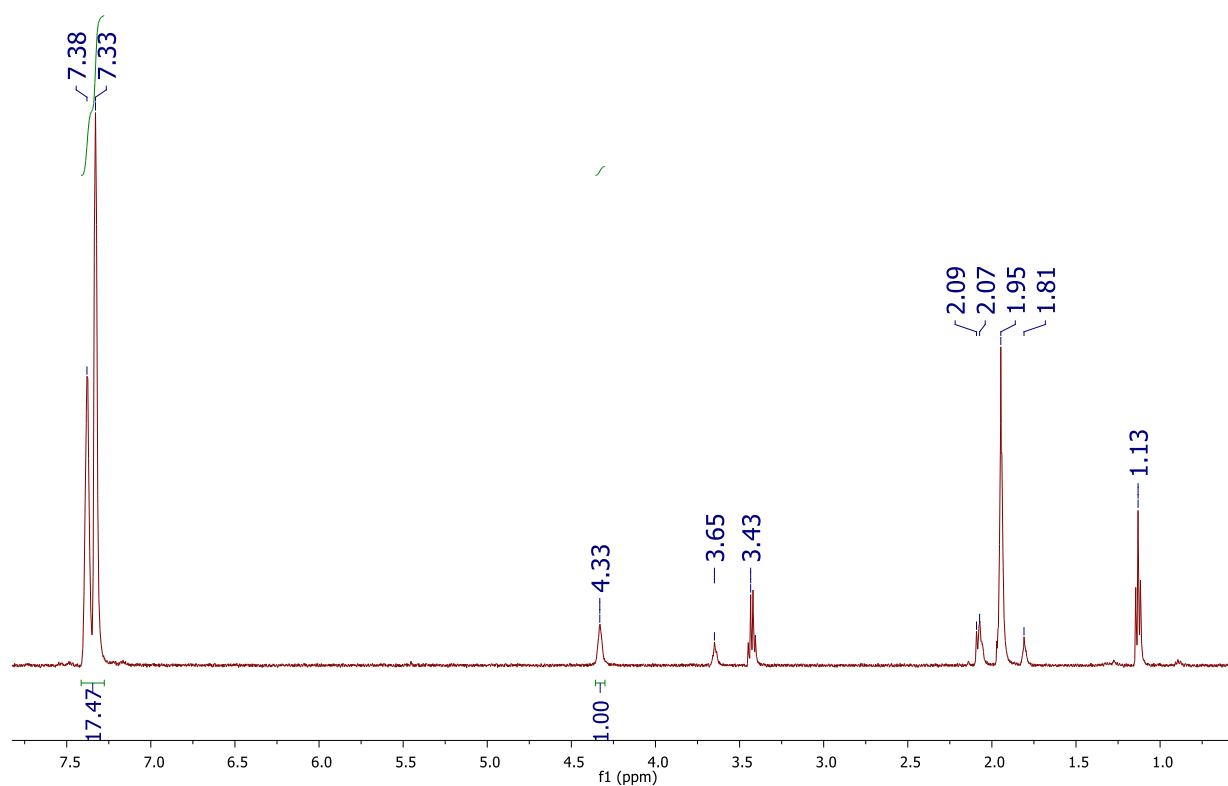


FIGURE 5.1 ^1H NMR (500 MHz) of bis(diphenylphosphino)amine ligand in CD_3CN synthesized from modified literature procedure.¹⁷⁶ Note: Integration values for solvent impurities were neglected from spectrum.

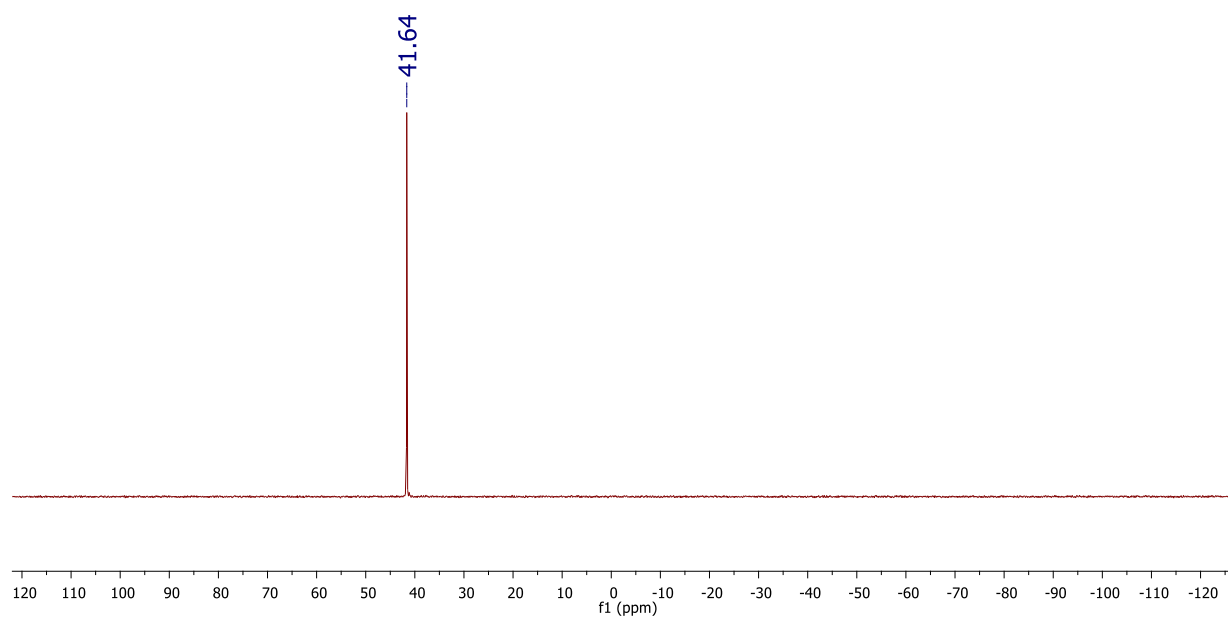


FIGURE 5.2 ^{31}P NMR (500 MHz) of bis(diphenylphosphino)amine ligand in CD_3CN synthesized from modified literature procedure.¹⁷⁶

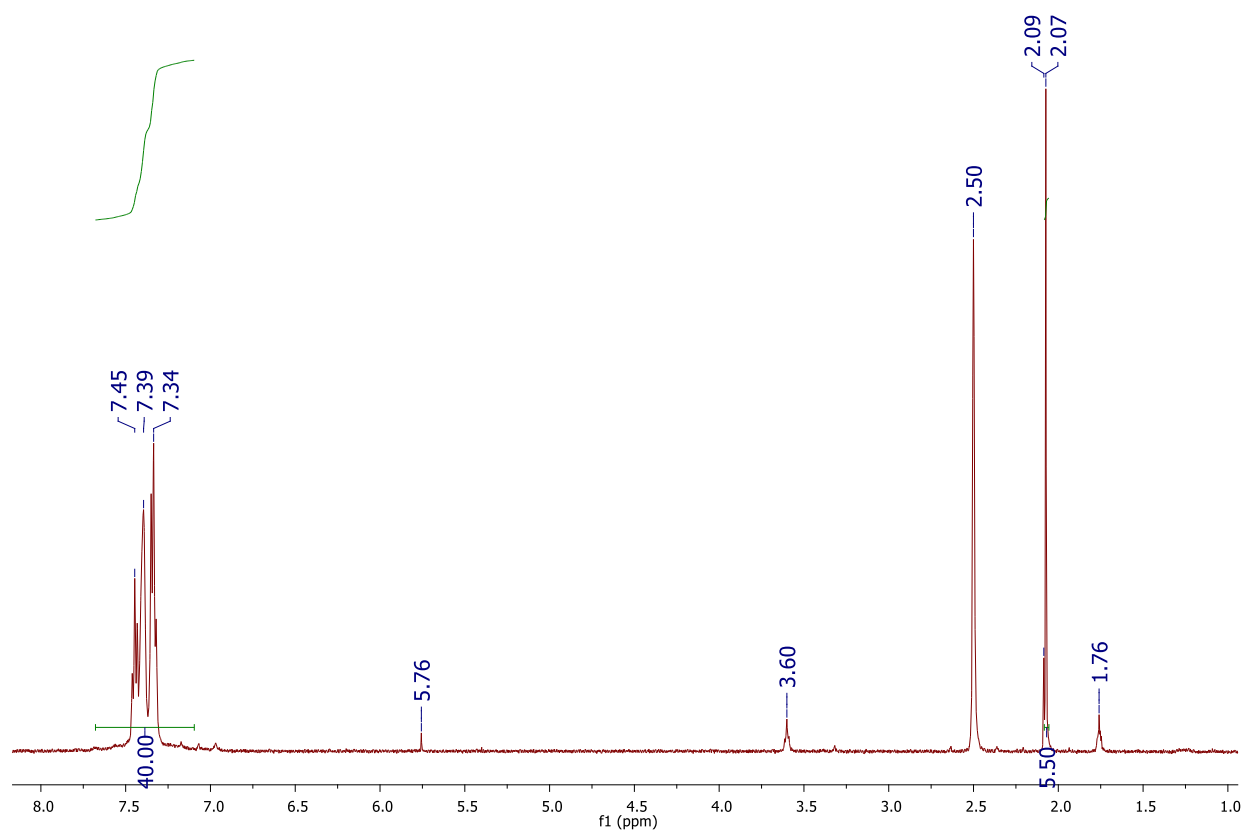


FIGURE 5.3 ¹H NMR (500 MHz) of **2.1** in DMSO-d₆ synthesized from literature procedure.¹⁶⁸ Calibration of integral for phenyl protons to 40.0 reveals only 2 acetonitrile molecules maximum coordinated to dicopper complex. Note: Integration values for solvent impurities were neglected from spectrum.

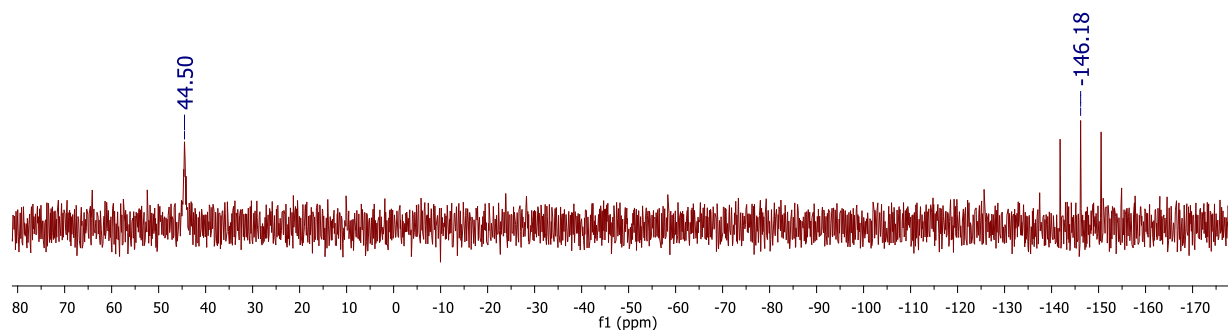


FIGURE 5.4 ³¹P NMR (500 MHz) of **2.1** in CD₃CN synthesized from literature procedure.¹⁶⁸

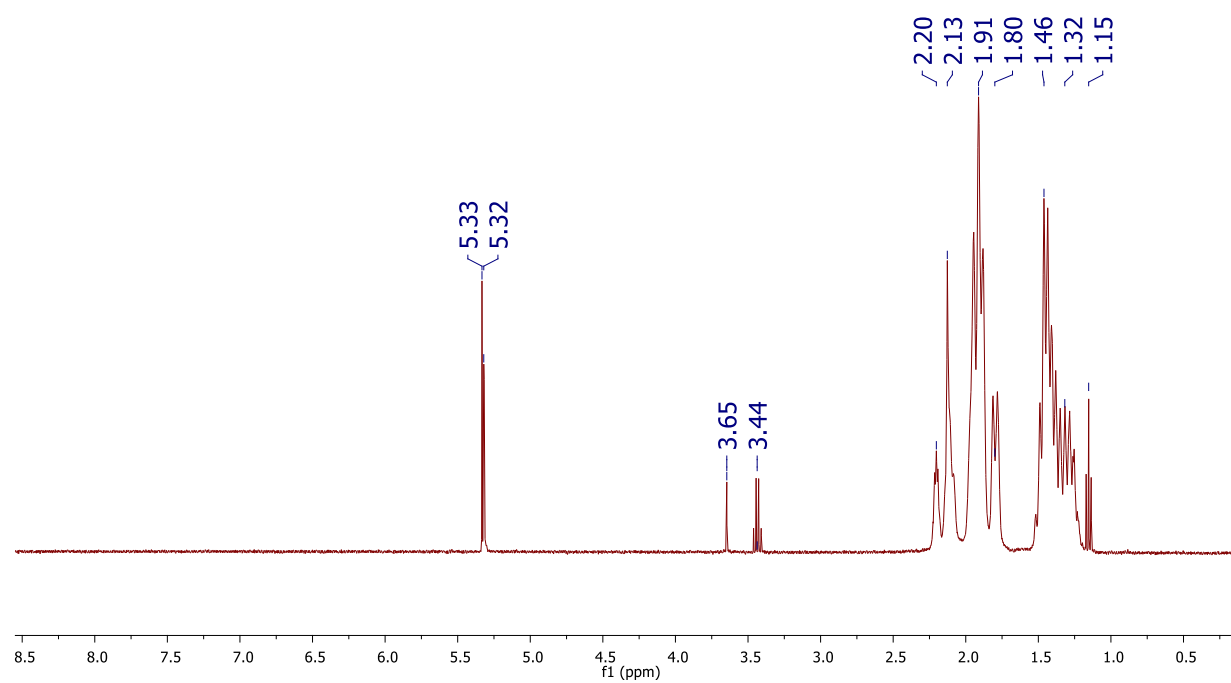


FIGURE 5.5 ^1H NMR (500 MHz) of **2.3** in CD_2Cl_2 synthesized from literature procedure.¹⁷⁹ Note: Some peaks present in spectrum are solvent impurities.

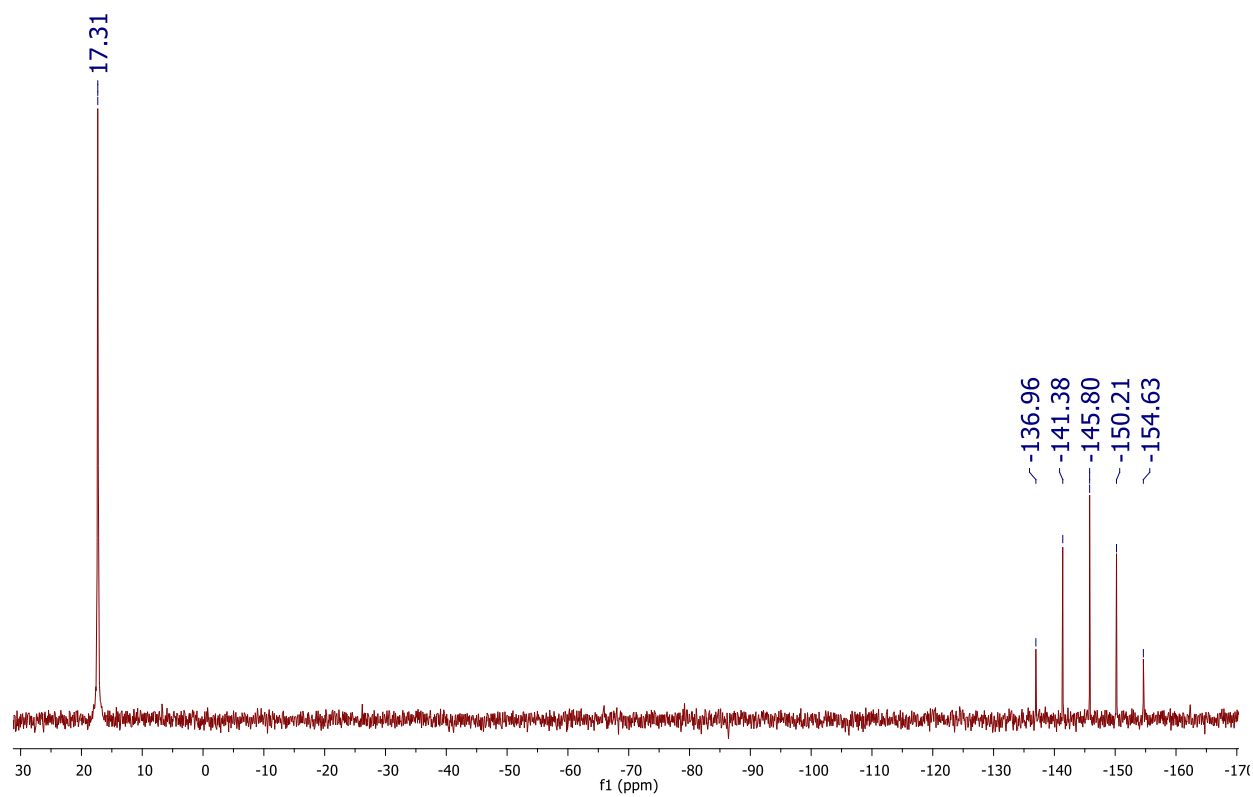


FIGURE 5.6 ^{31}P NMR (500 MHz) of **2.3** in CD_2Cl_2 synthesized from literature procedure.¹⁷⁹

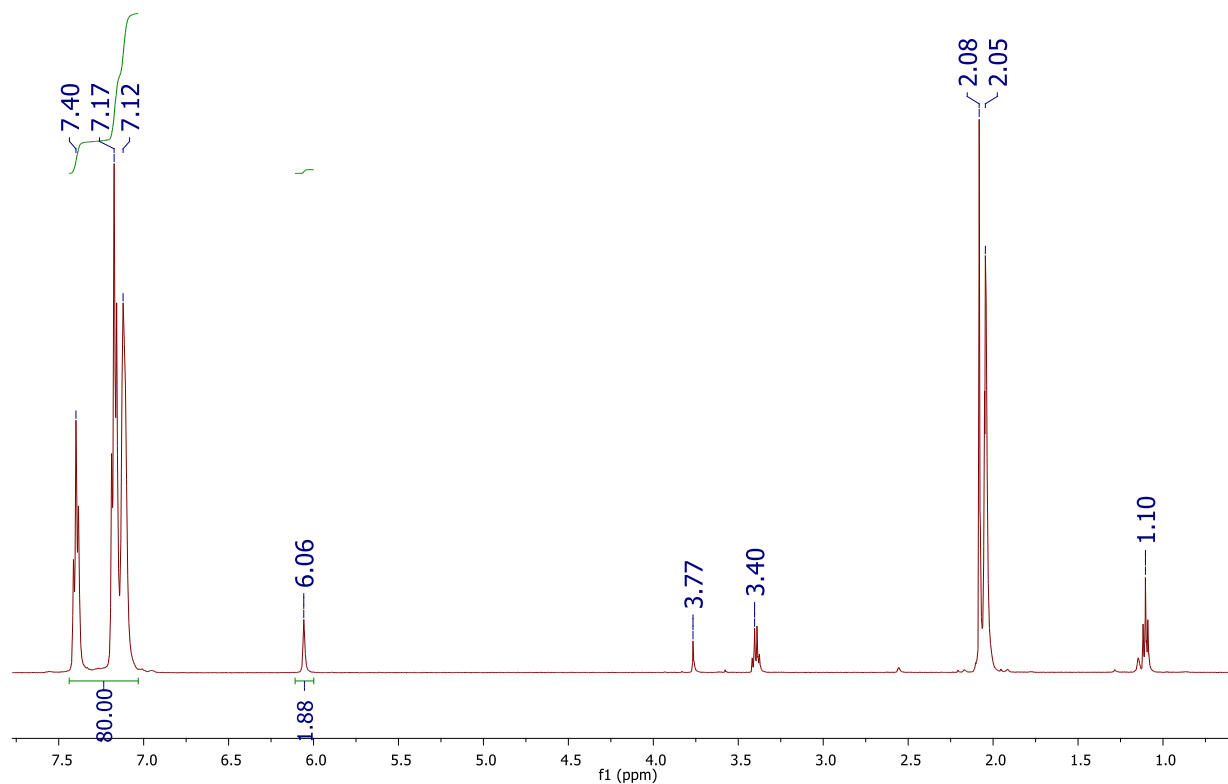


FIGURE 5.7 ¹H NMR (500 MHz) of **2.2** in (CD₃)₂CO. Note: Integration values for solvent impurities were neglected from spectrum. Peak at 3.77 ppm was not identified as a solvent impurity however it does appear in ¹H NMR spectrum of just (CD₃)₂CO.

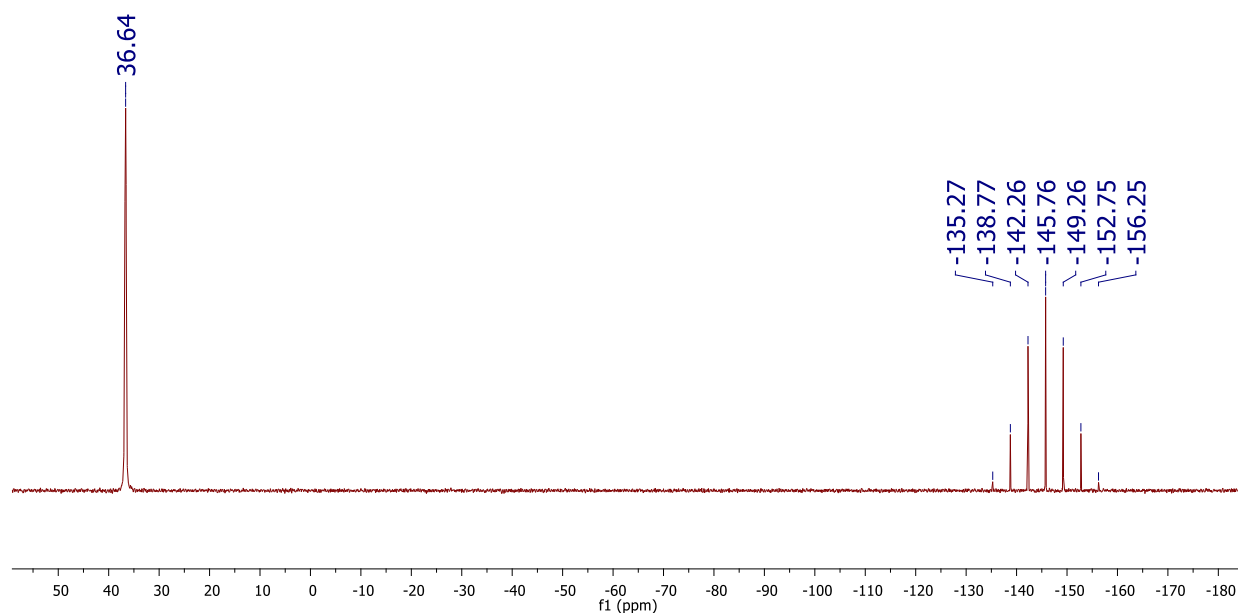


FIGURE 5.8 ³¹P NMR (500 MHz) of **2.2** in (CD₃)₂CO.

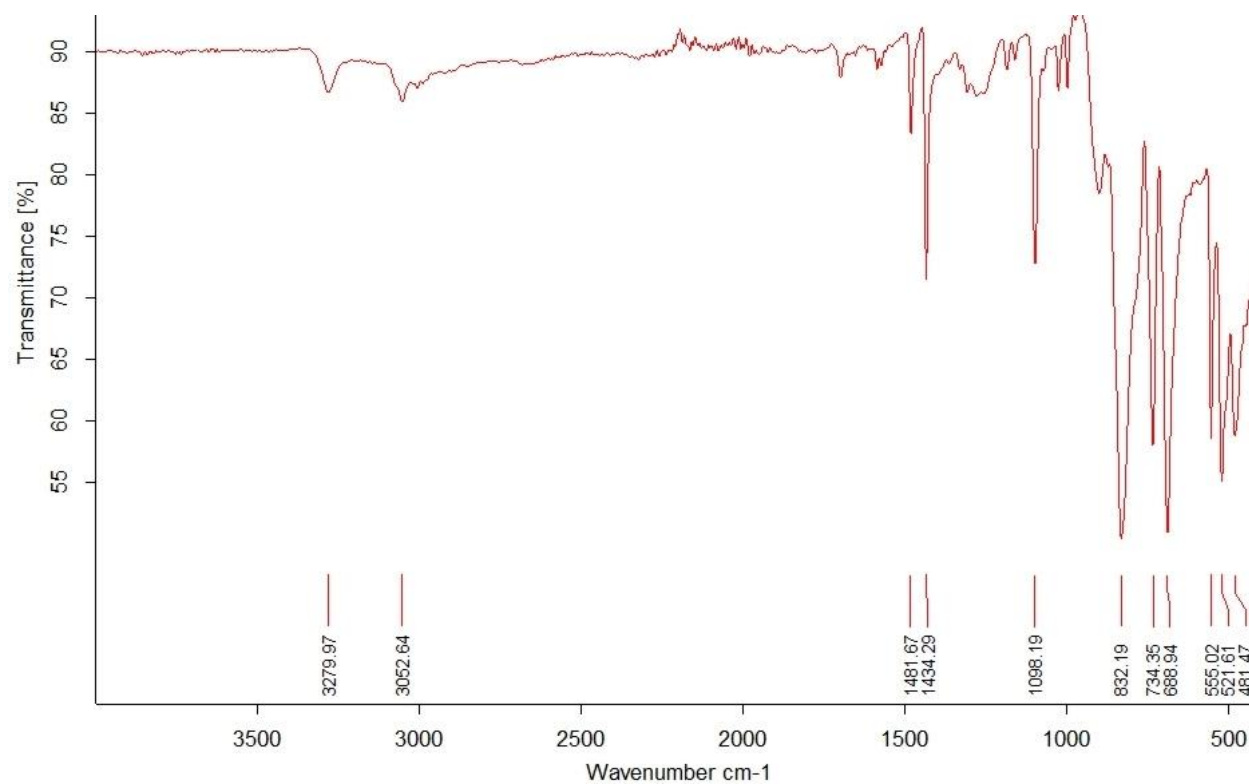


FIGURE 5.9 Infrared spectrum of 2.2

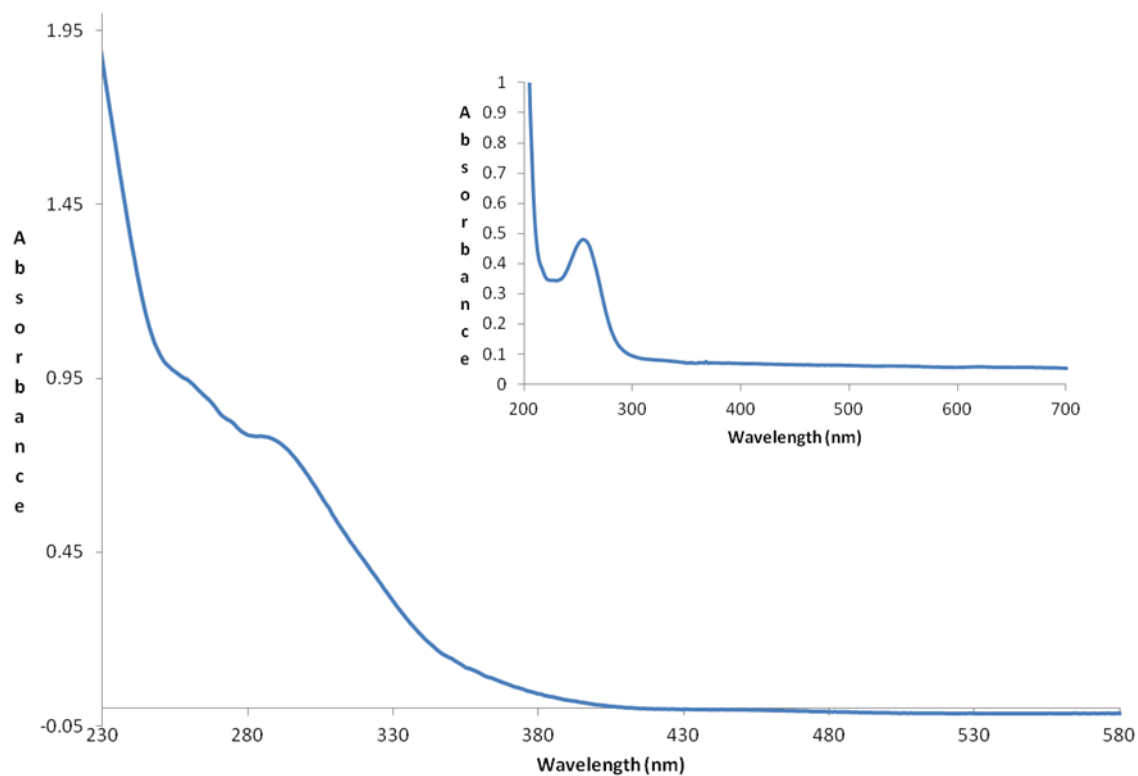


FIGURE 5.10 Absorption spectrum of **2.2** (2×10^{-5} M) in MeCN at room temperature. Shoulder appears at 284 nm. Note: Shoulder appearing at ~ 250 nm is from acetonitrile solvent and not a characteristic property of **2.2** (inset is MeCN solvent).

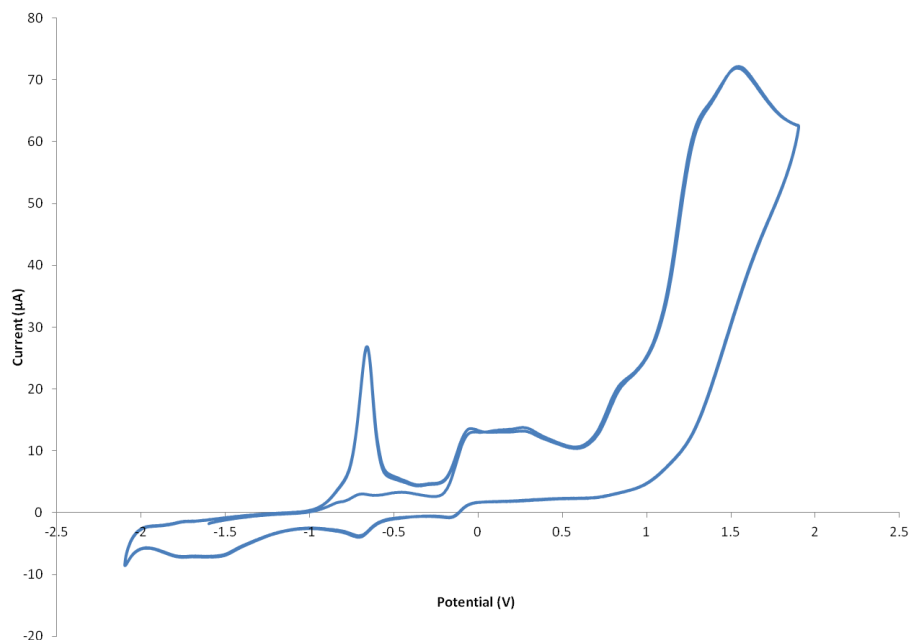


FIGURE 5.11 Cyclic voltammogram of **2.2** (1.88×10^{-3} M solution in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{MeCN}$). Potentials referenced to $\text{FeCp}_2^{+/0}$. The large feature at approximately -0.7 V does not appear in the first scan, but only after a complete oxidative scan has been conducted.

TABLE 5.1 Cyclic Voltammetry Parameters Used for Obtaining CV in Figure 5.11

Number of segments	Initial Potential (V)	Initial Direction	Upper Potential (V)	Lower Potential (V)	Final Potential (V)	Sweep Rate (V/s)
5	-1.5	Rising	2	-2	0	0.1

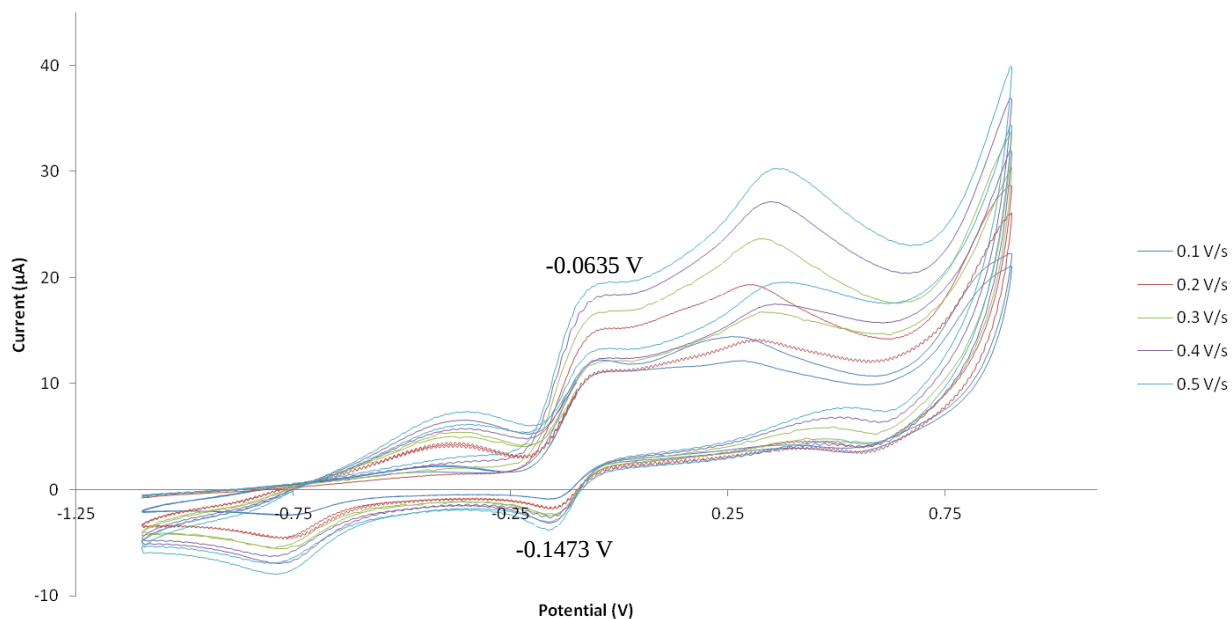


FIGURE 5.12 Cyclic voltammograms with differing scan rates of **2.2** (1.88×10^{-3} M solution in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{MeCN}$). Potentials referenced to $\text{FeCp}_2^{+/0}$.

TABLE 5.2 Cyclic Voltammetry Parameters Used for Acquiring CVs in Figure 5.12

Number of segments	Initial Potential (V)	Initial Direction	Upper Potential (V)	Lower Potential (V)	Final Potential (V)	Sweep Rate (V/s)
5	-1	Rising	1	-1	0	0.1, 0.2, 0.3, 0.4, 0.5

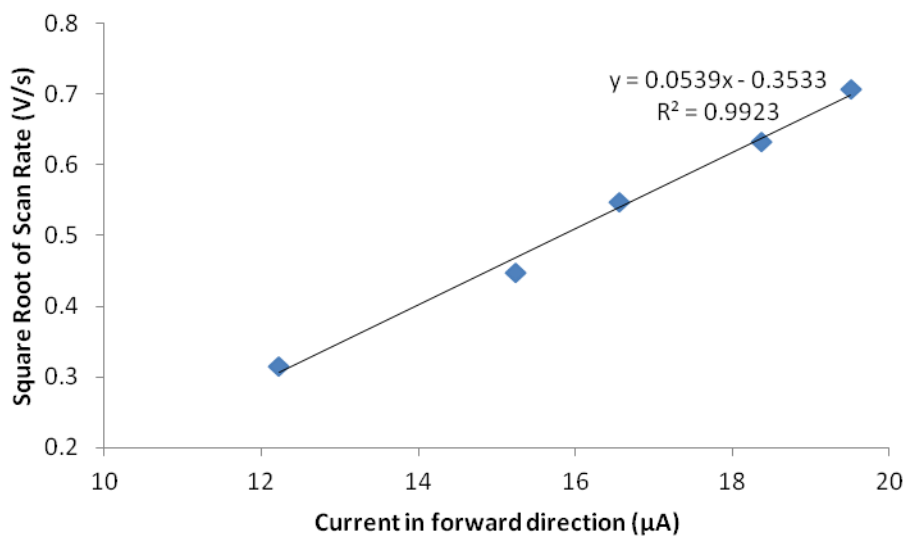


FIGURE 5.13 Plot of square root of scan rate vs. current in forward direction, demonstrating the reversibility of the first oxidation for **2.2**.

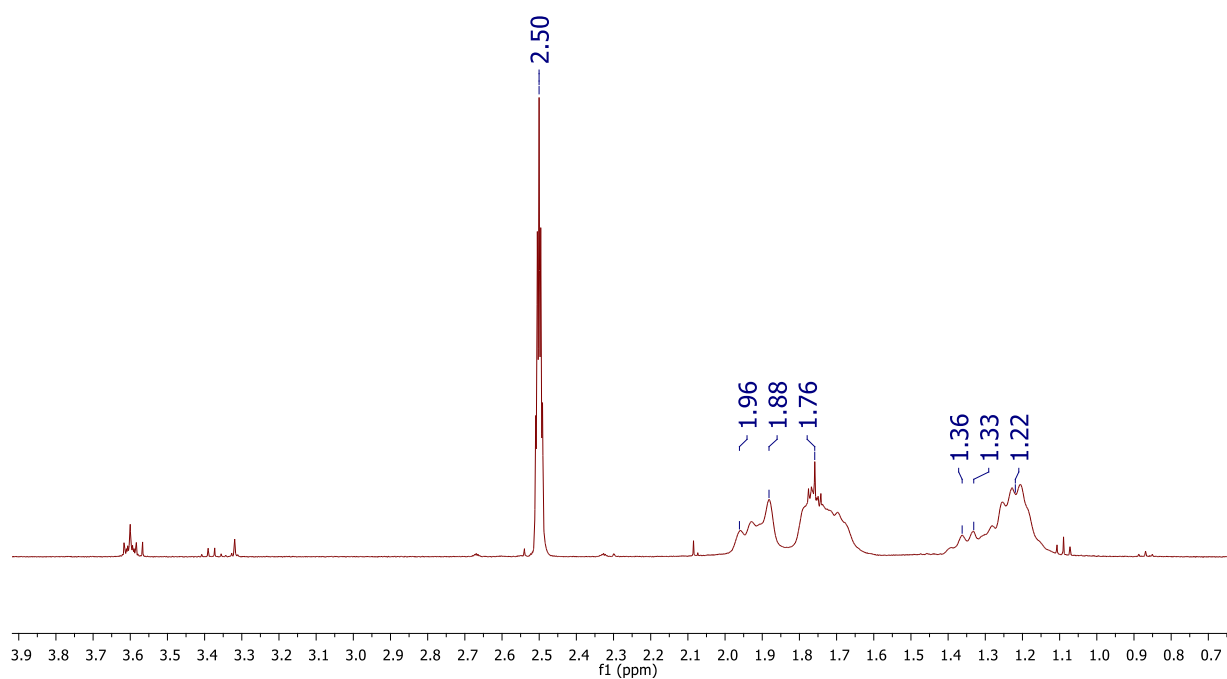


FIGURE 5.14 ^1H NMR (400 MHz) of **2.4** in DMSO-d_6 . Note: Solvent impurities are not peak picked.

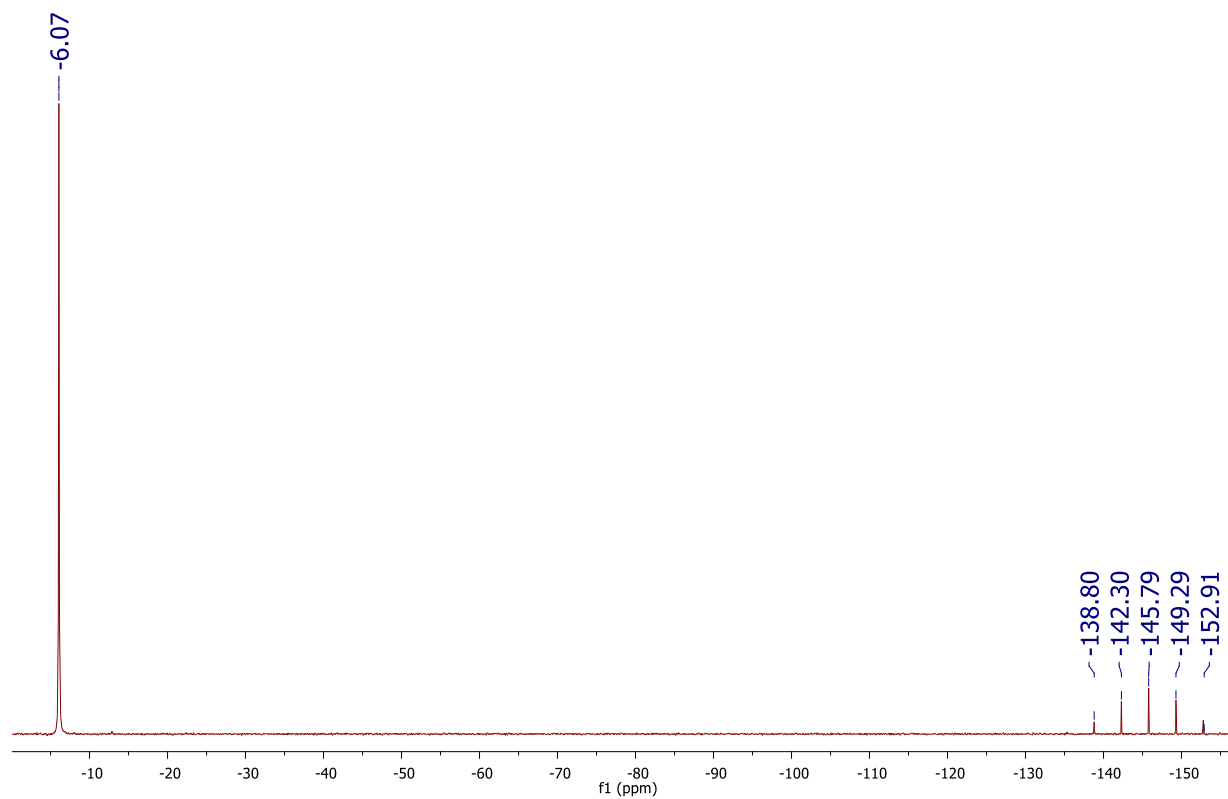


FIGURE 5.15 ^{31}P NMR (500 MHz) of **2.4** in $(\text{CD}_3)_2\text{CO}$.

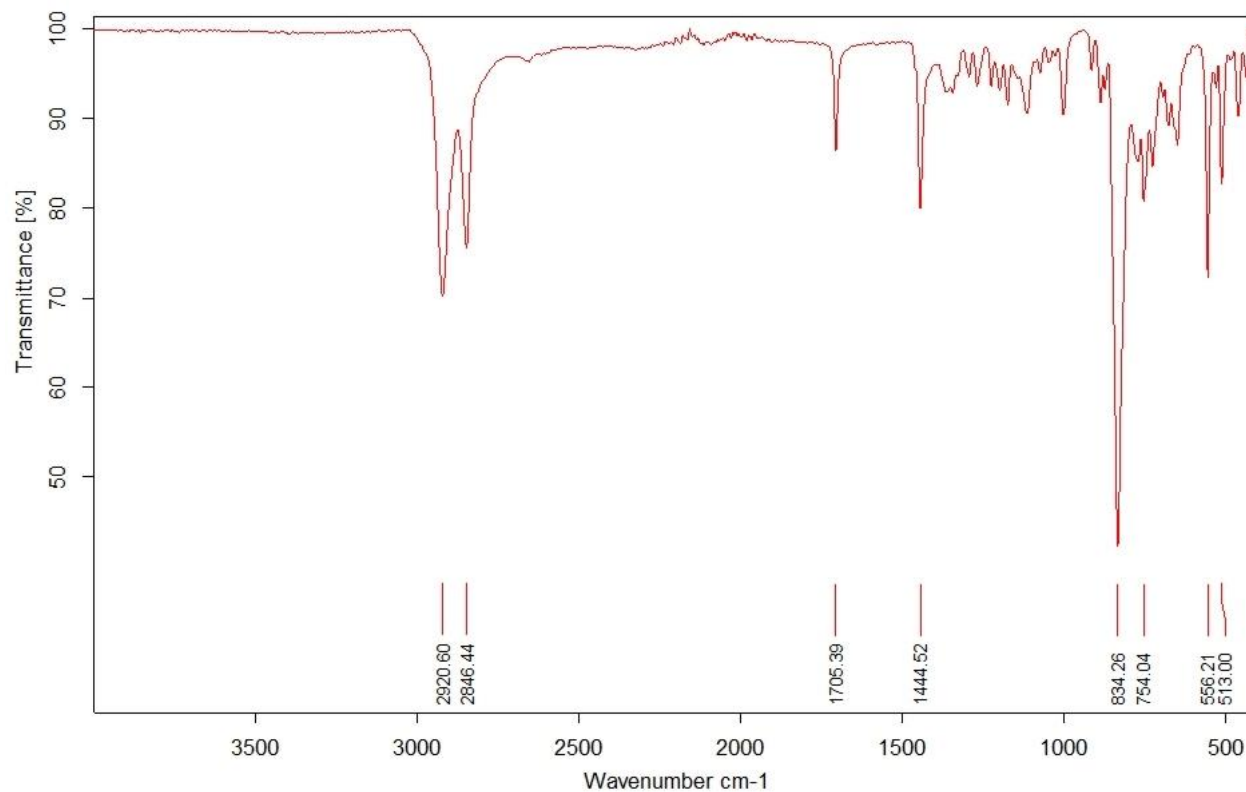


FIGURE 5.16 Infrared spectrum of **2.4**.

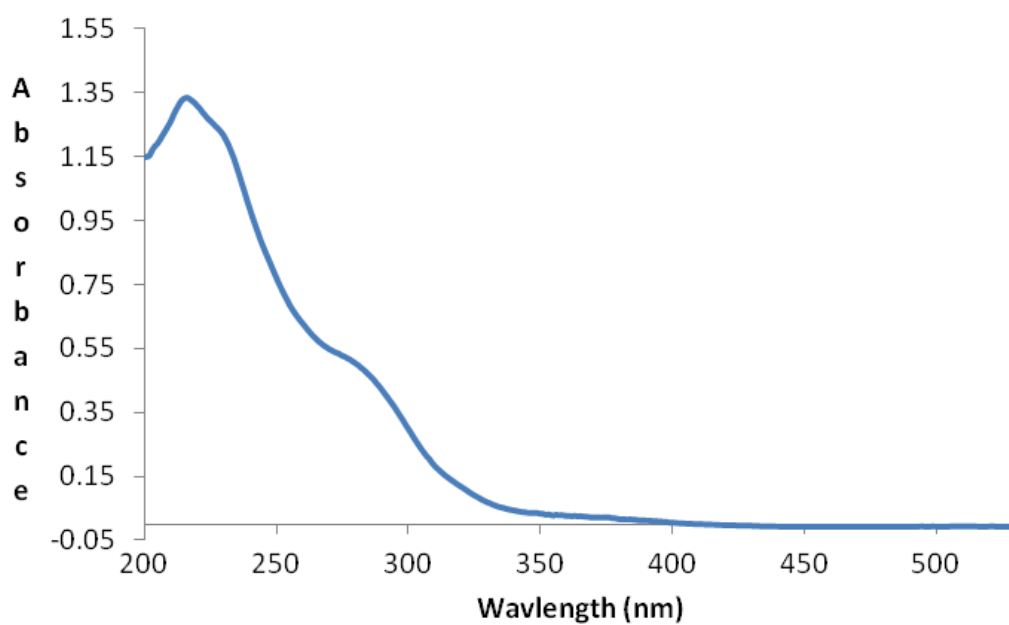


FIGURE 5.17 Absorption spectrum of **2.4** (4.0×10^{-5} M) in MeCN at room temperature. Shoulder appears at 279 nm, 229 nm and a peak appears at 216 nm.

