SORPTION OF AQUEOUS COPPER(II) AND 2,2'-BIPYRIDINE ON AMORPHOUS SILICA AND ALUMINA:
A SOLUTION AND SPECTROSCOPIC STUDY

A DISSERTATION SUBMITTED
TO THE DEPARTMENT OF
GEOLOGICAL AND ENVIRONMENTAL SCIENCES
AND THE COMMITTEE ON GRADUATE STUDIES
OF STANFORD UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Sing-Foong Cheah
April 1997
© Copyright by Sing-Foong Cheah 1997

All Rights Reserved
I certify that I have read this dissertation and that in my opinion it is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Gordon E. Brown, Jr. (Principal Adviser)

George A. Parks (Co-Adviser)

I certify that I have read this dissertation and that in my opinion it is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

George D. Redden

I certify that I have read this dissertation and that in my opinion it is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Garrison Sposito

Approved for the University Committee on Graduate Studies:
ABSTRACT

This thesis examines the effects of 2,2'-bipyridine (bipy for short) and oxide surfaces on Cu(II) sorption. The Cu(II)/bipy/oxide ternary system was chosen for in depth study to increase understanding of the interactions between metal cations, organic compounds, and mineral surfaces and because it represents a simplified model of more complex natural aquatic systems.

X-ray Absorption Fine Structure (XAFS) shows that, in the absence of bipy, at surface concentrations ≤ 0.05 μmol m⁻², monomeric Cu(II) species bind directly to oxygen or hydroxyl groups on γ-Al₂O₃ surfaces in bidentate or monodentate mode. At similar surface concentrations, Cu(II) on amorphous SiO₂ (am-SiO₂) is predominantly dimeric. At even higher surface concentrations, sizes of Cu(II) multimeric complexes and/or precipitates are larger on am-SiO₂ than on γ-Al₂O₃ or anatase.

Fourier Transform Infrared Spectroscopy (FTIR) indicates that in the absence of Cu(II), bipy adsorbs to am-SiO₂ surfaces through physisorption and hydrogen-bonding, but to γ-Al₂O₃ surfaces through chemisorption.

For the Cu(II)/bipy/am-SiO₂ system, bipy enhances net Cu(II) sorption onto am-SiO₂ at the lowest Cu solution concentration, ΣCu = 0.1 mM, but reduces net Cu(II) sorption at ΣCu = 1.6 mM. The ratio of Σ bipy adsorbed to Σ Cu(II)adsorbed (= bipyads/Cu(II)ads) = n where the predominant aqueous complex is Cu(II)-bipy₂. Electron Paramagnetic Resonance Spectroscopy, XAFS, and FTIR results suggest that Cu(II) and bipy are mutually bonded on the surface. For Cu(II)-bipy₁, spectroscopic results suggest that the dominant Cu(II) surface species is an inner-sphere, mononuclear, monodentate Type A ternary surface complex [i.e., is bonded to the surface through the Cu(II)].

In the Cu(II)/bipy/γ-Al₂O₃ system, bipy decreases Cu(II) sorption at all concentrations studied. The ratio bipyads/Cu(II)ads is a non-integer smaller than bipy tot/Cu(II) tot, suggesting that some bipy dissociates from Cu(II) during sorption. Based on uptake and spectroscopic measurements, there are both bipy-bound and free Cu(II) on the γ-Al₂O₃ surface, whether the dominant species in solution is Cu(II)-bipy₁ or Cu(II)-bipy₂. The differences in Cu(II) sorption in the presence of bipy on am-SiO₂ and γ-Al₂O₃ might be explained by differences in strength of surface bonding, stereochemistry, or coprecipitate formation.
ACKNOWLEDGMENTS

I would like to thank the Department of Energy for providing funding during my graduate career. Additional funding also came from the NSF/MRSEC (National Science Foundation/Material Research Science and Engineering Center) Graduate Research Assistantship for Women and the Ernest Gale Martin Memorial Fund Fellowship. I would also like to thank the McGee Fund of Stanford University for providing the funding for the infrared experiments.