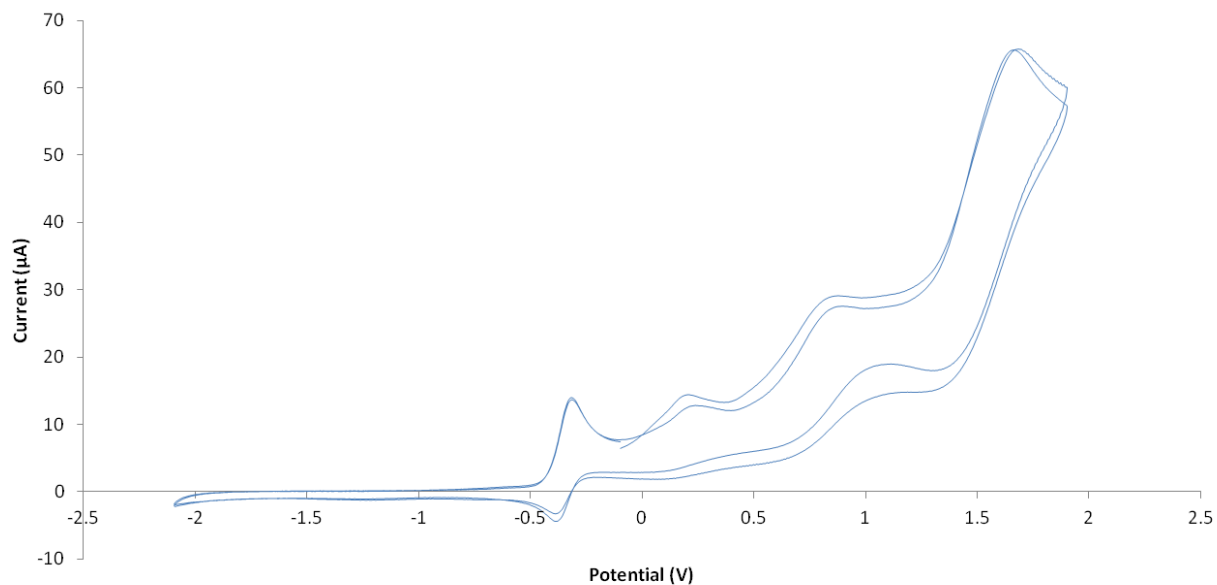


FIGURE 5.18 Cyclic voltammogram of **2.4** (1.88×10^{-3} M solution in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{MeCN}$) solution. Potentials referenced to $\text{FeCp}_2^{+/0}$.

TABLE 5.3 Cyclic Voltammetry Parameters Used for Obtaining CV in Figure 5.18

Number of segments	Initial Potential (V)	Initial Direction	Upper Potential (V)	Lower Potential (V)	Final Potential (V)	Sweep Rate (V/s)
5	0	Rising	2	-2	0	0.1

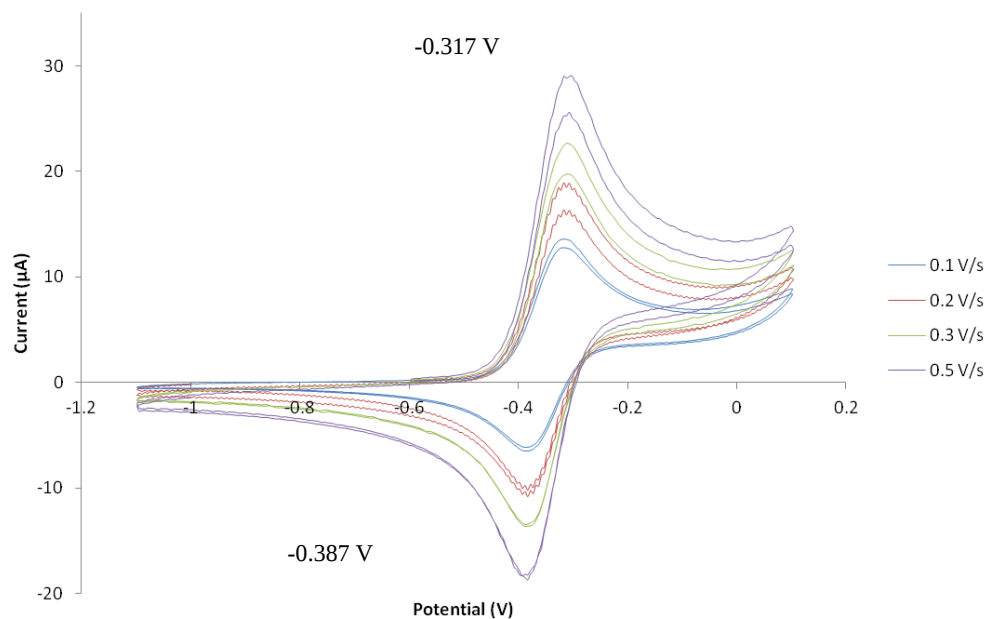


FIGURE 5.19 Cyclic voltammograms with differing scan rates of **2.4** (1.88×10^{-3} M solution in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{MeCN}$). Potentials referenced to $\text{FeCp}_2^{+/0}$.

TABLE 5.4 Cyclic Voltammetry Parameters for Acquiring CVs in Figure 5.19

Number of segments	Initial Potential (V)	Initial Direction	Upper Potential (V)	Lower Potential (V)	Final Potential (V)	Sweep Rate (V/s)
5	-0.5	Rising	0.2	-1	-0.9	0.1, 0.2, 0.3, 0.4, 0.5

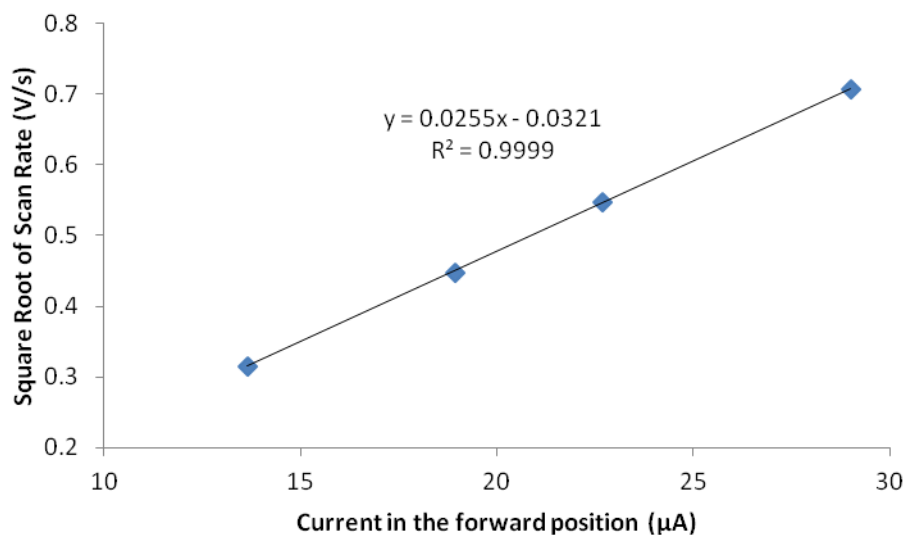


FIGURE 5.20 Plot of square root of scan rate vs. current in forward direction, demonstrating the reversibility of the first oxidation for **2.4**.

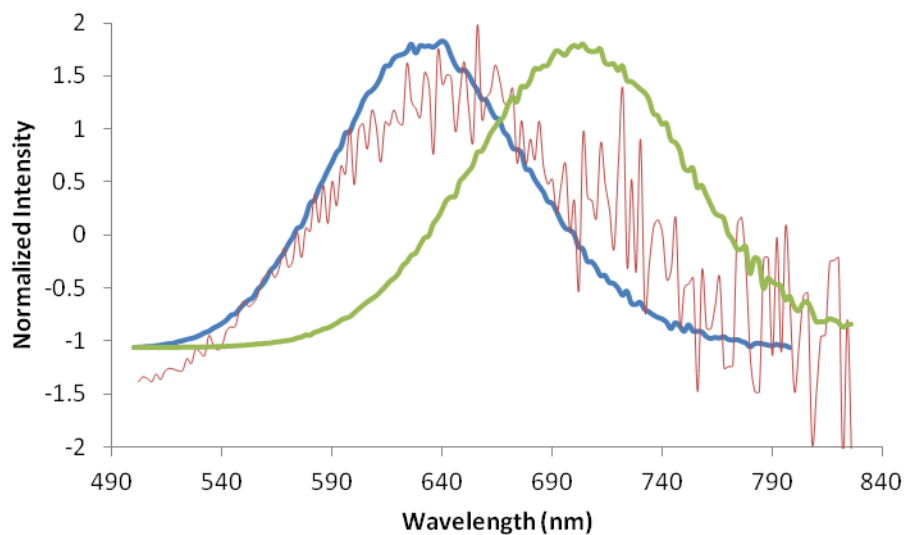


FIGURE 5.21 Normalized emission spectra for compounds **1.3** (blue trace), **2.2** (green trace) and **2.4** (red trace) using 415 nm as the excitation wavelength in all cases. Large signal to noise ratio for **2.4** resulted from decomposition during emission acquisition and intensity was below detection limit for instrument.

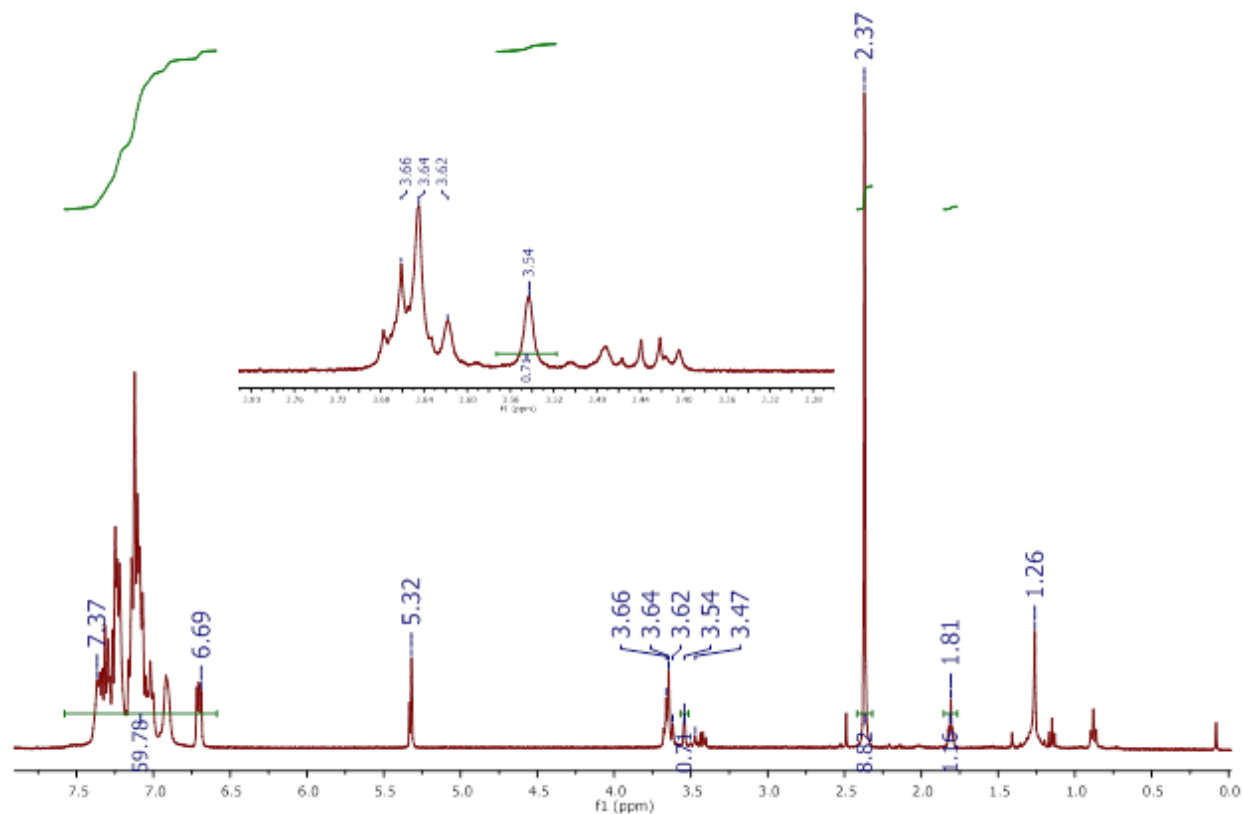


FIGURE 5.22 ^1H NMR (400 MHz) of reaction mixture of **2.2** and excess NaN_3 in CD_2Cl_2 with tri(*o*-tolyl)phosphine as the internal standard. Peak at 3.62 ppm is unreacted **2.2**. Integration values for **2.2**, **2.5** and coordinated THF molecules at 3.66 ppm could not be determined due to spectral peak overlap (see spectra inset).

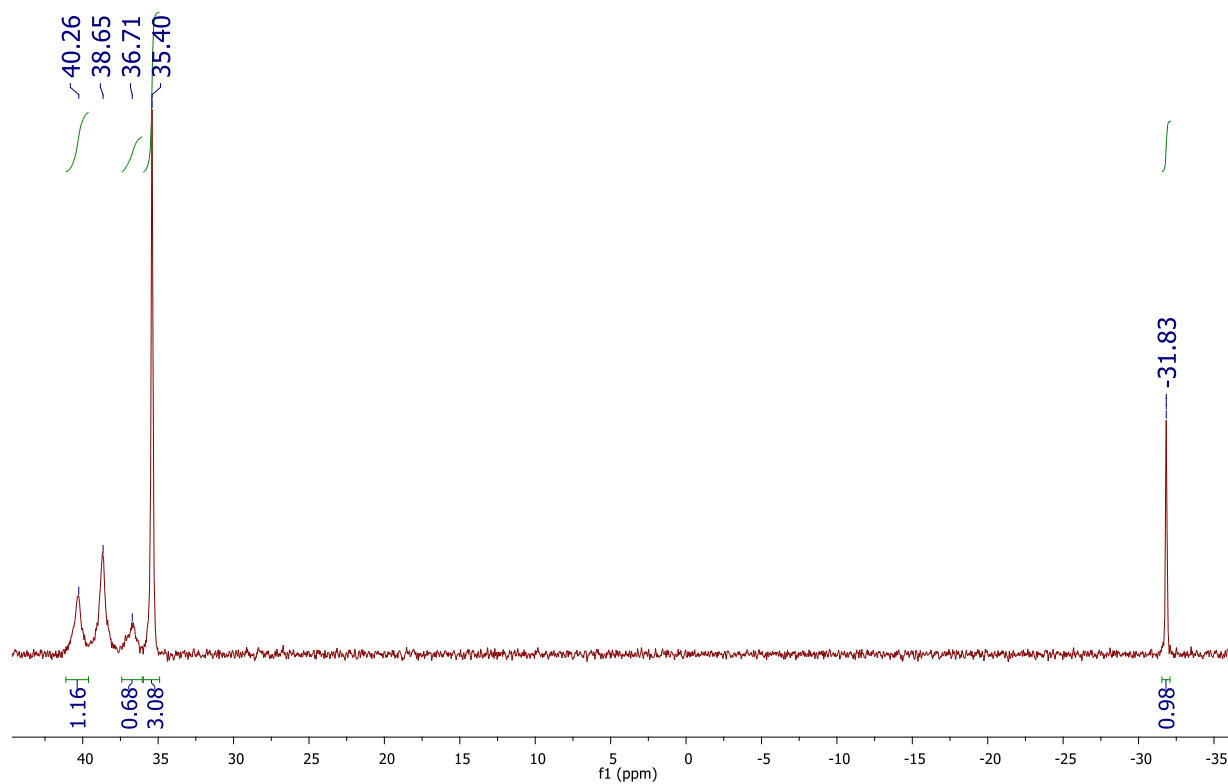


FIGURE 5.23 ^{31}P NMR (400 MHz) of reaction mixture of **2.2** and excess NaN_3 in CD_2Cl_2 with tri(*o*-tolyl)phosphine as the internal standard. Anion (PF_6^-) at -146.1 ppm is omitted from spectra.

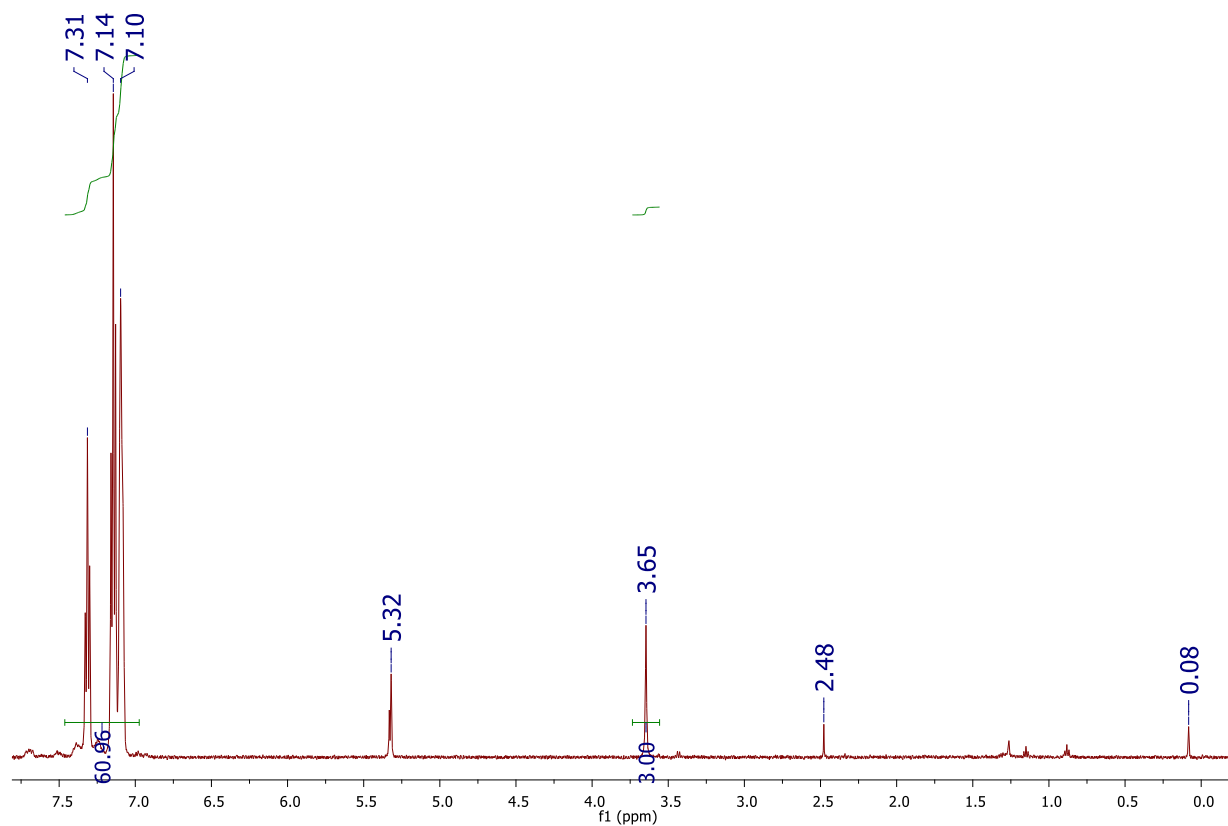


FIGURE 5.24 ^1H NMR (400 MHz) of **2.6** from N_3SiMe_3 in CD_2Cl_2 . Note: Integration values for solvent impurities were neglected from spectrum. Peak at 2.48 ppm is unknown as a solvent but is predicted to be an impurity in NMR tube because of its reoccurrence in other, different experimental spectra.

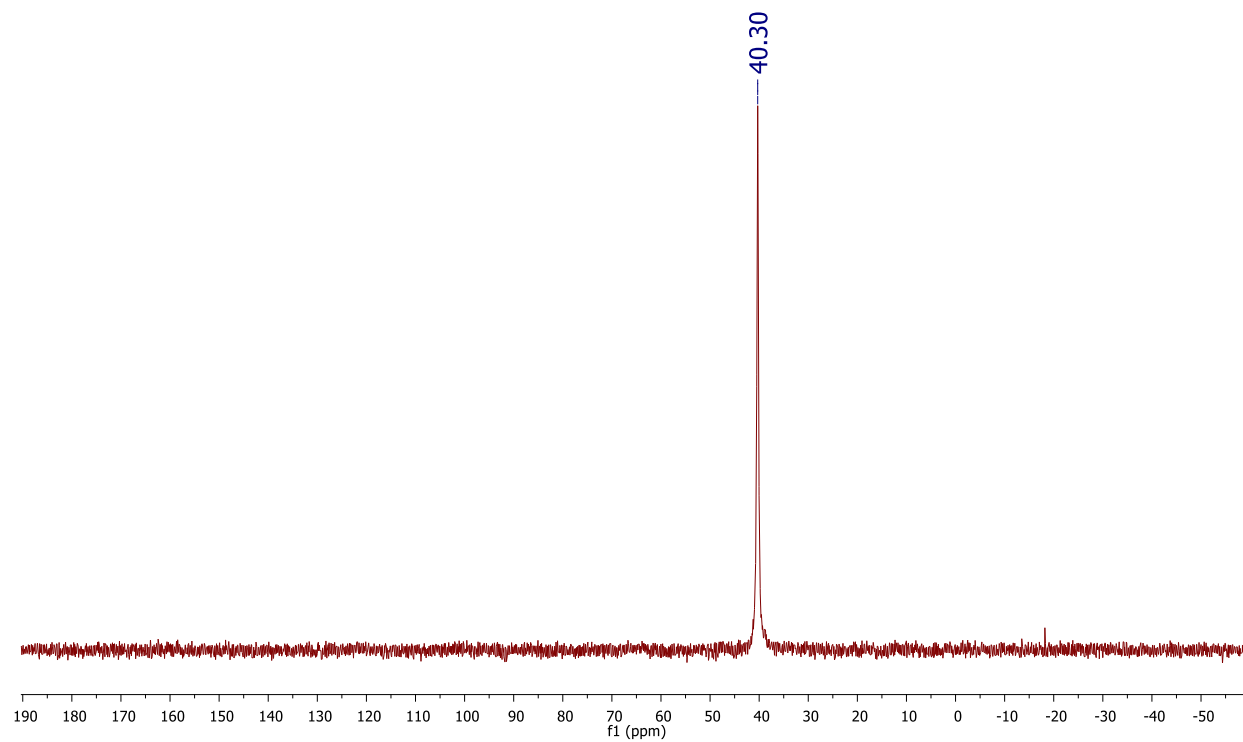


FIGURE 5.25 ^{31}P NMR (400 MHz) of **2.6** from N_3SiMe_3 in CD_2Cl_2 . Anion (PF_6^-) at -146.1 ppm omitted from spectra.

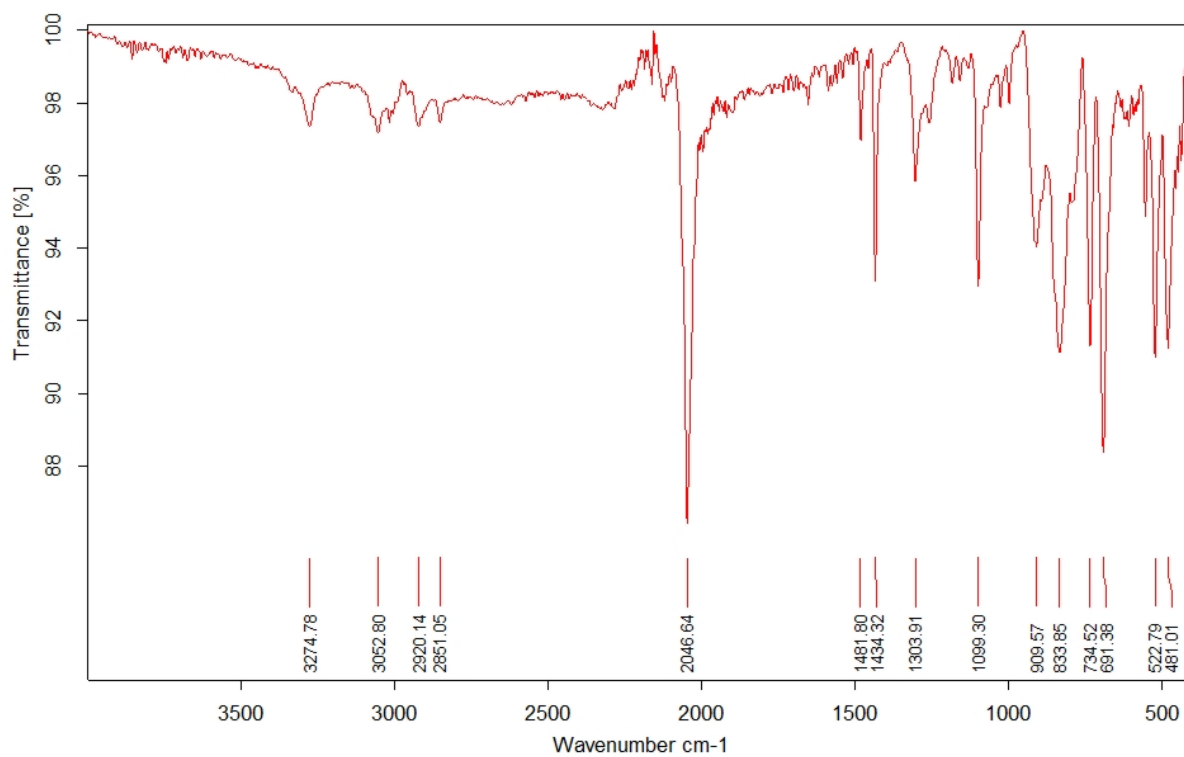


FIGURE 5.26 Infrared spectrum of **2.6**

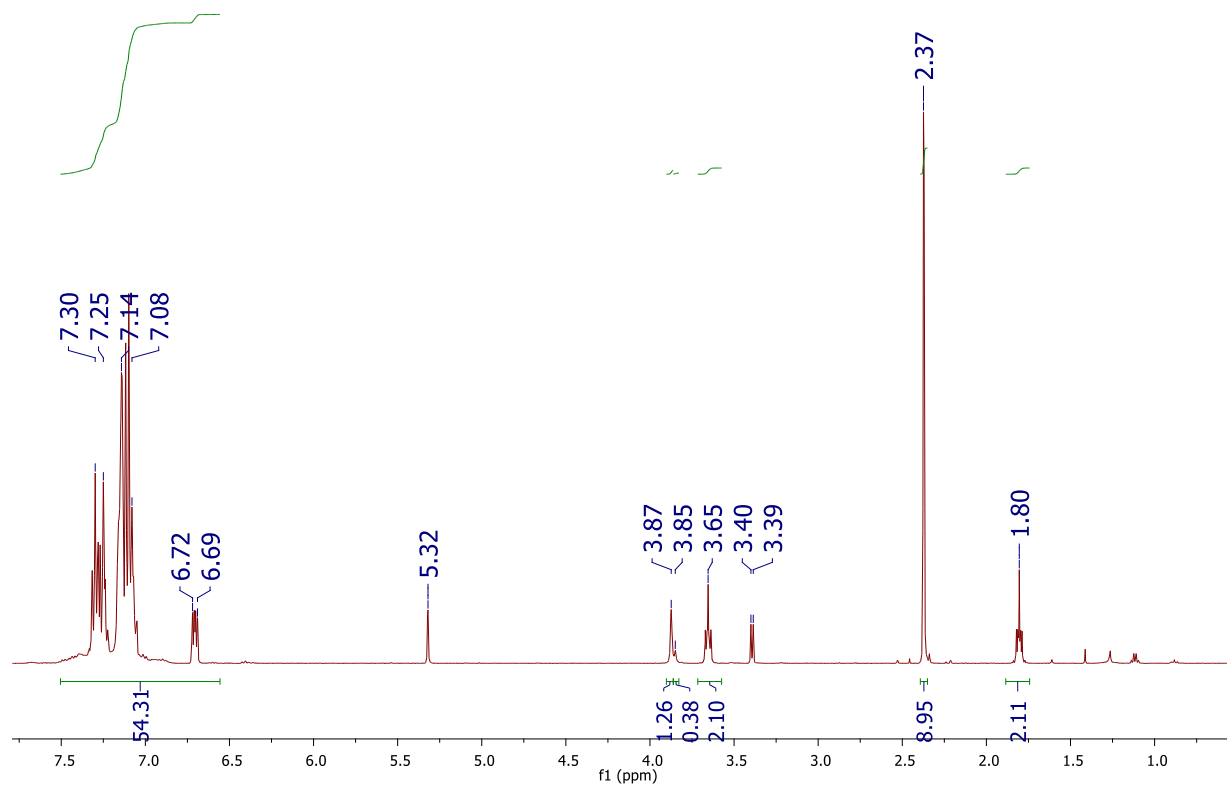


FIGURE 5.27 ^1H NMR (400 MHz) of reaction mixture of **2.2** and excess NaI in CD_2Cl_2 with tri(*o*-tolyl)phosphine as the internal standard. Doublet appearing at 3.40 ppm is unknown, however it never appeared in any other ^1H NMR spectra for this reaction.

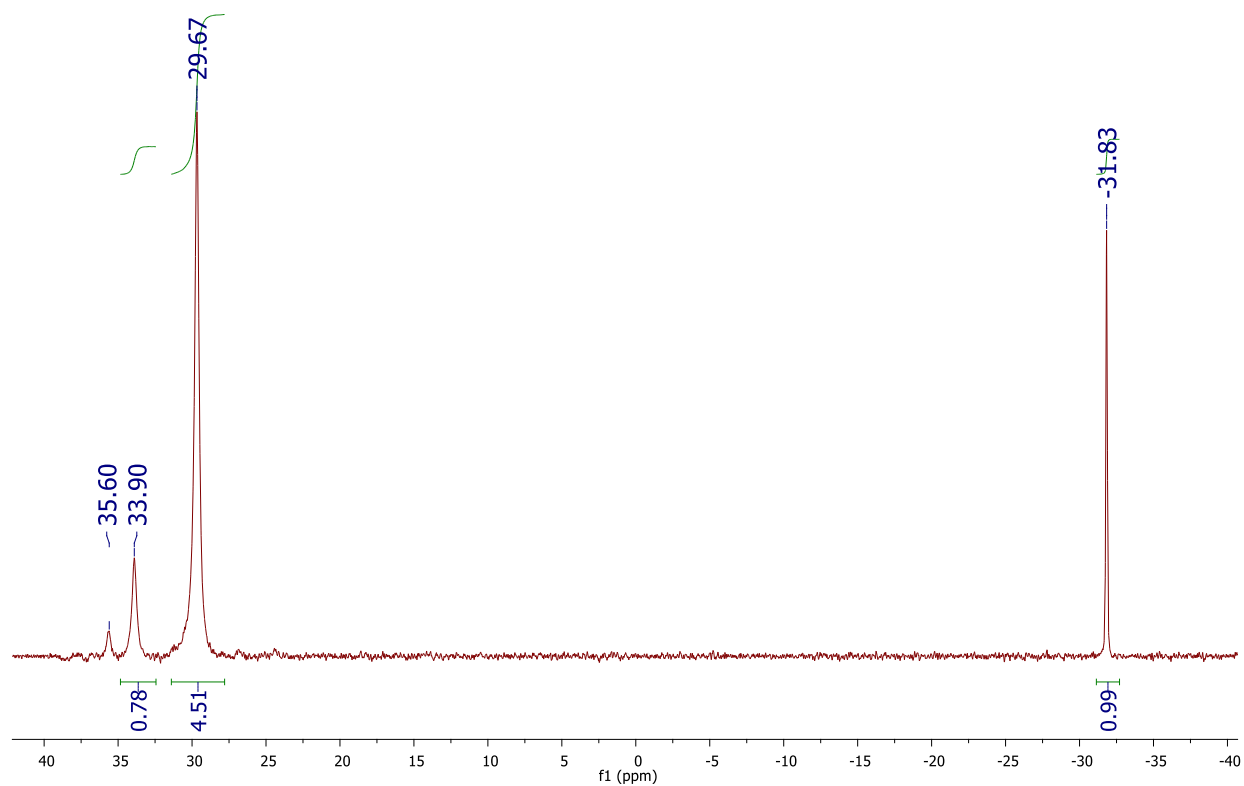


FIGURE 5.28 ^{31}P NMR (400 MHz) of reaction mixture of **2.2** and excess NaI in CD_2Cl_2 with tri(*o*-tolyl)phosphine as the internal standard. Unknown product at 35.60 ppm usually is not observed as a byproduct in this reaction.

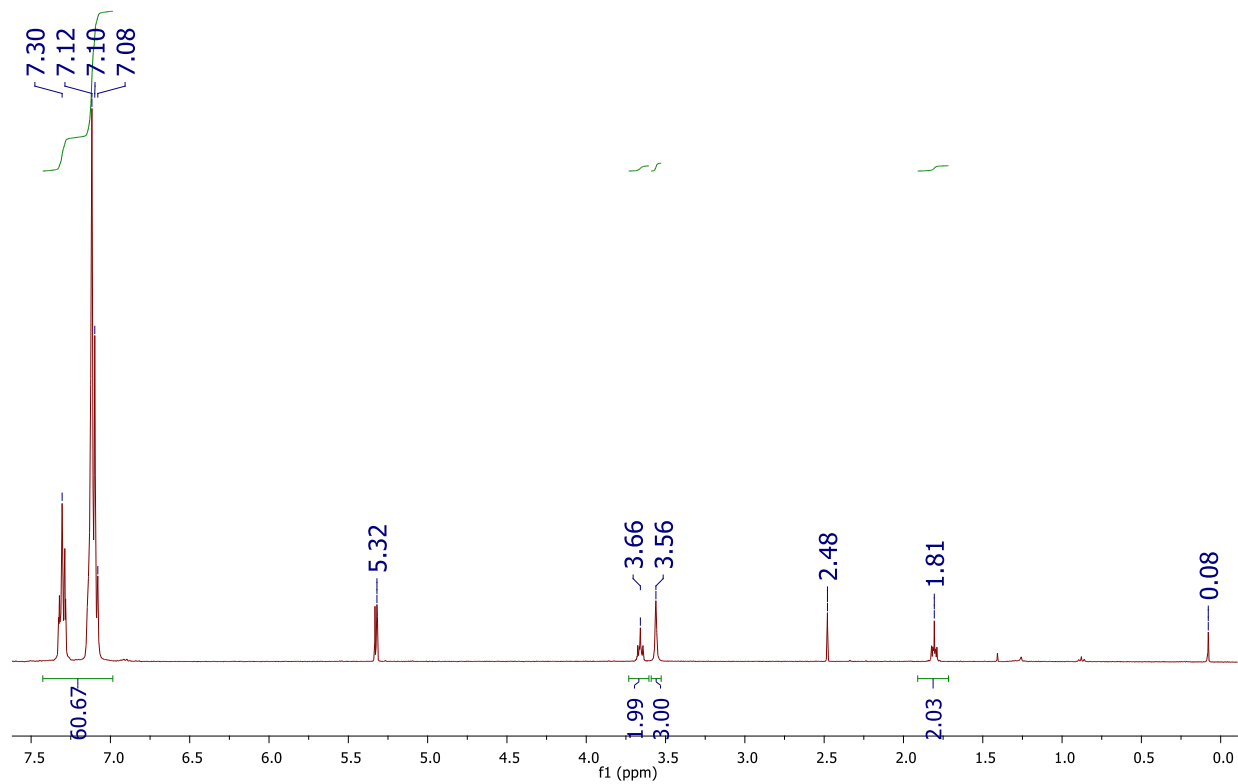


FIGURE 5.29 ^1H NMR (400 MHz) of isolation of **2.8** by toluene in CD_2Cl_2 . Peak at 2.48 ppm is unknown as a solvent impurity but is predicted to be an impurity in NMR tube because of its reoccurrence in other, different experimental spectra.

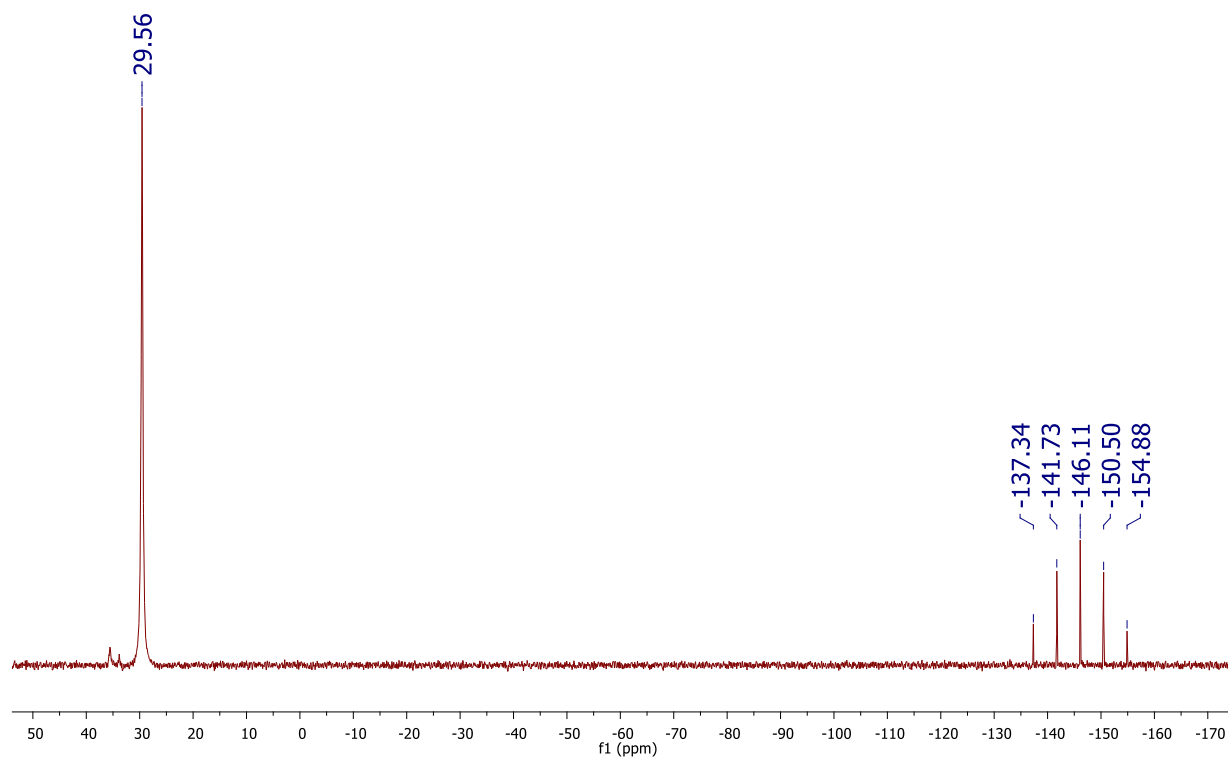


FIGURE 5.30 ^{31}P NMR (400 MHz) of isolation of **2.8** by toluene in CD_2Cl_2 .

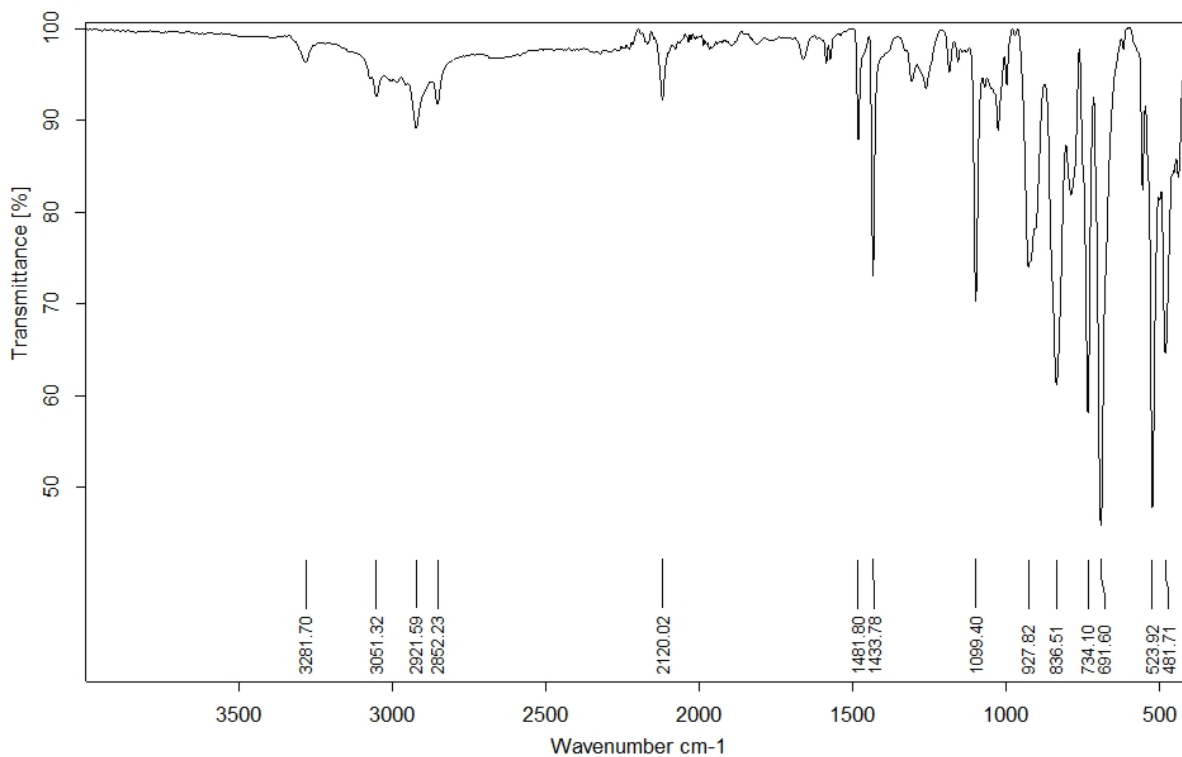


FIGURE 5.31 Infrared spectrum of **2.8**.

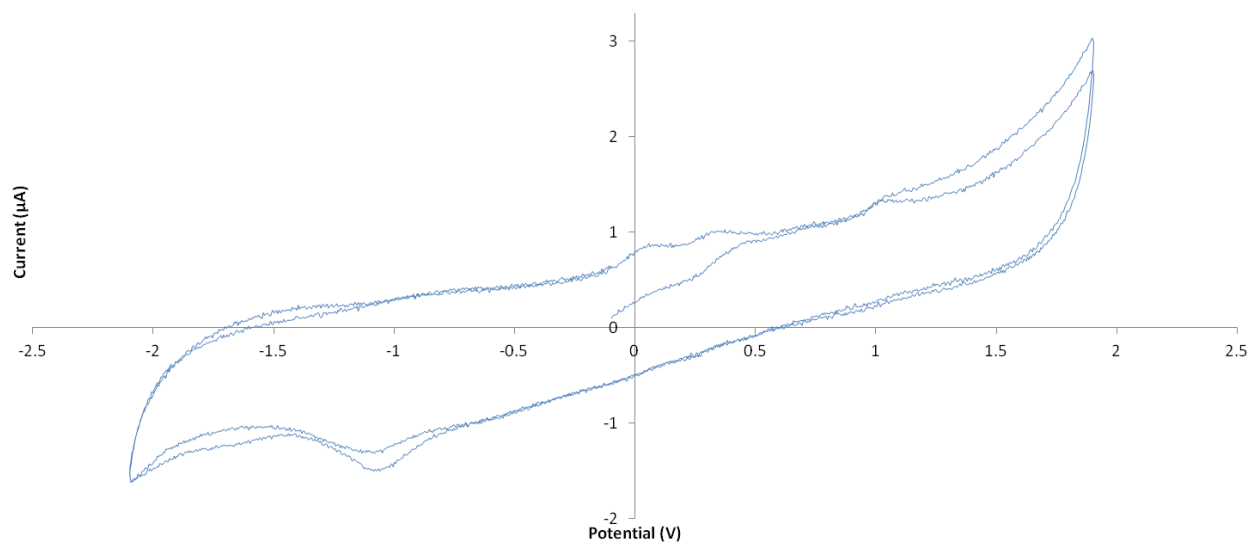
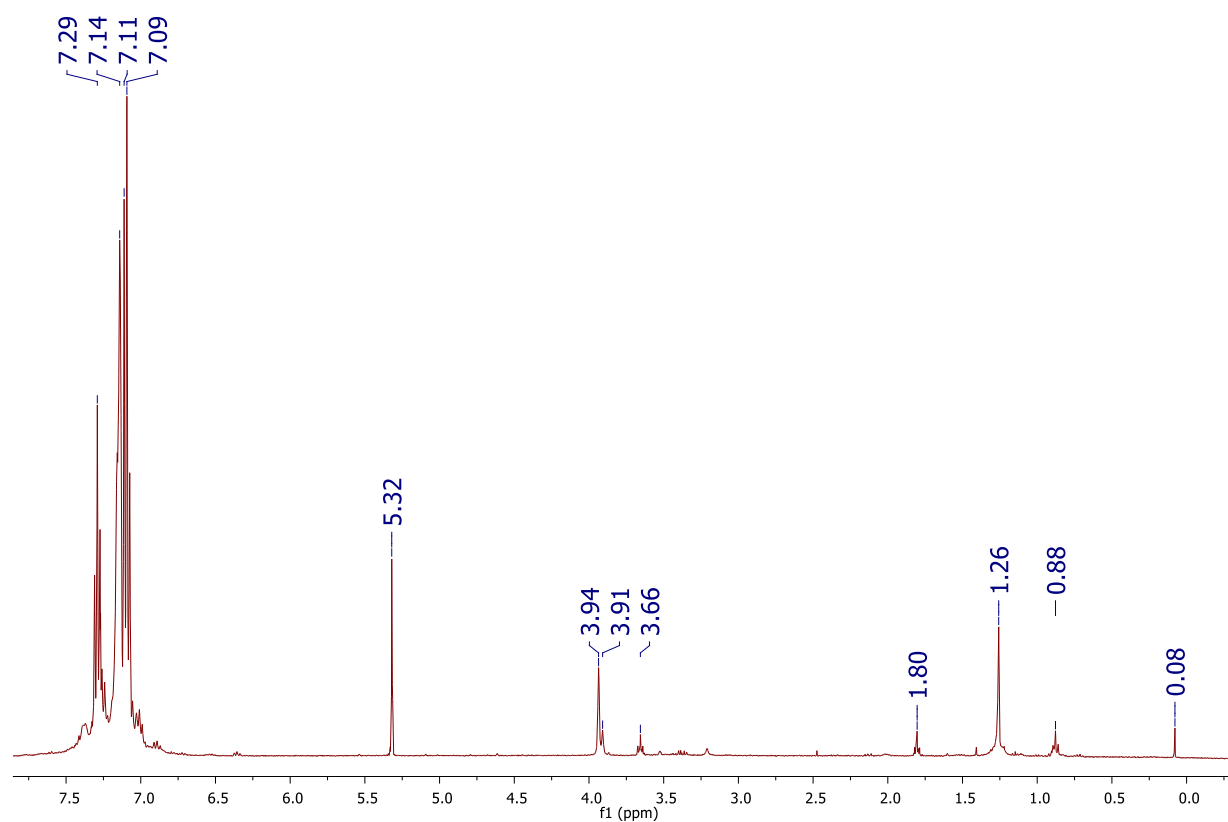


FIGURE 5.32 Cyclic voltammogram of 0.1 M Bu₄NPF₆/MeCN electrolyte solution used in CV measurements of **2.2** and **2.4**. Potentials referenced to FeCp₂⁺⁰. Irreversible oxidations occurring at 0.032 V, 0.33 V, 1.02 V and an irreversible reduction at -1.09 V.