There are many individuals whom I would like to thank. First and foremost, I want to thank my advisors Gordon E. Brown, Jr. and George A. Parks for their guidance and encouragement for this work. I thank Gordon for sharing his enthusiasm, insight to science, and technical knowledge to this research. His ability to provide a steady funding environment and his extensive contacts also help to provide a stable and simulating research environment. I thank George for always challenging me to think through a problem more thoroughly—the many discussions I had with him about ternary surface complexes have been very important for my scientific education at Stanford. If Gordon's optimism is irresistible, George's worrying about the actual time taken and all the details that need to be done to ensure a good piece of work also is infectious. I am very grateful to have both of their guidance.

Next, I would like to thank George Redden for his careful reading of my thesis and excellent comments, and for sharing his extensive knowledge about aquatic chemistry and laboratory techniques. I also thank Gary Sposito for providing concise, insightful suggestions about my thesis research.

I was extremely fortunate to start out my geochemistry laboratory experience under the guidance and training of a former postdoc in the research group, Dr. Per Persson. Per was instrumental in getting my hands wet: guiding me through the ins and outs of wet chemistry, as well as infrared spectroscopy. The trip to do infrared experiments in Sweden was definitely a high point in my graduate career. Anna's and his hospitality while I was there were greatly appreciated.

I thank Professor Ed Solomon for letting me use the EPR spectrometer, and Uma and Tim for teaching me how to use the machine and how to do EPR data analysis. I thank members of the SSRL staff, in particular, Ingrid Pickering, Britt Hedman, and Graham George, for their help during data collection and interesting discussions on XAFS data.
analysis. I would also like to express my gratitude to Professor Brian J. Hathaway, University College, Cork, Republic of Ireland for donating two model compounds.

Members of the geochemistry group at Stanford deserve special thanks for making the environment fun and stimulating. John Bargar, Steve Towle, Patricia Maurice, Trish Dove, Peggy O'Day, Hillary Thompson, Andrea Foster, Ning Xu, Jeff Fitts, Ping Liu, Maria Peterson, John Ostergren, Chris Kim, and Tom Trainor share their respective knowledge and insights in science, as well as professional advice which was very much appreciated.

I thank members of the Stanford Kenpo Karate club, for their consistent encouragement, beliefs, and the highest standards demanded of my mental and physical abilities. These include Barbara Minneti, Thomas Carson, Kenneth Van Vleck, Charles "Chip" Schmelz, Rod Martin, William "BJ" Jackson, Jeff Reichard, Paula Rickert, Chad Jennings, Ben Schwartz, Sunil Vemuri, and Max Kanevsky. I want to especially thank Linda Bickham for her kindness and the legendary Mr. Kurt Schnoor for instilling a belief in me that I can, and should, always push for the best in me, plus a little more.

I want to thank Bill Simpson, David Adelman, Jed Mosenfelder, Angus Miller, Lim Suat Guat and Song Fei Loong for their friendship. I wish for the best for Suat Guat, and hope Fei Loong can one day fulfill his dreams of publishing a collection of his short stories.

I want to thank my family, and Garth, for many things, but I am at a loss for words. I love them deeply.
Dedicated to the memory of my grandmother Lee Kon Lan
# TABLE OF CONTENTS

**ABSTRACT** ........................................................................................................ iv

**ACKNOWLEDGMENTS** ......................................................................................... v

**TABLE OF CONTENTS** ......................................................................................... viii

**LIST OF TABLES** ................................................................................................ xiii

**LIST OF FIGURES** .............................................................................................. xiv

**CHAPTER I. Introduction** .................................................................................... 1

**CHAPTER II. XAFS Spectroscopy Study of Cu(II) Sorption on Amorphous SiO₂ and γ-Al₂O₃: Effect of Substrate and Time on Sorption Complexes** ......................................................................................... 7