TABLE 5.5 Cyclic Voltammetry Parameters for Acquiring CVs in Figure 5.32

Number of segments	Initial Potential (V)	Initial Direction	Upper Potential (V)	Lower Potential (V)	Final Potential (V)	Sweep Rate (V/s)
5	0	Rising	2	-2	0	0.1

**FIGURE 5.33** ^1H NMR (400 MHz) of products from competition experiment between NaI/ NaN_3 and **2.2** in CD_2Cl_2 .

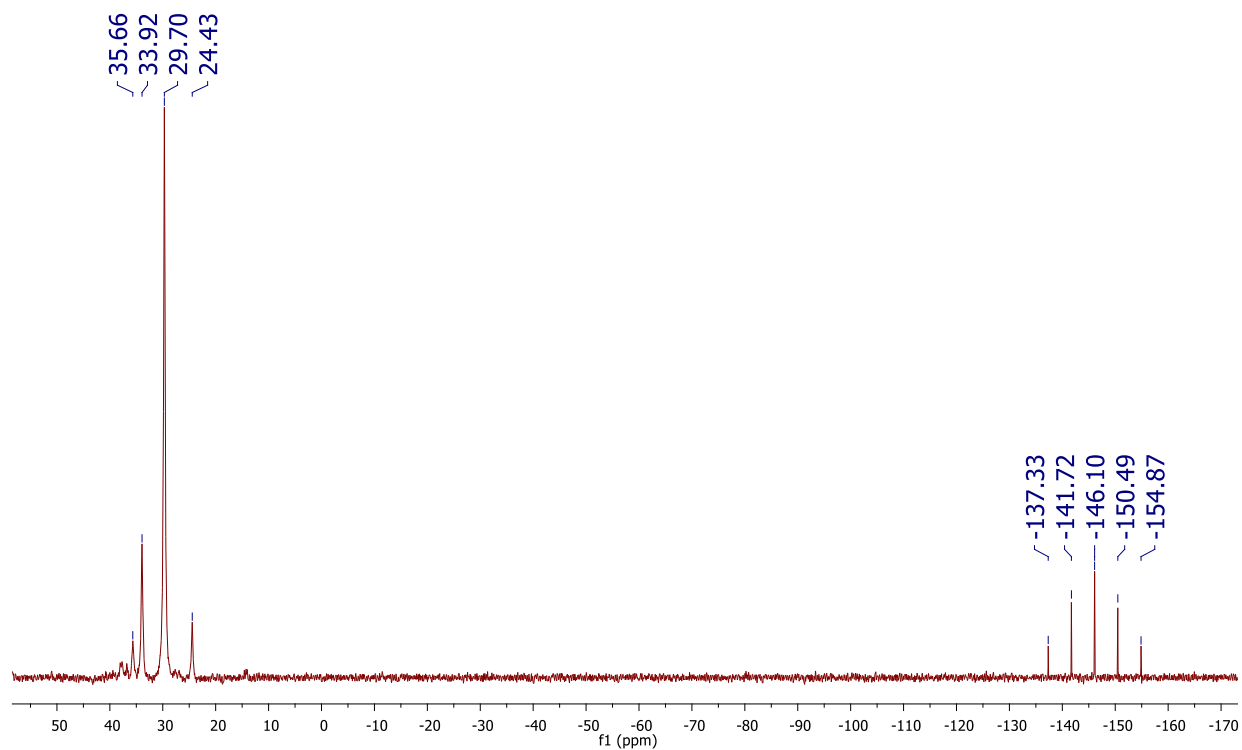


FIGURE 5.34 ^{31}P NMR (400 MHz) of products from competition experiment between NaI/ NaN_3 and **2.2** in CD_2Cl_2 .

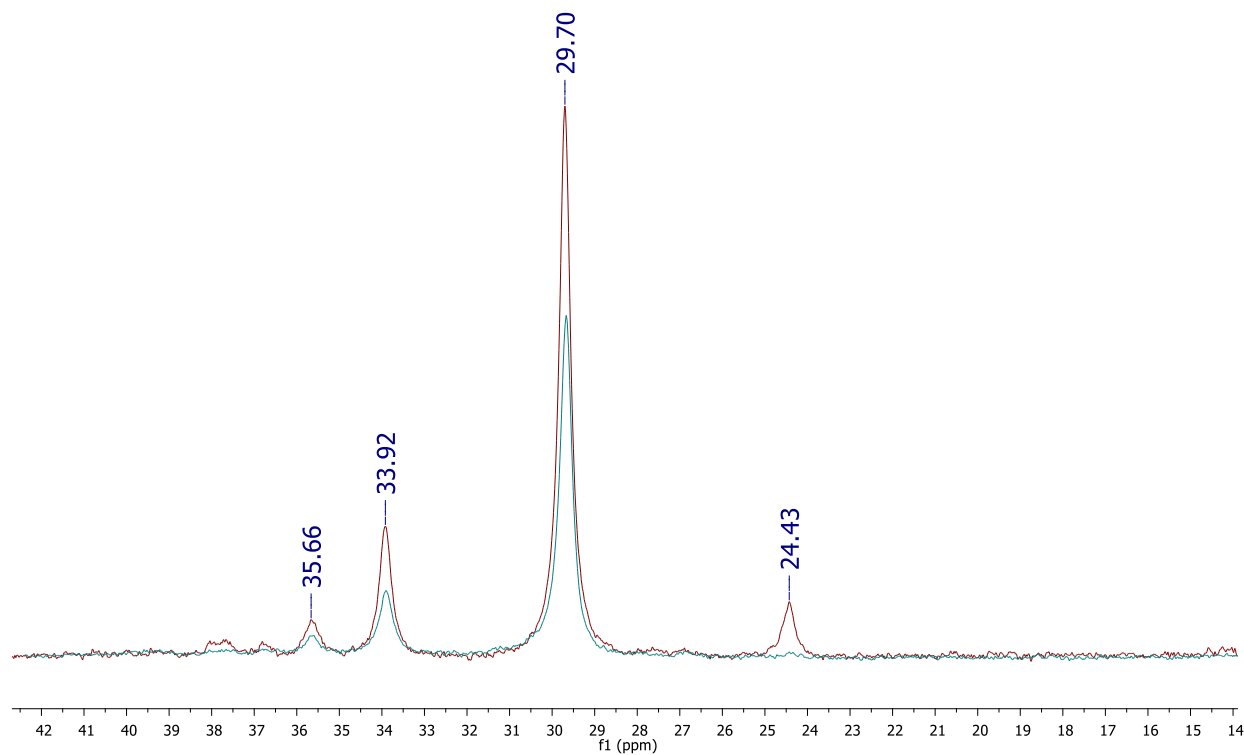


FIGURE 5.35 ^{31}P NMR (400 MHz) of Figure 5.34 (red trace) and Figure 5.28 (blue trace). Peak at 24.43 ppm is unknown but is sometimes seen during purification attempts in the reaction between **2.2** and excess NaI as a minor impurity.

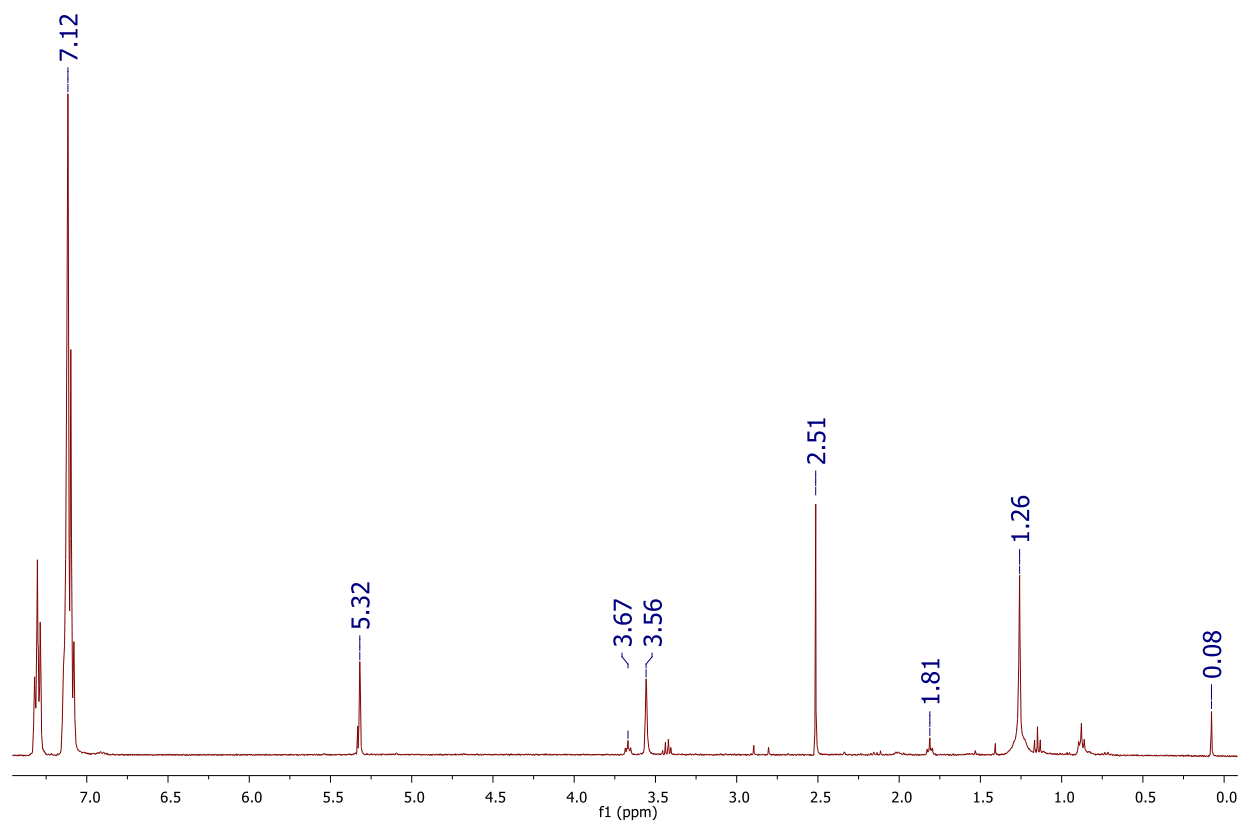


FIGURE 5.36 ^1H NMR (400MHz) of resulting mixture of 2.6 and excess NaI in CD_2Cl_2 .

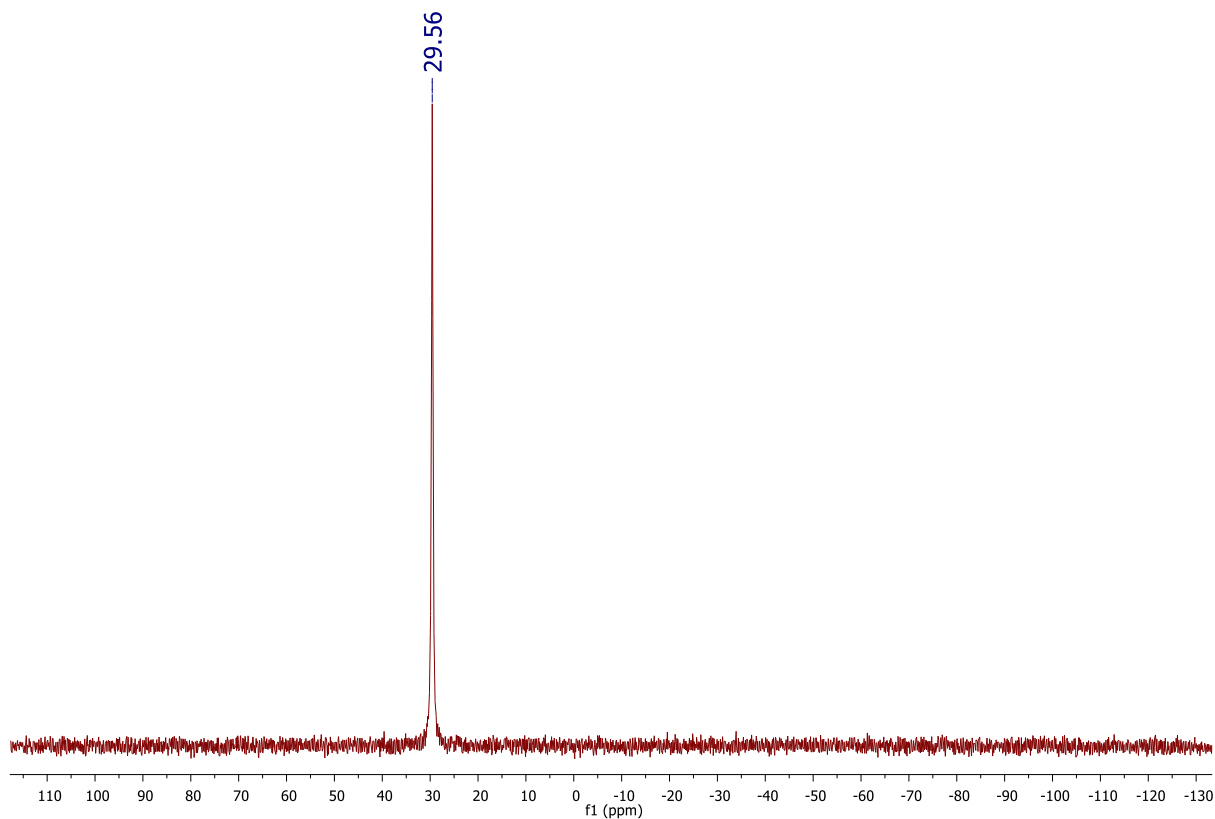


FIGURE 5.37 ^{31}P NMR (400MHz) of resulting mixture of **2.6** and excess NaI in CD_2Cl_2 . Anion (PF_6^-) at -146.1 ppm omitted from spectrum.

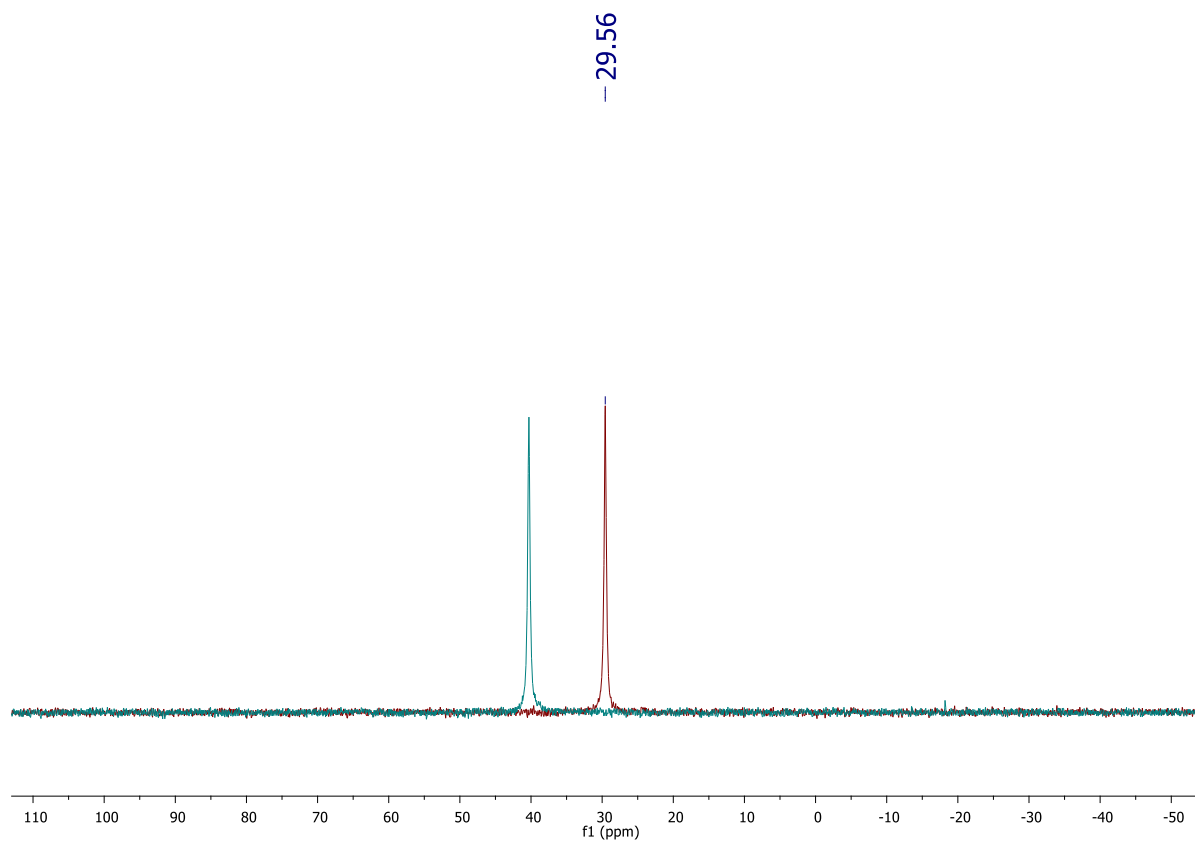


FIGURE 5.38 ^{31}P NMR (400MHz) comparison of resulting mixture of **2.6** and excess NaI (red trace) and **2.6** starting material (blue trace, at 40.31 ppm) in CD_2Cl_2 .

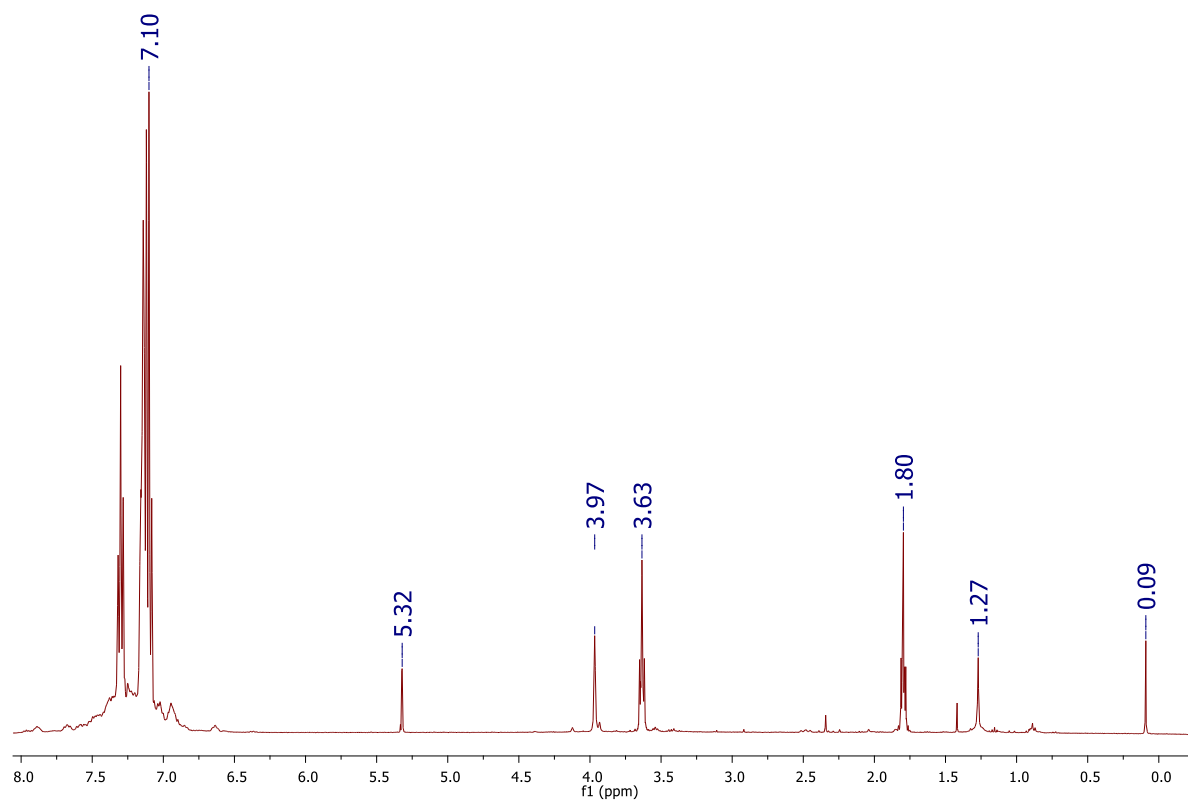


FIGURE 5.39 ^1H NMR (400 MHz) of resulting mixture of **2.7** and **2.8** with excess NaN_3 in CD_2Cl_2 .

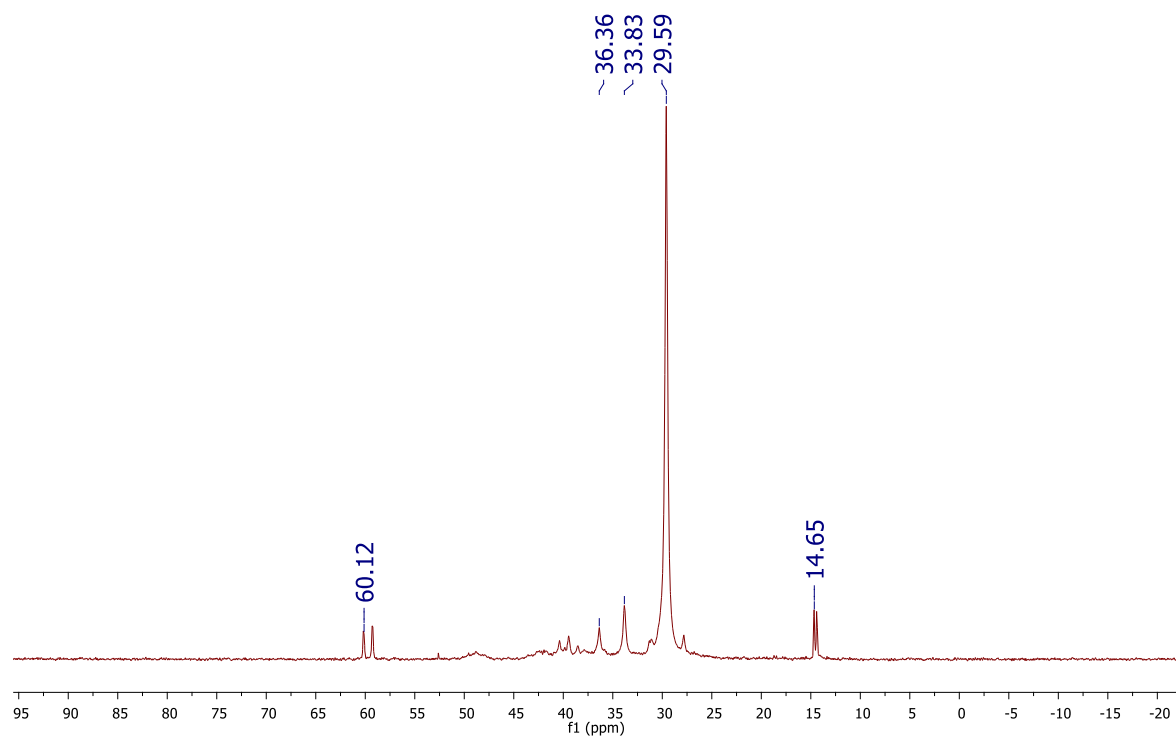


FIGURE 5.40 ^{31}P NMR (400 MHz) of resulting mixture of **2.7** and **2.8** with excess NaN_3 in CD_2Cl_2 . Anion (PF_6^-) at -146.1 ppm omitted from spectrum.

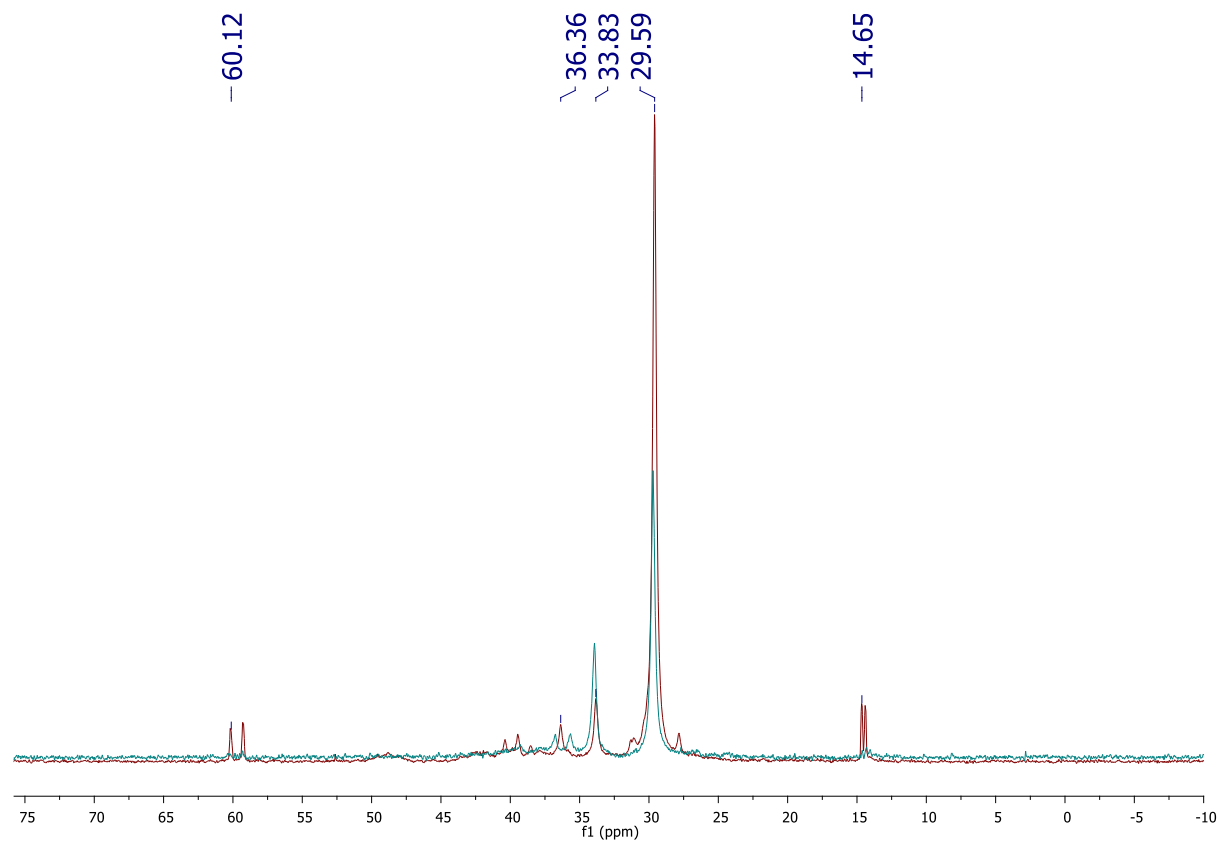


FIGURE 5.41 ^{31}P NMR (400 MHz) comparison of resulting mixture of **2.7** and **2.8** with excess NaN_3 (red trace) and **2.7** and **2.8** starting material (blue trace) in CD_2Cl_2 .

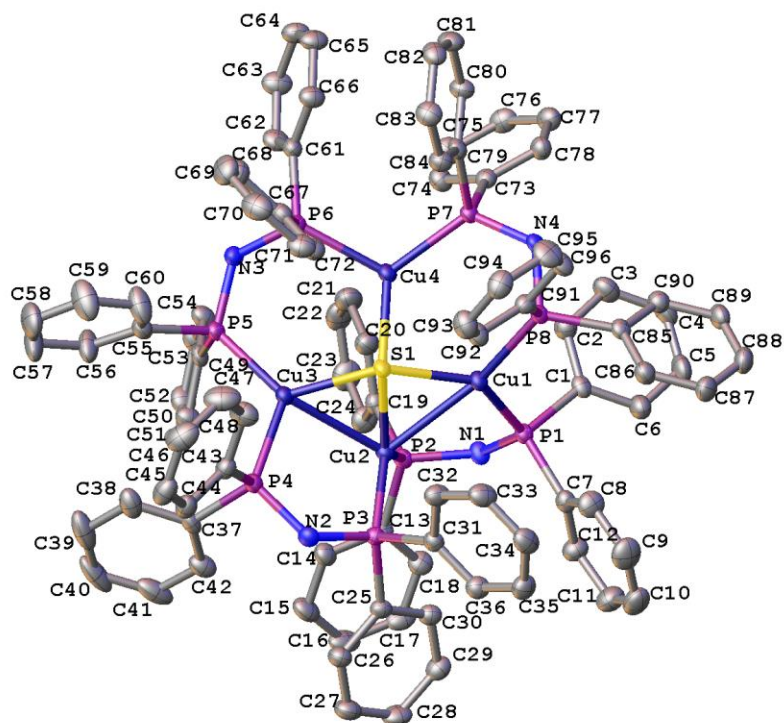


FIGURE 5.42 Fully labeled ORTEP of the dicationic unit in complex **2.2** (50% probability ellipsoids). Solvents, anions, and hydrogen atoms omitted.

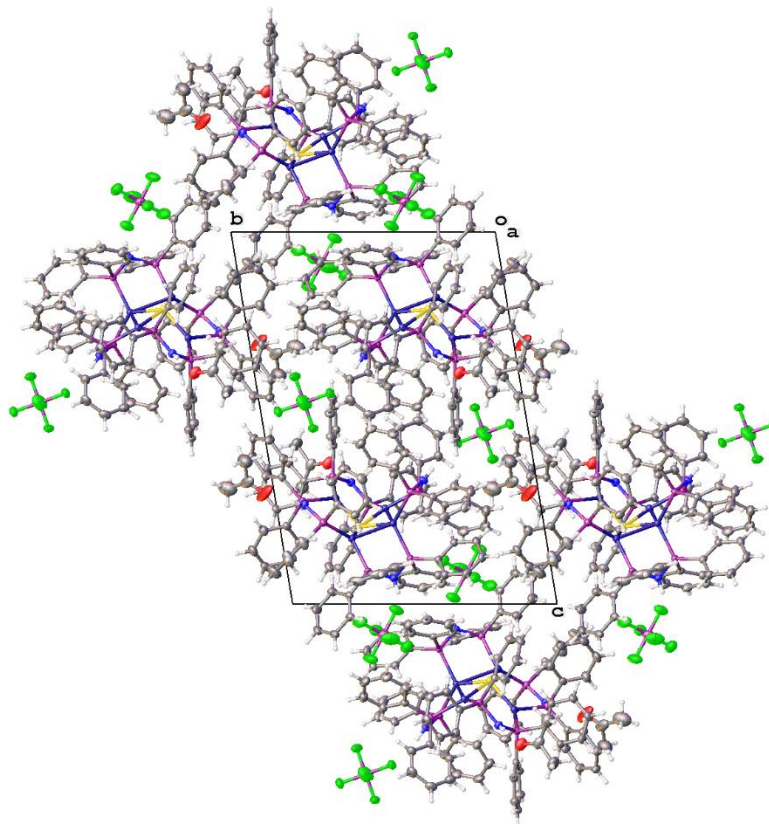


FIGURE 5.43 Crystal packing diagram for 2.2 (50% probability ellipsoids).

TABLE 5.6 Crystal Data and Structure Refinement for **2.2**

Empirical formula	C ₁₀₂ H ₉₆ Cu ₄ F ₁₂ N ₄ O ₂ P ₁₀ S
Formula weight	2233.75
Temperature/K	99.8(5)
Crystal system	triclinic
Space group	P-1
a/Å	14.9822(4)
b/Å	16.5538(5)
c/Å	21.8707(4)
$\alpha/^\circ$	96.934(2)
$\beta/^\circ$	94.5451(18)
$\gamma/^\circ$	112.432(3)
Volume/Å ³	4930.5(2)
Z	2
ρ_{calc} /mg/mm ³	1.505
m/mm ⁻¹	3.333
F(000)	2284.0
Crystal size/mm ³	0.1933 × 0.0776 × 0.0241
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection	5.86 to 147.48°
Index ranges	-18 ≤ h ≤ 17, -20 ≤ k ≤ 20, -27 ≤ l ≤ 19
Reflections collected	46350
Independent reflections	19350 [R_{int} = 0.0339, R_{sigma} = 0.0383]
Data/restraints/parameters	19350/0/1236
Goodness-of-fit on F ²	1.026
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0404, wR_2 = 0.1028
Final R indexes [all data]	R_1 = 0.0488, wR_2 = 0.1096
Largest diff. peak/hole / e Å ⁻³	1.02/-0.67

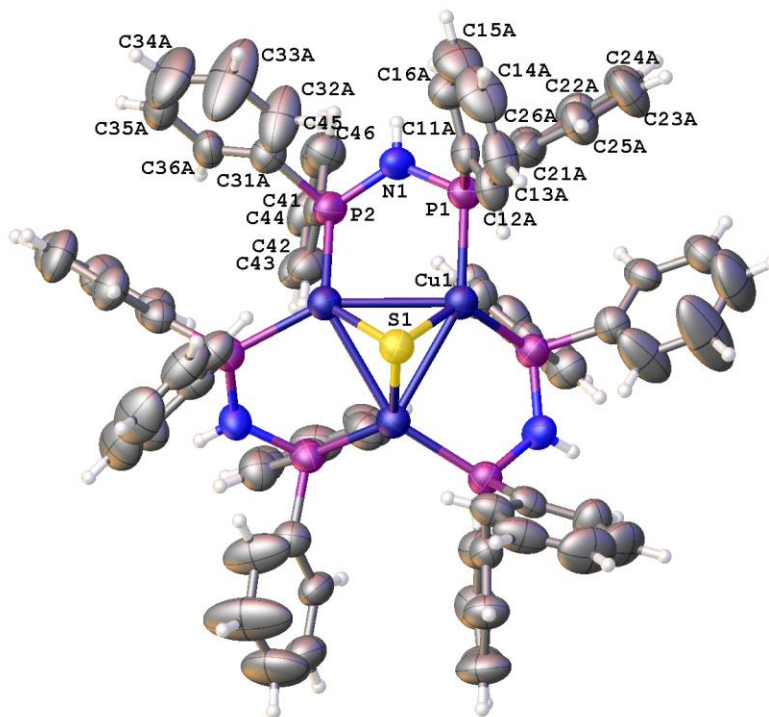


Figure 5.44 Fully labeled ORTEP of the cationic unit in complex **2.5** (50% probability ellipsoids). The cation is positioned on a crystallographic 3-fold axis of symmetry. The solvent/anion region was extremely disordered and was modeled using a solvent-mask procedure to account for its contribution to structural factors.

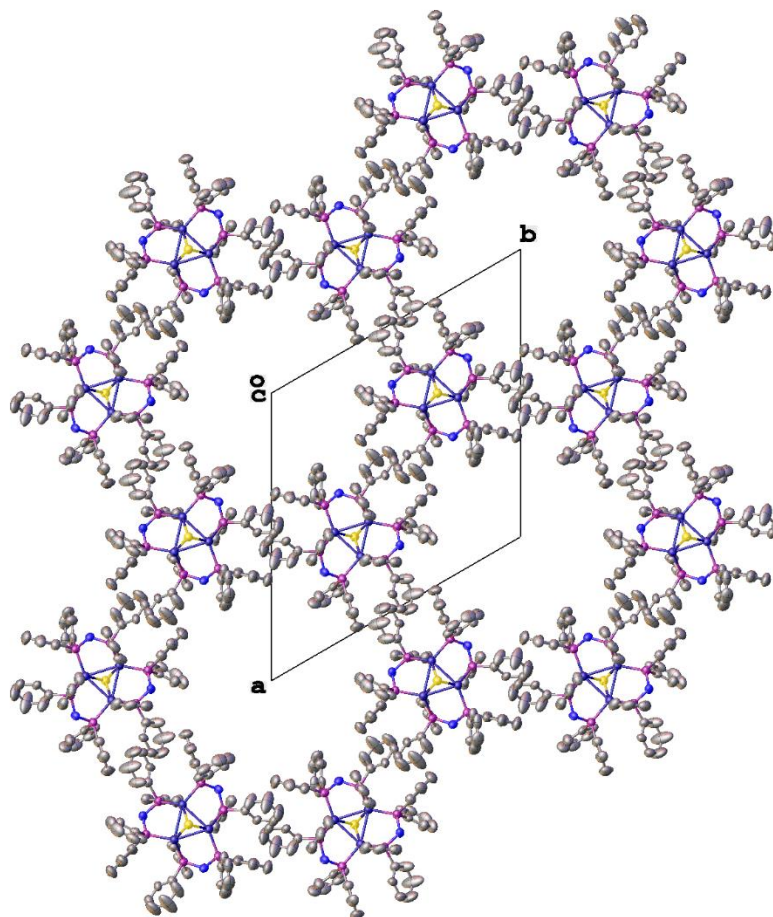
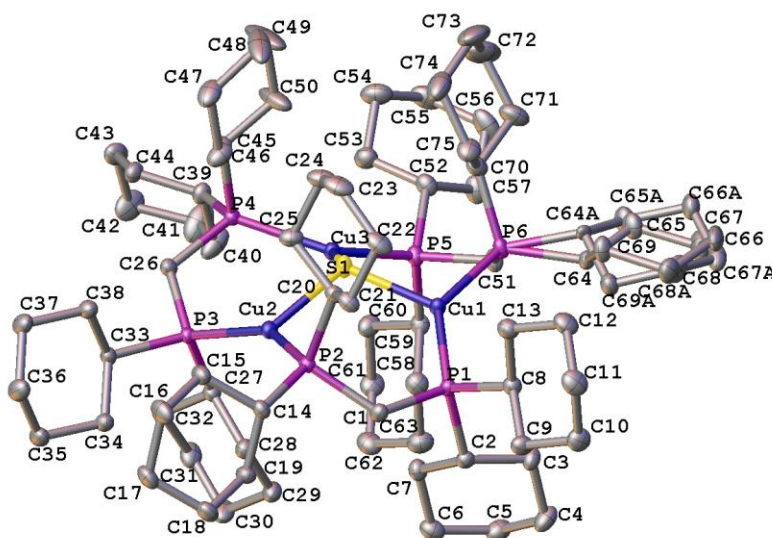


FIGURE 5.45 Crystal packing diagram for **2.5** (50% probability ellipsoids). The spacious channels along the 3-fold axis contain solvent/anion electron density modeled using a solvent-mask procedure.

TABLE 5.7 Crystal Data and Structure Refinement for **2.5**

Empirical formula	C ₇₂ H ₆₃ Cu ₃ N ₃ P ₆ S
Formula weight	1378.75
Temperature/K	100.00(10)
Crystal system	trigonal
Space group	P-3
a/Å	22.6945(7)
b/Å	22.6945(7)
c/Å	9.9881(5)
$\alpha/^\circ$	90.00
$\beta/^\circ$	90.00
$\gamma/^\circ$	120.00
Volume/Å ³	4455.1(3)
Z	2
ρ_{calc} /mg/mm ³	1.028
m/mm ⁻¹	2.321
F(000)	1418.0
Crystal size/mm ³	0.7300 × 0.0498 × 0.0379
Radiation	Cu K α (λ = 1.5418)
2 θ range for data collection	7.8 to 147.22°
Index ranges	-27 ≤ h ≤ 28, -27 ≤ k ≤ 28, -10 ≤ l ≤ 11
Reflections collected	28120
Independent reflections	5901[R _{int} = 0.0556]
Data/restraints/parameters	5901/270/310
Goodness-of-fit on F ²	1.055
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0773, wR ₂ = 0.2178
Final R indexes [all data]	R ₁ = 0.0876, wR ₂ = 0.2253
Largest diff. peak/hole / e Å ⁻³	0.75/-0.70

**FIGURE 5.46** Fully labeled ORTEP of the cationic unit in complex **2.4** (50% probability ellipsoids). Solvents, anions, and hydrogen atoms omitted. One of the cyclohexyl groups is disordered in a 3:1 ratio.

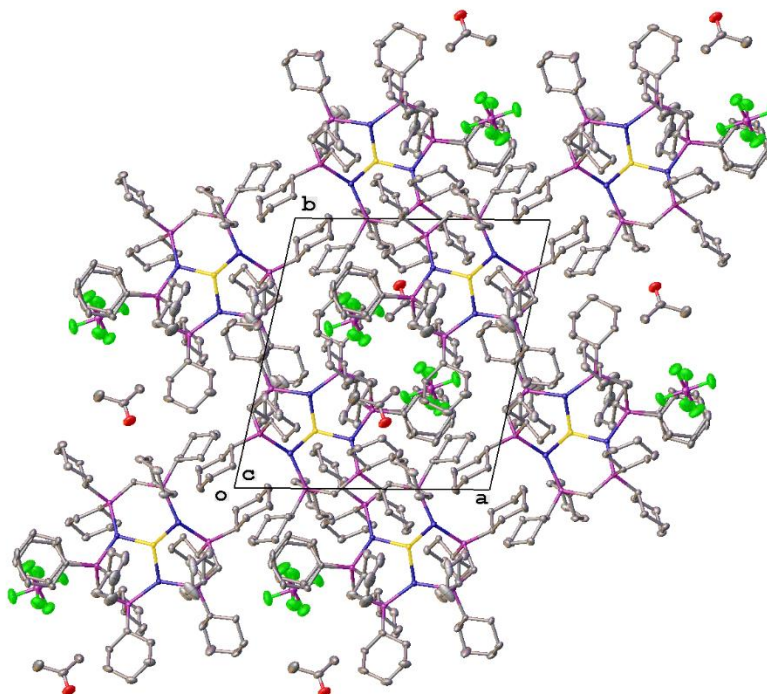


FIGURE 5.47 Crystal packing diagram for **2.4** (50% probability ellipsoids). Whereas the PF_6^- anion and one equivalent of acetone were localized, the structure contains relatively small ($261.5 \text{ \AA}^3$) centrosymmetric cavities apparently containing disordered Et_2O molecules. However, the complex distribution of electron density suggests a presence of some other solvents. Therefore, a solvent-mask procedure was applied to account for the contributions of this relatively minor but highly disordered and mixed area into the structural factors.

TABLE 5.8 Crystal Data and Structure Refinement for **2.4**

Empirical formula	C ₇₈ H ₁₄₄ Cu ₃ F ₆ OP ₇ S
Formula weight	1651.40
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	14.7920(3)
b/Å	16.0721(4)
c/Å	18.7434(4)
$\alpha/^\circ$	83.8839(17)
$\beta/^\circ$	86.2996(15)
$\gamma/^\circ$	77.4184(17)
Volume/Å ³	4320.34(15)
Z	2
ρ_{calc} /mg/mm ³	1.269
m/mm ⁻¹	2.728
F(000)	1764.0
Crystal size/mm ³	0.1891 × 0.1305 × 0.1121
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection	5.66 to 147.42°
Index ranges	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -22 ≤ l ≤ 23
Reflections collected	80468
Independent reflections	17149 [R _{int} = 0.0269, R _{sigma} = 0.0169]
Data/restraints/parameters	17149/36/916
Goodness-of-fit on F ²	1.056
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0280, wR ₂ = 0.0734
Final R indexes [all data]	R ₁ = 0.0302, wR ₂ = 0.0750
Largest diff. peak/hole / e Å ⁻³	1.08/-0.54

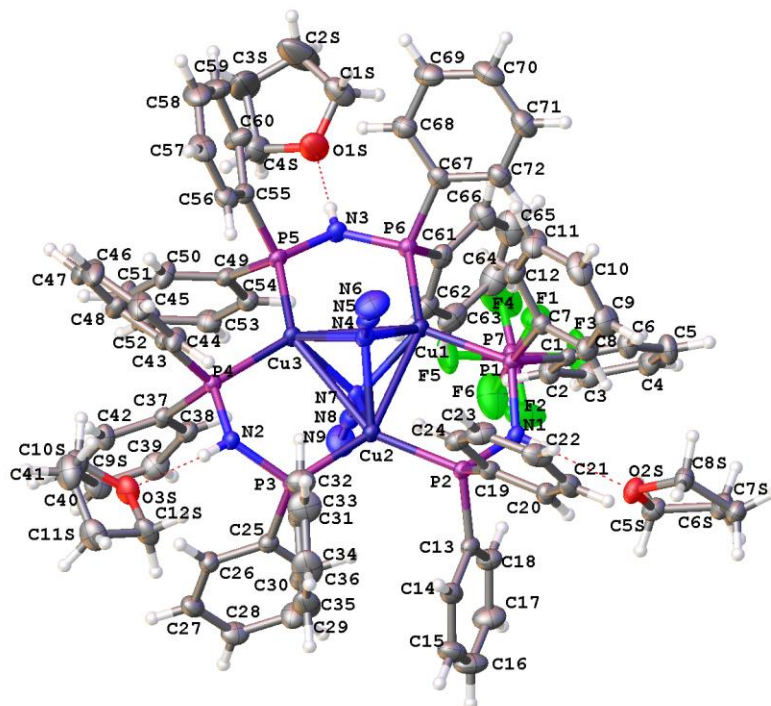


Figure 5.48 Fully labeled ORTEP of complex **2.6** (50% probability ellipsoids). There are two symmetrically independent formula units in the crystal (only one shown).

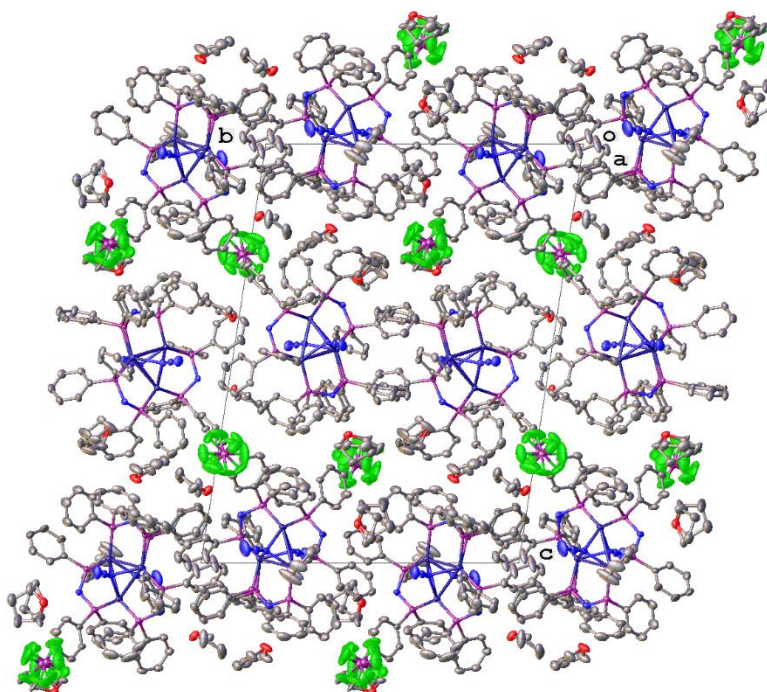


FIGURE 5.49 Crystal packing diagram for **2.6** (50% probability ellipsoids). There are multiple instances of disorder in the structure.