2.1. INTRODUCTION ............................................................................................... 7

2.1.1. Choice of Systems ....................................................................................... 8

2.2. PREVIOUS WORK .......................................................................................... 9

2.3. EXPERIMENTAL ............................................................................................ 13

2.3.1. Uptake Studies and Sample Preparation .................................................... 13

2.3.2. XAFS Data Collection ............................................................................. 14

2.4. RESULTS ......................................................................................................... 17

2.4.1. Uptake Measurements ............................................................................ 17

2.4.2. XAFS Results ......................................................................................... 18

2.5. DISCUSSION .................................................................................................. 33

2.5.1. Cu(II)-Surface Interaction based on Polyhedral Approach ............... 33

2.5.2. Structural Mismatch and Dimer Formation ............................................. 39

2.5.2.1. Detailed Structure of the Cu(II) Dimers on am-SiO₂ ...................... 41
2.5.3. Observed Changes in the XAFS Spectra of Cu/SiO2 Samples as a Function of Time ................................................................. 44

2.6. CONCLUSIONS ..................................................................... 46

CHAPTER III. XAFS Study of Copper(II) Model Compounds and Sorption of Copper(II) on Amorphous SiO2, γ-Al2O3, and Anatase ........... 47

3.1. INTRODUCTION .................................................................. 47

3.2. EXPERIMENTAL ................................................................. 50

3.2.1. Uptake Measurements and Sorption Sample Preparation .......... 50

3.2.2. Sources and Verification of Model Compounds ...................... 50

3.3. RESULTS--XAFS STUDY OF MODEL COMPOUNDS ................. 51

3.3.1. Detection of Equatorial and Axial Oxygens in the Coordination Sphere of Cu ............................................................... 51

3.3.2. Detection of Cu Atoms Surrounding the Central Cu Atom ........... 56

3.3.2.1. Second shell Cu atoms ............................................... 56

3.3.2.2. Fourth shell Cu atoms ............................................... 56

3.3.3. Detection of Si Second Neighbors ......................................... 57

3.3.4. Cu→Oeq→Oeq Multiple Scattering ....................................... 57

3.4. RESULTS--SORPTION SAMPLES ......................................... 58

3.4.1. Solution Uptake Results ................................................... 58

3.4.2. XAFS Results--Sorption Samples ....................................... 58

3.4.2.1. Cu/am-SiO2 ........................................................... 59

3.4.2.2. Cu/γ-Al2O3 ............................................................ 64

3.4.2.3. Cu/a-TiO2 ............................................................. 64

3.5. DISCUSSION ..................................................................... 65

3.5.1. Cu/am-SiO2 Samples ..................................................... 65

3.5.2. Cu/γ-Al2O3 Samples ..................................................... 66

3.5.3. Cu/a-TiO2 Sample ....................................................... 67
3.5.4. Summaries and Comparison to Other Studies ........................................... 67
3.6. CONCLUSIONS .............................................................................................. 68

CHAPTER IV. Infrared Studies of Sorption of 2,2'-Bipyridine on
Amorphous SiO₂ and γ-Al₂O₃ in the Presence and Absence of
Copper(II) ............................................................................................................. 69
4.1. INTRODUCTION .......................................................................................... 69
4.2. EXPERIMENTAL ......................................................................................... 70
  4.2.1. Uptake Measurements and Sorption Sample Preparation............... 70
  4.2.2. Infrared Data Collection ................................................................. 70
  4.2.3. Infrared Data Analysis ................................................................. 71
  4.2.4. Sample Nomenclature ......................................................................... 72
4.3. RESULTS AND DISCUSSION .................................................................... 72
  4.3.1. Uptake studies .................................................................................. 72
  4.3.2. FTIR Spectroscopy ........................................................................ 73
    4.3.2.1. Sample BSiO₂ ........................................................................... 74
    4.3.2.2. Sample BAl₂O₃ ........................................................................ 75
    4.3.2.3. Sample Cu/bipy/Al₂O₃ ............................................................ 77
    4.3.2.4. Samples Cu/bipy/am-SiO₂ .................................................... 79
4.4. CONCLUSION ............................................................................................. 82

CHAPTER V. XAFS and EPR Study of Ternary Surface Complexes
of Copper(II) and 2,2'-Bipyridine on Amorphous SiO₂ .................................... 83
5.1. INTRODUCTION ......................................................................................... 83
  5.1.1. Previous Studies .............................................................................. 85
  5.1.2. Experimental Strategy ....................................................................... 86
5.2. EXPERIMENTAL ....................................................................................... 89
  5.2.1. Materials and Reagents ................................................................... 89
  5.2.2. Uptake Experiments-Procedure ..................................................... 89
5.2.3. Uptake Experiments—Analytical Methods and Error .................... 91
5.2.4. Sample Labeling ......................................................................... 93
5.2.5. EPR Data Collection .................................................................. 93
5.2.6. XAFS--Data Collection ............................................................... 94
5.2.7. XAFS--Data Analysis ................................................................. 95

5.3. RESULTS ....................................................................................... 96
5.3.1. Uptake Results ........................................................................... 96
5.3.2. Spectroscopic Results ................................................................. 103
  5.3.2.1. EPR Results ........................................................................ 103
  5.3.2.2. XAFS--XANES Results ...................................................... 107
  5.3.2.3. XAFS--EXAFS Results ...................................................... 107

5.4. DISCUSSION ................................................................................. 115
  5.4.1. Composition and Structure of the Surface Complexes ................ 115
    5.4.1.1. Bonding mode of Cu(II)-bipy1 on am-SiO2 surface .......... 119
    5.4.1.2. Bonding mode of Cu(II)-bipy2 on am-SiO2 surface .......... 120
  5.4.2. The Influence of bipy on Cu(II) sorption on am-SiO2 ................ 121
  5.4.3. Site Limitation ....................................................................... 123

5.5. CONCLUSIONS ............................................................................ 125

CHAPTER VI. Solution and Spectroscopic Studies of the Influence of 2,2'-bipyridine on the Sorption of Copper(II) on γ-Al2O3 .......... 126

6.1. INTRODUCTION ........................................................................ 126

6.2. BACKGROUND ........................................................................... 127

6.3. EXPERIMENTAL ....................................................................... 132

6.4. RESULTS .................................................................................... 132
  6.4.1. Uptake Results ................................................................. 132
  6.4.2. Spectroscopic Results ......................................................... 134
    6.4.2.1. EPR Results ................................................................. 137
6.4.2.2. XAFS--XANES Results ........................................... 138
6.4.2.3. XAFS--EXAFS Results ........................................... 138

6.5. DISCUSSION ........................................................................ 141
  6.5.1. Composition and Structure of the Surface Complexes ........ 141
  6.5.2. Comparison of Cu(II)-bipy Sorption on Different Oxides .... 142

6.6. CONCLUSIONS ...................................................................... 147

REFERENCES ............................................................................. 149
LIST OF TABLES

Table 2.1. Summary of EPR parameters of Cu(II) sorption on surfaces containing SiOH and AlOH groups................................................................. 12

Table 2.2. Experimental conditions for XAFS sorption samples............................ 16

Table 2.3. Solubility product $K_{sp}$ for Cu precipitates that might form in the experiments. .......................................................................................... 19

Table 2.4. EXAFS results of Cu/SiO$_2$ and Cu/Al$_2$O$_3$ ........................................ 24

Table 3.1. Results of least square fits of Cu K-EXAFS of model compounds compared to the reported structures......................................................54-55

Table 3.2. Experimental conditions for XAFS sorption samples............................... 59

Table 3.3. Results of quantitative analysis of EXAFS data ........................................ 63

Table 4.1. IR band positions for sorption samples BSiO$_2$ and BAl$_2$O$_3$ ............. 77