TABLE 5.9 Crystal Data and Structure Refinement for **2.6**

Empirical formula	C ₈₄ H ₈₇ Cu ₃ F ₆ N ₉ O ₃ P ₇
Formula weight	1792.04
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.1050(2)
b/Å	22.7156(3)
c/Å	29.5406(4)
$\alpha/^\circ$	79.6448(10)
$\beta/^\circ$	82.6818(13)
$\gamma/^\circ$	75.0872(13)
Volume/Å ³	8328.8(2)
Z	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.429
μ/mm^{-1}	2.720
F(000)	3696.0
Crystal size/mm ³	0.4436 × 0.3995 × 0.1324
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/ $^\circ$	6.1 to 147.58
Index ranges	-15 ≤ h ≤ 16, -28 ≤ k ≤ 28, -36 ≤ l ≤ 36
Reflections collected	156426
Independent reflections	33081 [R_{int} = 0.0487, R_{sigma} = 0.0299]
Data/restraints/parameters	33081/513/2538
Goodness-of-fit on F ²	1.018
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0423, wR_2 = 0.1062
Final R indexes [all data]	R_1 = 0.0499, wR_2 = 0.1131
Largest diff. peak/hole / e Å ⁻³	0.88/-0.81

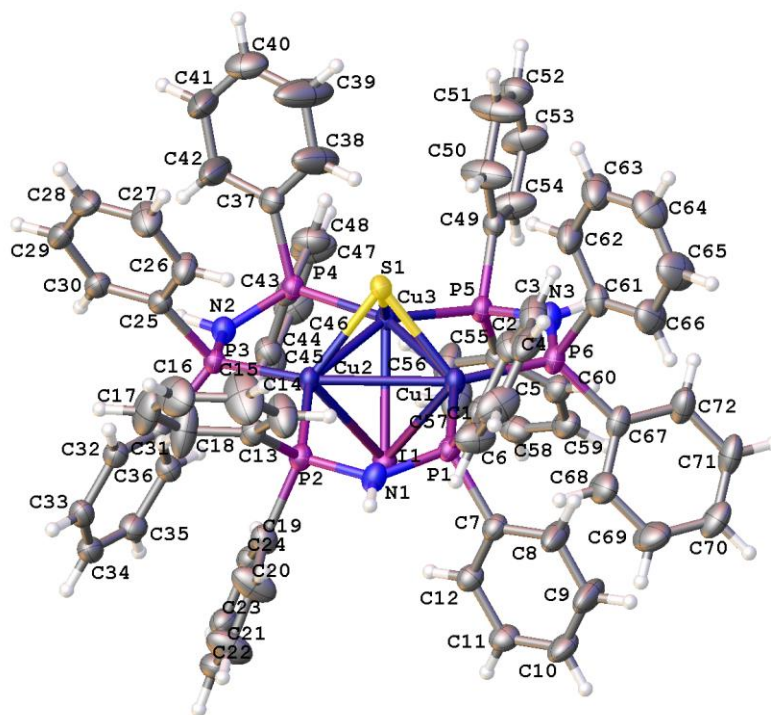


FIGURE 5.50 Fully labeled ORTEP of complex **2.7** (50% probability ellipsoids). It is disordered in a roughly 3:1 ratio with the outside ligand scaffold in place and I and S ligand changing places. The alternative positions of I and S practically coincide and only the Cu triangle position shifts along I...S axis.

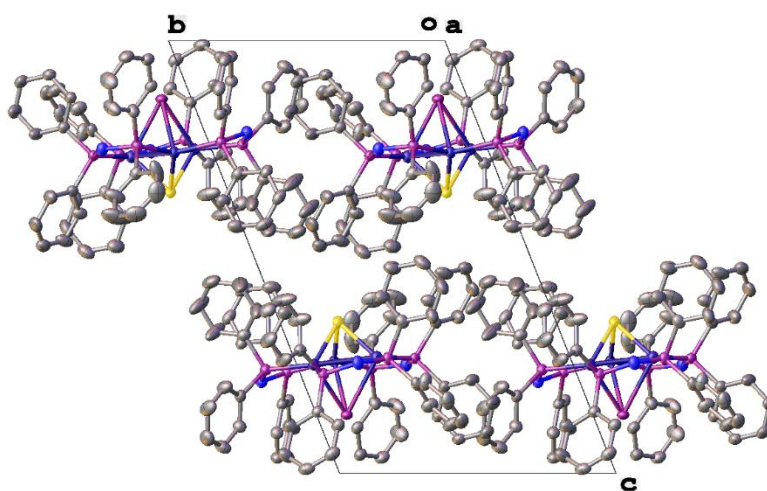


FIGURE 5.51 Crystal packing diagram for **2.7** (50% probability ellipsoids).

TABLE 5.10 Crystal Data and Structure Refinement for **2.7**

Empirical formula	C ₇₂ H ₆₃ Cu ₃ IN ₃ P ₆ S
Formula weight	1505.65
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.7161(3)
b/Å	13.9702(4)
c/Å	20.5980(5)
$\alpha/^\circ$	108.460(2)
$\beta/^\circ$	90.8367(19)
$\gamma/^\circ$	118.571(3)
Volume/Å ³	3221.94(14)
Z	2
ρ_{calc} /mg/mm ³	1.552
m/mm ⁻¹	6.977
F(000)	1524.0
Crystal size/mm ³	0.5342 × 0.2676 × 0.128
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection	7.42 to 147.54°
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -25 ≤ l ≤ 25
Reflections collected	47311
Independent reflections	12805 [R_{int} = 0.0412, R_{sigma} = 0.0317]
Data/restraints/parameters	12805/10/816
Goodness-of-fit on F ²	1.083
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0447, wR_2 = 0.1148
Final R indexes [all data]	R_1 = 0.0476, wR_2 = 0.1168
Largest diff. peak/hole / e Å ⁻³	1.27/-0.69

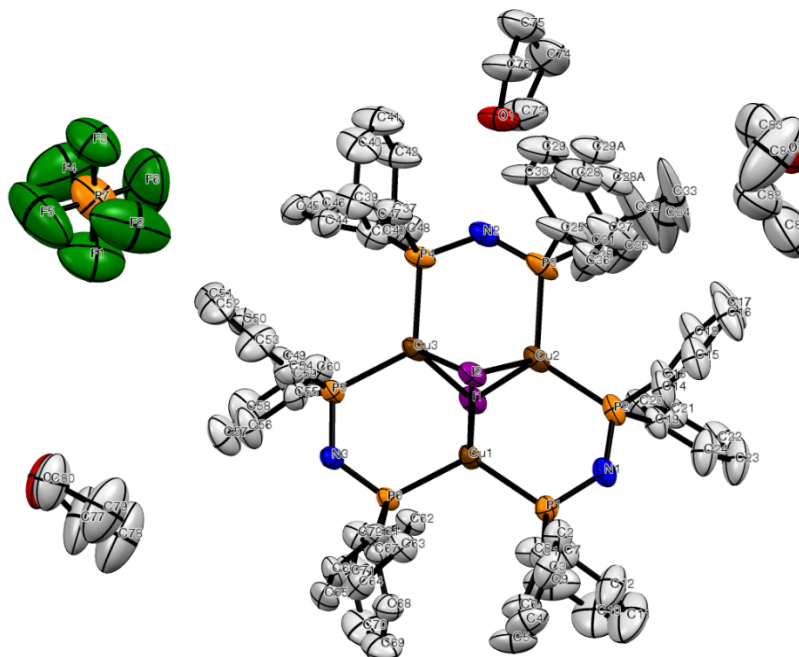


FIGURE 5.52 Fully labeled ORTEP of complex **2.8** (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

TABLE 5.11 Crystal Data and Structure Refinement for **2.8**

Empirical formula	C ₈₄ H ₈₂ Cu ₃ F ₆ I ₂ N ₃ O ₆ P ₇
Formula weight	2004.73
Temperature/K	200(2)
Crystal system	triclinic
Space group	P-1
a/Å	13.0898(6)
b/Å	18.5702(10)
c/Å	19.7003(10)
$\alpha/^\circ$	107.3385(16)
$\beta/^\circ$	101.4419(15)
$\gamma/^\circ$	98.1390(16)
Volume/Å ³	4376.0(4)
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.521
Absorption coefficient /mm ⁻¹	1.620
F(000)	2014
Crystal size/mm ³	0.07 × 0.21 × 0.51
Θ range for data collection	1.12 to 26.37°
Index ranges	-16 ≤ h ≤ 12, -23 ≤ k ≤ 23, -24 ≤ l ≤ 24
Reflections collected	59232
Independent reflections	17542 [R _{int} = 0.0658]
Completeness to theta = 26.37°	97.6 %
Absorption correction	Multiscan
Max. and min. transmission	0.8950 and 0.4920
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	17542/308/1003
Goodness-of-fit on F ²	1.004
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0511, wR ₂ = 0.1359
R indexes [all data]	R ₁ = 0.1045, wR ₂ = 0.1733
Largest diff. peak/hole / e Å ⁻³	1.653/-1.197

5.2 Supporting Information for Construction of Copper-sulfide Complexes Using Amidinate Ligands

Experimental information and data collected for **3.2**, reproduced from reference 229 with permission from the Royal Society of Chemistry. Experimental information and data collected for **3.3**, reproduced with permission from Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. “A One-Hole Cu₄S Cluster with N₂O Reductase Activity: A Structural and Functional Model for Cu_z*” *J. Am. Chem. Soc.* **2016**, *138*, 13107. Copyright 2016 American Chemical Society.

5.2.1 General Considerations for Complex 3.2

Unless otherwise specified, all reactions and manipulations were performed under purified N₂ in a glovebox or using standard Schlenk line techniques. Glassware was oven-dried prior to use. Reaction solvents (diethyl ether, toluene, tetrahydrofuran, dichloromethane, acetonitrile, pentane) were sparged with argon and dried using a Glass Contour Solvent System built by Pure Process Technology, LLC. Chloroform was degassed, dried and distilled. Unless otherwise specified, all chemicals were purchased from commercial sources and used without further purification.

5.2.2 Physical Measurements for Complex 3.2

NMR spectra for compound characterization were recorded at ambient temperatures using Bruker Avance DPX-400 or Bruker Avance DRX-500 MHz spectrometers. Low temperature NMR spectra were recorded on a Bruker Avance DRX-500 MHz spectrometer and low temperatures were attained from liquid nitrogen boiloff. Equations (2) and (3) were used to calculate magnetic moment (B.M.) and molar susceptibility, respectively, using Evans' Method.

$$\mu_{eff} = \sqrt{8 \times X_m \times T (K)} \quad (2)$$

$$X_m = \frac{477 \times \Delta(Hz)}{2 \times \text{Instrument frequency (Hz)} \times \text{Molar concentration}} \quad (3)$$

¹H and ¹³C NMR chemical shifts were referenced to residual solvent peaks. FT-IR spectra were recorded on solid samples in a glovebox using a Bruker ALPHA spectrometer fitted with a diamond-ATR detection unit. Elemental analyses were performed by the Midwest Microlab, LLC in Indianapolis, IN. Deuterated solvents were degassed by repeated freeze-pump-thaw cycles and then stored over 3-Å molecular sieves. UV-Vis absorbance spectra were taken at room temperature using a Cary 300 Bio UV-Visible Spectrophotometer.

Electrochemical data was measured at room temperature using a WaveNow USB Potentiostat from Pine Research Instrumentation. In a classic three-electrode system, a platinum working electrode, platinum counter electrode and a Ag/AgNO₃ (0.01 M AgNO₃/0.1M Bu₄NPF₆ in THF or dichloromethane) reference electrode was used. Compound **3.2** was dissolved in a 0.1 M solution of Bu₄NPF₆ in THF or

dichloromethane at approximately 1 mM concentrations. Electrochemical measurements were referenced to approximately 1mM solutions of $\text{FeCp}_2^{+/0}$ in same electrolyte solution.

X-band EPR spectra at 110 K to 150 K were obtained with a Bruker EMX spectrometer located at the National Biomedical EPR Center at the Medical College of Wisconsin. Spectra were simulated (not shown) with EasySpin.²⁶⁷ Samples of 5 mM **3.2** and Cu(II) impurity (Figure 5.70) were glassed in toluene spiked with 3-5 drops of dichloromethane. The full spectrum of **3.2** and Cu(II) impurity shown in Figure 5.71A utilized microwave frequency 9.297 GHz, temp 115 K, 9 scans, microwave power 5 mW, mod. Amp. 5G, mod. Freq. 100 kHz, time constant 81.92 ms, sweep time 83.886 s. The insert focusing on the $g_{\parallel}$ region (Figure 5.71B) utilized microwave frequency 9.277 GHz, 25 scans, time constant 81.92 ms, sweep time 42.943 s.

5.2.3 X-ray Crystallography for Complex 3.2

X-ray crystallography data was collected at the X-ray Structural Laboratory at Marquette University (Milwaukee, WI). The X-ray single-crystal diffraction data were collected with an Oxford Diffraction SuperNova diffractometer equipped with dual microfocus Cu/Mo X-ray sources, X-ray mirror optics, Atlas CCD detector and low-temperature Cryojet device. Data was collected using $\text{Cu(K}\alpha\text{)}$ radiation at 100 K. The data was processed with CrysAlisPro program package (Oxford Diffraction Ltd., 2010) typically using a numerical Gaussian absorption correction (based on the real shape of the crystal) followed by an empirical multi-scan correction using SCALE3 ABSPACK routine. The structures were solved using SHELXS program and refined with SHELXL program²⁶⁵ within Olex2 crystallographic package.²⁶⁶ All computations were performed on an Intel PC computer under Windows 7 OS. The structure contained a certain degree of disorder, as described in Section 3.3 and Appendix F, which was detected in difference Fourier syntheses of electron density and was taken care of using capabilities of SHELX package (see Figure 5.67 and caption for more information). Hydrogen atoms were localized in difference syntheses of electron density but were refined using appropriate geometric restrictions on the corresponding bond lengths and bond angles within a riding/rotating model (torsion angles of Me hydrogens were optimized to

better fit the residual electron density). A solvent-mask procedure was applied to account for additional electron density that could not be assigned definitively to a co-crystallized solvent.

5.2.4 Preparation of Bis(2,4,6-trimethylphenyl)formamidine

A literature procedure was followed for the isolation of bis(2,4,6-trimethylphenyl)formamidine.²²⁸

This synthesis took place in open air and acetone was used as the recrystallization solvent.

5.2.5 Preparation of Complex 3.1

A modified version of the reported literature procedure for **3.1**²¹³ was used with the following modifications: bis(2,4,6-trimethylphenyl)formamidine (1.83 g, 6.53 mmol) was dissolved in THF (approximately 120 mL). Sodium bis(trimethylsilyl)amide (1.34 g, 7.31 mmol) was added to the stirring THF solution at room temperature, and the yellow solution was stirred for 1 h. Tetrakis(acetonitrile)copper(I) hexafluorophosphate (2.43 g, 6.52 mmol) was added to the stirring solution, which became instantly cloudy white. Stirring was continued at room temperature overnight. The solution volume was completely evaporated by vacuum. The evaporated residue was reconstituted in dichloromethane and filtered through Celite to remove insoluble NaPF₆. The resulting yellow filtrate was vacuum evaporated until a precipitate formed. This solid was collected by filtration and washed with diethyl ether (2 x 5 mL). The resulting white solid was dried under vacuum, and the filtrate was further vacuum evaporated to collect multiple crops. Yield of **3.1**: 93%. ¹H NMR (400 MHz, CDCl₃): δ 2.21 (s, 12H, *p*-CH₃), 2.30 (s, 24H, *o*-CH₃), 6.79 (s, 8H, Ar C-H), 6.98 (s, 2H, NCH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 169.8 (NC(H)N), 144.4 (quat C, Ar), 133.4 (quat *p*-C, Ar), 132.8 (quat *o*-C, Ar), 128.7 (*m*-CH, Ar), 20.6 (Ar *p*-CH₃), 19.3 (Ar *o*-CH₃). FT-IR (cm⁻¹): 3002, 2903, 2848, 1611 (N=C), 1567, 1474, 1429, 1372, 1334, 1231, 1210, 1146, 1007, 846, 624, 583, 513, 418.

5.2.6 Preparation of 3.2 using Elemental Sulfur

Complex **3.1** (0.300 g, 0.437 mmol) was dissolved in minimum amount of THF (~ 3 mL) using a magnetic stir bar. In a separate vessel, S₈ (0.007 g, 0.027 mmol) was stirred in 0.5 mL toluene until completely dissolved. The toluene solution of S₈ was then added to the solution of **3.1** dropwise, with stirring, at room temperature. Once all the S₈ solution had been added, the color began to change steadily

to purple. The solution was stirred vigorously at 40-43° C overnight. The next day the solution was black. The solution was completely evaporated by vacuum. To the evaporated residue was added a small amount (~ 1 mL) of dichloromethane to make a super saturated solution and was filtered. The dark solid was then washed with dichloromethane (2 x 4 mL) to remove unreacted **3.1**, then diethyl ether (approximately 10 mL) to remove any remaining dichloromethane solvent and finally acetonitrile (approximately 10 mL or until filtrate is clear) to remove any polar Cu(II) impurities or side products. Using a new, clean vacuum flask, the purple solid was collected with copious amounts of dichloromethane until filtrate appeared clear. The purple filtrate was then pipette-filtered through Celite, and the solution was then completely evaporated under vacuum. After filtrate is pipette-filtered through Celite, it should be evaporated as soon as possible to avoid thermal decomposition into **3.1**. Yield of **3.2**: 0.107 g, 34%. Compound **3.2** was stored in a freezer (-36°C) and is not stable in solution at room temperature for long periods of time. Note: Trace amounts (5-10%) of the starting material, **3.1**, were often detected by ¹H NMR regardless of multiple purification attempts. Best method for removing unwanted **3.1** is by adding a small amount of dichloromethane to the purple solid so that trace amount of **3.1** dissolves but **3.2** is super saturated and doesn't dissolve entire sample. Saturated solution is filtered, purple solid is washed with a small amount of dichloromethane and then diethyl ether to remove dichloromethane solvent. Purple solid can then be collected and dried under vacuum. Usually this purification method is done twice to achieve elemental analysis purity. Dark black crystals may be obtained by dissolving purple **3.2** in a minimum amount of chloroform and allowing pentane vapors to diffuse in through a pin sized hole. ¹H NMR (400 MHz, CDCl₃): δ 1.30 (s, 12 H, CH₃), 1.38 (s, 12 H, CH₃), 2.16 (s, 12 H, CH₃), 2.18 (s, 12 H, CH₃), 2.68 (s, 12 H, CH₃), 2.75 (s, 12 H, CH₃), 6.12 (s, 2 H, NC(H)N), 6.24 (s, 4 H, Ar CH), 6.30 (s, 4 H, Ar CH), 6.65 (s, 2 H, NC(H)N), 6.70 (s, 8 H, Ar CH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 172 (NC(H)N), 160 (NC(H)N), 144.5 (Ar), 144.3 (Ar), 133.6 (Ar), 133.4 (Ar), 132.7 (Ar), 132.58 (Ar), 132.53 (Ar), 128.7 (Ar), 128.5 (Ar), 128.2 (Ar), 128.0 (Ar), 21 (Ar *p*-CH₃), 20.7 (Ar *p*-CH₃), 20.4 (Ar *o*-CH₃), 18 (Ar *o*-CH₃), 17 (Ar *o*-CH₃). FT-IR (cm⁻¹): 2981, 2912, 2851, 1610 (N=C), 1553, 1530, 1471, 1372, 1339, 1325, 1224, 1206, 1144, 1029, 850, 735, 588, 571, 505, 460, 442, 412. Anal. calcd. for C₇₆H₉₂Cu₄N₈S: C, 65.0; H, 6.61; N, 7.98. Found: C, 64.91; H, 6.60; N, 8.06.

5.2.7 Preparation of 3.2 using Triphenylantimony Sulfide

Complex **3.1** (0.258 g, 0.376 mmol) was dissolved in minimum amount of THF (~ 3 mL) using a magnetic stir bar. In a separate vessel, Ph₃SbS (0.0727 g, 0.188 mmol) was dissolved in 2 mL THF. The solution of Ph₃SbS solution was then added to the solution of **3.1** dropwise, with stirring, at room temperature. Once all the Ph₃SbS solution had been added, the color rapidly began to change from yellow to orange then maroon. The solution was stirred vigorously at room temperature overnight. The next day the solution was black. The solution was completely evaporated by vacuum. To the evaporated residue was added a small amount (~ 1 mL) of dichloromethane to make a super saturated solution and was filtered through Celite. The dark solid on the Celite pad was then washed with dichloromethane (2 x 6 mL) to remove unreacted **3.1**, then diethyl ether (approximately 6 mL) to remove any remaining dichloromethane solvent and finally acetonitrile (approximately 10 mL or until filtrate is clear) to remove any remaining triphenyl-antimony containing byproducts (usually appearing in ¹H NMR δ: 7.24- 7.15 ppm in CDCl₃). Using a new, clean vacuum flask, the purple solid remaining on the Celite was collected with copious amounts of dichloromethane until the filtrate became clear (~ 100 mL). The dark purple filtrate was completely evaporated by vacuum. This filtrate should be evaporated as soon as possible to avoid decomposition into **3.1**. Yield of **3.2**: 0.1144 g, 43%. Note: Trace amounts (5-10%) of the starting material, **3.1**, were often detected by ¹H NMR regardless of multiple purification attempts. Best method for removing trace amounts of **3.1** is by adding a small amount of dichloromethane to the purple solid so that **3.1** dissolves but **3.2** remains super saturated and doesn't dissolve entire sample. Saturated solution is filtered, purple solid is washed with a small amount of dichloromethane and then diethyl ether to remove dichloromethane solvent. Purple solid can then be collected and dried under vacuum. Dark black crystals may be obtained by dissolving purple **3.2** in a minimum amount of chloroform and allowing pentane vapors to diffuse in through a pin sized hole.

5.2.8 Experimental Conditions for Low Temperature ¹H NMR Evans' Method with Complex 3.2

Complex **3.2** and unknown amount of the Cu(II) impurity shown in Figure 5.70 (total mass of sample was 0.0015 g) was dissolved in CDCl₃ and 100 µL of CHCl₃ was added. Total weight of solution

was 1.7571 g. The solution was then pipette-filtered through Celite into an NMR tube. A glass capillary tube (approximately 17 cm in length and approximately 3 mm in diameter) was syringe filled with CHCl_3 and then inserted into the NMR tube containing the solution mixture of **3.2** and $\text{Cu}^{\text{II}}\text{S}_2\text{NCN}_2$. The difference in chloroform peak chemical shifts in the ^1H NMR spectrum (Figure 5.54) were analyzed to determine magnetic moment using Evans' Method analysis (Figure 5.53) and falsely identified complex **3.2** as possessing paramagnetic properties.

5.2.9 Computational Methods for **3.2**

All calculations were performed using Gaussian09, Revision B.01.²⁶⁸ Density functional theory (DFT) calculations were carried out using a hybrid functional, BVP86, consisting of Becke's 1988 gradient-corrected Slater exchange functional²⁶⁹ combined with the VWNS local electron correlation functional and Perdew's 1986 nonlocal electron correlation functional.²⁷⁰ Mixed basis sets were employed: the LANL2TZ(f) triple- ζ basis set^{271–273} with effective core potential^{271,274,275} was used for Cu, the Gaussian09 internal 6-311+G(d) basis set was used for S, and the Gaussian09 internal 6-31+G(d) basis set was used for C, H, and N. The crystal structure of **3.2** was used as a starting point for constructing the input file: the mesityl groups were changed to methyl groups, and only one set of Cu_4S coordinates were used. All calculations were spin-unrestricted and symmetry-unrestricted. Final output wavefunctions were tested for stability against antiferromagnetic coupling and were found to be stable. Orbital surfaces were analyzed using Gaussview, and orbital populations were determined using the Pop=Orbitals keyword in Gaussian09. Optimized coordinates for the singlet state of **3.2'** are enclosed in Table 5.13.

5.2.10 Experimental Spectra and Relevant Data Tables

TABLE 5.12 Data Used in Calculating Magnetic Moment and Molar Susceptibility of **3.2** for Low Temperature NMR Evans' Method Analysis.

Temperature (K)	Peak 1 (ppm)	Peak 2 (ppm)
298	7.272	7.259
280	7.274	7.261
261	7.275	7.262
240	7.275	7.262
221	7.274	7.262

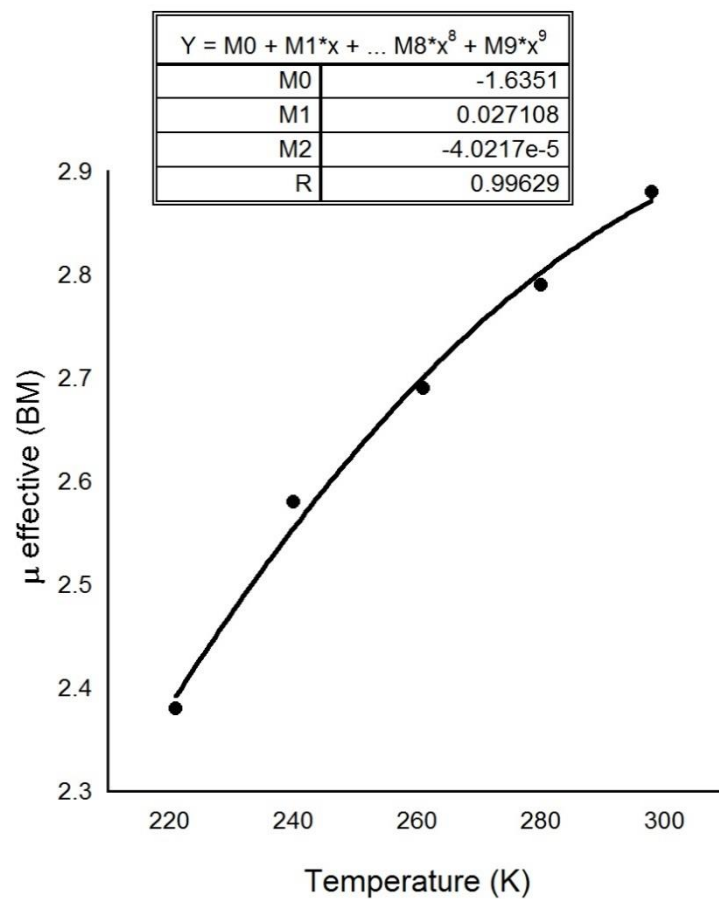


FIGURE 5.53 Change in magnetic moment of solution containing **3.2** and $\text{Cu}^{\text{II}}\text{S}_2\text{NCN}_2$, depending on temperature studied by ^1H NMR Evans' Method analysis.

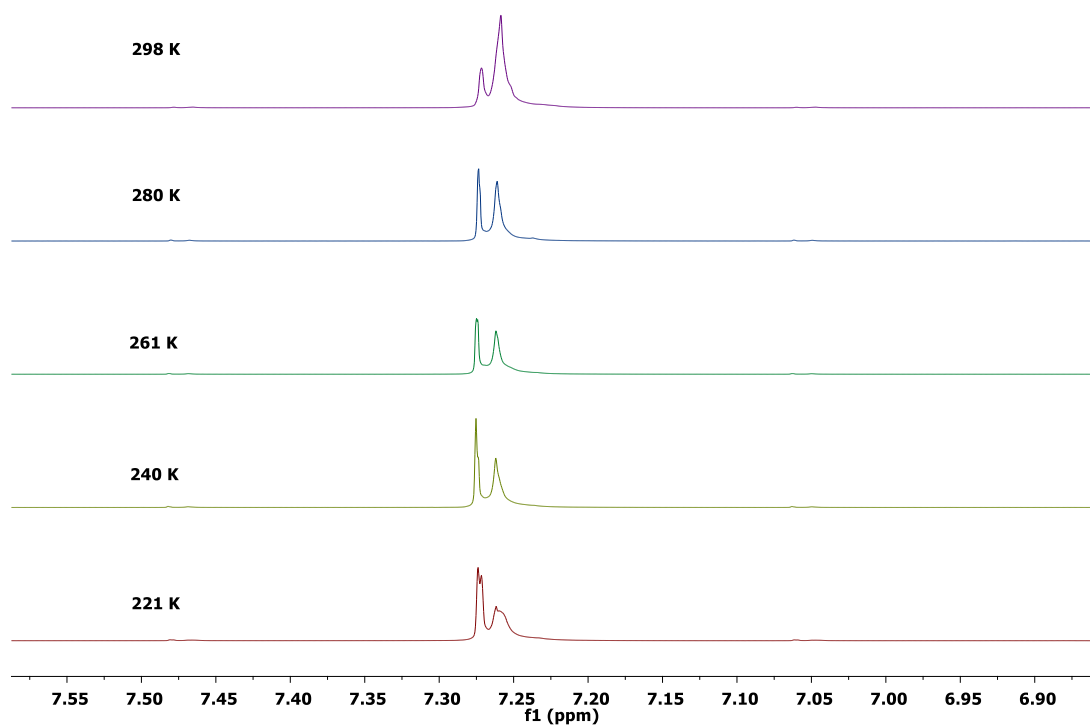


FIGURE 5.54 ^1H NMR (500 MHz) of 3.2 and $\text{Cu}^{\text{II}}\text{S}_2\text{NCN}_2$ solution mixture at different temperatures for Evans' Method analysis.

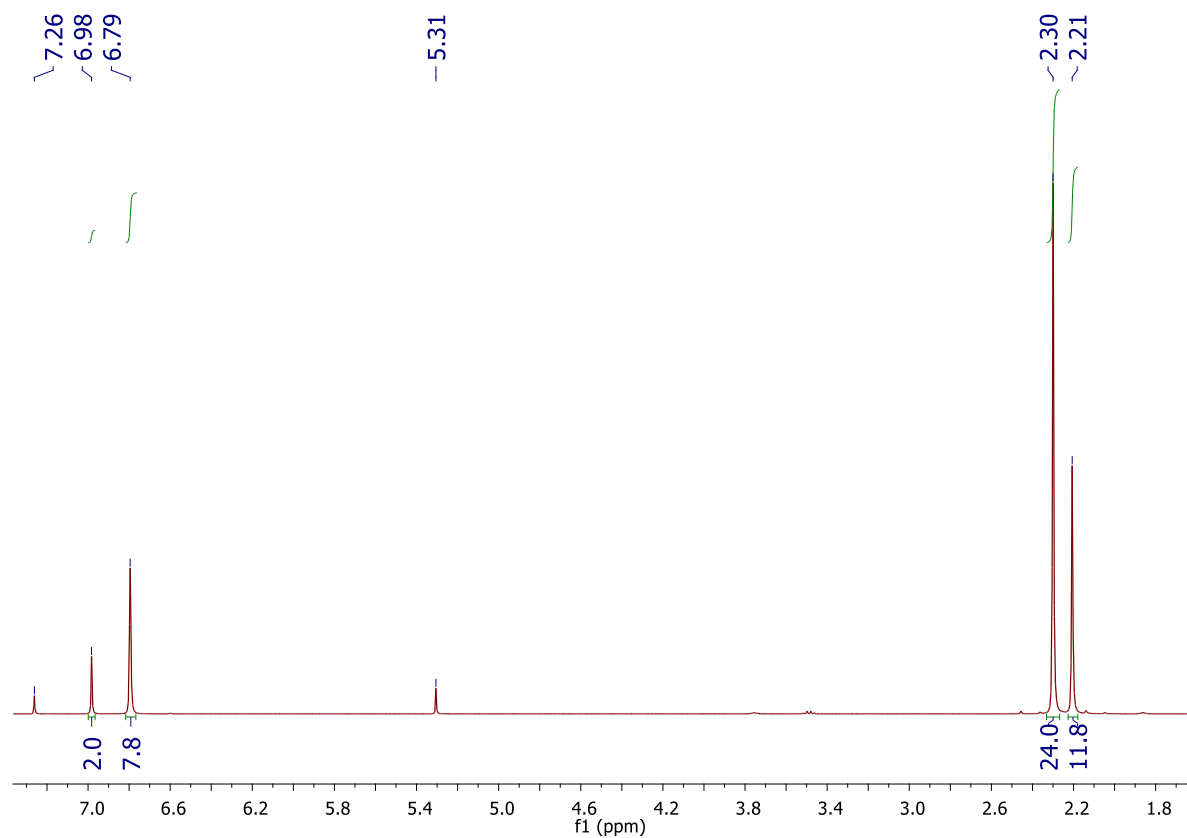


FIGURE 5.55 ^1H NMR (400 MHz) of **3.1** in CDCl_3 . Peak observed at 5.31 ppm is residual dichloromethane.

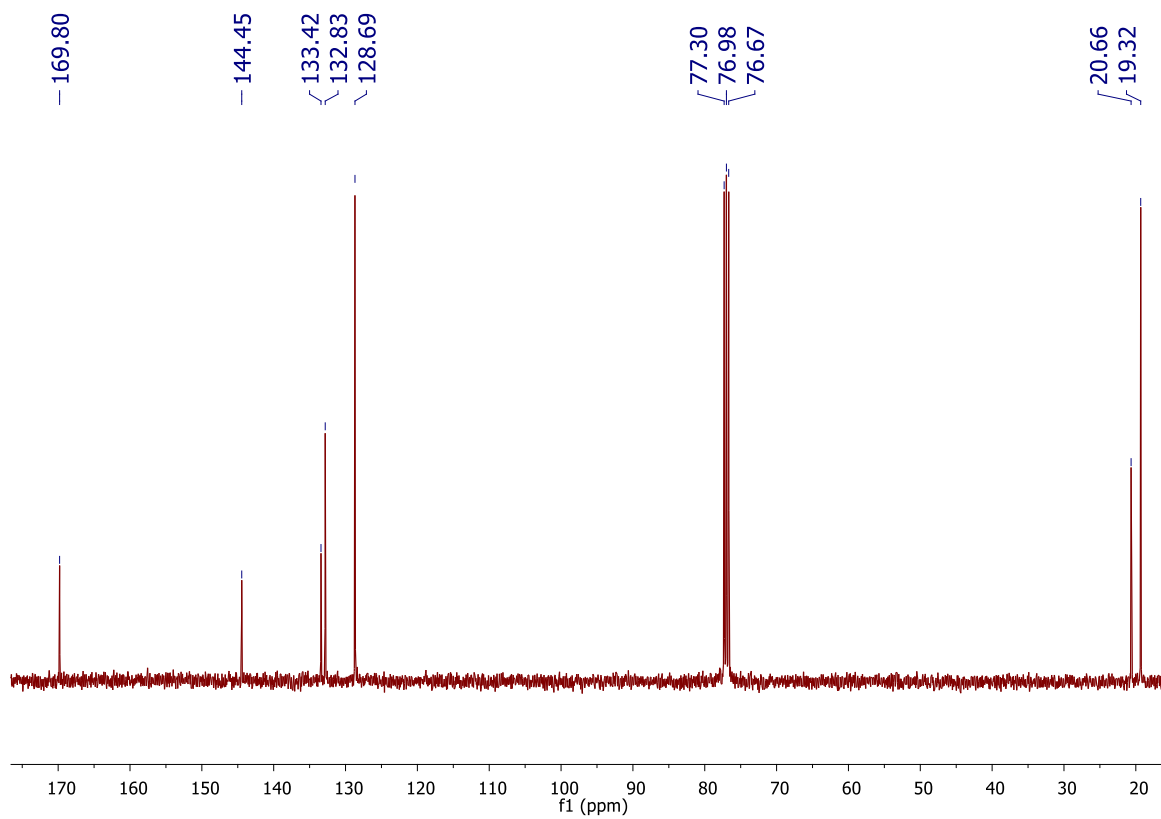


FIGURE 5.56 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) of **3.1** in CDCl_3 .

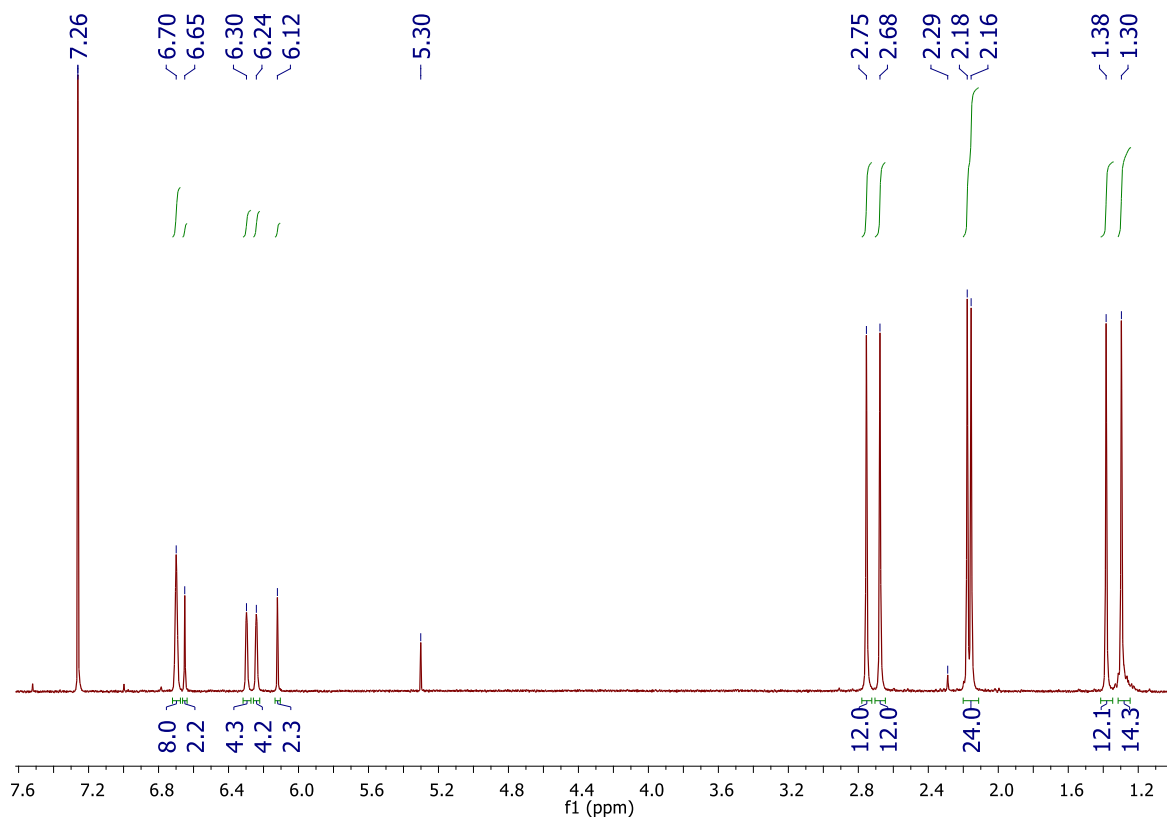


FIGURE 5.57 ¹H NMR (400 MHz) of **3.2** in CDCl₃. Peak observed at 5.30 ppm is residual dichloromethane. Peak observed at 2.29 ppm is trace amount of **3.1**.

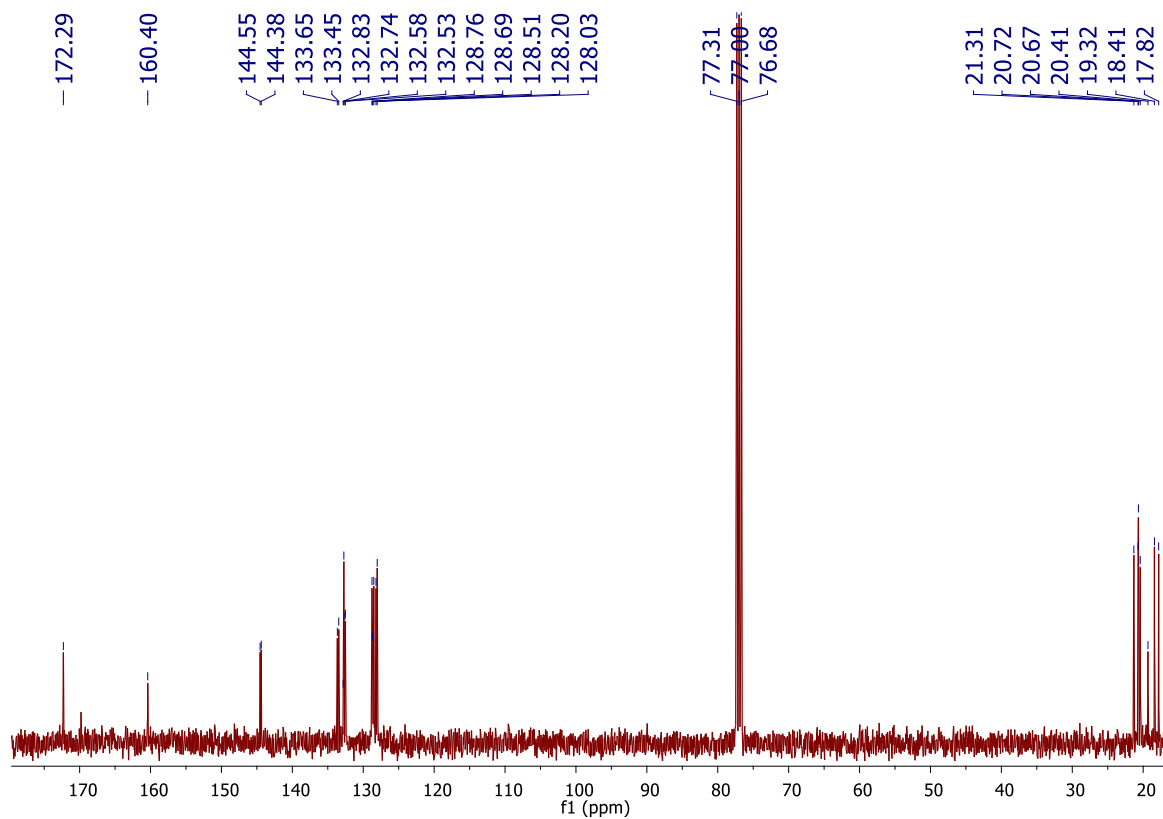


FIGURE 5.58 ^{13}C NMR (100 MHz) of **3.2** in CDCl_3 . Peak observed at the following chemical shifts are residual amounts of **3.1**; 132.8 ppm, 128.69 ppm, 20.67 ppm and 19.3 ppm.

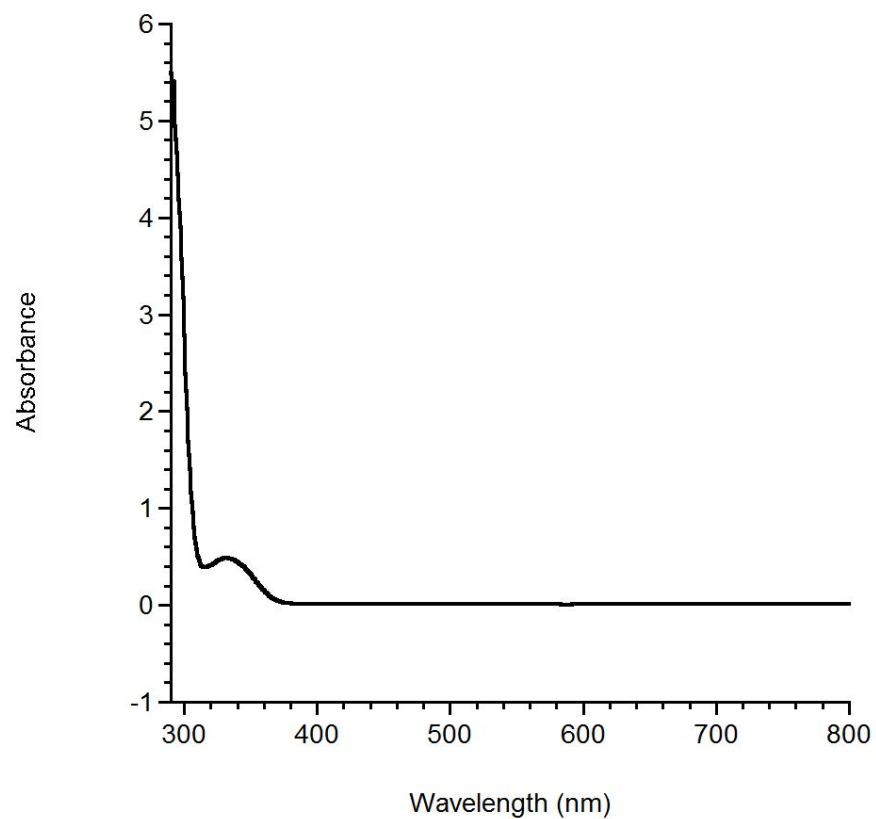


FIGURE 5.59 Absorption spectra for 0.3 mM **3.1** in dichloromethane.

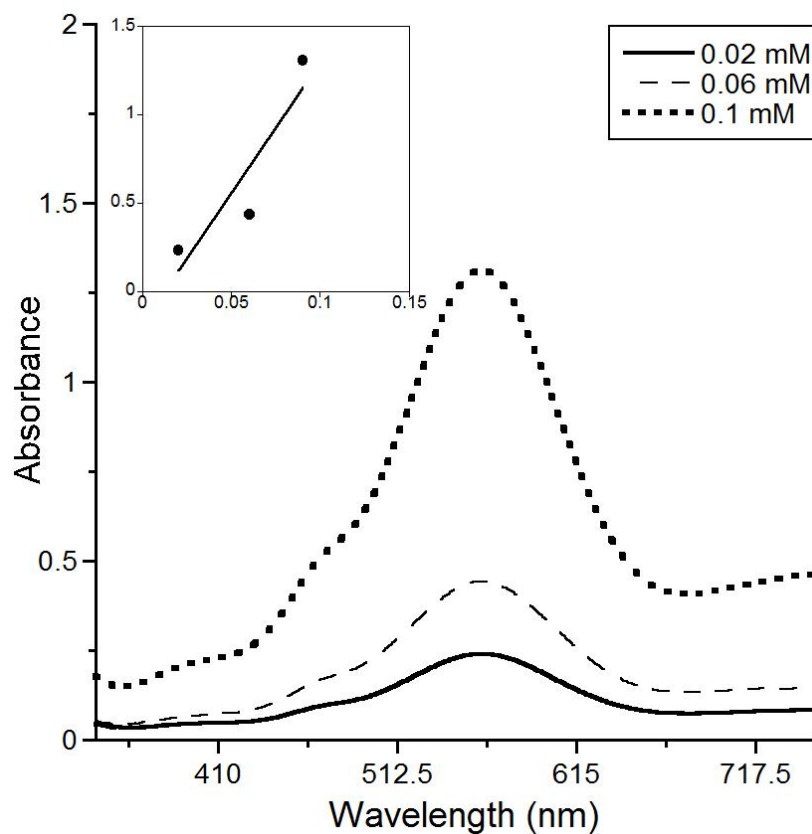


FIGURE 5.60 Absorption spectra for 3.2 in dichloromethane at different concentrations. Inset plot of absorbance vs. concentration (mM); $\epsilon = 14000 \text{ M}^{-1} \text{ cm}^{-1}$ ($y = -0.1712 + 14.746x$; $R^2 = 0.9100$).