Table 4.2. IR band positions for sorption samples Cu/bipy/SiO$_2$ and Cu/bipy/Al$_2$O$_3$ ................................................................................................. 81

Table 5.1 Experimental conditions for XAFS sorption samples............................... 103

Table 5.2. Spectral parameters derived from EPR data............................................. 106

Table 5.3. Results of quantitative EXAFS analysis .................................................... 116-117

Table 5.4. Summary of spectroscopic results for sorption samples.......................... 117

Table 6.1. Summary of EPR parameters of Cu(II)-organic sorption complexes on oxides and oxyhydroxides from previous studies........................................ 129
LIST OF FIGURES

Figure 2.1. Cu uptake on am-SiO₂ and γ-Al₂O₃ as a function of pH ......................... 17

Figure 2.2. Relative degrees of saturation of initial and final solution conditions of XAFS samples with respect to Cu(OH)₂ and CuO precipitation ................................. 20

Figure 2.3. X-ray absorption edges and second derivatives of Cu(II) on γ-Al₂O₃ and am-SiO₂ ................................................................. 22

Figure 2.4. EXAFS and Fourier transforms of Cu(II) on γ-Al₂O₃ and am-SiO₂ ........... 23

Figure 2.5. (a-f) Experimental EXAFS spectra and non-linear least squares fit ...........25-26

Figure 2.6. X-ray absorption edges and second derivatives of Cu/SiO₂ (0.05) as a function of time ................................................................. 29

Figure 2.7. Change in coordination number in the second Cu shell of Cu/SiO₂ (0.05) as a function of time ................................................................. 30

Figure 2.8. Trends in dimeric versus monomeric Cu(II) species on the am-SiO₂ surface as a function of time ................................................................. 31-32

Figure 2.9. Schematic drawing of CuO₆ distorted octahedron adsorbed on SiO₄ tetrahedron ......................................................................................... 35

Figure 2.10. Schematic drawing of CuO₆ distorted octahedron adsorbed on Al(O,OH)₆ octahedron .............................................................................. 36

Figure 2.11. Schematic drawing of Cu(II) complexes on γ-Al₂O₃ and am-SiO₂ ...... 38

Figure 2.12. Types of possible Cu(II) dimer arrangements ...................................... 43

Figure 3.1. X-ray absorption edges and second derivatives of model compounds...... 52

Figure 3.2. EXAFS and Fourier transforms of model compounds .......................... 53
Figure 3.3. Cu uptake on γ-Al₂O₃ and am-SiO₂ as a function of total Cu(II) concentration and pH ................................................................. 58

Figure 3.4. Relative degrees of saturation of initial and final solution conditions of XAFS samples with respect to Cu(OH)₂ and CuO precipitation........................................ 60

Figure 3.5. X-ray absorption edges and second derivatives of Cu(II) on γ-Al₂O₃ and am-SiO₂, and α-TiO₂ .................................................................................. 61

Figure 3.6. EXAFS and Fourier transforms of Cu(II) on γ-Al₂O₃ and am-SiO₂, and α-TiO₂ .................................................................................. 62

Figure 4.1. The bipy molecule........................................................................ 69

Figure 4.2. Sorption of bipy on am-SiO₂ ............................................................ 73

Figure 4.3. FTIR spectra of BSiO₂ and bipy (aq) .............................................. 75

Figure 4.4. FTIR spectra of BAl₂O₃ and bipy (aq) ............................................ 76

Figure 4.5. FTIR spectra of Cu(II)-bipy₁ (aq) and Cu(II)-bipy₂ (aq) ................. 78

Figure 4.6. FTIR spectra of Cu/bipy/solid samples .......................................... 80

Figure 5.1. The bipy molecule........................................................................ 85

Figure 5.2. Uptake of Cu(II) and bipy, and the ratio bipy_{ads}/Cu(II)_{ads} on am-SiO₂ ... 98

Figure 5.3. Uptake of Cu(II) and bipy, and the ratio bipy_{ads}/Cu(II)_{ads} on am-SiO₂ at high concentrations ................................................................. 99

Figure 5.4. Effect of concentration and pH on Cu(II) and bipy sorption on am-SiO₂ .............................................................................................. 100

Figure 5.5. Effect of ionic strength and pH on Cu(II) and bipy sorption on am-SiO₂ .............................................................................................. 101-102

Figure 5.6. EPR spectra of sorption and aqueous samples .................................. 105

Figure 5.7. X-ray absorption edges and second derivatives of Cu/bipy/am-SiO₂ sorption samples compared to those of Cu/am-SiO₂ ............................................. 108
Figure 5.8. X-ray absorption edges and second derivatives of Cu/bipy/am-SiO$_2$ sorption samples and model compounds ................................................................. 109

Figure 5.9. Deconvolution of Cu K-XANES spectrum of sorption sample and Cu(II)-bipy$_1$ (aq) ................................................................. 110

Figure 5.10. EXAFS and Fourier transforms of Cu/bipy/am-SiO$_2$ sorption samples compared to those of Cu/am-SiO$_2$ ................................................................. 111

Figure 5.11. EXAFS and Fourier transforms of Cu/bipy/am-SiO$_2$ sorption samples and model compounds ................................................................. 112

Figure 5.12. Experimental EXAFS spectrum and least square fit of model compound Cu(bipy(NO$_2$)$_2$) ................................................................. 114

Figure 5.13. Least-squares gradient search profile for the coordination number (N) and distance (R) of Si second neighbors in Cu/bipy/SiO$_2$ sorption sample .......... 115

Figure 5.14. Schematic drawing of possible arrangement of Cu(II)-bipy$_1$ bonded to a SiO$_4$ tetrahedron in monodentate mode ................................................................. 120

Figure 5.15. Schematic drawing of the relative sizes of the various sorbate molecules on the am-SiO$_2$ surface ................................................................. 124

Figure 6.1. Uptake of Cu(II) and bipy on $\gamma$-Al$_2$O$_3$ as a function of pH and bipy to Cu(II) ratio ................................................................. 133

Figure 6.2. Effect of concentration on Cu(II) and bipy sorption on $\gamma$-Al$_2$O$_3$ ............ 135

Figure 6.3. Effect of ionic strength on Cu(II) and bipy sorption on $\gamma$-Al$_2$O$_3$ ............ 136

Figure 6.4. EPR spectrum of Cu/bipy/$\gamma$-Al$_2$O$_3$ sorption sample ................................................................. 137

Figure 6.5. X-ray absorption edges and second derivatives of Cu/bipy/$\gamma$-Al$_2$O$_3$ sorption samples ................................................................. 139

Figure 6.6. EXAFS and Fourier transforms of Cu/bipy/$\gamma$-Al$_2$O$_3$ sorption samples .......... 140

Figure 6.7. Comparison of bipy$_{ads}$/Cu(II)$_{ads}$ on $\gamma$-Al$_2$O$_3$ and a-TiO$_2$ ............ 144
CHAPTER I

INTRODUCTION

The goal of this thesis is to examine the effects of both (1) an organic ligand, 2,2'-bipyridine, and (2) choice of oxide surface, on Cu(II) sorption. The Cu(II)/bipy/oxide (bipy designates 2,2'-bipyridine) ternary system was chosen as a simplified example of more complex natural aquatic systems in which metal cations, organic compounds, and mineral surfaces co-exist. In this study, both spectroscopic and solution uptake methods were used to examine the ternary (Cu(II)/bipy/oxide) systems as well as the "parent" binary (Cu(II)/oxide and bipy/oxide) systems. The knowledge gained in the study of the binary systems is used to help interpret results of the ternary system studies.