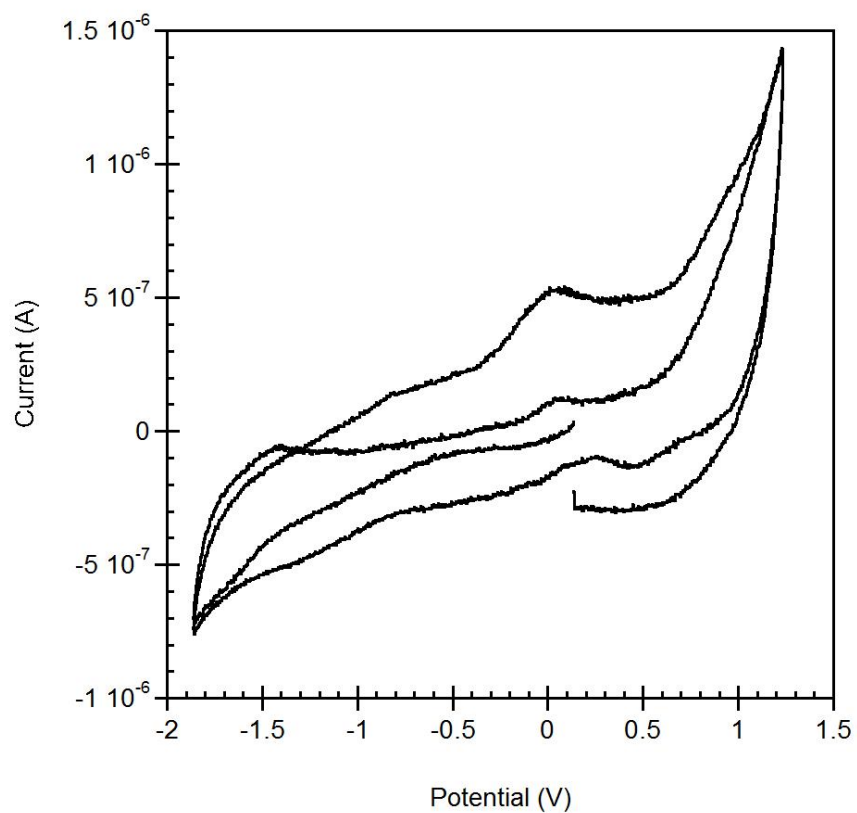


FIGURE 5.61 Cyclic voltammogram of 0.1 M Bu_4NPF_6 background in dichloromethane vs $\text{FeCp}_2^{+/0}$.

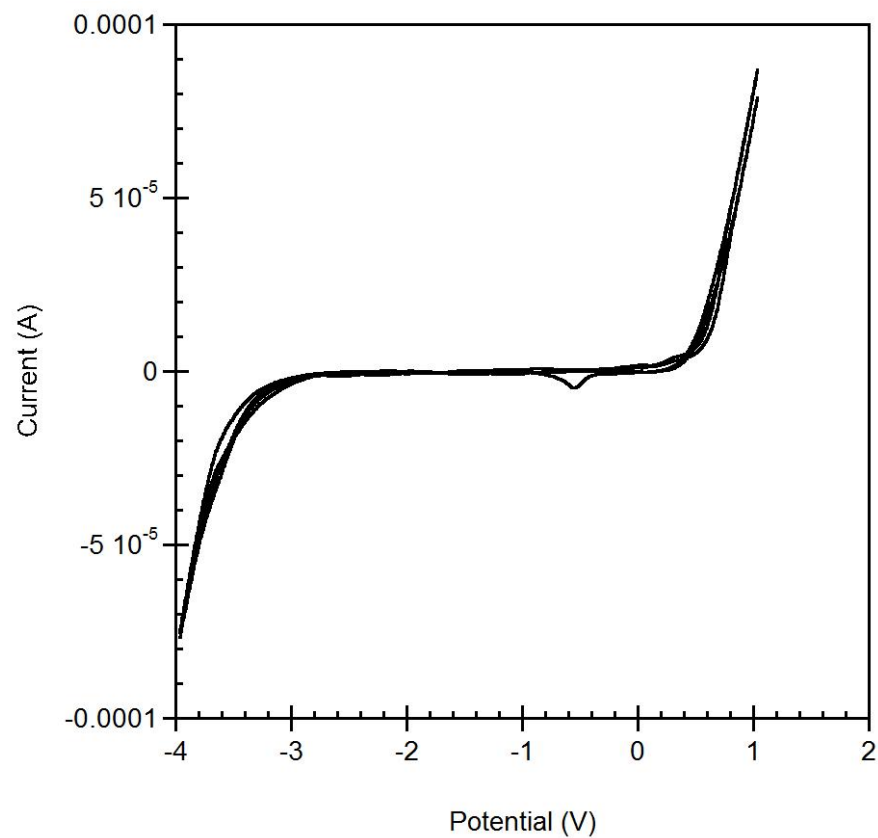


FIGURE 5.62 Cyclic voltammogram of 0.1 M Bu_4NPF_6 background in THF vs. $\text{FeCp}_2^{+/0}$.

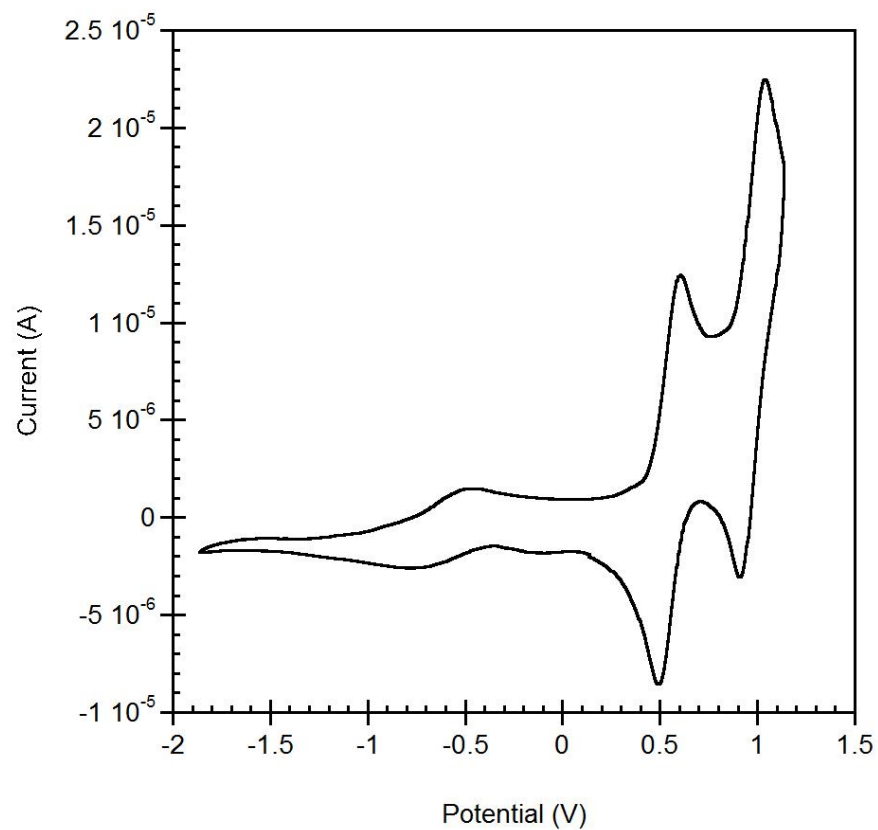


FIGURE 5.63 Cyclic voltammogram of 1.48 mM **3.1** in dichloromethane vs. $\text{FeCp}_2^{+/0}$.

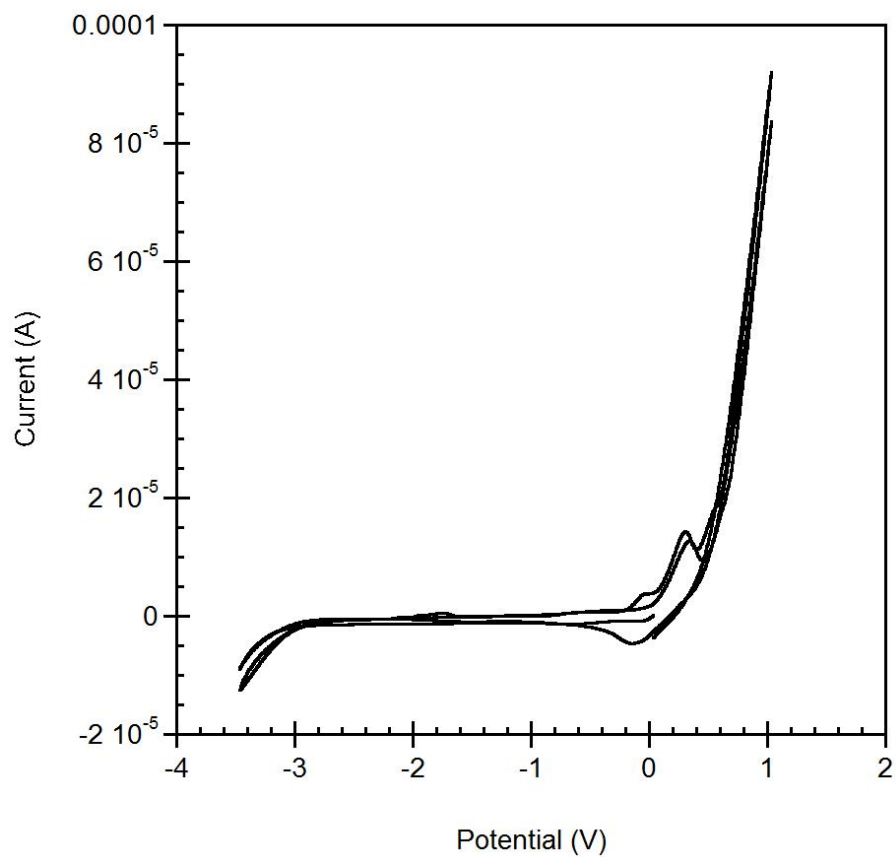


FIGURE 5.64 Cyclic voltammogram of 0.63 mM **3.1** in THF vs. $\text{FeCp}_2^{+/0}$.

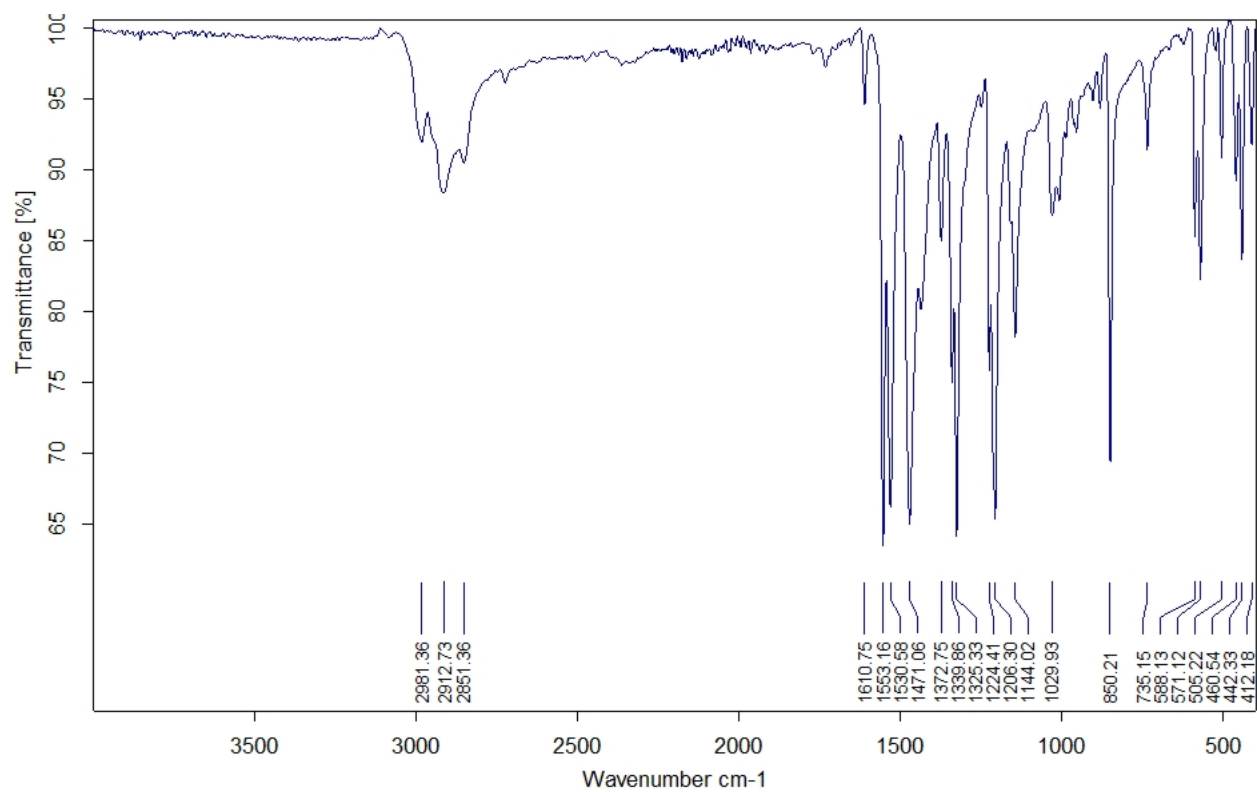


FIGURE 5.65 Infrared spectrum of **3.2**.

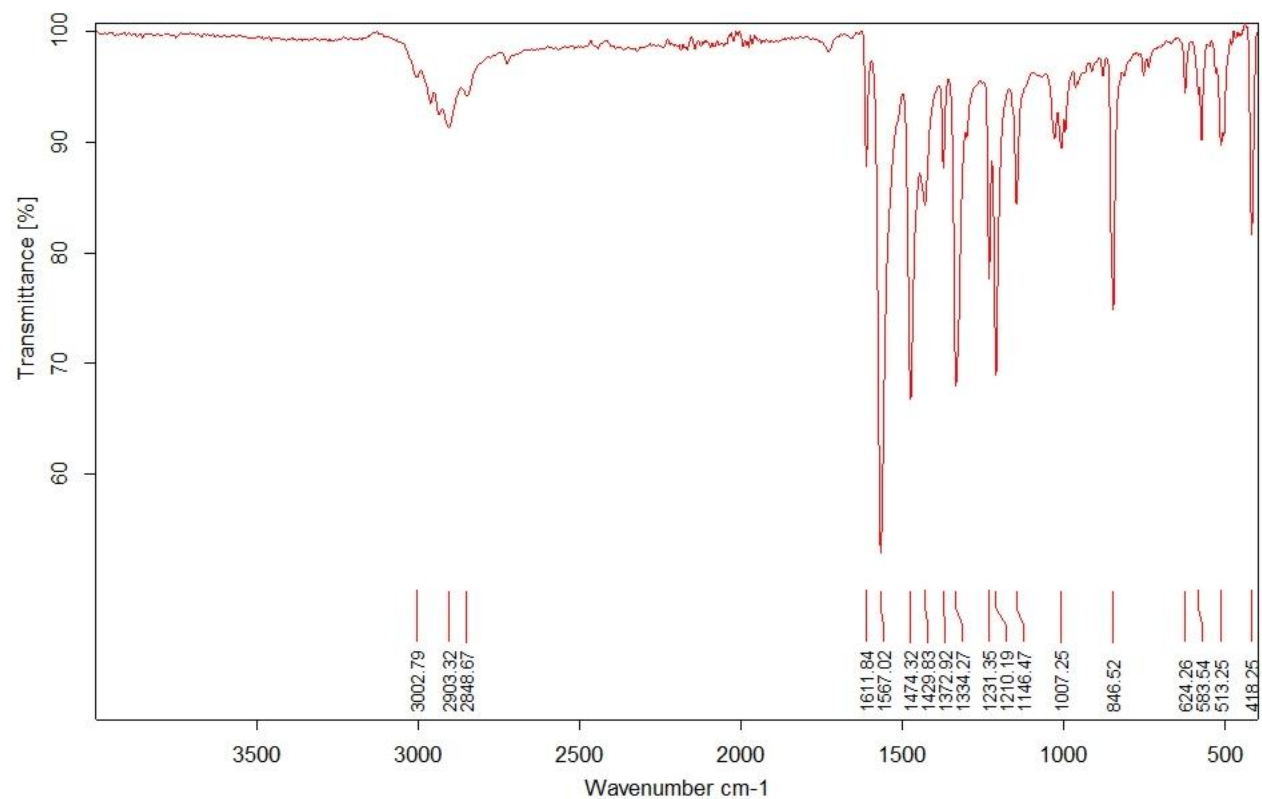


FIGURE 5.66 Infrared spectrum of **3.1**.

TABLE 5.13 Optimized Coordinates for the Singlet State of **3.2'**

Cu1	Cu	-1.3232	1.3228	-0.2204
S2	S	9.01401e-17	-0.0001	-1.472
Cu7	Cu	1.3231	-1.3227	-0.2202
Cu12	Cu	1.1189	1.4595	-0.15
N13	N	0.951	2.6674	1.375
N14	N	-1.4014	2.5711	1.2715
C15	C	-0.2624	2.9922	1.8152
H16	H	-0.3289	3.6517	2.706
Cu17	Cu	-1.1189	-1.4595	-0.1498
N18	N	-0.9509	-2.6671	1.3754
N19	N	1.4016	-2.5707	1.2719

C20 C 0.2626 -2.992 1.8156
H21 H 0.3291 -3.6515 2.7063
C30 C 2.1006 3.2074 2.094
H31 H 2.8286 2.4073 2.3177
H32 H 2.6238 3.98 1.4974
H33 H 1.7988 3.6724 3.0545
C34 C -2.654 3.0268 1.8641
H35 H -3.345 2.1765 2.0013
H36 H -2.4893 3.5005 2.8533
H37 H -3.1614 3.7695 1.2166
C46 C -2.1005 -3.2072 2.0944
H47 H -1.7986 -3.6726 3.0547
H48 H -2.8283 -2.407 2.3185
H49 H -2.624 -3.9794 1.4976
C50 C 2.6542 -3.0266 1.8644
H51 H 2.4896 -3.5002 2.8536
H52 H 3.1615 -3.7693 1.2168
H53 H 3.3453 -2.1763 2.0014
N3 N -3.1307 0.9736 -0.9666
N4 N -2.9782 -1.3951 -0.8587
C5 C -3.5863 -0.257 -1.1737
H6 H -4.5845 -0.3419 -1.6504
C38 C -3.9049 2.0935 -1.4931
H39 H -4.8927 1.7673 -1.8774
H40 H -4.082 2.8517 -0.7085
H41 H -3.3694 2.5931 -2.3242

C42 C -3.6538 -2.647 -1.1882
H43 H -3.8477 -3.2471 -0.2795
H44 H -4.6269 -2.4703 -1.6895
H45 H -3.0327 -3.2617 -1.867
N8 N 3.1306 -0.9739 -0.9666
N9 N 2.9783 1.3948 -0.8589
C10 C 3.5862 0.2567 -1.1738
H11 H 4.5844 0.3415 -1.6506
C22 C 3.9042 -2.0938 -1.494
H23 H 4.0794 -2.8534 -0.7103
H24 H 3.3694 -2.5915 -2.3266
H25 H 4.893 -1.7681 -1.8762
C26 C 3.6542 2.6467 -1.1877
H27 H 4.6266 2.4699 -1.6904
H28 H 3.0326 3.2625 -1.865
H29 H 3.8496 3.2457 -0.2786

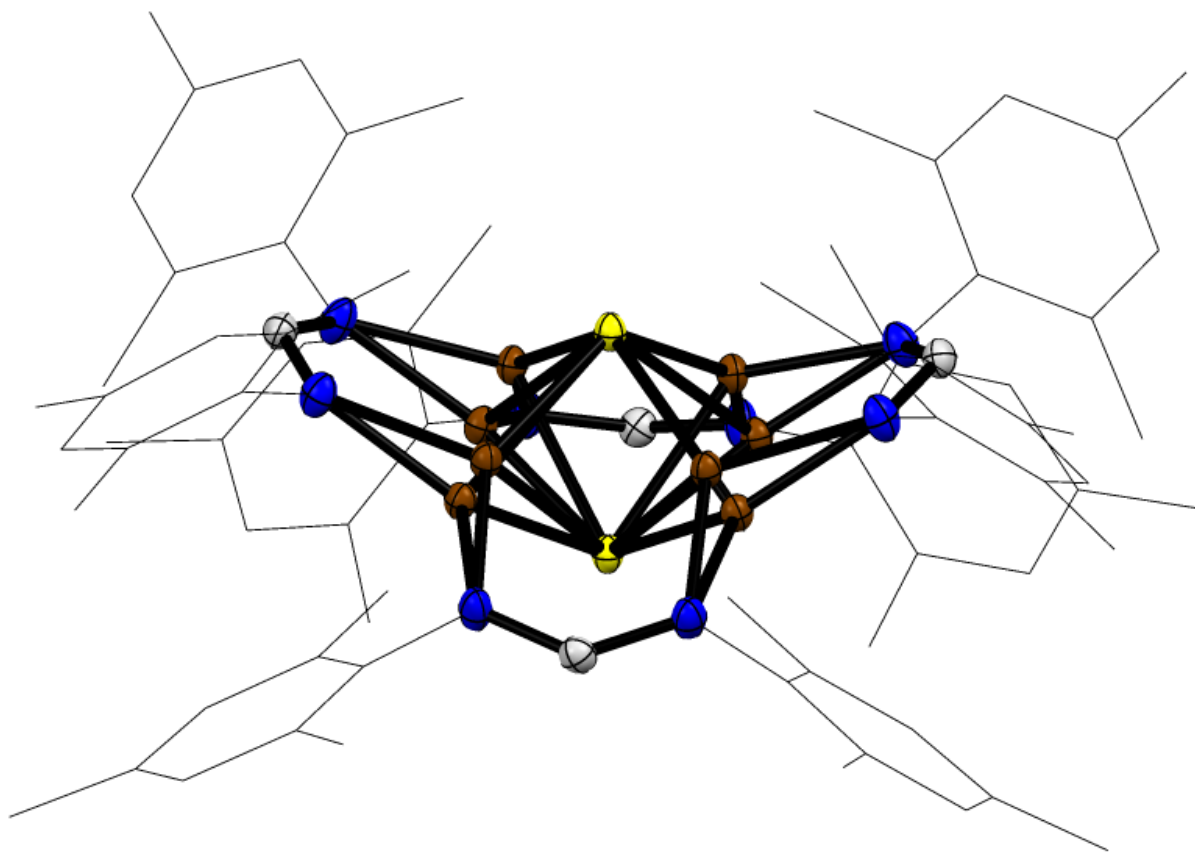


FIGURE 5.67 Solid state structure of **3.2** determined by X-ray crystallography, with both disordered Cu₄S units shown. Mesityl groups are shown as wireframes and other atoms are displayed as 50% probability thermal ellipsoids. Hydrogen atoms and any co-crystallization solvents have been omitted. Atom colors include: Cu, brown; S, yellow; N, blue; C, gray. The molecule is positioned on crystallographic element of symmetry (-4) and experiences two types of disorder: (a) the S cap alternatively occupies 2 symmetrically equivalent position over and under the Cu₄ moiety, and (b) each of the Cu ions of the central moiety deviates alternatively up or down from the mean plane that corresponds to a superposition of two tetrahedral distortions of opposite sign. The ligands do not show any perceptible disorder. Apparently, they form a significantly robust scaffold around the central metal nucleus owing to stacking between overlapping mesityl groups.

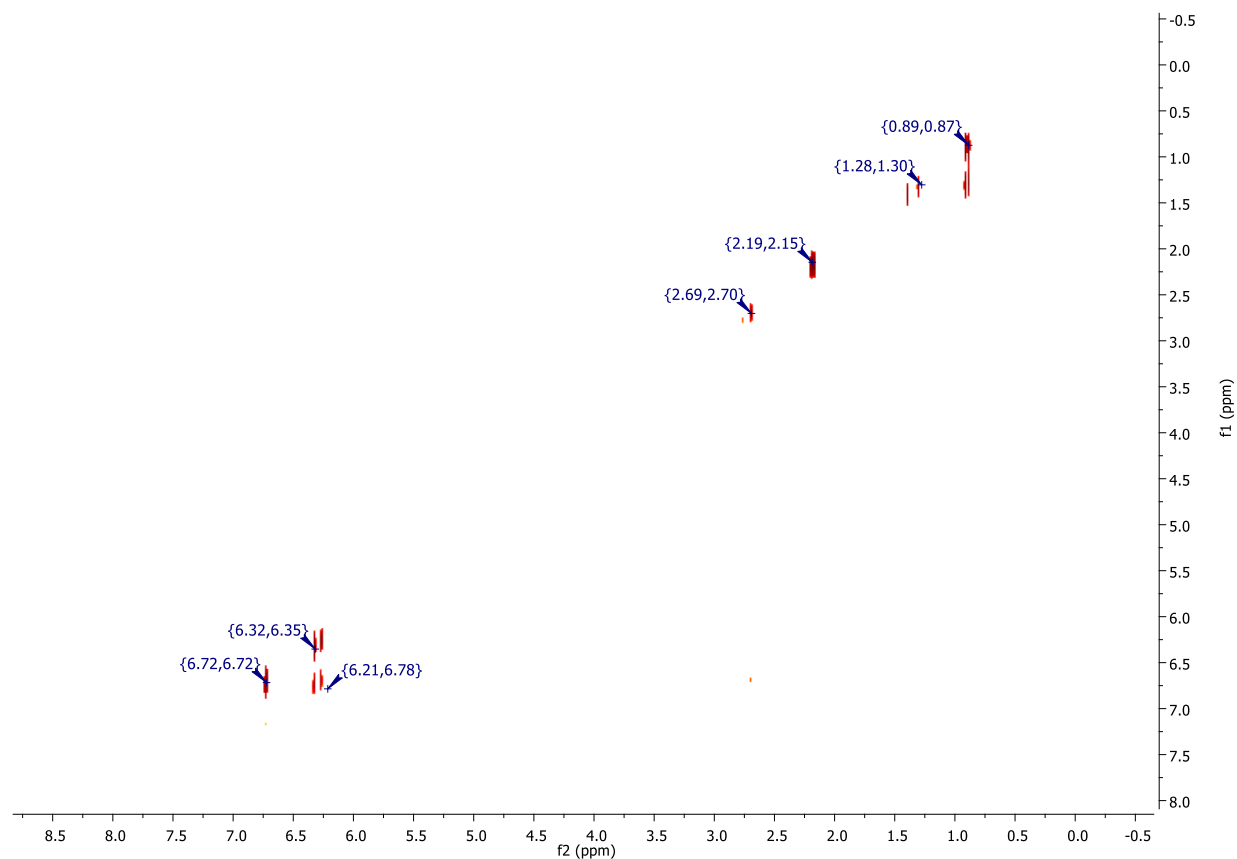


FIGURE 5.68 ^1H - ^1H COSY (500 MHz) of **3.2** in CDCl_3 . Correlation seen at 0.89 ppm is residual pentane solvent.

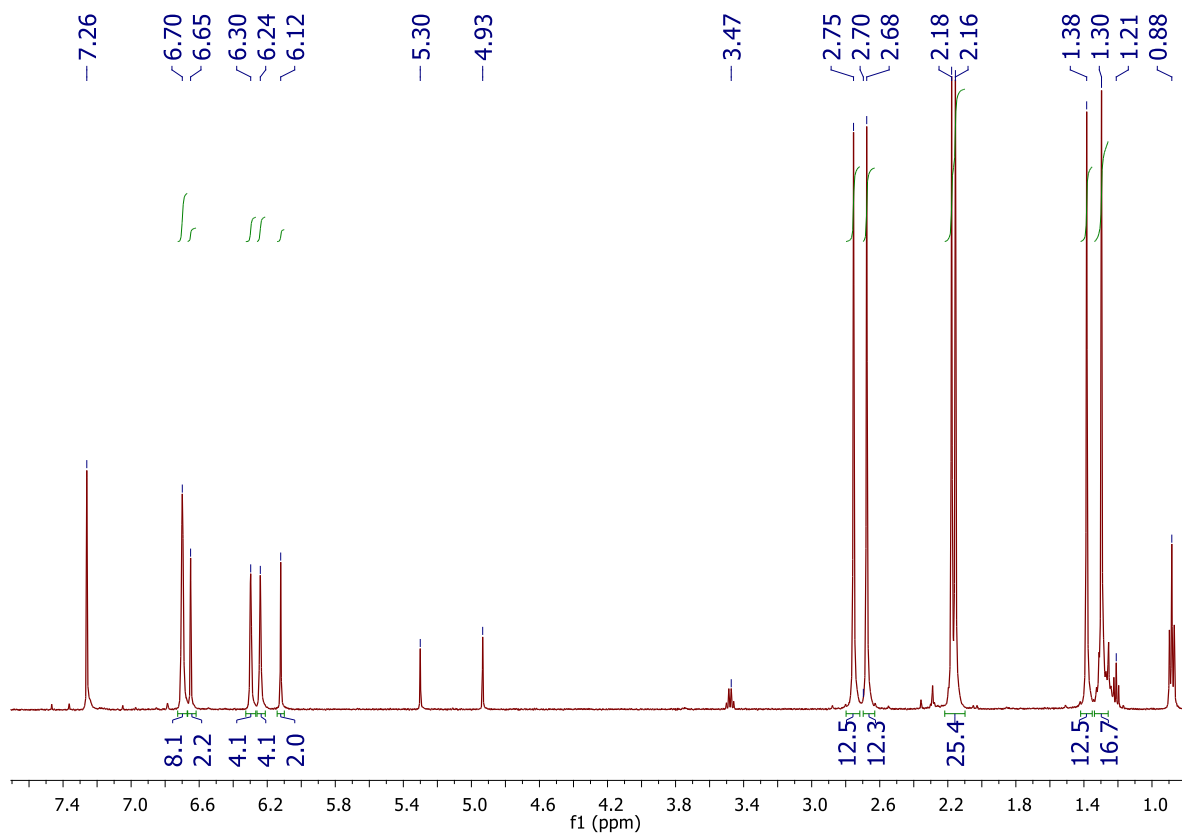


FIGURE 5.69 ^1H NMR (500 MHz) of **3.2** in CDCl_3 sample used for ^1H - ^1H COSY experiment in Figure 5.68. Peaks observed at the following chemical shifts are residual solvents in sample: 0.88 ppm (pentane), 1.21 ppm and 3.47 ppm (diethyl ether), 4.93 ppm (dibromomethane), 5.30 ppm (dichloromethane).

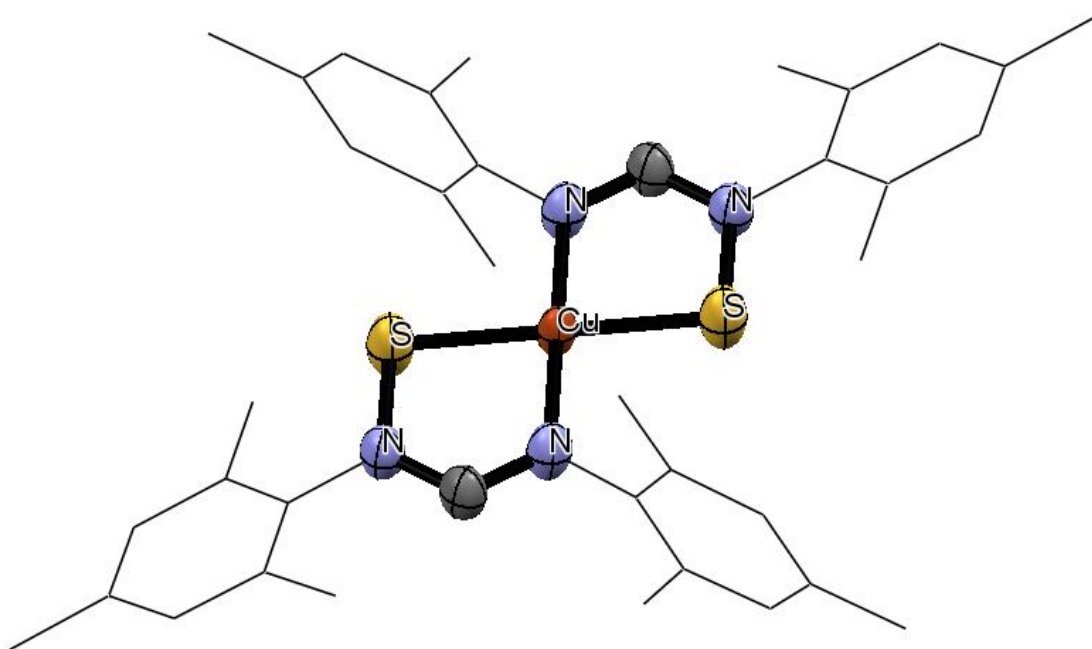


FIGURE 5.70 Solid state structure of $\text{Cu}^{\text{II}}\text{S}_2\text{NCN}_2$ paramagnetic impurity determined by single-crystal X-ray diffraction.²³² Mesityl groups are shown as wireframes and other atoms are displayed as 50% probability thermal ellipsoids. Hydrogen atoms and any co-crystallization solvents have been omitted. Atom colors include: Cu, orange; S, yellow; N, blue; C, gray. The $\text{Cu}^{\text{II}}\text{S}_2\text{NCN}_2$ impurity was isolated following the procedure described in Section 5.2.6 with S_8 and the following modifications: the reaction mixture was stirred for two days at room temperature. The crude reaction solution was filtered through Celite and the filtrate was completely evaporated by vacuum. Recrystallization by vapor diffusion of the filtrate residue in CHCl_3 and pentane vapors leads to the formation of maroon crystals.

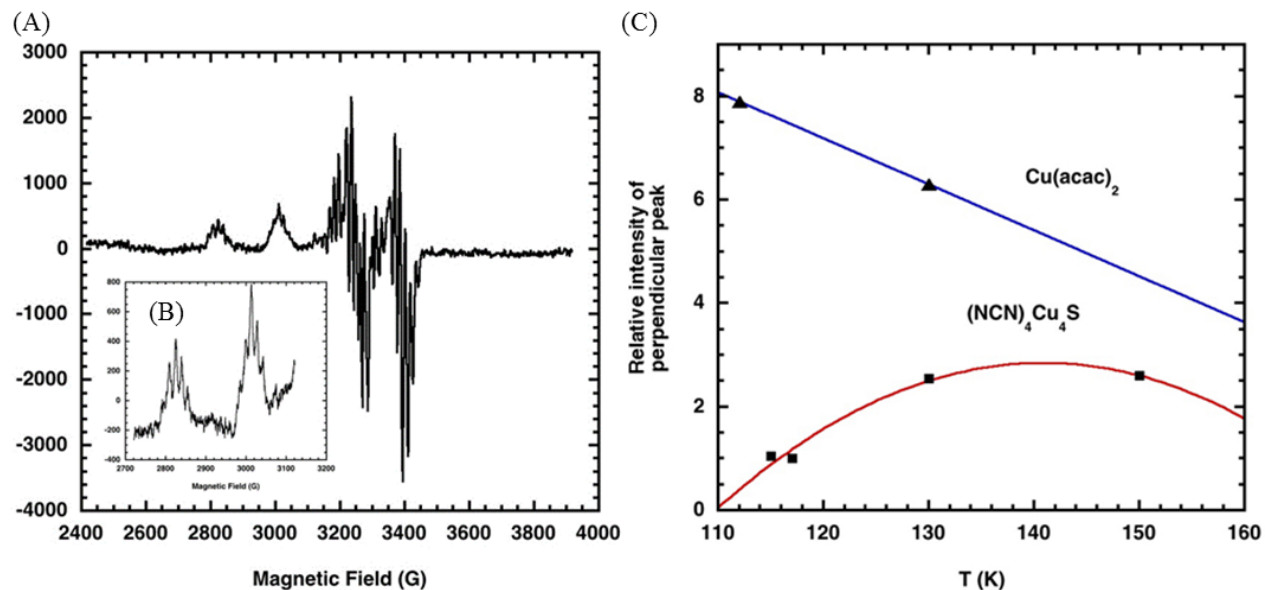


FIGURE 5.71 EPR data collected for 3.2 and Cu(II) impurity shown in Figure 5.70. (A) X-band EPR spectrum in toluene glass at 115K. (B) the $g_{\parallel}$ region of the EPR spectrum and (C) temperature dependence of EPR signal intensity for 3.2 and Cu(II) impurity mixture (red trace) and the $\text{Cu}(\text{acac})_2$ control, with curves drawn to guide the eye.

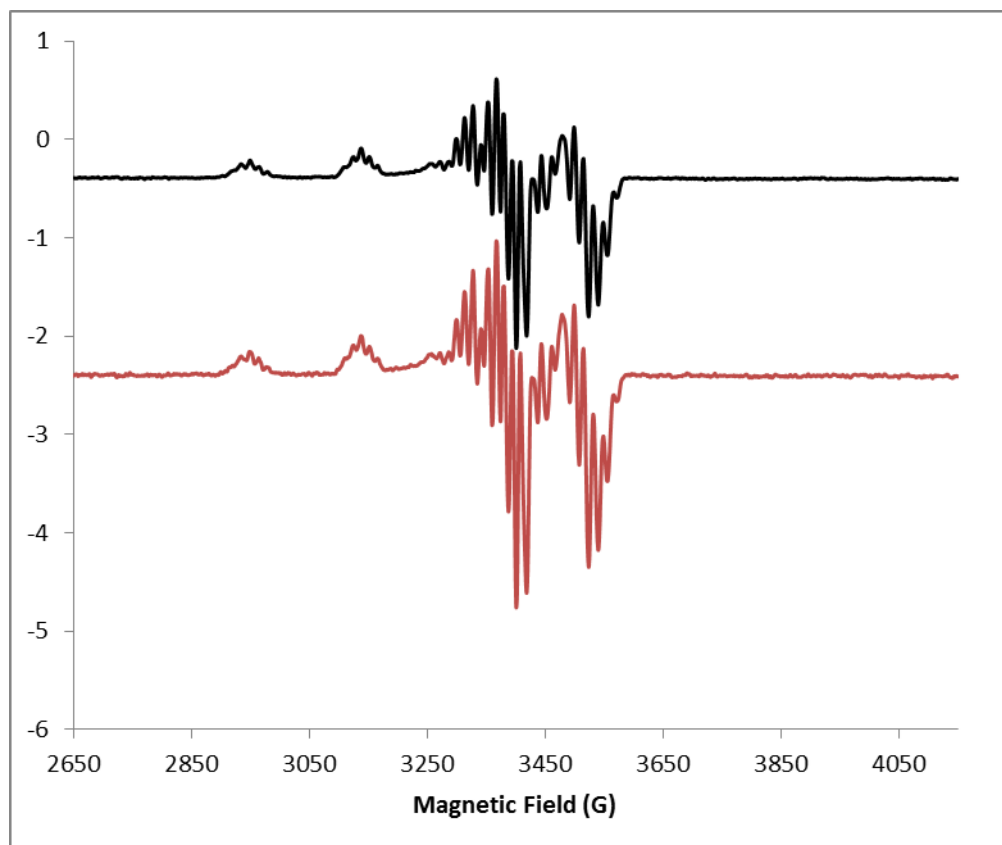


FIGURE 5.72 X-band EPR spectrum of sample containing $\text{Cu}^{\text{II}}\text{S}_2\text{NCN}_2$ impurity (Figure 5.70) glassed in 2-methyltetrahydrofuran at 34 K (black trace) and 24 K (red trace), power 46 dB.

5.2.11 General Considerations for Complex 3.3

Unless otherwise specified, all reactions and manipulations were performed under purified N_2 in a glovebox or using standard Schlenk line techniques. Glassware was oven-dried prior to use. Reaction solvents (diethyl ether, toluene, tetrahydrofuran, dichloromethane, acetonitrile, pentane) were sparged with argon and dried using a Glass Contour Solvent System built by Pure Process Technology, LLC. Deuterated solvents were degassed by repeated freeze-pump-thaw cycles and then stored over 3-Å molecular sieves. Unless otherwise specified, all other chemicals were purchased from commercial sources and used without further purification. 1 L of Nitrous Oxide ($^{15}\text{N}_2$, 98%+) was purchased from Cambridge Isotope Laboratories, Inc. A 460 mL Stainless Steel 1/4" NPT Stainless Steel Whitey Straight/Male adaptor was also purchased and assembled from Cambridge Isotope Laboratories packaging prior to shipment.

5.2.12 Spectroscopic Measurements for Complex 3.3

The NMR spectra for compound characterization were recorded at ambient temperature using Bruker Avance DPX-400 or Bruker Avance DRX-500 MHz spectrometers. ^1H NMR chemical shifts were referenced to residual solvent peaks. FT-IR spectra were recorded on solid samples in a glovebox using a Bruker ALPHA spectrometer fitted with a diamond-ATR detection unit. Elemental analyses were performed by the Midwest Microlab, LLC in Indianapolis, IN. UV-Vis absorbance spectra were taken at room temperature using a JASCO V-660 Spectrophotometer. Absorbance was measured at 0.5 nm intervals and with a continuous scan speed of 1000 nm/min. X-band spectra were obtained at 10 K with an Elexsys E500 spectrometer, Bruker, Billerica, MA located at the National Biomedical EPR Center at the Medical College of Wisconsin. Q-band spectra were obtained on a Varian E109 spectrometer at -150°C located at the National Biomedical EPR Center at the Medical College of Wisconsin. Spectra were simulated with EasySpin.²⁶⁷ The 1st harmonic spectra were obtained using SumSpec (a program available from the National Biomedical EPR Center) using pseudomodulation with a 1% or 3% Bessel function.

Magnetic measurements were performed on polycrystalline samples in a sealed polyethylene bag or in a sealed quartz tube restrained with eicosane. All data were collected using a Quantum Design MPMS-XL SQUID magnetometer in a temperature range of 1.8 to 400 K at applied dc fields of 0.1 T and 7 T. A quartz tube was employed for high temperature measurements to avoid melting the polyethylene bag, and a high-field was employed with the quartz-tube sample to ensure sufficient signal-to-noise at high temperatures.

Headspace gas was analyzed by a JEOL GCMate II (JEOL USA, Peabody MA) gas chromatograph/mass spectrometer, the gas chromatograph was an Agilent 6890Plus (Wilmington DE) equipped with a G1513A autoinjector with 100 vial sample tray connected to a G1512A controller. The gas chromatography column was a J&W GS-CarbonPLOT (Agilent Tech), 60 m long, 0.320 mm diameter, 1.50 μm film thickness. The carrier gas was helium (99.999% Ultra High Purity) run through a STG triple filter (Restek Corp.) at a constant flow rate of 2.5 mL/min. The inlet temperature was 250°C and was fitted with an Agilent 4 mm ID single taper split liner containing deactivated glass wool. The static headspace analysis

was performed using 5 μL of the experimental gas mixture manually injected via syringe. The GC inlet split ratio was 20:1. The GC oven was run in isothermal mode at a temperature of 30 $^{\circ}\text{C}$ for 5 minutes then ramped 10 $^{\circ}\text{C}/\text{min}$ to 80 $^{\circ}\text{C}$. Total run time was approximately 10 min. The mass spectrometer was a benchtop magnetic sector operating at a nominal resolving power of 500 using an accelerating voltage of 2500 V. The spectrometer was operated in full scan EI mode (+Ve) with the filament operating at 70 eV scanning from m/z 10 to m/z 850 using a linear magnet scan. The scan speed was 0.2 s/scan. Data analysis was performed using the TSSPro software (Shrader Analytical & Consulting Laboratories, Inc., Detroit MI) provided with the spectrometer. Mass calibration was performed using perfluorokerosene (PFK).

5.2.13 X-ray Crystallography for Complex 3.3

The X-ray crystallography data on dark violet tablets of **3.3** was collected at the X-ray Structural Laboratory at Marquette University (Milwaukee, WI). The X-ray single-crystal diffraction data were collected with an Oxford Diffraction SuperNova diffractometer equipped with dual microfocus Cu/Mo X-ray sources, X-ray mirror optics, Atlas CCD detector and low-temperature Cryojet device. Data was collected using $\text{Cu}(\text{K}\alpha)$ radiation at 100 K. The data was processed with CrysAlisPro program package (Oxford Diffraction Ltd., 2010) typically using a numerical Gaussian absorption correction (based on the real shape of the crystal) followed by an empirical multi-scan correction using SCALE3 ABSPACK routine. The structures were solved using SHELXS program and refined with SHELXL program²⁶⁵ within Olex2 crystallographic package.²⁶⁶ All computations were performed on an Intel PC computer under Windows 7 OS. Hydrogen atoms were localized in difference syntheses of electron density but were refined using appropriate geometric restrictions on the corresponding bond lengths and bond angles within a riding/rotating model (torsion angles of Me hydrogens were optimized to better fit the residual electron density). The crystal was twinned: regular twins with 180 $^{\circ}$ rotation around direct -101 vector. Because of quasi-rational cell dimensions, all reflections with $h+l=2n$ overlap exactly (but not with identical indexes - HKL transformation matrix $\begin{pmatrix} -.5 & 0 & -.5 & 0 & -1 & 0 & -1.5 & 0 & .5 \end{pmatrix}$). Reflections with $h+l=2n+1$ are separate. The structure contains two symmetrically independent tetranuclear units having a similar geometry. Two $\text{K}^+/\text{18-crown-6}$ counter ions are disordered to a different degree. The disorder affects as the position of K atom (swinging

alternatively in axial direction to make $K^+ \dots Ar$ contacts with neighboring anions) as well as the crown-ether itself. The structure contains well-ordered 1 eq of solvate DCM solvent. It also contains large areas of highly-disordered solvent only partially localized/identified as diethyl ether. Because of the twinning, an application of a solvent mask procedure was prohibited.

5.2.14 Preparation of Complex 3.3

Complex **3.2** (0.10 g, 0.079 mmol) was dissolved in approximately 60 mL of toluene using a magnetic stir bar. Solid $[K(18\text{-crown-}6)_2][Fp]^{231}$ (0.057 g, 0.076 mmol) was added slowly to stirring solution at room temperature. The solution was stirred vigorously overnight. The next day the solution was filtered. The collected dark solid was washed with pentane to remove any Fp_2 (cyclopentadienyliron dicarbonyl dimer) until filtrate was clear, and then washed with toluene to remove any unreacted **3.2** until filtrate was clear. The solid was collected and dried under vacuum. Yield of **3.3**: 0.091 g, 75%. Compound **3.3** was stored in a freezer (-36°C) and is not stable in solution at room temperature for more than an hour. Note: Trace amounts (2-5%) of **3.1** were often detected by ^1H NMR regardless of multiple purification attempts. The best method for removing **3.1** is by adding a small amount of tetrahydrofuran (2 mL) to solid **3.3** (0.091 g) so that **3.1** dissolves but **3.3** is super-saturated and doesn't dissolve entirely. This solution is filtered, and the resulting purple solid is washed with a small amount of tetrahydrofuran (2 mL) and then pentane (2 mL) to remove any remaining tetrahydrofuran solvent. The purple solid can then be collected and dried under vacuum. Usually this purification method is done once to achieve experimental purity. Dark black crystals may be obtained by dissolving **3.3** in a minimum amount of dimethoxyethane, pipette-filtering through Celite, and leaving solution at -36°C for four days. NMR samples were dissolved in acetone- d_6 and pipette-filtered through Celite into NMR tube. ^1H NMR (500 MHz, acetone- d_6): δ 3.66 (s, 24 H, 18-crown-6). FT-IR (cm^{-1}): 2992, 2903, 2854, 2724, 1717, 1652, 1609, 1556, 1538, 1469, 1330, 1209, 1104, 959, 847, 738, 586, 504, 422. Anal. calcd. for $C_{88}H_{116}Cu_4N_8O_6SK$: C, 61.90; H, 6.85; N, 6.56. Found: C, 60.37; H, 6.50; N, 6.57. Repeated attempts at obtaining satisfactory combustion analysis results (with %C within $\pm 0.4\%$ of the calculated value) gave results with a large degree of variance, indicating

either that the spectroscopically pure samples were compromised during shipping/handling or that the compound does not combust cleanly.

5.2.15 Detection of **3.2** After Reaction Between Nitrous Oxide and Complex **3.3**

Inside a N₂ filled glovebox, to a Schlenk tube equipped with a Teflon screw cap and magnetic stir bar, **3.3** (0.006 g, 0.0035 mmol) was added and dissolved in approximately 2.5 mL dichloromethane. The tube was sealed with the Teflon screw cap and taken out of the glovebox and connected to a Schlenk line streaming N₂O. The solution was cooled to -78° C (dry ice and acetone bath) with stirring. The solution was then exposed to N₂O for 6.5 hours while maintaining the cooling bath at -78° C. Once cooling bath was removed, solvent was removed by vacuum evaporation and Schlenk tube was closed and pumped back into the glovebox. Evaporated residue was dissolved in CD₂Cl₂ and pipette-filtered through Celite into an NMR tube for analysis. A control experiment was conducted by same procedure using 0.005 g (0.0029 mmol) of **3.3** in approximately 2 mL of dichloromethane while under N₂. Using integration of 18-crown-6 as an internal standard (24 H) in ¹H NMR reveals 45% NMR yield of **3.2** in the reaction with N₂O (Figure 5.79) with respect to any Ar-CH₃ peak of **3.2** (12 H) and 0% yield in N₂ control experiment (Figure 5.80).

5.2.16 Recovery of **3.2** After Reaction Between Nitrous Oxide and Complex **3.3**

Inside a N₂ filled glovebox, to a Schlenk tube equipped with a Teflon screw cap and magnet stir bar, **3.3** (0.021 g, 0.012 mmol) was added and dissolved in dichloromethane (10 mL). The tube was sealed with the Teflon cap and taken out of the glovebox and connected to Schlenk line streaming with N₂O. The solution in the flask was cooled to -78° C (dry ice and acetone bath) with stirring, and then opened to N₂O for 6 hours while maintaining the cooling bath at -78° C. Solvent was removed by vacuum evaporation and Schlenk tube was closed and pumped back into the glovebox. Purple evaporated residue inside Schlenk tube was washed with acetonitrile (approximately 20 mL), in which **3.2** is insoluble, and then pipette-filtering through Celite until filtrate became clear. Dark purple solid remaining was collected using dichloromethane and the solution was completely evaporated by vacuum. The same procedure was followed in a control experiment using 0.021 g (0.012 mmol) of **3.3** in 10 mL of dichloromethane under N₂. Amount of **3.2** isolated from N₂O reaction residue: 0.015 g (0.010 mmol, 88% yield, Figure 5.81);

amount of **3.2** isolated from N₂ control reaction residue: 0.0052 g (0.0035 mmol, 30% decomposition, Figure 5.82).

5.2.17 Oxygen Trapping Experiment with Chlorotrimethylsilane

Inside a N₂ filled glovebox, to a Schlenk tube equipped with a Teflon screw cap and magnet stir bar, **3.3** (0.003 g, 0.0017 mmol) was added and dissolved in dichloromethane (3 mL). The tube was sealed with the Teflon cap and taken out of the glovebox and connected to Schlenk line streaming with N₂O. The solution in the flask was cooled to -78° C (dry ice and acetone bath) with stirring, and then opened to N₂O for 3.5 hours while maintaining the temperature at -78° C. Solvent was removed by vacuum evaporation and Schlenk tube was closed and pumped back into the glovebox. Purple evaporated residue inside Schlenk tube was dissolved in approximately 1 mL of CD₂Cl₂, and 95 µL of a 0.092 M solution of TMS-Cl (0.0087 mmol) in CD₂Cl₂ was added. Contents were stirred for 1 hour at room temperature and were then pipette-filtered through Celite into an NMR tube for analysis (Figure 5.83). The same procedure was followed in a control experiment using 0.006 g (0.0035 mmol) of **3.3** in 3 mL of dichloromethane, under N₂, followed by addition of 190 µL of 0.092 M TMS-Cl in CD₂Cl₂ solution (0.017 mmol) in the same manner as described in the N₂O experiment (Figure 5.84). ¹H NMR (400 MHz, CD₂Cl₂): δ 0.07 (s, (Me₃Si)₂O), 0.43 (s, unreacted TMS-Cl), 1.31 (s, **3.2** Ar-CH₃), 1.39 (s, **3.2** Ar-CH₃), 2.15 (s, **3.2** Ar-CH₃), 2.17 (s, **3.2** Ar-CH₃), 2.69 (s, **3.2** Ar-CH₃), 2.77 (s, **3.2** Ar-CH₃), 3.63 (s, 18-crown-6), 6.10 (s, **3.2** NC(H)N), 6.25 (s, **3.2** Ar-CH), 6.31 (s, **3.2** Ar-CH), 6.61 (s, **3.2** NC(H)N), 6.71 (s, **3.2** Ar-CH).

5.2.18 Oxygen Trapping Experiment with Benzoyl Chloride

Inside a N₂ filled glovebox, to a Schlenk tube equipped with a Teflon screw cap and magnet stir bar, **3.3** (0.010 g, 0.0058 mmol) was added and dissolved in dichloromethane (5 mL). The tube was sealed with the Teflon cap and taken out of the glovebox and connected to Schlenk line streaming with N₂O. The solution in the flask was cooled to -78° C (dry ice and acetone bath) with stirring, and then opened to N₂O for 3 hours while maintaining the temperature at -78° C. Solvent was removed by vacuum evaporation and Schlenk tube was closed and pumped back into the glovebox. Purple evaporated residue inside Schlenk tube was mixed with approximately 8 mL of diethyl ether and 20 µL of a 0.287 M solution of cold (-32° C)

benzoyl chloride (0.0057 mmol) in diethyl ether was added. Contents stirred for 1 hour at room temperature, pipette-filtered through Celite and solvent was removed by vacuum evaporation. Resulting residue was dissolved in C_6D_6 and pipette-filtered through Celite into an NMR tube for analysis (Figures 5.85 – 5.86). 1H NMR (400 MHz, C_6D_6): δ 1.46 (s, **3.2** Ar-CH₃), 1.57 (s, **3.2** Ar-CH₃), 2.18 (s, **3.2** Ar-CH₃), 2.20 (s, **3.2** Ar-CH₃), 2.83 (s, **3.2** Ar-CH₃), 2.97 (s, **3.2** Ar-CH₃), 3.52 (s, 18-crown-6), 6.37 (s, **3.2** Ar-CH), 6.44 (s, **3.2** Ar-CH), 6.94 (m, benzoic anhydride Ar-CH), 7.07 (m, benzoic anhydride Ar-CH), 7.96 (m, benzoic anhydride Ar-CH).

5.2.19 Reaction Headspace Analysis of $^{15}N_2$ Produced from the Reaction Between $^{15}N_2O$ and **3.3**

Inside a N_2 filled glovebox, to a 100 mL round bottom Schlenk flask with a magnetic stir bar, **3.3** (0.125 g, 0.0732 mmol) was added and dissolved in THF (60 mL). The flask was sealed with an unpunctured septa wrapped in copper wire and a Keck clip. The flask was taken out of the glovebox and connected to a T-shaped stopcock connected to a Schlenk line streaming N_2 and $^{15}N_2O$ gas cylinder. After five freeze-pump-thaw cycles, the flask was cooled to $-78^\circ C$ (dry ice and acetone bath) and headspace was backfilled quickly with $^{15}N_2O$ (~3 seconds) and then the flask was closed. The reaction was stirred at $-78^\circ C$ for three hours, and then the cooling bath was removed. The reaction was then stirred for 3 hours at room temperature to initialize equilibrium of the gases in the reaction headspace and gas dissolved in the solution. The gases in the reaction headspace were then analyzed by 5 μL injections into GC-MS (Figure 5.91). After the 6 hour GC-MS headspace measurement, the reaction flask sat for 48 hours at room temperature, without stirring to prevent high pressure build-up within the flask. After 48 hours, the gases in the headspace were again analyzed by 5 μL injections into the GC-MS (Figures 5.87 and 5.89). To serve as a blank, a 50 mL round bottom Schlenk flask was sealed using an unpunctured septa wrapped in copper wire and a keck clip. The blank flask was evacuated by vacuum and refilled with $^{15}N_2O$ and then closed. Gases in blank flask were analyzed by a 5 μL injection (Figure 5.92). Blank flask then sat alongside the reaction flask for 48 hours at room temperature and was re-analyzed by GC-MS (Figure 5.88 and 5.90).

5.2.20 Computational Methods for Complex 3.3 and Optimized Calculations for Complex 3.2

All calculations were performed using Gaussian09, Revision B.01.²⁶⁸ Density functional theory (DFT) calculations were carried out using the B3LYP functional.^{276–279} Mixed basis sets were employed: the LANL2TZ(f) triple- ζ basis set^{271–273} with effective core potential^{271,274,275} was used for Cu, the Gaussian09 internal 6-311+G(d) basis set was used for S, and the Gaussian09 internal 6-31+G(d) basis set was used for C, H, and N. All calculations included a polarizable continuum model for dichloromethane solvation.²⁸⁰ The optimized coordinates for model **3.2'** (where the mesityl groups of **3.2** were replaced with methyls) at a slightly different level of theory were reported previously in Section 5.2.9, and were used as the starting point for obtaining optimized coordinates for neutral **3.2'** and anion **3.3'** (where the mesityl groups of **3.3** were replaced with methyls). Optimized coordinates for both structures are enclosed below (Tables 5.20 and 5.21), along with comparisons of **3.2'** and **3.3'** to the experimental structures of **3.2** and **3.3** (Table 5.19). These optimized coordinates were used for single-point TD-DFT calculations (35 states for **3.2'**, 25 states for **3.3'**) at the same level of theory (see Figures 5.95 – 5.97). Lists of these transitions are included as Tables 5.22 and 5.23, below. Natural transition orbital analysis²⁸¹ was used to examine the nature of the dominant transition (State 9, 578 nm, 6000 M⁻¹cm⁻¹) in the predicted electronic spectrum of **3.3'**. The broken-symmetry S = 0 and S = 1 states of **3.2'** were found to be higher in energy than the closed-shell S = 0 state presented in Chapter 3, although all three states were within ± 2 kcal/mol of each other, indicating that high-level calculations are in order to accurately model **3.2**. Orbital surfaces and Mulliken spin density were plotted using Gaussview 4.1²⁸² and are presented with isovalues indicated in figure captions.

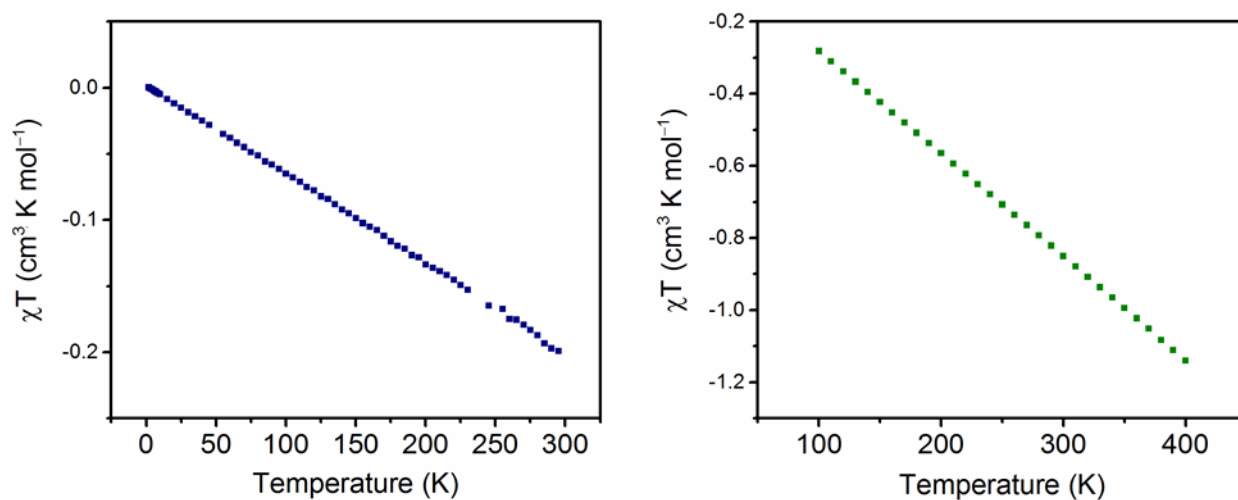
5.2.21 Experimental Spectra and Relevant Data Tables

FIGURE 5.73 χT vs. temperature plots of **3.2** in a polyethylene bag at a field of 0.1 T (left) and a separate sample of **3.2** in a sealed quartz tube at a field of 7 T (right). Both depict a downward-sloping, linear curve, indicative of a diamagnetic sample. The significantly larger diamagnetic moment exhibited by the quartz-tube sample (right) is attributable to the additional mass of the quartz and eicosane.

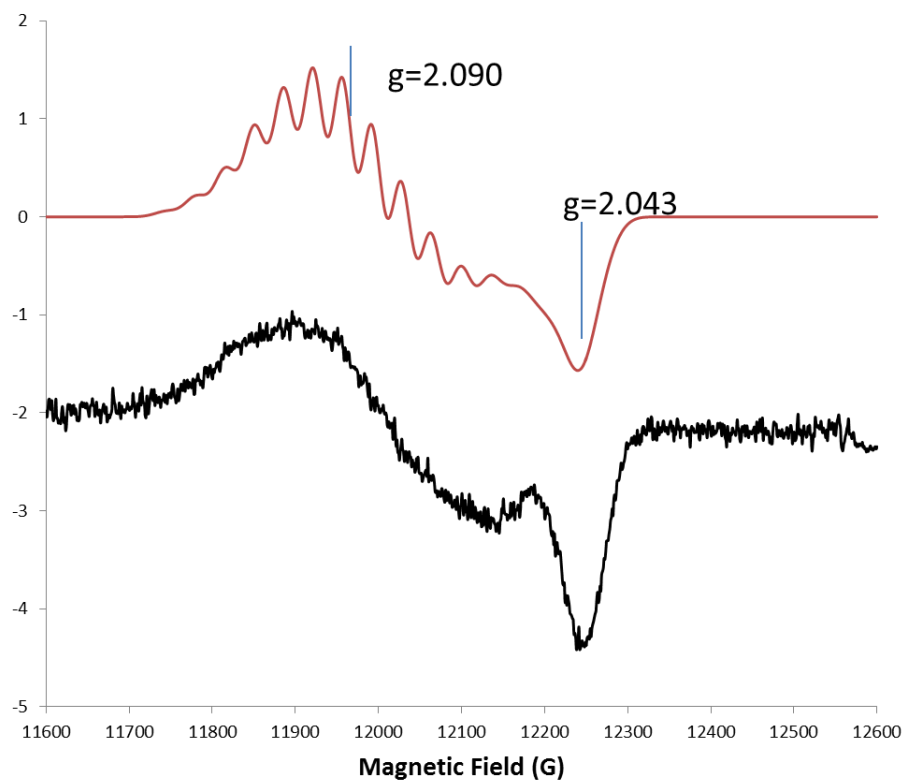


FIGURE 5.74 Q-band EPR spectrum for **3.3** (black scan): 34.99 GHz, -150 °C, 9 scans, power 22 dB, 10 G, mod.; time constant 0.1 sec; 2 min scans; Simulation (EasySpin, red scan): $g= 2.09, 2.043$; four Cu's (both isotopes), $A= 100, 15$ MHz; $lwpp=0.5$; $HStrain=100$ 90.

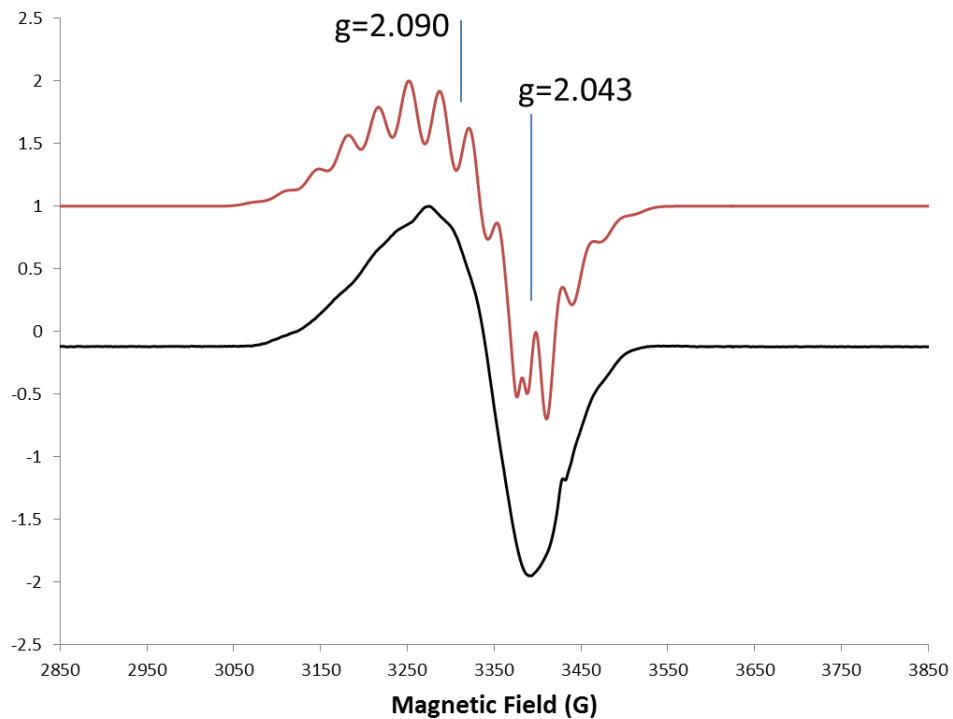


FIGURE 5.75 X-band EPR spectrum of **3.3** (black scan): 9.632 GHz, 9.9 K, 9 scans, power 46 dB; Simulation (red scan, EasySpin): $g = 2.09, 2.043$; both 63 and 65 isotopes, $A = 100, 15$ MHz, $lwpp=0.5$; Hstrain:100 20.

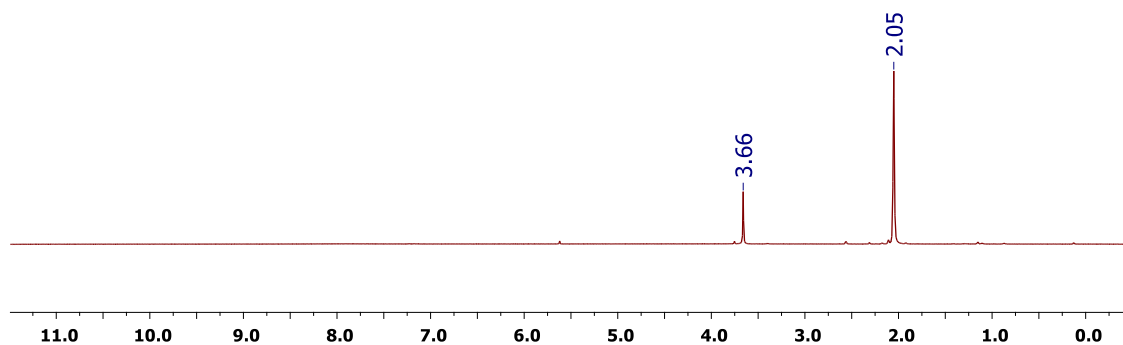


FIGURE 5.76 ^1H NMR (500 MHz) of **3.3** in $(\text{CD}_3)_2\text{CO}$.

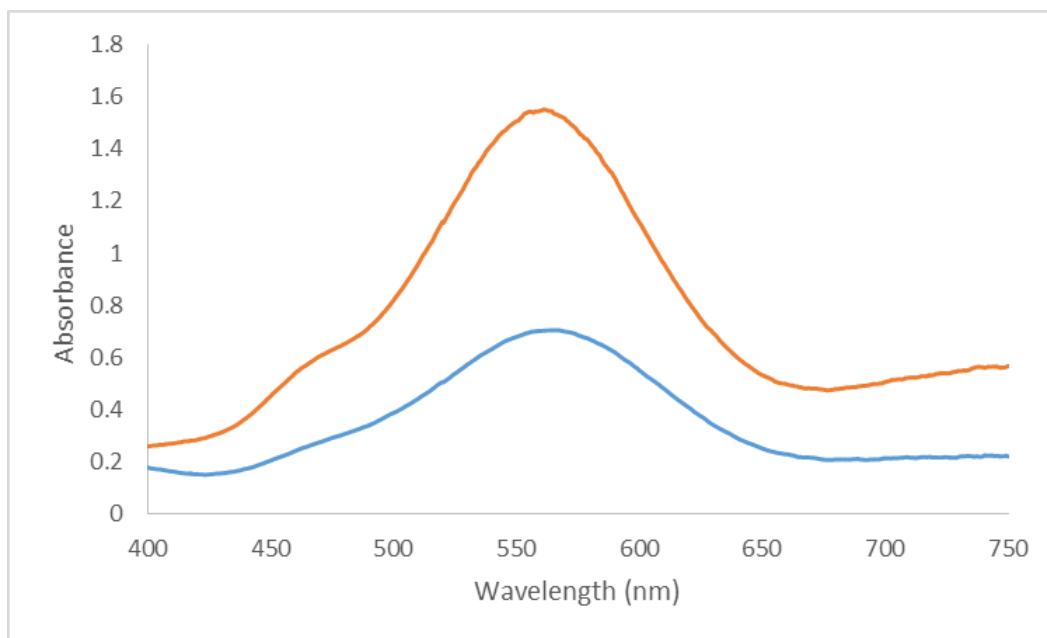


FIGURE 5.77 Absorption spectra for 0.082 mM **3.3** (blue trace; absorption maxima at 565.5 nm; $\epsilon = 8601 \text{ M}^{-1} \text{ cm}^{-1}$) and 0.085 mM **3.2** (orange trace; absorption maxima at 561 nm; $\epsilon = 18132 \text{ M}^{-1} \text{ cm}^{-1}$) in THF at room temperature.

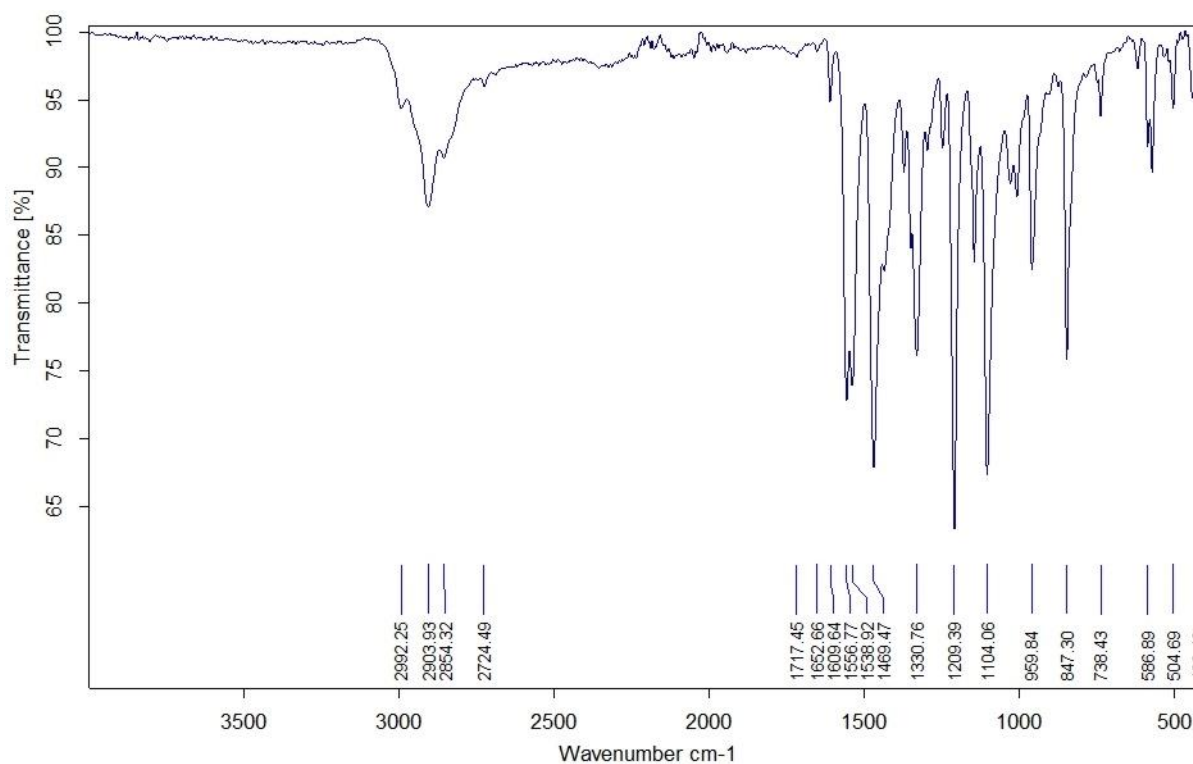


FIGURE 5.78 Infrared spectrum of **3.3**

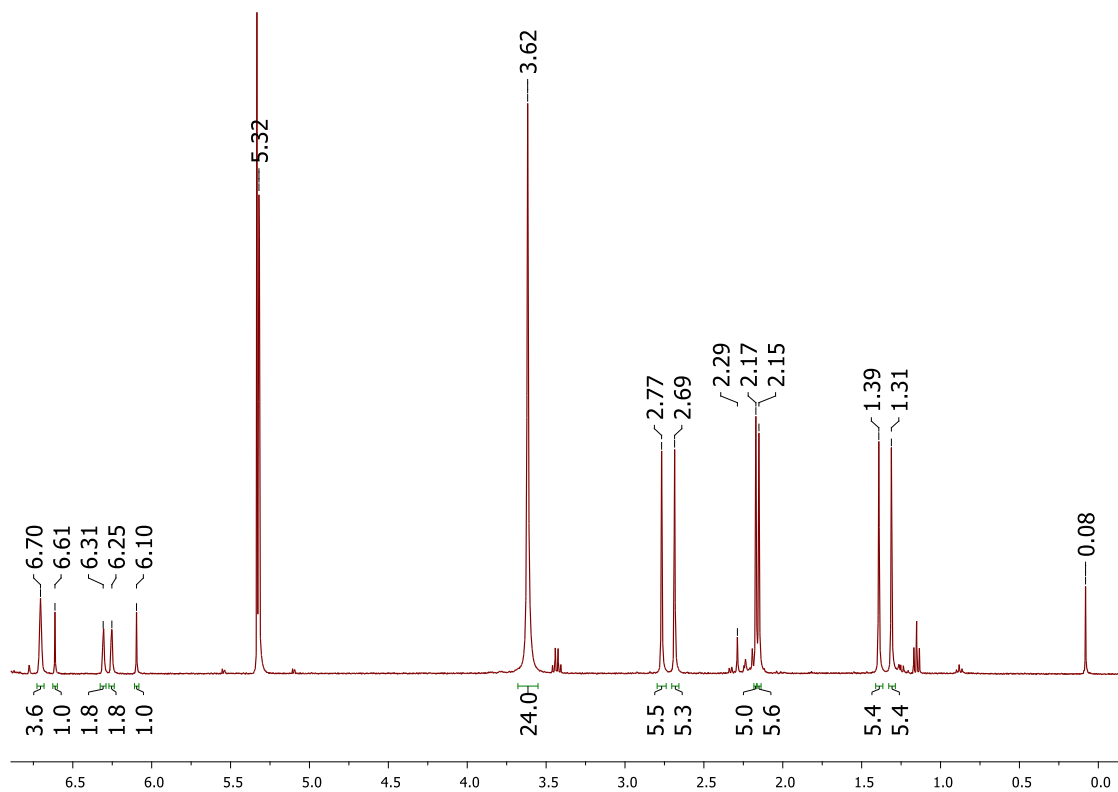


FIGURE 5.79 ^1H NMR (400 MHz, CD_2Cl_2) of reaction products from **3.3** and N_2O with appearance of **3.2** in 45% yield compared to integration of 18-crown-6 as the internal standard. Residual solvents in spectra are not peak picked. Peak appearing at 2.29 ppm is **3.1** from thermal decomposition.

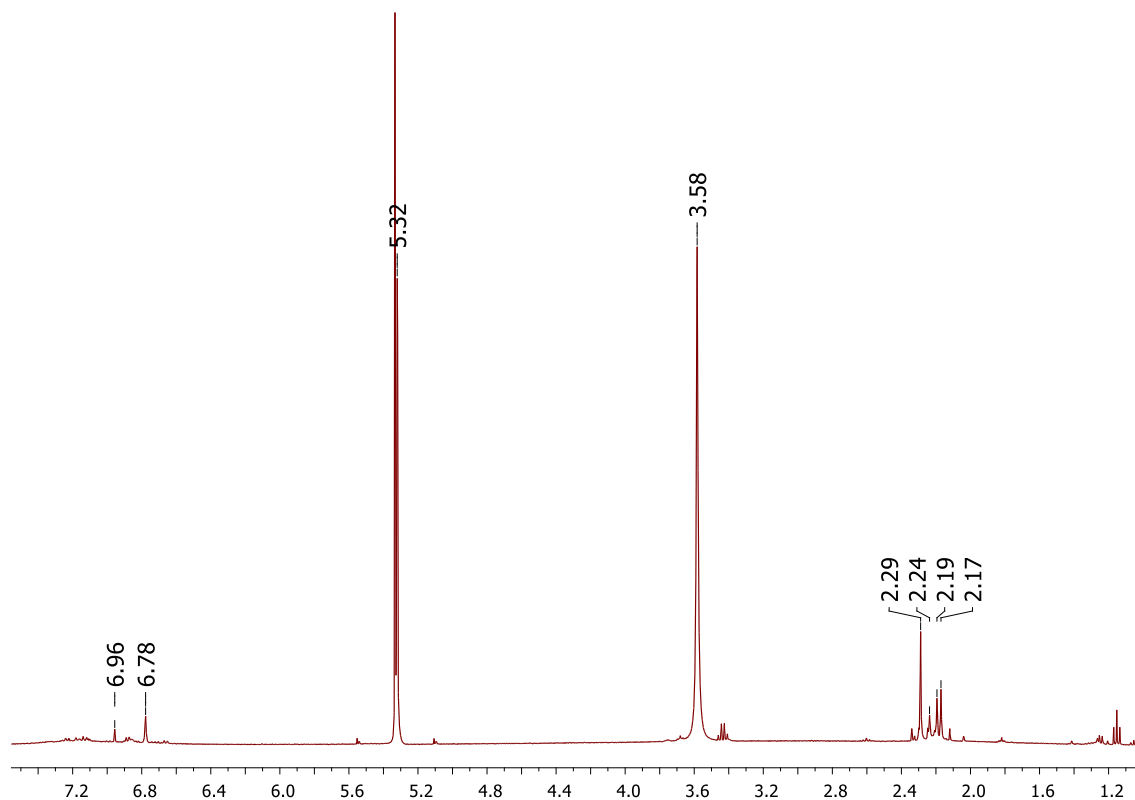


FIGURE 5.80 ^1H NMR (400 MHz, CD_2Cl_2) of control experiment between **3.3** and N_2 . Residual solvents in spectra are not peak picked. Peaks appearing at 2.17- 2.29 ppm and 6.78- 6.96 ppm are decomposition products (**3.1**) and free ligand (bis(2,4,6-trimethylphenyl)formamidine). No presence of **3.2** is evident.

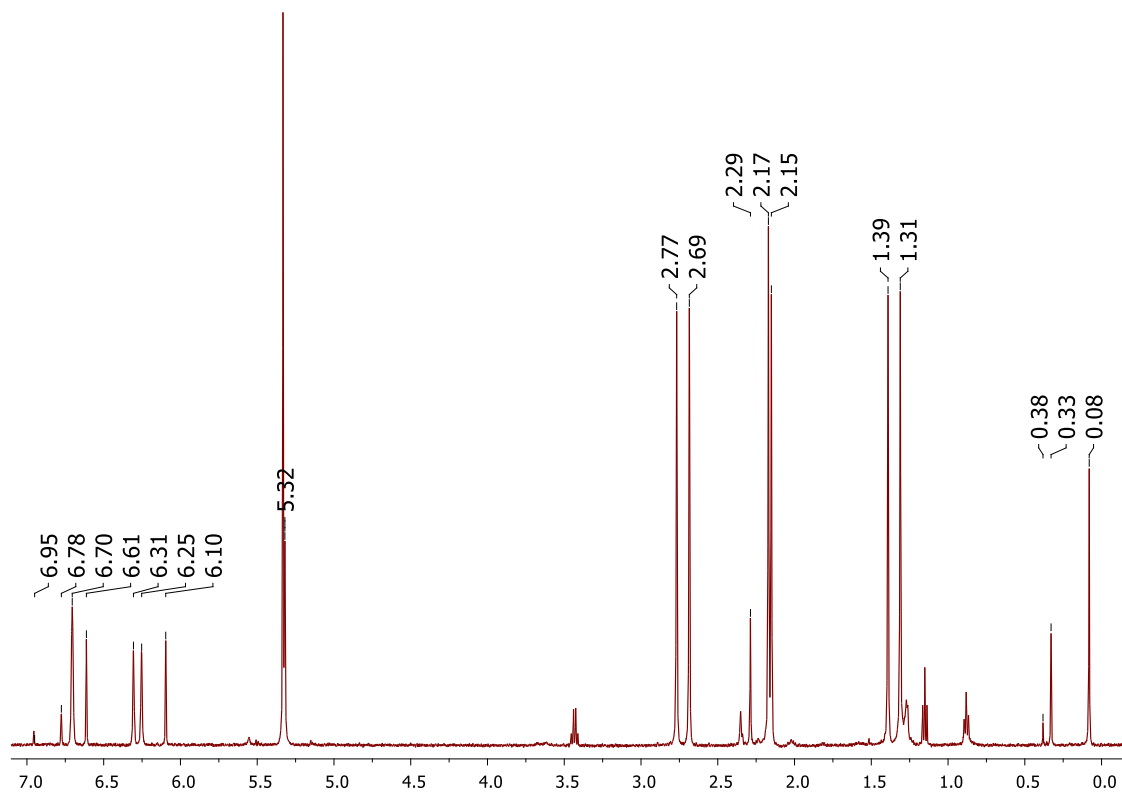


FIGURE 5.81 ^1H NMR (500 MHz, CD_2Cl_2) of **3.2** isolated after reaction between **3.3** and N_2O in CD_2Cl_2 (88% yield). Residual solvents in spectra are not peak picked. Peaks observed at 2.29, 6.78 and 6.95 ppm are the decomposition product, **3.1**.

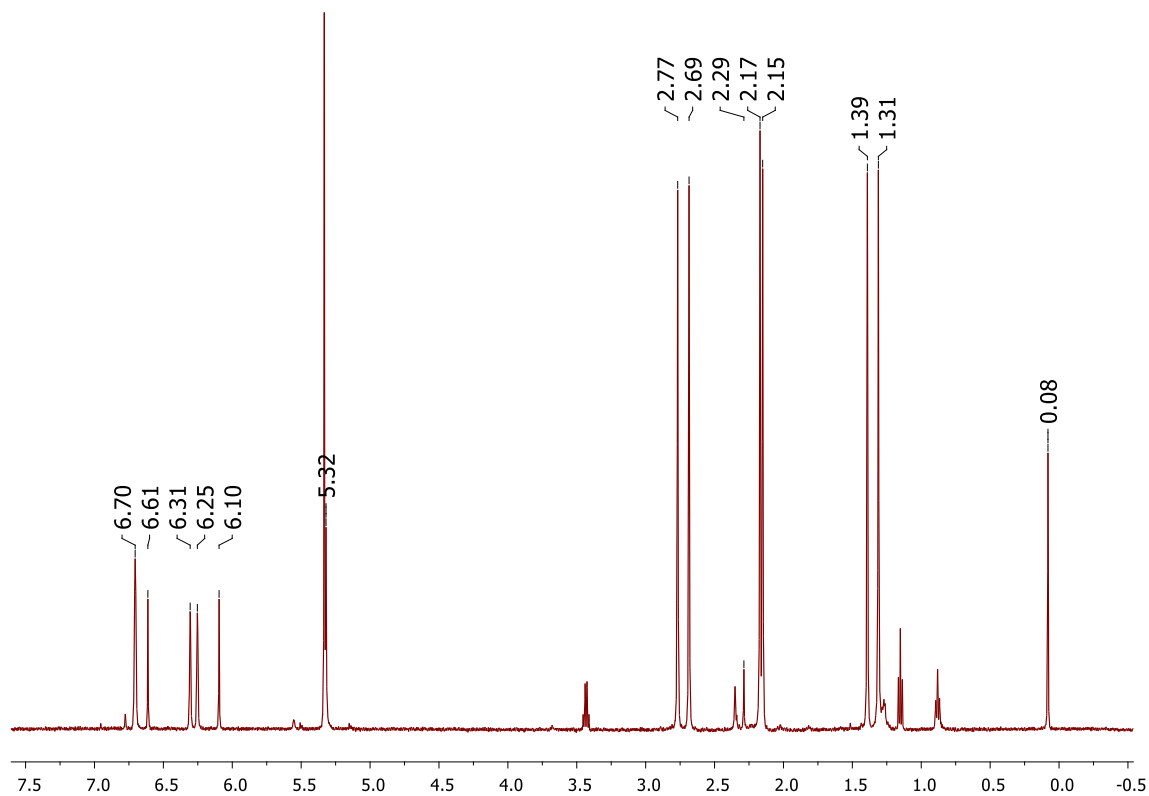


FIGURE 5.82 ^1H NMR (500 MHz, CD_2Cl_2) of **3.2** recovered after control experiment between **3.3** and N_2 (30% decomposition). Residual solvents in spectra are not peak picked. Peak observed at 2.29 ppm is the decomposition product, **3.1**.

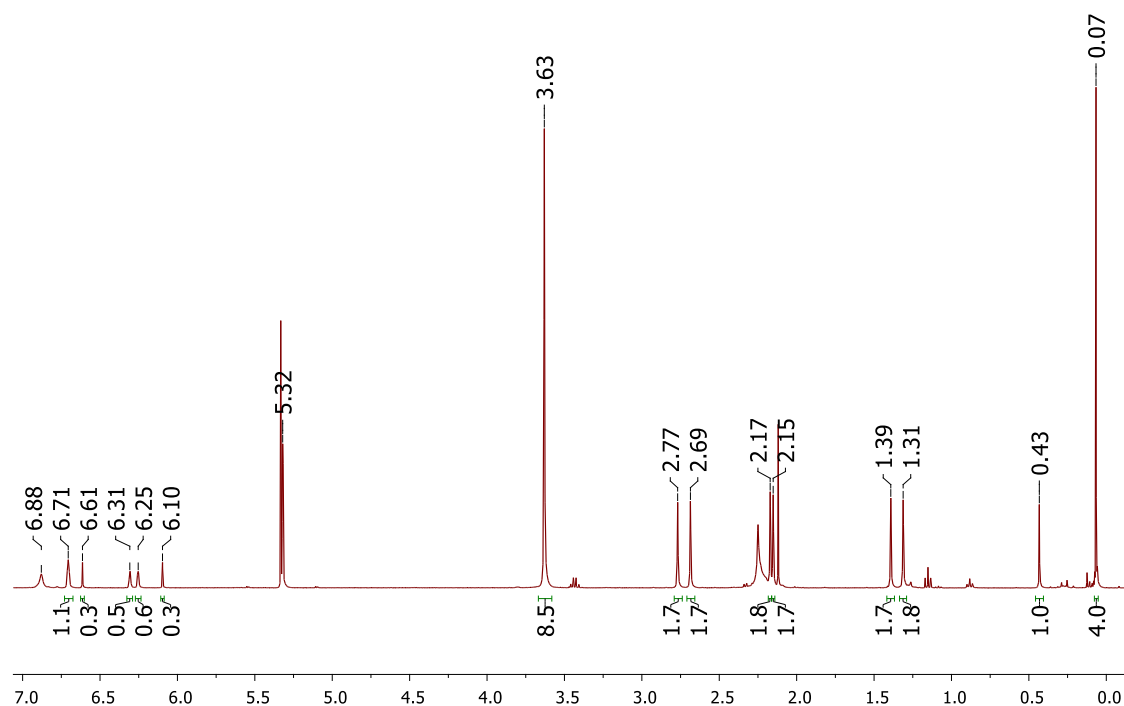


FIGURE 5.83 ^1H NMR (400 MHz, CD_2Cl_2) of reaction products from **3.3** and N_2O , using 5 equivalents of TMS-Cl as an oxygen trap. Hexamethyldisiloxane appearing at 0.07 ppm is the major product and some unreacted TMS-Cl appears at 0.43 ppm. Residual solvents in spectra are not peak picked.

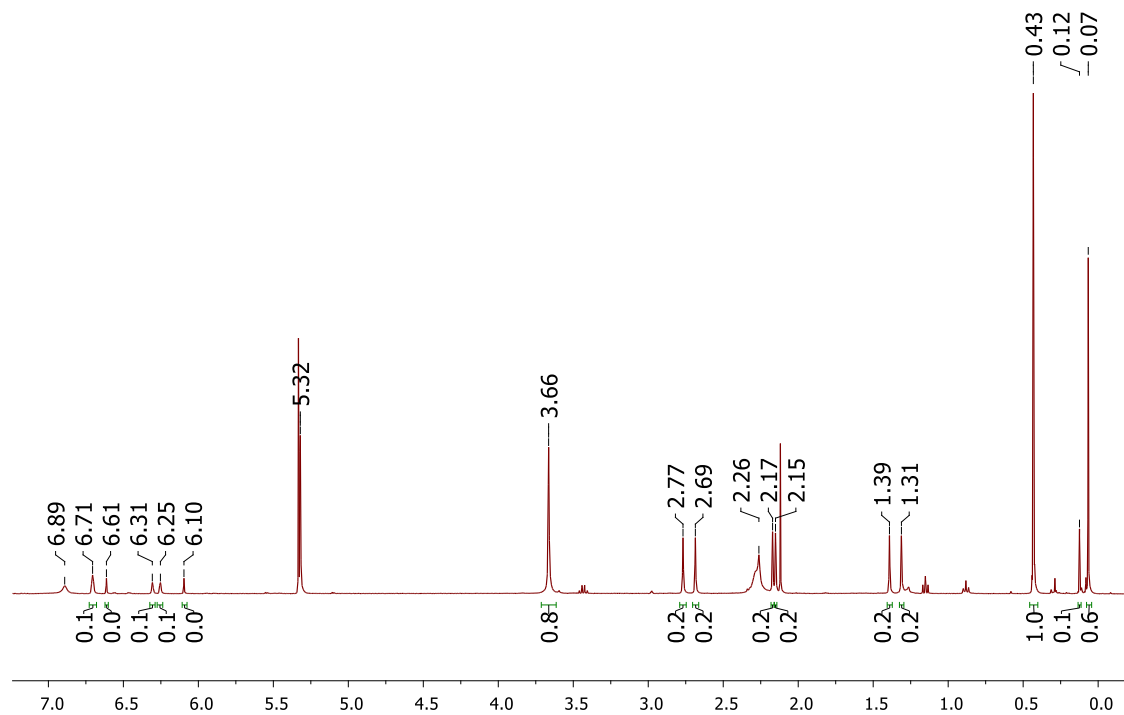


FIGURE 5.84 ^1H NMR (400 MHz, CD_2Cl_2) of resulting control experiment between **3.3** and N_2 and 5 equivalents of TMS-Cl. Residual solvents in spectra are not peak picked.

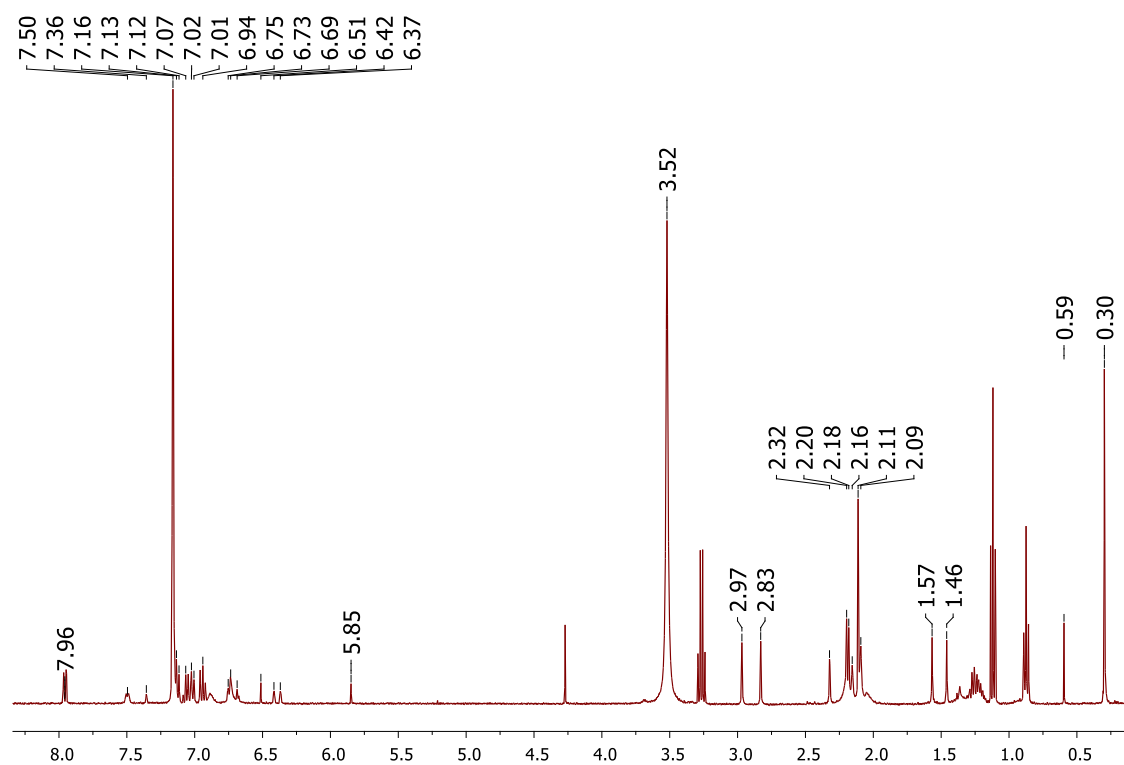


FIGURE 5.85 ^1H NMR (400 MHz, C_6D_6) of reaction products from **3.3** and N_2O , using benzoyl chloride as an oxygen trap to form benzoic anhydride. Residual solvents in spectra are not peak picked.

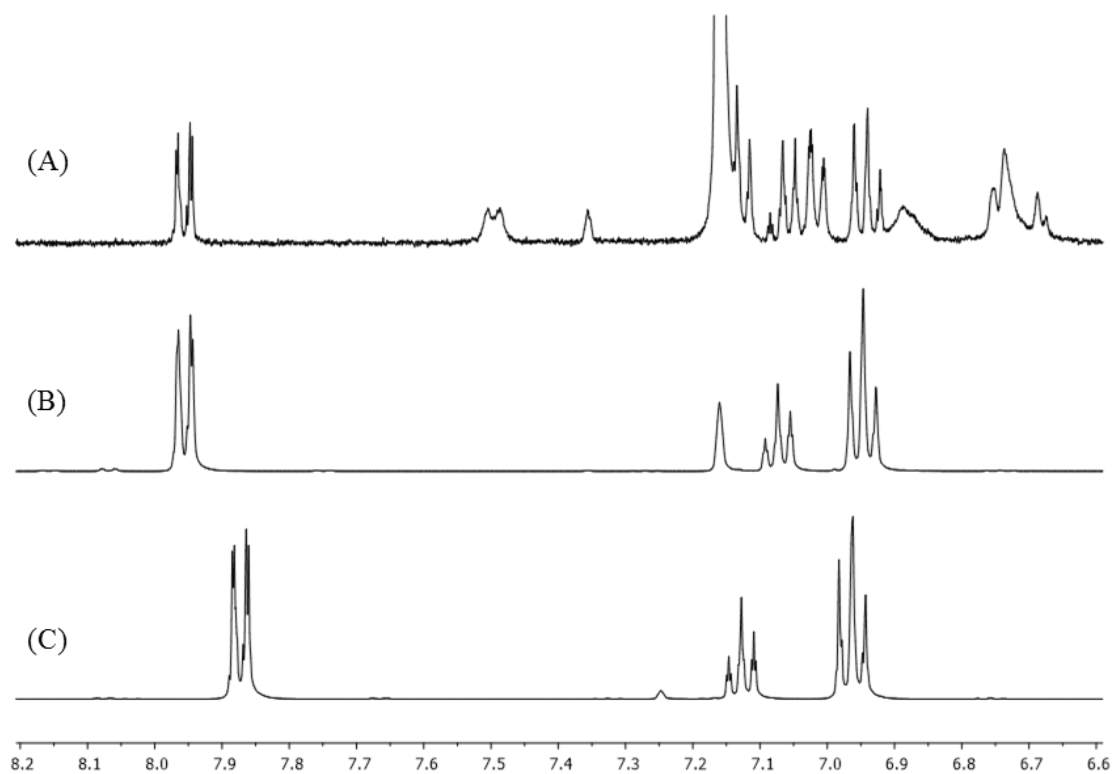


FIGURE 5.86 Comparison of ^1H NMR (400 MHz, C_6D_6) of (A) reaction products from **3.3** and N_2O using benzoyl chloride as an oxygen trap to form benzoic anhydride; (B) authentic sample of benzoic anhydride and (C) authentic sample of benzoyl chloride.