In natural aquatic and soil systems, metal ions are often complexed or bound by organic matter or mineral surfaces or both. This complexation affects the distribution of metal ions between solid and aqueous phases and their speciation in each. This, in turn, affects the mobility, transport, cycling, bioavailability, and toxicity [1] of these ions. Similarly, the thermodynamic stability and the degradation rates of contaminant organic compounds depend on the composition and structure of aqueous and surface complexes in which they are present.

Because of the importance of such reactions in natural systems, there is considerable research interest in the effect of complexing inorganic and organic ligands on the sorption of metal ions, and in relating their uptake behavior to sorption modes at the molecular scale. In the absence of ligands, cations normally sorb weakly or not at all at low pH and strongly at high pH. This behavior is easily understood as cations competing with H\(^+\) ions for surface sites. Likewise, anion sorption normally exhibits the opposite pH dependence, with weak sorption at high pH and strong sorption at low pH, suggesting that anions compete with OH\(^-\) ions for surface sites. For cation-ligand complexes, it is generally believed that the pH dependence of their sorption should depend on whether it is the cation or ligand that directly bonds to the surface. What is known as a type A ternary surface complex [2] is a complex where the cation is directly bound to the surface and still bound to the ligand, and therefore its sorption is generally believed to have a pH dependence that is "cation-like" [2]. In parallel, a type B ternary surface complex is one where the ligand is directly bound to the surface and still bound to the cation, and therefore its sorption is generally believed to have a pH dependence that is "anion-like" [2].
To better understand the interaction of metal cations, ligands, and solid surfaces requires examination of the dominant reactions involved in surface complex formation. A conceptual model has been developed by Benjamin and Leckie [3] to provide a systematic framework from which to consider the possible sets of reactions. This model is based on the relative stability constants of reactions between the various components (i.e., metal cations, ligands, and solid surface functional groups). Letting M designate the metal cation, L the ligand, and X the surface functional group, the Benjamin-Leckie model considers the following reactions and equilibrium constants:

\[
\begin{align*}
M + L &\rightleftharpoons ML & K_{ML} \\
M + X &\rightleftharpoons MX & K_{MX} \\
L + X &\rightleftharpoons LX & K_{XL} \\
X + ML &\rightleftharpoons X-ML & K_{X-ML} \\
X + ML &\rightleftharpoons X-LM & K_{X-LM}
\end{align*}
\]

Based on this conceptual model, there are eight limiting cases describing sorption of "cation-like" and "anion-like" complexes. Mathematically, however, the equations describing two separate pairs of limiting cases are similar, resulting in six unique cases as follows:

(i) The affinity between the metal ion and the ligand is high \((K_{ML} \text{ large})\), the affinity between metal-ligand complex \((M-L)\) and the solid surface is high, and a bond between the metal center and the Lewis basic sites (electron-pair donating sites) on the solid surface is responsible for sorption \((K_{X-ML} \text{ larger than } K_{X-LM})\). A type A ternary surface sorption complex [2] is formed in this case.

(ii) \(K_{ML}\) is large, but the affinity between the surface and the metal cation is much higher than the affinity between the ligand and the metal cation \((K_{MX} \gg K_{ML})\), therefore the surface functional group should replace the ligand from the coordinating sphere of the metal cation. The resulting surface complex in this case is the same as would have formed in the binary system consisting of only the surface and the metal cations. Either the functionality of the ligand, or steric hindrance may explain why the metal cation is not coordinated to both the surface and the organic ligand at the same time.
(iii) $K_{ML}$ is large and the metal-organic complex has a high affinity for the solid, adsorbing on the solid through bonding between the ligand and the solid ($K_{X-LM}$ larger than $K_{X-ML}$). A type B surface complex is then formed [2].

(iv) The affinity between the metal cation and the organic ligand is low ($K_{ML}$ small), and both the metal cation and the ligand have low affinity for the surface ($K_{X-M}$, $K_{X-L}$, $K_{X-ML}$, and $K_{X-LM}$ are all small). In this case, M doesn't adsorb or complex with L, and L doesn't adsorb, in other words, the various components do not react or influence each other's behavior.