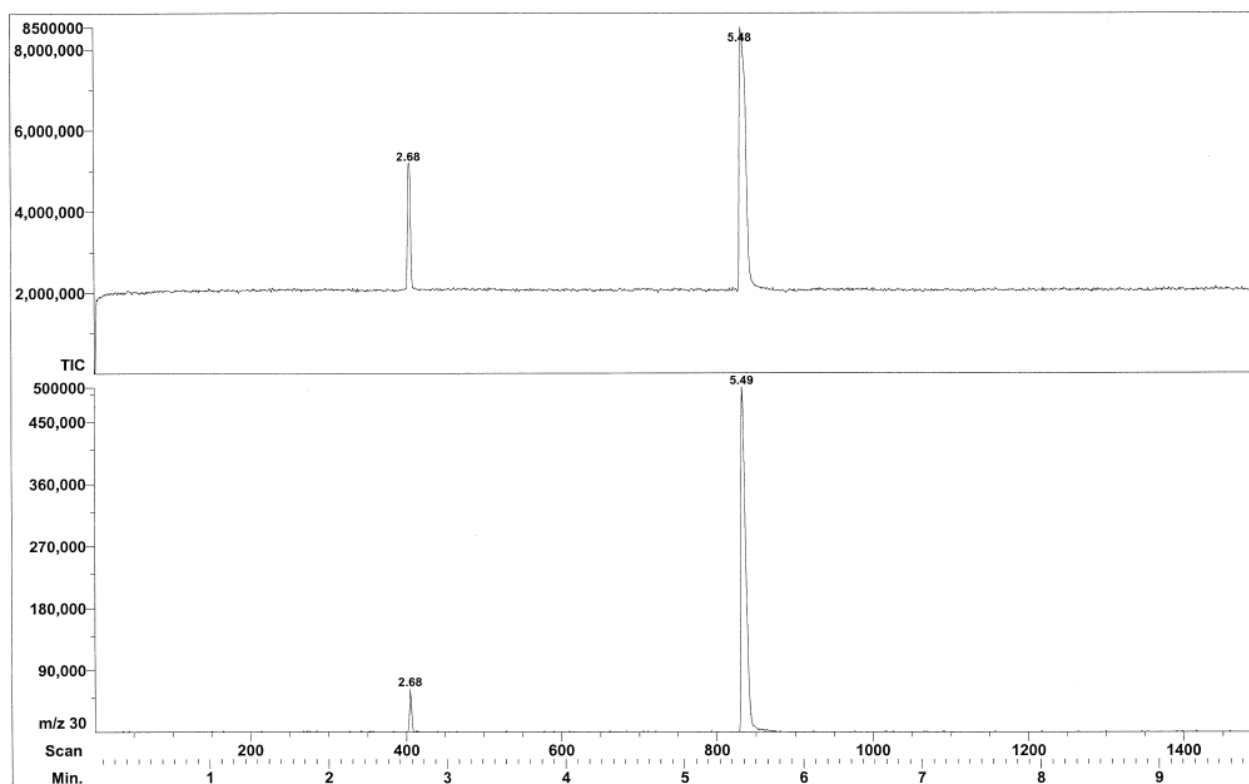


FIGURE 5.87 Total chromatogram (top) and extracted ion chromatogram for m/z 30 (bottom) from the reaction headspace after 48 hours of $^{15}\text{N}_2\text{O}$ and 3.3.

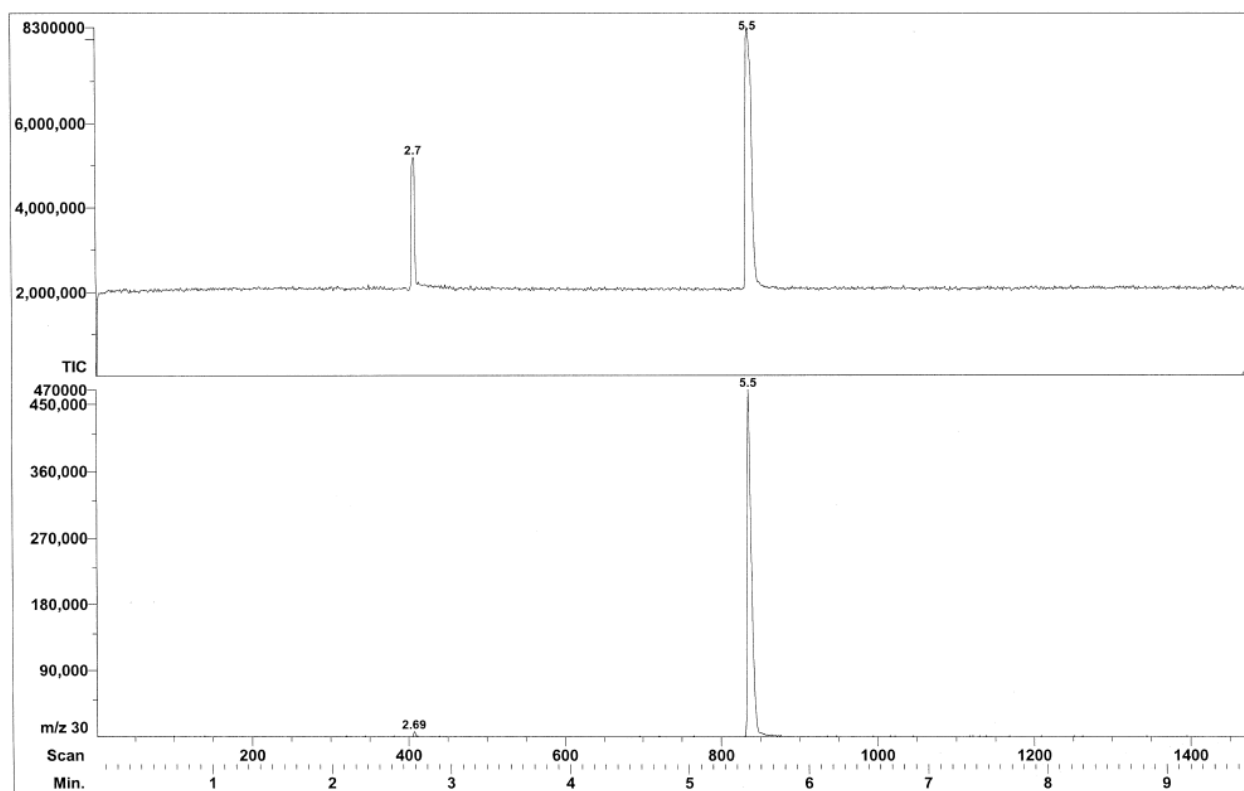


FIGURE 5.88 Total chromatogram (top) and extracted ion chromatogram for m/z 30 (bottom) from blank flask containing $^{15}\text{N}_2\text{O}$ for 48 hours.

Scan: 405 R.T.: 2.68
 Base: m/z 28; 100%FS #Ions: 28 TIC: 5173296 (Max Inten : 4193876)

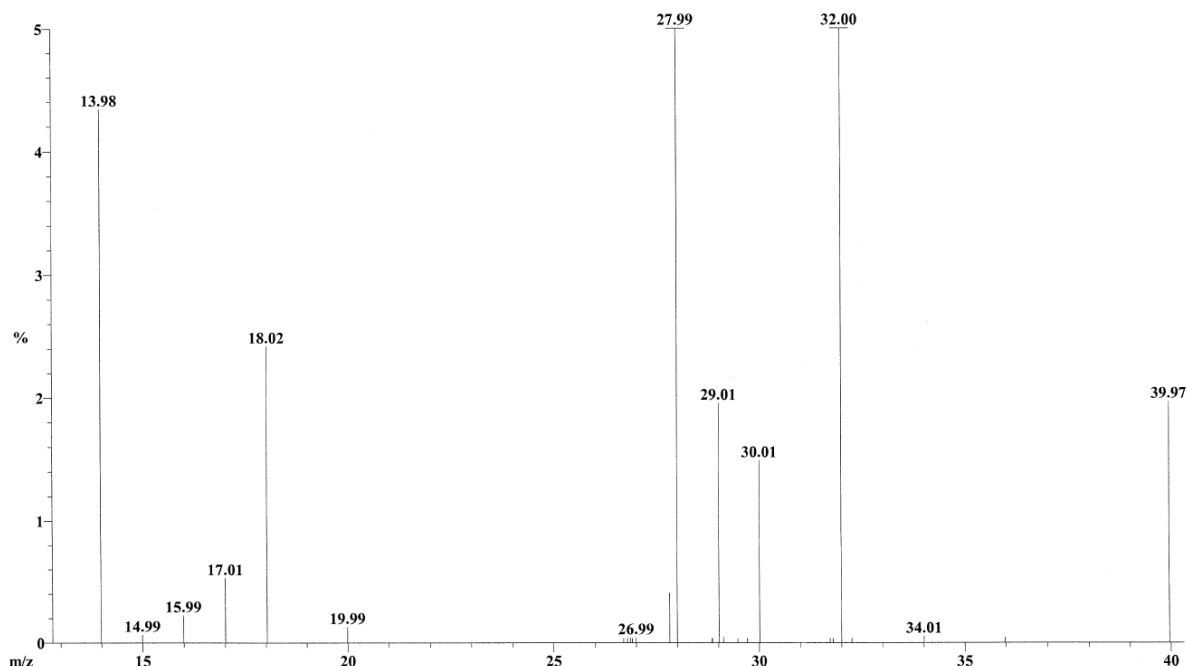


FIGURE 5.89 Mass spectrum of species at 2.68 minutes from the reaction headspace of $^{15}\text{N}_2\text{O}$ and 3.3 after 48 hours.

TABLE 5.14 Percent Composition of Species in Figure 5.89.

Scan: 405 R.T.: 2.68
 Base: m/z 28; 100%FS#Ions: 28 TIC: 5173296 (Max Inten : 4193876)

Threshold: .1% of Base

Displayed TIC: 5173296

Mass	%Base	%TIC	Intensity	Mass	%Base	%TIC	Intensity	Mass	%Base	%TIC	Intensity
13.9815	4.3	3.519	182,036	19.9908	.1	0.106	5,460	30.0124	1.5	1.209	62,548
15.9851	.2	0.182	9,428	27.8101	.4	0.328	16,980	31.9988	9.1	7.405	383,060
17.0069	.5	0.428	22,164	27.9929	100.0	81.068	4,193,876	39.9675	2.0	1.596	82,580
18.0212	2.4	1.961	101,460	29.0135	2.0	1.586	82,068				

Scan: 405 R.T.: 2.68
 Base: m/z 28; 58.7%FS #Ions: 18 TIC: 3112296 (Max Inten : 2461140)

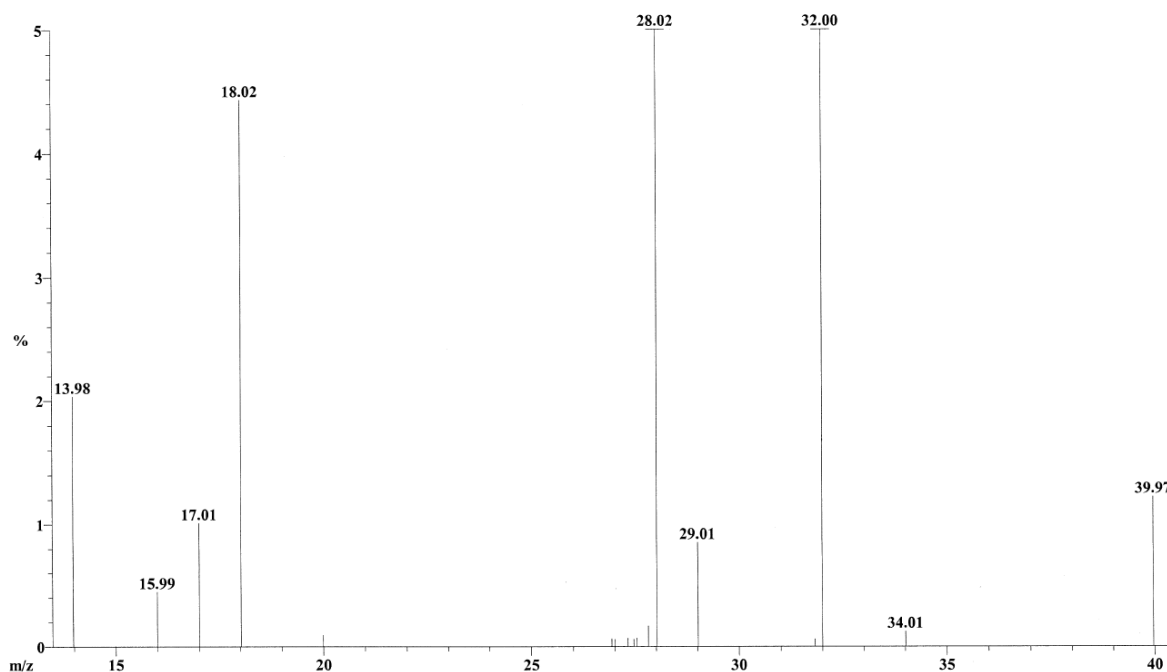


FIGURE 5.90 Mass spectrum of species at 2.68 minutes from blank flask containing $^{15}\text{N}_2\text{O}$ after 48 hours.

TABLE 5.15 Percent Composition of Species in Figure 5.90

Scan: 406 R.T.: 2.68
 Base: m/z 28; 100%FS#Ions: 26 TIC: 4968712 (Max Inten : 4193876)

Threshold: .1% of Base

Displayed TIC: 49687

Mass	%Base	%TIC	Intensity	Mass	%Base	%TIC	Intensity	Mass	%Base	%TIC	Intensity
13.9815	2.9	2.468	122,644	18.0212	2.5	2.132	105,940	29.0135	1.1	0.965	47,956
15.9924	.2	0.195	9,684	27.8293	.2	0.196	9,748	31.9988	9.2	7.794	387,284
17.0069	.5	0.432	21,460	28.0121	100.0	84.406	4,193,876	39.9790	.8	0.715	35,540

Scan: 406 R.T.: 2.68
Base: m/z 28; 100%FS #Ions: 24 TIC: 5072672 (Max Inten : 4193876)

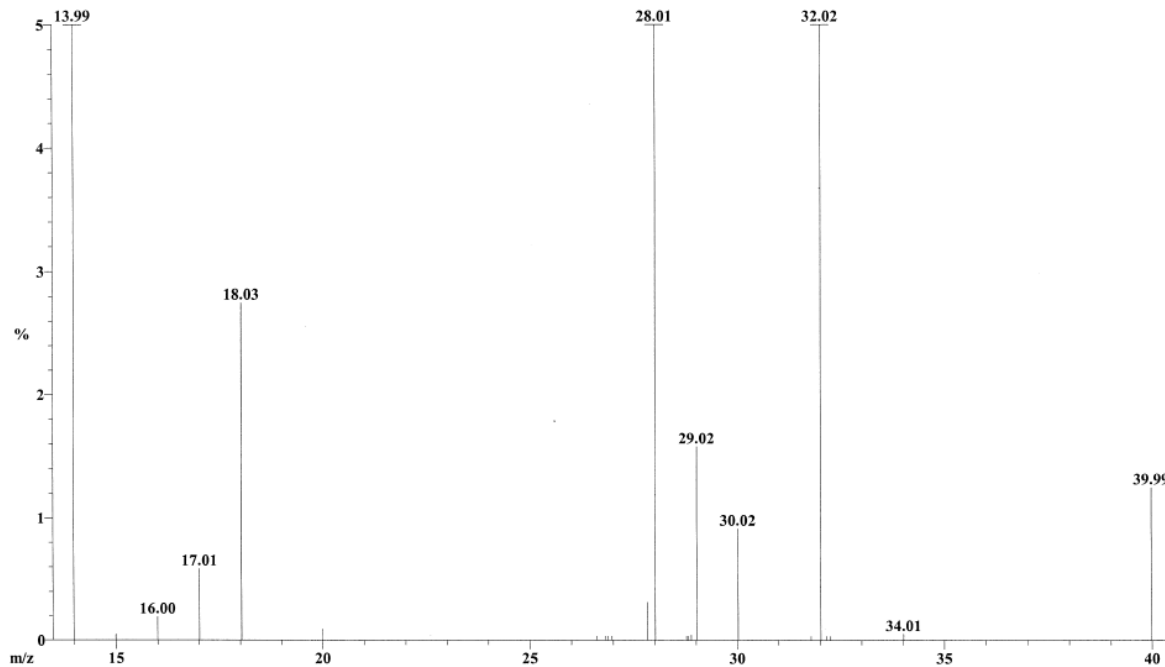


FIGURE 5.91 Mass spectrum of species at 2.68 minutes from the reaction headspace of $^{15}\text{N}_2\text{O}$ and **3.3** after 6 hours.

TABLE 5.16 Percent Composition of Species in Figure 5.91

Scan: 406 R.T.: 2.68
Base: m/z 28; 100%FS#Ions: 24 TIC: 5072672 (Max Inten : 4193876)

Threshold: .1% of Base

Displayed TIC: 50726

Mass	%Base	%TIC	Intensity	Mass	%Base	%TIC	Intensity	Mass	%Base	%TIC	Intensity
13.9855	5.1	4.175	211,796	27.8257	.3	0.259	13,140	32.0156	7.7	6.338	321,492
15.9969	.2	0.158	8,020	28.0085	100.0	82.676	4,193,876	39.9904	1.3	1.034	52,436
17.0115	.6	0.484	24,532	29.0195	1.6	1.304	66,132				
18.0261	2.7	2.273	115,284	30.0185	.9	0.756	38,356				

Scan: 408 R.T.: 2.69
 Base: m/z 28; 93.2%FS #Ions: 21 TIC: 4576356 (Max Inten : 3907156)

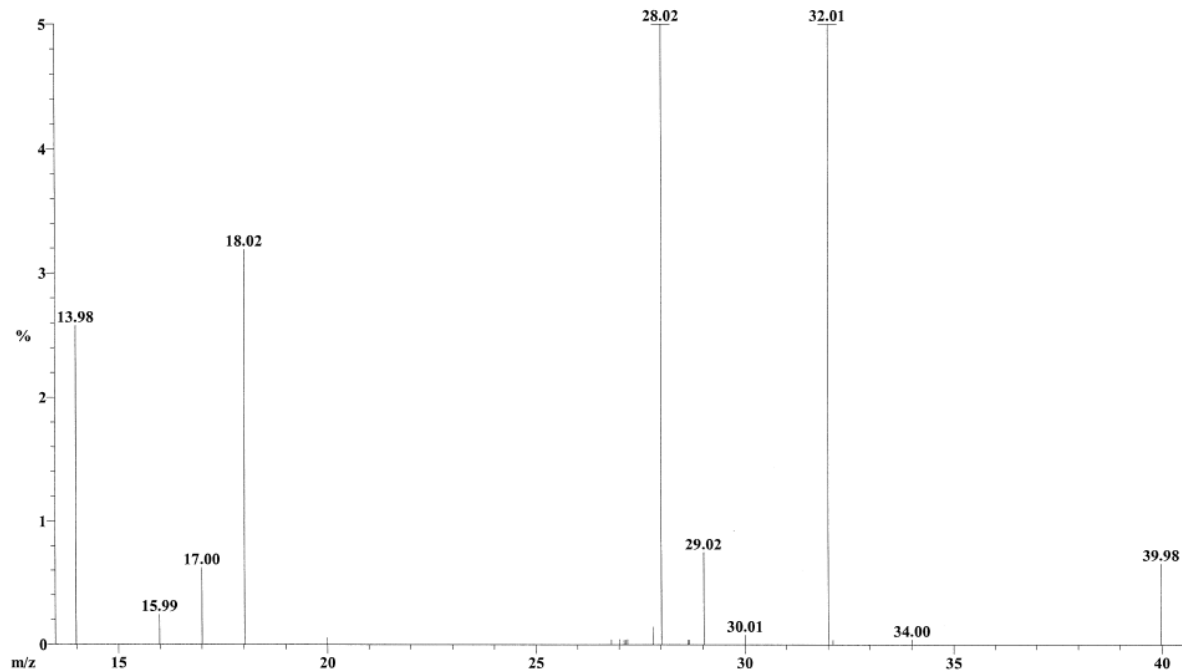


Figure 5.92 Mass spectrum of species at 2.69 minutes from blank flask containing $^{15}\text{N}_2\text{O}$.

TABLE 5.17 Percent Composition of Species in Figure 5.92

Scan: 408 R.T.: 2.69
 Base: m/z 28; 93.2%FS#Ions: 21 TIC: 4576356 (Max Inten : 3907156)

Threshold: .1% of Base

Displayed TIC: 457635

Mass	%Base	%TIC	Intensity	Mass	%Base	%TIC	Intensity	Mass	%Base	%TIC	Intensity
13.9786	2.6	2.200	100,692	18.0183	3.2	2.722	124,564	29.0195	.7	0.638	29,204
15.9895	.2	0.206	9,428	27.8257	.1	0.125	5,716	32.0052	8.4	7.137	326,612
17.0040	.6	0.530	24,276	28.0181	100.0	85.377	3,907,156	39.9789	.7	0.561	25,684

Scan: 832 R.T.: 5.48
 Base: m/z 46; 100%FS #Ions: 40 TIC: 8115232 (Max Inten : 4193876)

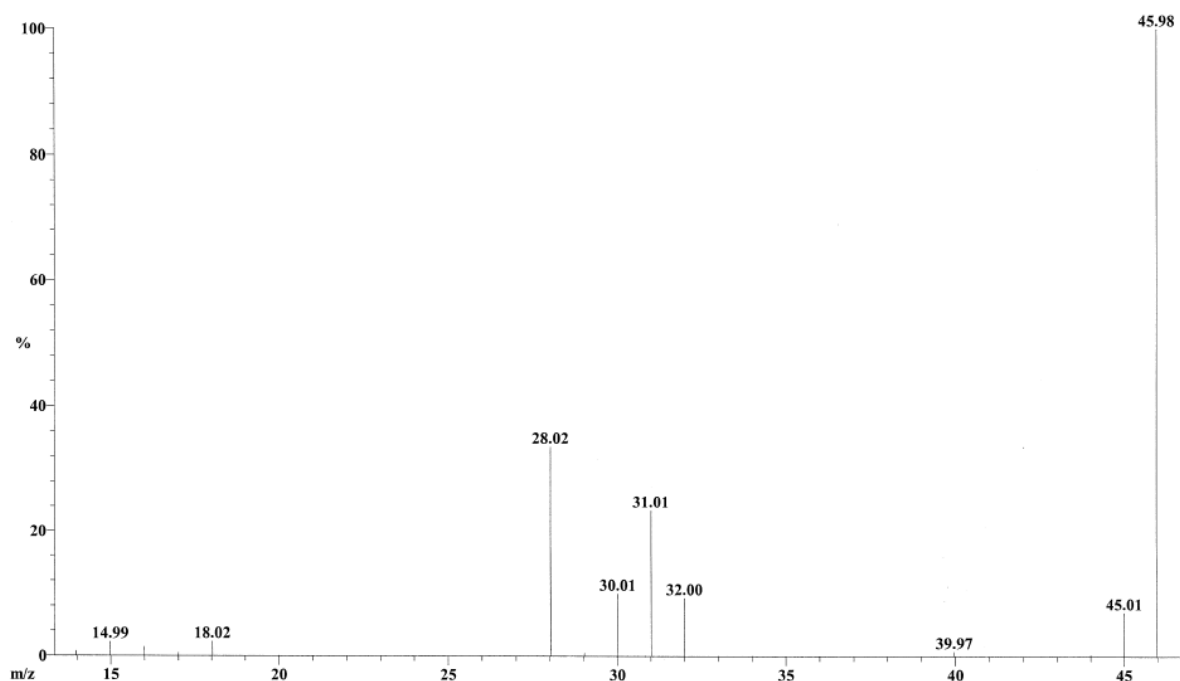


FIGURE 5.93 Mass spectrum of species at 5.48 minutes from the chromatogram of the reaction headspace of $^{15}\text{N}_2\text{O}$ and **3.3** in Figure 5.87.

TABLE 5.18 Summary Integration Values of $^{15}\text{N}_2$ From Reaction Headspace Experiments with $^{15}\text{N}_2\text{O}$ and **3.3**, After 6 and 48 Hours Compared to the $^{15}\text{N}_2\text{O}$ Blank. Integration values were obtained from the extracted ion chromatogram for m/z 30 for the peak with the retention time of 2.68 minutes (bottom of Figure 5.87 and Figure 5.88)

Rxn Time	Reaction $^{15}\text{N}_2$ Peak Integration	Blank $^{15}\text{N}_2$ Peak Integration
48 Hours	181,583	21,394
6 Hours	109,835	22,868

TABLE 5.19 Comparison of Calculated and Experimental Bond Distances (Å).

	3.2' (calculated)	3.2 (experimental)	3.3' (calculated)	3.3 (experimental)
Cu1-Cu2	2.469	2.4226(6)	2.584	2.502(1), 2.486(1)
Cu2-Cu3	2.928	3.0353(6)	2.827	2.809(1), 2.854(1)
Cu3-Cu4	2.469	2.4226(6)	2.584	2.532(1), 2.500(1)
Cu1-Cu4	2.928	3.0353(6)	2.827	2.831(1), 2.844(1)
Average Cu-S	2.261	2.180	2.302	2.217

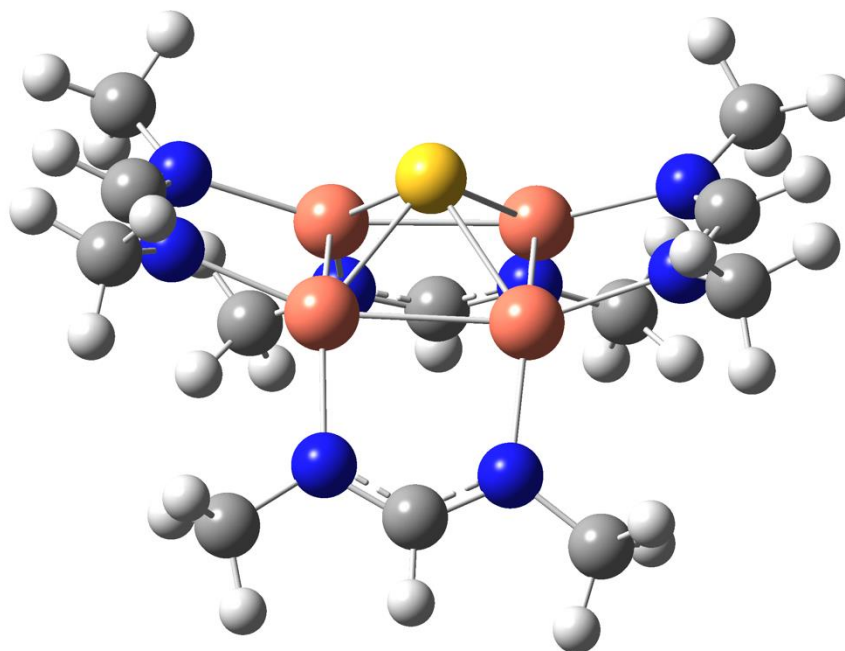


FIGURE 5.94 Optimized structure of **3.3'**.

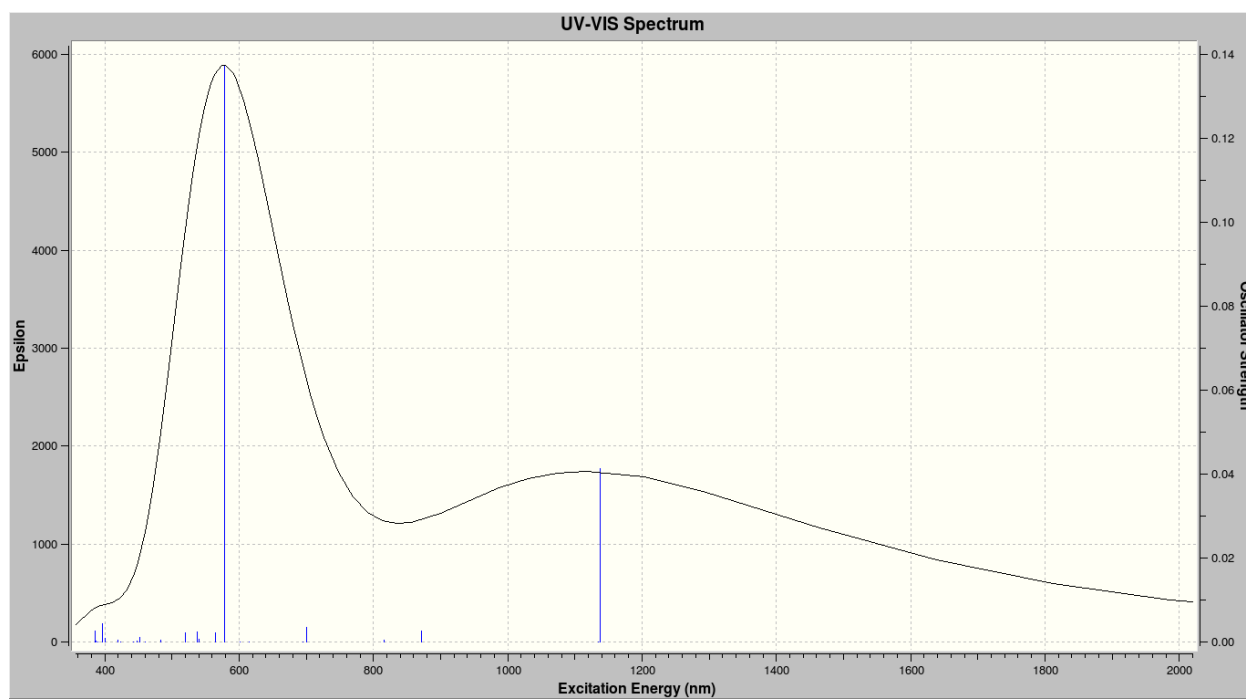


FIGURE 5.95 Calculated UV-Vis spectrum of **3.3'**.

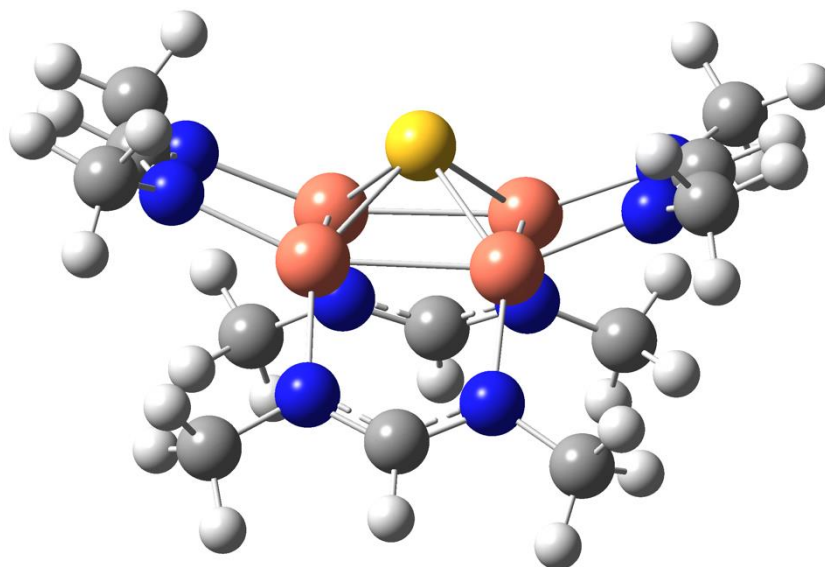


FIGURE 5.96 Optimized structure of 3.2'.

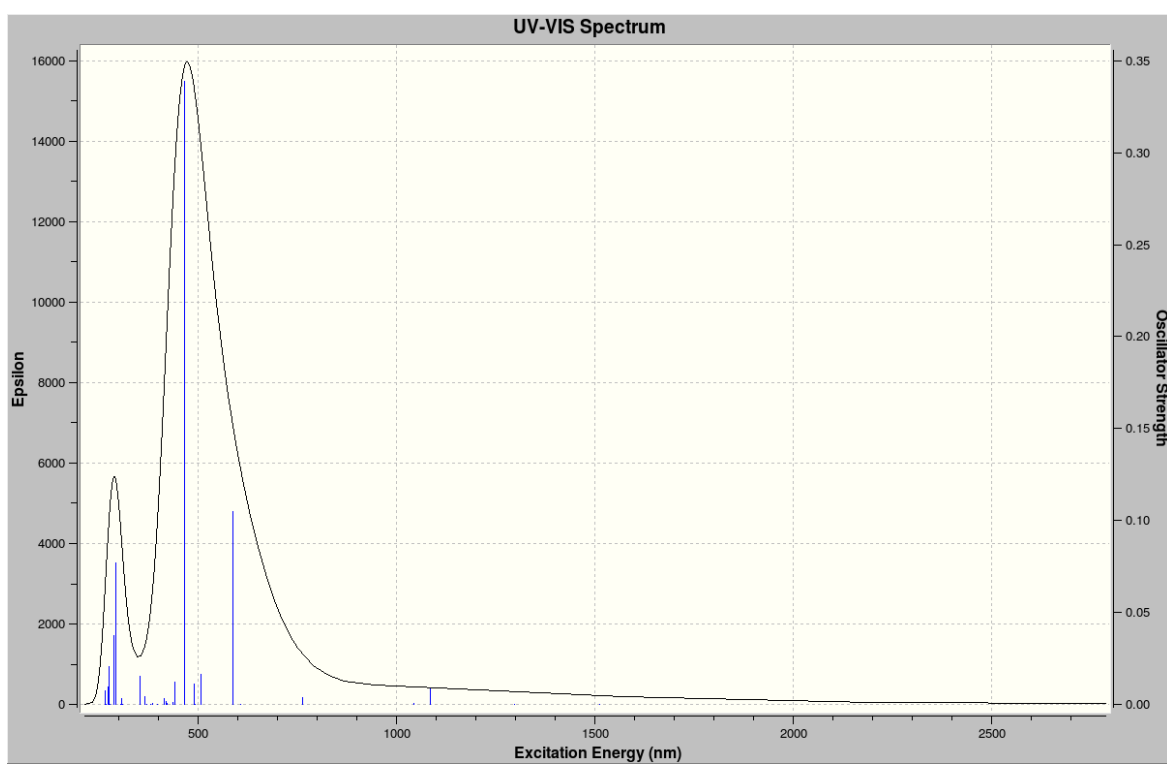


FIGURE 5.97 Calculated UV-Vis spectrum of 3.2'.

TABLE 5.20 Optimized Coordinates of **3.3'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	29	0	1.386449	-1.349982	-0.224024
2	16	0	0.000002	-0.000076	-1.474806
3	7	0	3.281351	-0.976101	-0.923119
4	7	0	3.126323	1.380414	-0.861635
5	6	0	3.733485	0.243940	-1.159060
6	1	0	4.723098	0.321561	-1.645214
7	29	0	-1.386447	1.349952	-0.224154
8	7	0	-3.281346	0.976012	-0.923222
9	7	0	-3.126316	-1.380499	-0.861544
10	6	0	-3.733473	-0.244049	-1.159074
11	1	0	-4.723075	-0.321712	-1.645242
12	29	0	-1.194111	-1.470350	-0.169276
13	7	0	-0.983854	-2.734209	1.363758
14	7	0	1.364907	-2.687537	1.258960
15	6	0	0.218929	-3.082077	1.789964
16	1	0	0.271111	-3.754926	2.662529
17	29	0	1.194104	1.470329	-0.169420
18	7	0	0.983846	2.734363	1.363467
19	7	0	-1.364915	2.687653	1.258698
20	6	0	-0.218937	3.082258	1.789654
21	1	0	-0.271117	3.755185	2.662158
22	6	0	-4.104976	2.086128	-1.378376
23	1	0	-4.335943	2.772439	-0.551923
24	1	0	-3.588327	2.676106	-2.150727
25	1	0	-5.062706	1.748165	-1.807901
26	6	0	-3.808144	-2.611006	-1.234625
27	1	0	-4.788424	-2.420762	-1.702280
28	1	0	-3.210188	-3.195840	-1.949527
29	1	0	-3.978270	-3.252732	-0.358617
30	6	0	-2.127197	-3.266063	2.093188
31	1	0	-2.789334	-2.456198	2.427473
32	1	0	-2.728135	-3.934564	1.460693
33	1	0	-1.820489	-3.837150	2.983909
34	6	0	2.587763	-3.192080	1.869003
35	1	0	3.264894	-2.367038	2.125869
36	1	0	2.386510	-3.760642	2.791011
37	1	0	3.133163	-3.856012	1.182523
38	6	0	4.104985	-2.086257	-1.378171
39	1	0	5.062724	-1.748332	-1.807706
40	1	0	4.335933	-2.772504	-0.551660
41	1	0	3.588346	-2.676293	-2.150485
42	6	0	3.808163	2.610891	-1.234795
43	1	0	3.978266	3.252684	-0.358834
44	1	0	4.788454	2.420608	-1.702409
45	1	0	3.210227	3.195670	-1.949759
46	6	0	2.127192	3.266324	2.092813

47	1	0	2.789424	2.456516	2.427042
48	1	0	2.728025	3.934883	1.460277
49	1	0	1.820497	3.837380	2.983559
50	6	0	-2.587772	3.192221	1.868715
51	1	0	-2.386519	3.760866	2.790672
52	1	0	-3.133196	3.856082	1.182186
53	1	0	-3.264882	2.367186	2.125659

TABLE 5.21 Optimized Coordinates of **3.2'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	29	0	1.309161	-1.408896	-0.176093
2	16	0	0.000030	-0.000018	-1.366232
3	7	0	3.123631	-1.031322	-0.923548
4	7	0	3.004493	1.333672	-0.894061
5	6	0	3.590064	0.180910	-1.162130
6	1	0	4.583731	0.236714	-1.629581
7	29	0	-1.309162	1.408912	-0.176201
8	7	0	-3.123593	1.031285	-0.923732
9	7	0	-3.004442	-1.333708	-0.894173
10	6	0	-3.590005	-0.180955	-1.162305
11	1	0	-4.583648	-0.236781	-1.629805
12	29	0	-1.157468	-1.514723	-0.152193
13	7	0	-1.027289	-2.830246	1.301666
14	7	0	1.317693	-2.747879	1.262167
15	6	0	0.167111	-3.191147	1.742215
16	1	0	0.206278	-3.905971	2.577536
17	29	0	1.157482	1.514715	-0.152169
18	7	0	1.027225	2.830266	1.301657
19	7	0	-1.317758	2.747935	1.262025
20	6	0	-0.167196	3.191189	1.742132
21	1	0	-0.206399	3.906025	2.577442
22	6	0	-3.927349	2.169324	-1.361351
23	1	0	-4.165283	2.829723	-0.518974
24	1	0	-3.385261	2.766474	-2.107040
25	1	0	-4.875848	1.848734	-1.815429
26	6	0	-3.693299	-2.557939	-1.292745
27	1	0	-4.671398	-2.346570	-1.747857
28	1	0	-3.098340	-3.120147	-2.025142
29	1	0	-3.859048	-3.212817	-0.429241
30	6	0	-2.193353	-3.416698	1.953617
31	1	0	-2.919871	-2.638329	2.215184
32	1	0	-2.700891	-4.136000	1.296463
33	1	0	-1.917232	-3.945138	2.877449
34	6	0	2.543713	-3.261118	1.863637

35	1	0	3.231249	-2.439063	2.094298
36	1	0	2.339983	-3.804238	2.797769
37	1	0	3.065933	-3.948915	1.184318
38	6	0	3.927278	-2.169374	-1.361332
39	1	0	4.875974	-1.848822	-1.815025
40	1	0	4.164834	-2.830094	-0.519102
41	1	0	3.385291	-2.766176	-2.107378
42	6	0	3.693513	2.557897	-1.292372
43	1	0	3.859656	3.212442	-0.428686
44	1	0	4.671436	2.346476	-1.747840
45	1	0	3.098468	3.120487	-2.024398
46	6	0	2.193256	3.416734	1.953655
47	1	0	1.917091	3.945163	2.877480
48	1	0	2.919775	2.638376	2.215245
49	1	0	2.700804	4.136048	1.296524
50	6	0	-2.543802	3.261181	1.863439
51	1	0	-2.340102	3.804360	2.797543
52	1	0	-3.066019	3.948928	1.184067
53	1	0	-3.231328	2.439128	2.094135

TABLE 5.22 Excitation Energies and Oscillator Strengths Calculated for **3.3'**

Excited State 1: 2.012-A 1.0901 eV 1137.34 nm $f=0.0412$ $\langle S^{**2} \rangle = 0.762$
124B ->125B 0.98494

Excited State 2: 2.014-A 1.0920 eV 1135.44 nm $f=0.0000$ $\langle S^{**2} \rangle = 0.764$
116B ->125B -0.27982
123B ->125B 0.95099

Excited State 3: 2.014-A 1.4216 eV 872.17 nm $f=0.0026$ $\langle S^{**2} \rangle = 0.764$
106B ->125B -0.17953
115B ->125B -0.14311
119B ->125B -0.14966
122B ->125B 0.95136

Excited State 4: 2.016-A 1.5197 eV 815.85 nm $f=0.0004$ $\langle S^{**2} \rangle = 0.766$
117B ->125B -0.28839
119B ->125B 0.93398
122B ->125B 0.14766

Excited State 5: 2.014-A 1.7681 eV 701.21 nm $f=0.0035$ $\langle S^{**2} \rangle = 0.764$
106B ->125B -0.12989
108B ->125B -0.21992
121B ->125B 0.95954

Excited State 6: 2.014-A 1.7853 eV 694.48 nm $f=0.0001$ $\langle S^{**2} \rangle = 0.764$
103B ->125B -0.13558
110B ->125B -0.12442

120B ->125B	0.96831				
Excited State 7:	2.018-A	2.0145 eV	615.45 nm	f=0.0000	<S**2>=0.768
107B ->125B	-0.11607				
116B ->125B	0.31707				
118B ->125B	0.91674				
Excited State 8:	2.017-A	2.0629 eV	601.01 nm	f=0.0000	<S**2>=0.767
107B ->125B	-0.17133				
114B ->125B	-0.38394				
116B ->125B	0.82481				
118B ->125B	-0.28052				
123B ->125B	0.23153				
Excited State 9:	2.009-A	2.1445 eV	578.16 nm	f=0.1373	<S**2>=0.759
117B ->125B	0.92381				
119B ->125B	0.28993				
Excited State 10:	2.019-A	2.1931 eV	565.35 nm	f=0.0021	<S**2>=0.770
106B ->125B	-0.10521				
115B ->125B	0.97445				
122B ->125B	0.12177				
Excited State 11:	2.021-A	2.2968 eV	539.81 nm	f=0.0006	<S**2>=0.771
113B ->125B	-0.41552				
114B ->125B	0.81505				
116B ->125B	0.25767				
118B ->125B	-0.18268				
123B ->125B	0.12055				
Excited State 12:	2.023-A	2.3075 eV	537.30 nm	f=0.0024	<S**2>=0.773
101B ->125B	0.14150				
103B ->125B	0.16943				
113B ->125B	0.86179				
114B ->125B	0.39427				
116B ->125B	0.13180				
Excited State 13:	2.022-A	2.3845 eV	519.95 nm	f=0.0022	<S**2>=0.772
108B ->125B	0.20952				
112B ->125B	0.96306				
Excited State 14:	2.022-A	2.5655 eV	483.27 nm	f=0.0004	<S**2>=0.772
110B ->125B	-0.50719				
111B ->125B	0.84862				
Excited State 15:	2.021-A	2.6971 eV	459.70 nm	f=0.0000	<S**2>=0.771
103B ->125B	-0.22846				
110B ->125B	0.81149				
111B ->125B	0.49847				
120B ->125B	0.11851				

Excited State 16: 2.024-A 2.7419 eV 452.18 nm f=0.0011 <S**2>=0.774
 108B ->125B -0.15892
 109B ->125B 0.96425

Excited State 17: 2.027-A 2.7674 eV 448.02 nm f=0.0002 <S**2>=0.778
 108B ->125B 0.91836
 109B ->125B 0.17454
 112B ->125B -0.20170
 121B ->125B 0.22317
 122B ->125B -0.11180

Excited State 18: 2.026-A 2.8010 eV 442.65 nm f=0.0000 <S**2>=0.776
 105B ->125B 0.65387
 107B ->125B 0.72969
 116B ->125B 0.10957

Excited State 19: 2.028-A 2.9282 eV 423.41 nm f=0.0000 <S**2>=0.778
 105B ->125B 0.73661
 107B ->125B -0.62098
 116B ->125B -0.17680
 123B ->125B -0.11599

Excited State 20: 2.026-A 2.9584 eV 419.09 nm f=0.0004 <S**2>=0.776
 104B ->125B 0.97627
 106B ->125B 0.15190

Excited State 21: 2.023-A 3.0904 eV 401.20 nm f=0.0009 <S**2>=0.773
 102B ->125B -0.16140
 104B ->125B -0.14710
 106B ->125B 0.93325
 121B ->125B 0.12978
 122B ->125B 0.19626

Excited State 22: 2.027-A 3.1250 eV 396.74 nm f=0.0044 <S**2>=0.777
 102B ->125B 0.96600
 106B ->125B 0.15586

Excited State 23: 2.865-A 3.1862 eV 389.13 nm f=0.0000 <S**2>=1.802
 124B ->126B 0.96849
 124B ->130B -0.17849

Excited State 24: 2.032-A 3.2040 eV 386.96 nm f=0.0002 <S**2>=0.783
 125A ->126A 0.97670
 125A ->130A 0.12024

Excited State 25: 2.025-A 3.2162 eV 385.50 nm f=0.0026 <S**2>=0.775
 101B ->125B -0.16399
 103B ->125B 0.92412
 110B ->125B 0.19048
 113B ->125B -0.14148
 120B ->125B 0.19548

TABLE 5.23 Excitation Energies and Oscillator Strengths Calculated for **3.2'**

Excited State	1:	Singlet-A	0.8195 eV	1512.85 nm	f=0.0000	<S**2>=0.000
	124 ->125	0.69812				
Excited State	2:	Singlet-A	0.9557 eV	1297.26 nm	f=0.0002	<S**2>=0.000
	120 ->125	-0.12684				
	122 ->125	0.34619				
	123 ->125	0.59919				
Excited State	3:	Singlet-A	1.1420 eV	1085.69 nm	f=0.0089	<S**2>=0.000
	120 ->125	0.21827				
	122 ->125	0.59859				
	123 ->125	-0.30230				
Excited State	4:	Singlet-A	1.1876 eV	1044.00 nm	f=0.0005	<S**2>=0.000
	121 ->125	0.70440				
Excited State	5:	Singlet-A	1.6223 eV	764.26 nm	f=0.0038	<S**2>=0.000
	118 ->125	-0.32957				
	119 ->125	0.62069				
Excited State	6:	Singlet-A	2.0442 eV	606.51 nm	f=0.0000	<S**2>=0.000
	113 ->125	0.10210				
	116 ->125	-0.48352				
	117 ->125	0.48766				
	124 ->125	0.10386				
Excited State	7:	Singlet-A	2.1103 eV	587.53 nm	f=0.1047	<S**2>=0.000
	115 ->125	-0.14336				
	120 ->125	0.64006				
	122 ->125	-0.12524				
	123 ->125	0.21890				
	120 <-125	-0.11134				
Excited State	8:	Singlet-A	2.4436 eV	507.39 nm	f=0.0163	<S**2>=0.000
	115 ->125	0.68200				
	120 ->125	0.12697				
Excited State	9:	Singlet-A	2.5187 eV	492.26 nm	f=0.0000	<S**2>=0.000
	113 ->125	0.66734				
	116 ->125	0.19973				
Excited State	10:	Singlet-A	2.5267 eV	490.71 nm	f=0.0111	<S**2>=0.000
	100 ->125	-0.13704				
	104 ->125	-0.12763				
	114 ->125	0.66842				
Excited State	11:	Singlet-A	2.6557 eV	466.86 nm	f=0.3389	<S**2>=0.000
	112 ->125	-0.10268				
	118 ->125	0.60542				
	119 ->125	0.31790				

Excited State 12:	Singlet-A	2.6650 eV	465.23 nm	f=0.0000	<S**2>=0.000
108 ->125	-0.14988				
113 ->125	-0.18960				
116 ->125	0.43924				
117 ->125	0.47689				
Excited State 13:	Singlet-A	2.8013 eV	442.60 nm	f=0.0123	<S**2>=0.000
107 ->125	0.18044				
110 ->125	0.66256				
120 ->125	0.10742				
Excited State 14:	Singlet-A	2.8478 eV	435.36 nm	f=0.0010	<S**2>=0.000
109 ->125	0.43980				
111 ->125	0.54322				
Excited State 15:	Singlet-A	2.9437 eV	421.19 nm	f=0.0006	<S**2>=0.000
101 ->125	-0.12153				
104 ->125	-0.20509				
109 ->125	0.50894				
111 ->125	-0.42265				
Excited State 16:	Singlet-A	2.9488 eV	420.45 nm	f=0.0018	<S**2>=0.000
112 ->125	0.68901				
Excited State 17:	Singlet-A	2.9848 eV	415.39 nm	f=0.0034	<S**2>=0.000
107 ->125	0.66881				
110 ->125	-0.19805				
Excited State 18:	Singlet-A	3.1279 eV	396.38 nm	f=0.0000	<S**2>=0.000
103 ->125	0.14705				
108 ->125	0.66723				
116 ->125	0.11342				
Excited State 19:	Singlet-A	3.2227 eV	384.72 nm	f=0.0006	<S**2>=0.000
105 ->125	0.56403				
106 ->125	-0.41055				
Excited State 20:	Singlet-A	3.2489 eV	381.62 nm	f=0.0001	<S**2>=0.000
105 ->125	0.40875				
106 ->125	0.56155				
Excited State 21:	Singlet-A	3.3478 eV	370.35 nm	f=0.0000	<S**2>=0.000
103 ->125	0.68142				
108 ->125	-0.12975				
Excited State 22:	Singlet-A	3.3857 eV	366.19 nm	f=0.0043	<S**2>=0.000
101 ->125	-0.20671				
104 ->125	0.64012				
109 ->125	0.13061				

Excited State 23:	Singlet-A	3.5036 eV	353.88 nm	f=0.0152	<S**2>=0.000
102 ->125	0.68398				
Excited State 24:	Singlet-A	4.0030 eV	309.73 nm	f=0.0000	<S**2>=0.000
120 ->126	0.12598				
122 ->126	-0.18612				
123 ->126	0.66239				
Excited State 25:	Singlet-A	4.0195 eV	308.46 nm	f=0.0032	<S**2>=0.000
124 ->126	0.69794				
Excited State 26:	Singlet-A	4.0779 eV	304.04 nm	f=0.0000	<S**2>=0.000
122 ->126	0.66474				
123 ->126	0.18888				
Excited State 27:	Singlet-A	4.2220 eV	293.66 nm	f=0.0769	<S**2>=0.000
121 ->126	0.69025				
Excited State 28:	Singlet-A	4.2988 eV	288.42 nm	f=0.0372	<S**2>=0.000
98 ->125	0.10538				
100 ->125	0.26640				
101 ->125	0.56354				
104 ->125	0.12178				
109 ->125	0.14037				
114 ->125	0.16931				
Excited State 29:	Singlet-A	4.4764 eV	276.97 nm	f=0.0000	<S**2>=0.000
120 ->126	-0.29542				
123 ->127	0.60347				
Excited State 30:	Singlet-A	4.4959 eV	275.77 nm	f=0.0206	<S**2>=0.000
123 ->129	0.10267				
124 ->127	0.68345				
Excited State 31:	Singlet-A	4.5198 eV	274.31 nm	f=0.0094	<S**2>=0.000
89 ->125	0.25955				
92 ->125	0.15191				
94 ->125	0.11845				
95 ->125	0.39205				
99 ->125	0.46736				
Excited State 32:	Singlet-A	4.5363 eV	273.32 nm	f=0.0000	<S**2>=0.000
96 ->125	-0.15886				
97 ->125	0.25528				
120 ->126	0.53293				
122 ->127	-0.10522				
123 ->127	0.25643				
Excited State 33:	Singlet-A	4.5538 eV	272.26 nm	f=0.0000	<S**2>=0.000
120 ->126	0.10775				
121 ->128	0.10769				

122 ->127 0.66340
122 ->133 0.11466

Excited State 34: Singlet-A 4.6004 eV 269.51 nm f=0.0000 <S**2>=0.000

87 ->125 0.12315
90 ->125 0.26954
96 ->125 -0.27646
97 ->125 0.43600
120 ->126 -0.28827
123 ->127 -0.13393

Excited State 35: Singlet-A 4.6488 eV 266.70 nm f=0.0072 <S**2>=0.000

99 ->125 -0.11687
121 ->127 0.64920
121 ->133 0.10600
122 ->128 0.17017

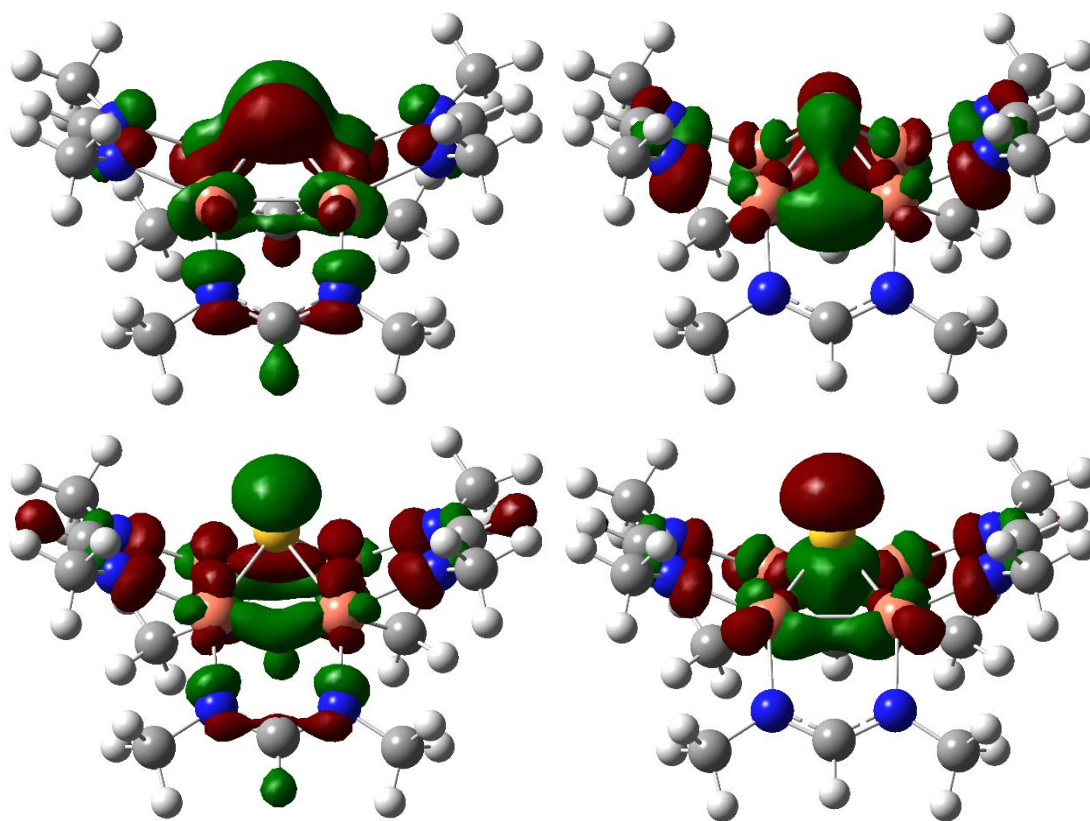


FIGURE 5.98 Frontier S(p) donor MOs for singlet **3.2'**: MOs 116-119 (i.e. HOMO-6 through HOMO-9; isovalue = 0.04).

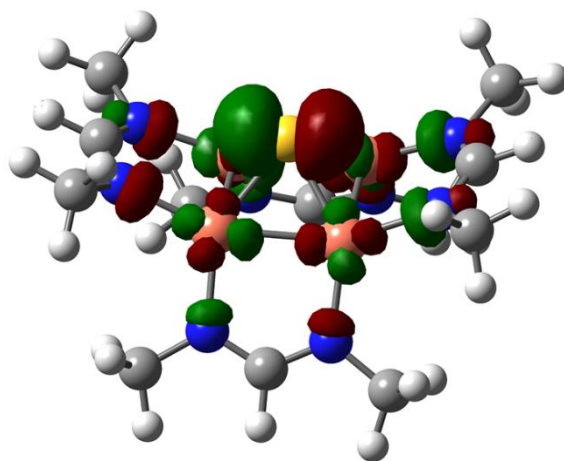


FIGURE 5.99 LUMO for singlet **3.2'** (MO 125, isovalue = 0.04).

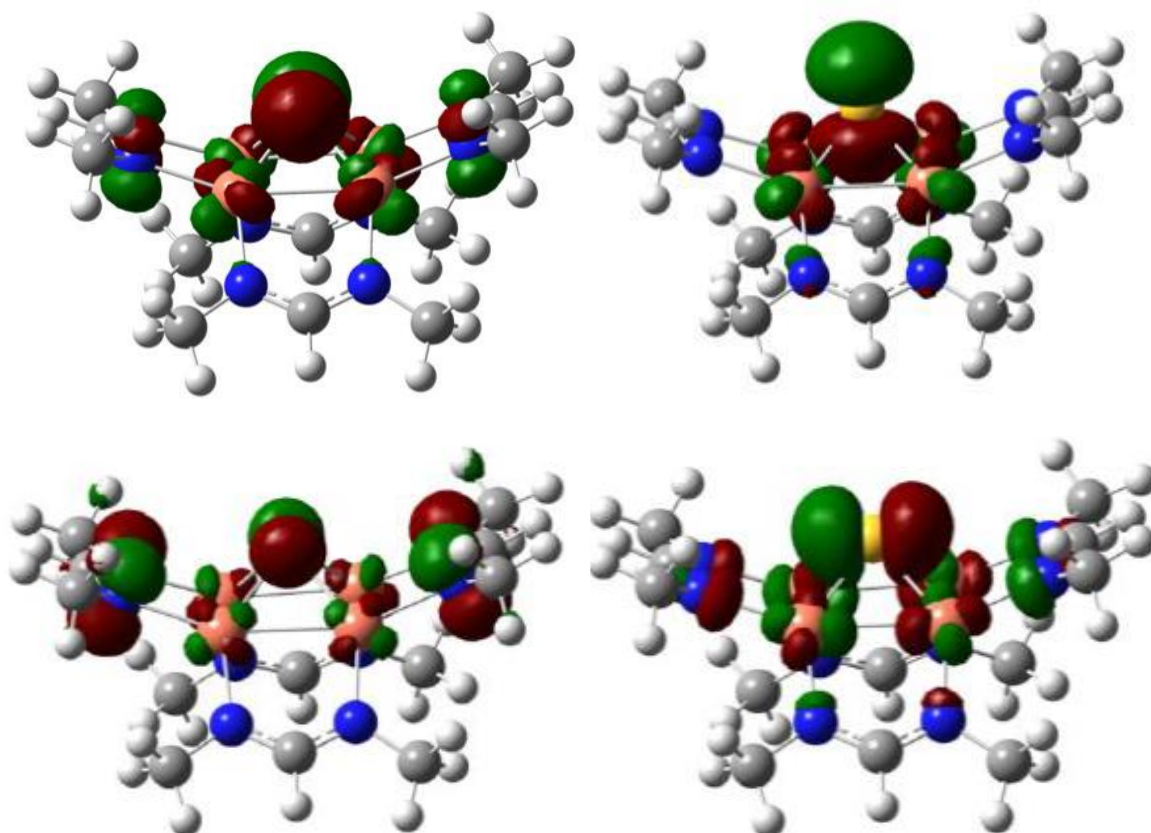


FIGURE 5.100 Filled S(p) α – MOs for singlet **3.3'**: MOs 118 α , 120 α , 124 α , 125 α (isovalue = 0.04).

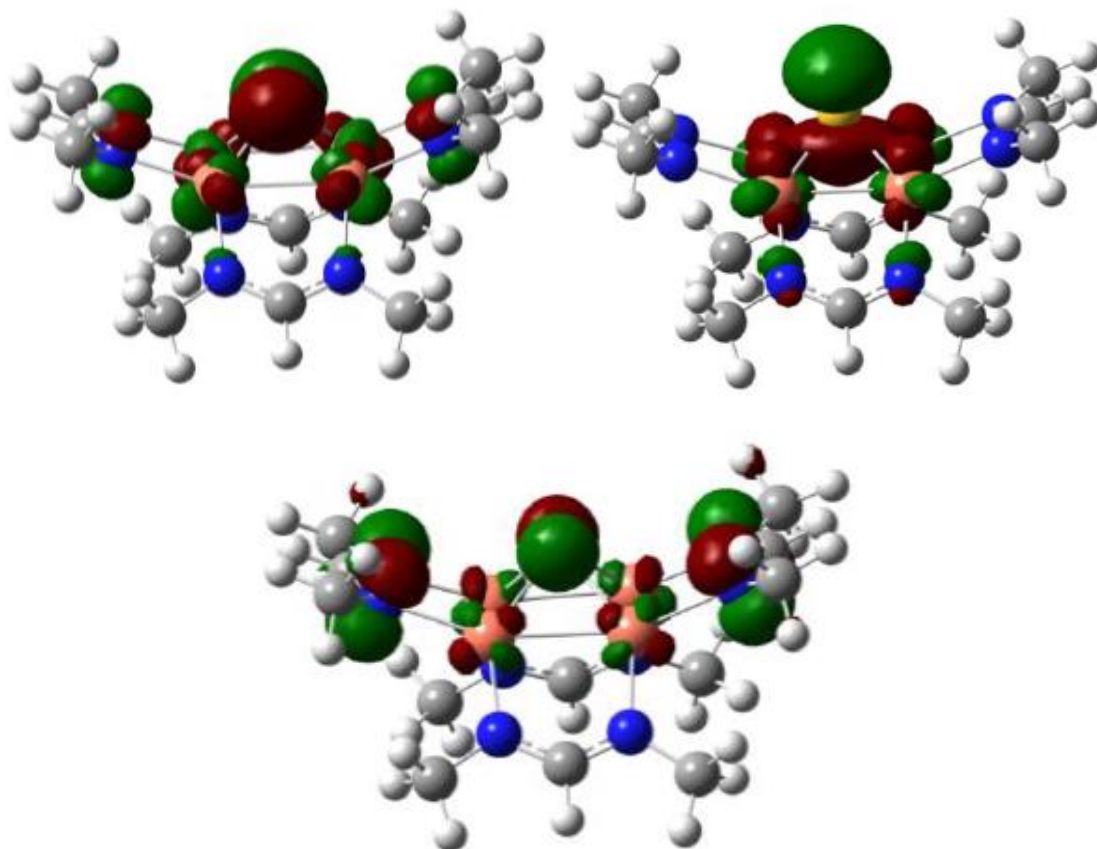


FIGURE 5.101 Filled S(p) β – MOs for singlet **3.3'**: MOs 116 β , 119 β , 123 β (isovalue = 0.04).

APPENDICES

APPENDIX A. Cu $\cdots$ Cu distances and Cu-S bond lengths (Å) reported for the Cu_Z* and Cu_Z resting states.

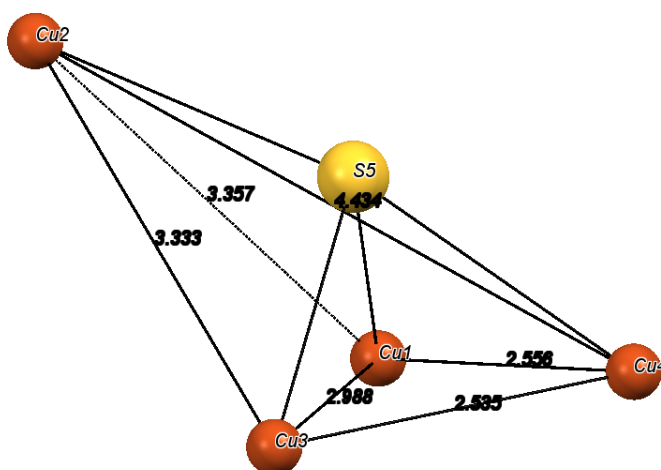


FIGURE A1. Cu $\cdots$ Cu distances in Cu_Z*. Coordinates analyzed from PDB code 1QNI.¹⁸ Structure shown in ball and stick style, histidine ligands removed for clarity.

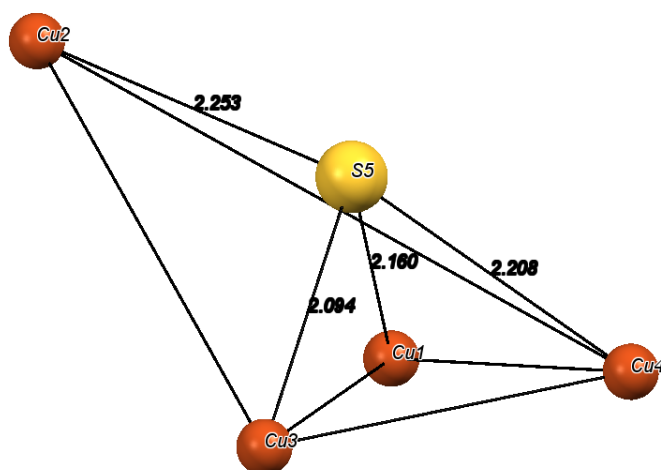


FIGURE A2. Cu-S bond lengths for Cu_Z*. Coordinates analyzed from PDB code 1QNI.¹⁸ Structure shown in ball and stick style, histidine ligands have been removed for clarity.

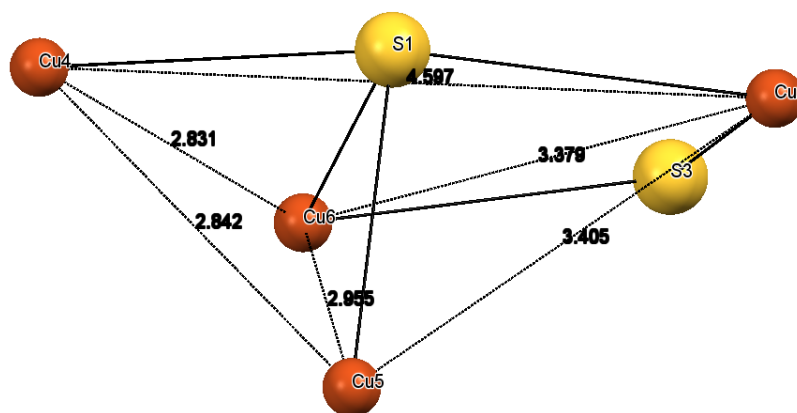


FIGURE A3. Cu...Cu distances for Cu₂. Coordinates analyzed from PDB code 3SBR.¹⁹ Structure shown in ball and stick style, histidine ligands have been removed for clarity.

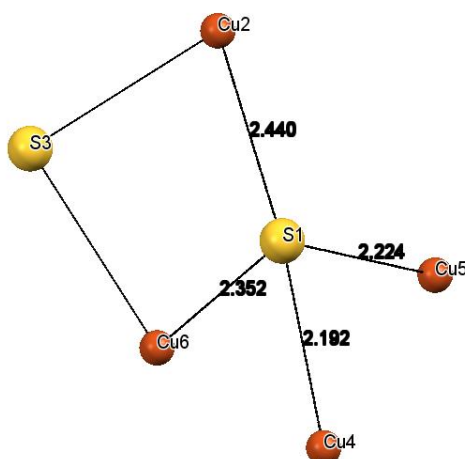


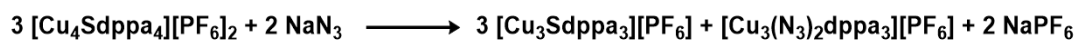
FIGURE A4. Cu-S bond lengths for Cu₂. Coordinates analyzed from PDB code 3SBR.¹⁹ Structure shown in ball and stick style, histidine ligands have been removed for clarity.

APPENDIX B. Calculation for quantum yields in Table 2.3 were determined based off Equation 1; A = measured absorbance at the excitation wavelength and I is the integrated emission intensity when samples were excited at 415 nm. A 7.10×10^{-4} M solution of **1.3** ($\Phi = 0.22$,¹¹⁸ excitation wavelength = 415 nm) in MeCN was used as the standard reference solution. Concentrations for **2.2** (5.66×10^{-4} M) and **2.4** (3.14×10^{-3} M) were also made in MeCN.

Equation 1:

$$\Phi_{\text{sample}} = \Phi_{\text{reference}} \frac{A_{\text{reference}} \times I_{\text{sample}}}{A_{\text{sample}} \times I_{\text{reference}}}$$

APPENDIX C. Balanced chemical equation for the reaction of **2.2** with excess sodium azide. Products **2.5** and **2.6** were produced in a ratio of ~ 3:1 in the crude reaction mixture.



APPENDIX D. Crystal structure of inorganic core in compound **2.6** determined by X-ray crystallography.

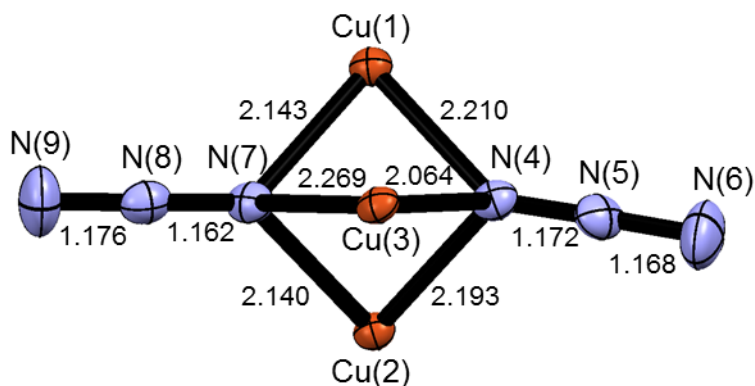
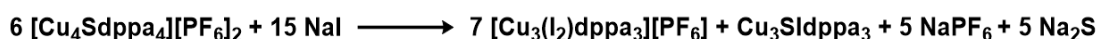


FIGURE A5. Crystal structure of compound **2.6** determined by X-ray crystallography. Complex drawn with 50% probability ellipsoids for the core atoms; ligands, co-crystallization solvent and anion molecules have been omitted. Bond lengths are in Å. $\angle\text{N}(9)\text{--N}(8)\text{--N}(7) = 178.53^\circ$; $\angle\text{N}(6)\text{--N}(5)\text{--N}(4) = 177.97^\circ$. Atom colors include: Cu, brown; N, blue.

APPENDIX E. Balanced chemical equation for the reaction of **2.2** with excess sodium iodide. Products **2.8** and **2.7** were produced in a ratio of ~ 6:1 in the crude reaction mixture.



APPENDIX E. Solid state structure and X-ray crystallographic analysis of complex **3.2**.

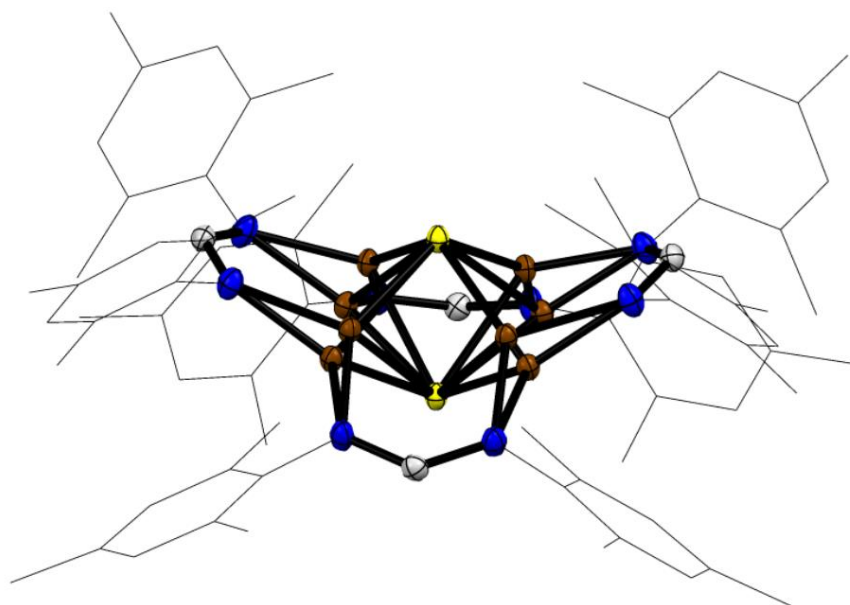


FIGURE A6. Solid state structure of **3.2** determined by X-ray crystallography, with both disordered Cu_4S units shown. The molecule is positioned on crystallographic element of symmetry (-4) and experiences two types of disorder: (a) the S cap alternatively occupies 2 symmetrically equivalent position over and under the Cu_4 moiety, and (b) each of the Cu ions of the central moiety deviates alternatively up or down from the mean plane that corresponds to a superposition of two tetrahedral distortions of opposite sign. The ligands do not show any perceptible disorder. Apparently, they form a significantly robust scaffold around the central metal nucleus owing to stacking between overlapping mesityl groups. X-ray crystallographic analysis also presented in Section 5.2.3 and Figure 5.67. Reproduced from reference 229 with permission from Royal Society of Chemistry.

APPENDIX G. Electrochemical analysis of compound **3.2**, using cyclic voltammetry.

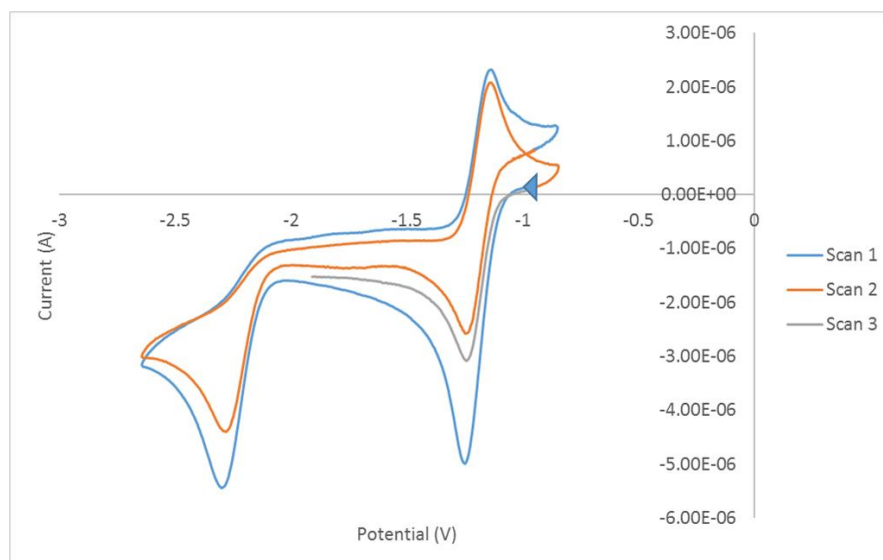


FIGURE A7. Cyclic voltammogram of **3.2** in 0.1 M [NBu₄][PF₆] electrolyte THF solution. Recorded at 100 mV/s with platinum working electrode and Ag/AgNO₃ reference electrode. Potentials are vs. Fc^{+/0}. After first scan (blue trace), current of reversible species at -1.25 V is decreased (orange and gray trace) indicating decomposition after onset of the second reduction at -2.36 V.

APPENDIX H. Contribution of two NCN[−] ligands taken from DFT calculated LUMO of **3.2'** (Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Mankad, N. P. *Chem. Commun.* **2015**, 51, 11860). Computational methods are described in Sections 5.2.9 and 5.2.20. The calculated spin densities in **3.2'** LUMO and calculated Mulliken population analysis for **3.3'** RAMO (Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. *J. Am. Chem. Soc.* **2016**, 138, 13107) are in fair agreement as shown in Table A1 below.

TABLE A1. Calculated LUMO of **3.2'** and SOMO **3.3'**^a

	Calculated LUMO 3.2'	Calculated SOMO 3.3' ^a
Cu(1)	12 %	10 %
Cu(2)	12 %	10 %
Cu(3)	12 %	10 %
Cu(4)	12 %	10 %
S	21 %	32 %

^a Spin densities are estimated from Mulliken population analysis.

APPENDIX I. Calibration data for quantifying N₂O and N₂ within flask headspace determined by GC-MS. For both set of standards, 50 mL round bottom Schlenk flasks were used, equipped with an unpunctured septa that was sealed using copper wire and a keck clip. For the N₂O standards, the flasks were purged three times with N₂ and then closed to Schlenk line. Using a syringe and a separate Schlenk flask containing N₂O, known volumes of N₂O were injected into the closed N₂ Schlenk flasks. Standards were injected and analyzed according to the procedure provided in Section 5.2.12. N₂ standards were prepared in the same fashion but He gas was used for the backfill and known volumes of N₂ were injected into the He flasks.

Under the GC-MS method conditions provided in Section 5.2.12, N₂ had the retention time of 2.7 minutes and N₂O had a retention time of 5.5 minutes. Resulting peaks in the chromatogram were manually integrated and integrated using instrument software (TSSPro, Shrader Analytical & Consulting Laboratories, Inc., Detroit, MI).

TABLE A2. Calibration Data for Quantifying N₂O^a

N ₂ O volume (mL)	TSSPro N ₂ O Integration	Manual N ₂ O Integration	Average N ₂ O Integration
0.1	159,520	107,584	133,552
0.3	308,736	278,912	293,824
0.5	540,704	465,216	502,960
0.8	819,168	796,576	807,872

^a Average N₂O Integration vs. Volume of N₂O in Standard: $y = 973987x + 20607$ ($R^2 = 0.9973$).

TABLE A3. Calibration Data for Quantifying N₂^a

N ₂ volume (mL)	TSSPro N ₂ Integration	Manual N ₂ Integration	Average N ₂ Integration
0	1,686,656	2,339,968	2,013,312
0.3	1,032,416	1,335,392	1,183,904
0.6	984,128	2,768,320	1,876,224
0.9	100,352	1,774,816	937,584
1.2	3,082,080	2,546,304	2,814,192
1.5	4,939,712	2,633,920	3,786,816

^a Average N₂ Integration vs. Volume of N₂ in Standard: $y = 10^6 x + 10^6$ ($R^2 = 0.419$).

APPENDIX J. Publisher (Royal Society of Chemistry) statement for the reuse of content originating in reference Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Mankad, N. P. *Chem. Commun.* **2015**, 51, 11860. URL link to source shown in Figures A8 and A9 below: <http://www.rsc.org/journals-books-databases/journal-authors-reviewers/licences-copyright-permissions/#reuse-permission-requests>. Any reprinted text or figures include the following statement before the text or in the figure caption: “Reproduced from reference 229 with permission from the Royal Society of Chemistry”.

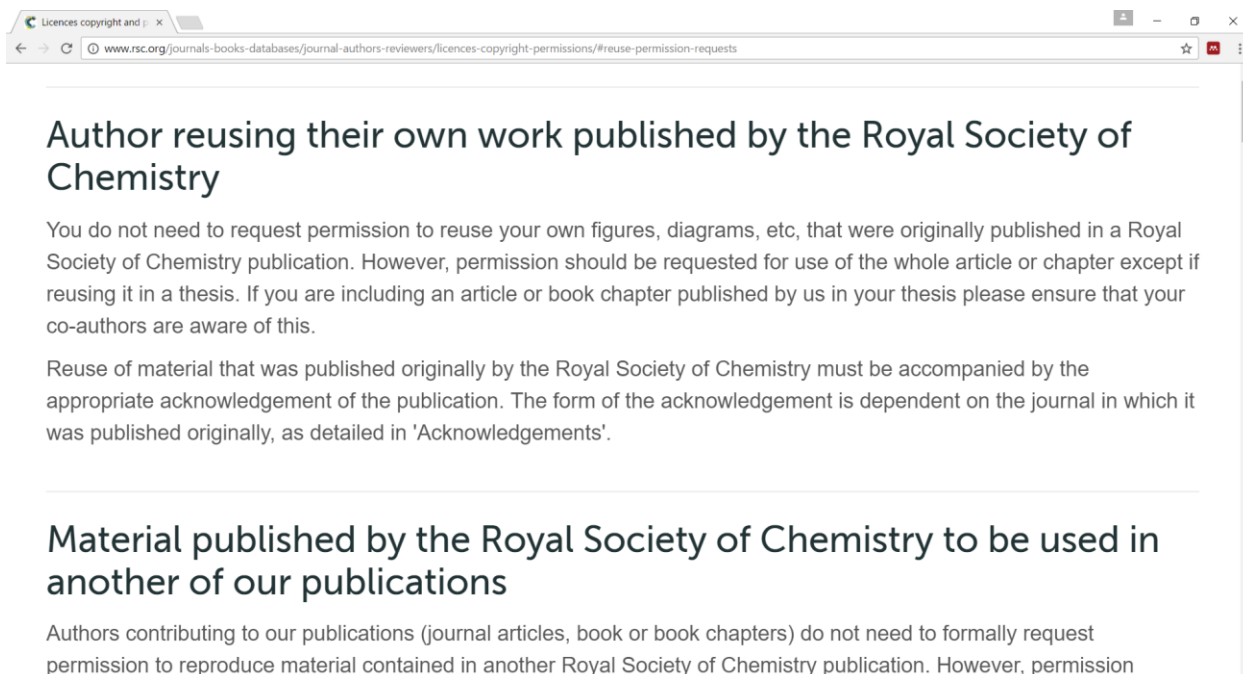


FIGURE A8. Top of webpage from RCS publisher, as a screen shot.

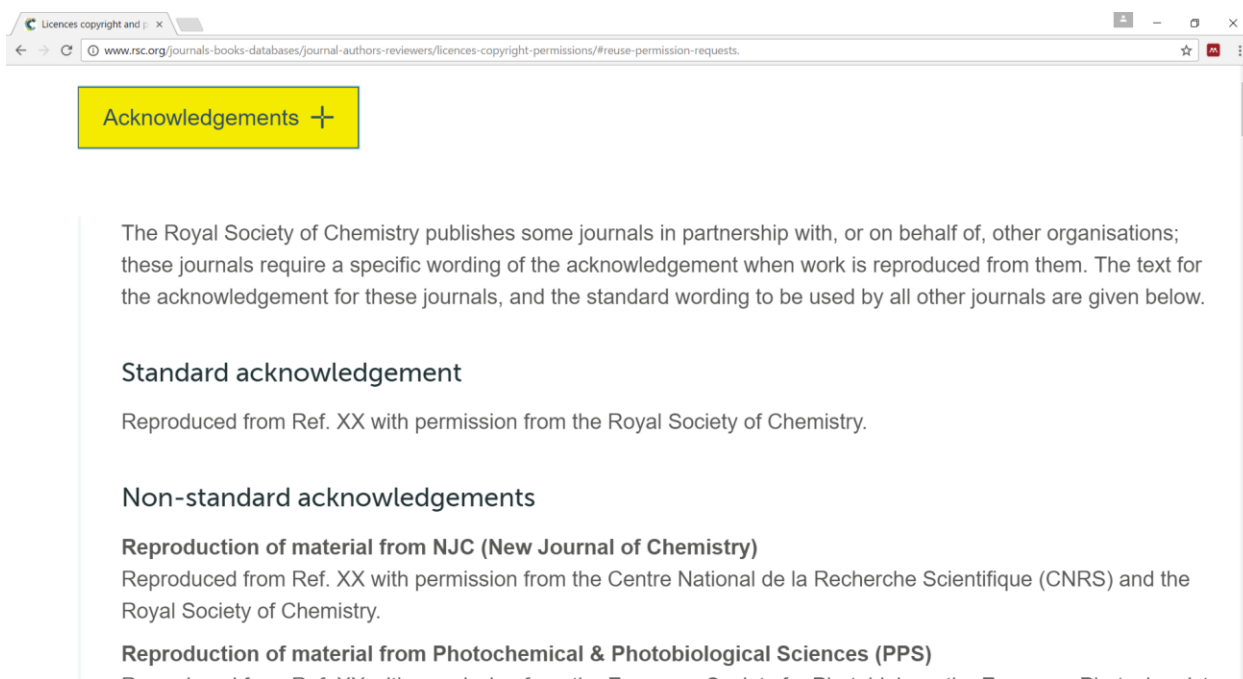


FIGURE A9. Bottom of webpage from RSC publisher, as a screen shot.

APPENDIX K. Publisher (American Chemical Society) statement for the reuse of content originating in references: Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. *Inorg. Chem.* **2014**, 53, 10611 and Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. *J. Am. Chem. Soc.* **2016**, 138, 13107. URL link to source shown in Figures A10, A11 and A12 below: <http://pubs.acs.org/pb-assets/acspubs/Migrated/dissertation.pdf>. Any reprinted figures or text include the following statement before the text or in the figure caption: “Reproduced with permission from Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. *Inorg. Chem.* **2014**, 53, 10611. Copyright 2014 American Chemical Society” and “Reproduced with permission from Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. *J. Am. Chem. Soc.* **2016**, 138, 13107. Copyright 2016 American Chemical Society”.

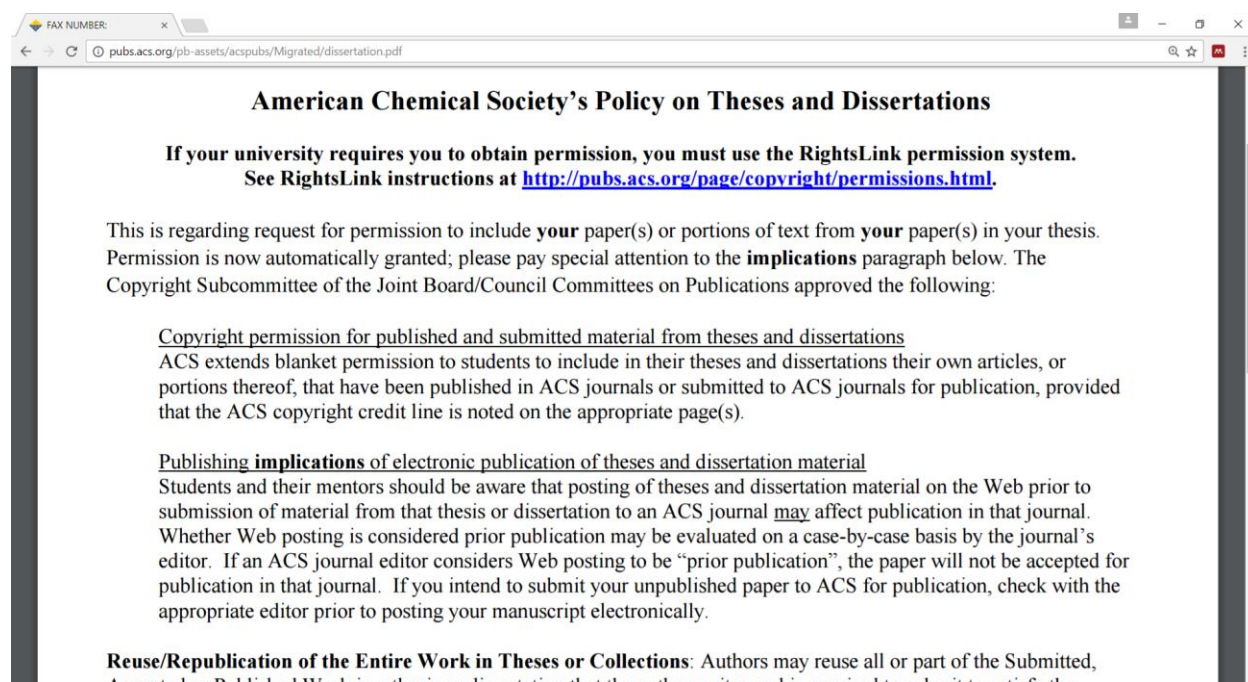


FIGURE A10. Top of webpage from ACS publisher, as a screen shot.

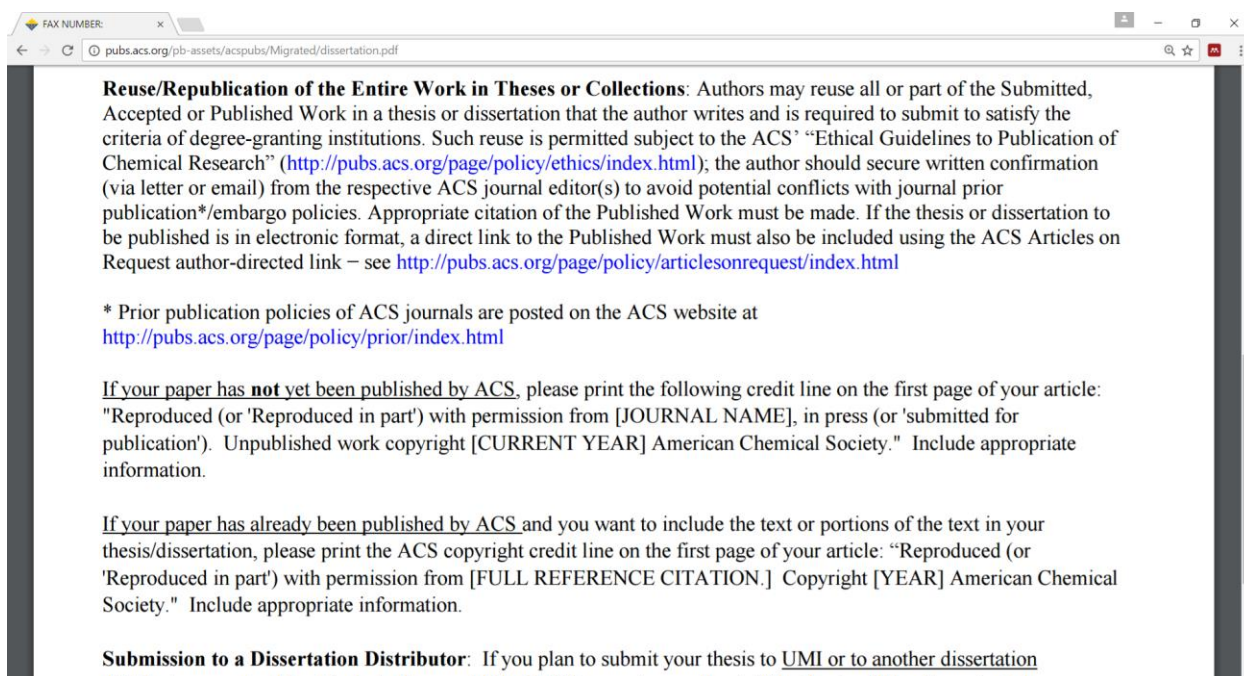


FIGURE A11. Middle of webpage from ACS publisher, as a screen shot.

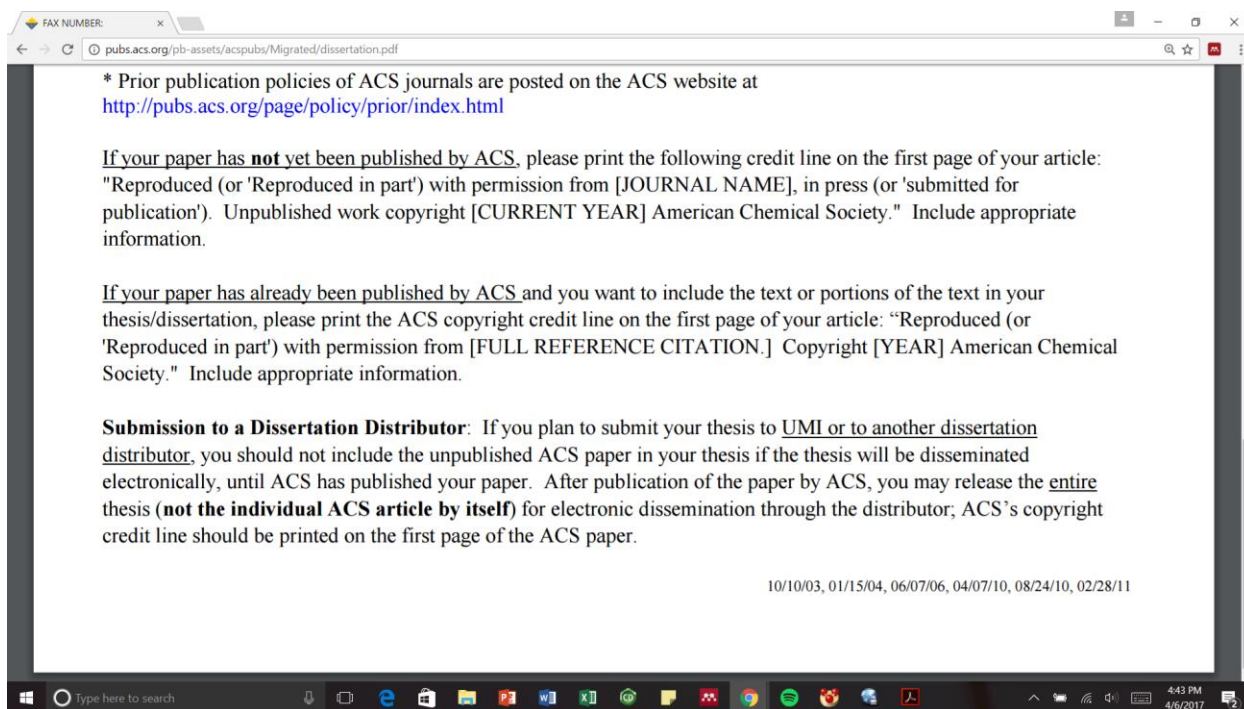


FIGURE A12. Bottom of webpage from ACS publisher, as a screen shot.

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