(v) $K_{ML}$ small, but $K_{X-ML}$ large. A type-A surface complex is formed.

(vi) $K_{ML}$ small, but $K_{X-LM}$ large. A type-B surface complex is formed.

Both case (v) and (vi) are conceptual cases where M and L bond together on the surface, even though they are not bonded to each other in the aqueous phase. These two cases are probably not likely in actual systems, and so far there is no experimental evidence to support such an occurrence.

Another possibility considered by Davis and Leckie [4], and Murphy and Zachara [5], which was not included in the Benjamin and Leckie formalism, is a two-step sorption process where first a multi-functional ligand bonds to the surface through one or more functional groups, then a metal cation bonds to a functional group on the "exposed" side of the ligand.

$$XL + M \rightleftharpoons XL-M \quad K_{XL-M} \quad (1.6)$$

In other words, if L is multifunctional and $K_{XL}$ and $K_{ML}$ are large, but $K_{XM}$ is small, then the metal cation is expected to coordinate to the surface only through the ligand and a type-B ternary complex results. Thermodynamically, we can probably not distinguish this $XL-M$ complex from the $X-LM$ produced by reaction 1.5, but the difference could be kinetically significant if the $X-L$ bond is much less labile than the $L-M$ bond. If the complex has the $XL-M$ structure, then, if a ligand functional group on the "exposed" side can bind to either a proton or a metal cation without large changes in $K_{XL}$, sorption of the metal ion would involve competition with protons for these sites. When the relative concentration of the ligand is high, uptake of the metal ion on the surface would then increase as pH increases, i.e., it would be "cation-like." Consequently, type B ternary surface complexation does not necessarily result in "anion-like" uptake behavior.
Conversely, observation of "cation-like" uptake does not require that a metal ion bonds directly to the surface. This type of behavior means that both molecular-scale and macroscopic-scale data are necessary to discern the structure of ternary surface complexes.

Ideally, we would ultimately like to use knowledge of the structure of the ligands and metal-ligand complexes, and of the equilibrium constants for the parent binary aqueous and sorption reactions (Eqs. 1.1-1.3), to predict which of the ternary reactions (Eqs. 1.4-1.6) dominates sorption behavior. This information is important in two contexts: (1) it helps in deciding sorption complex stoichiometry and structure for quasi-thermodynamic modeling, and (2) it is essential in developing absolute reaction rate models. Critical to the development of a predictive scheme is an understanding of the link between the structures of ligand and metal-ligand complexes in solution and the structures of ternary complexes on oxide surfaces. Such links might be established by systematic comparison of ternary systems to their binary counterparts on both macroscopic and microscopic scales. The Cu(II)/bipy/oxide systems studied in this thesis is one of the first such systems to receive systematic study. In the current work, macroscopic information is obtained from uptake studies. Surface spectroscopy is used to provide molecular-scale information, for example, by looking for M-X bonding or L-X bonding, and by verifying that ML exists as one entity on the surface.

Comparison of spectroscopic information with macroscopic uptake results will also help identify factors other than structure and mode of attachment that may affect the stability of ternary surface complexes. These additional factors may include hydrophobic interactions between the ligands, stereochemical effects, electrostatic effects, ligand induced changes in the electronic structure of the metal cation through π-bonding, or some combination of these factors [6, 7]. These additional factors can be important, as Schindler has shown [2], because the stability of ternary surface complexes can be much larger than that predicted from consideration of different ligand substitution reactions. Knowledge of the effect of such factors on the stability of ternary surface complexes is poor. However, ternary complexes in solution in which a metal cation is bonded to two organic ligands have been extensively studied due to considerable interest in such systems in the biology community. These studies show that after the metal cation bonds to the first ligand, the ability of the second ligand to substitute for a water molecule in the coordination sphere of the metal cation can be significantly larger or smaller than in the absence of the first ligand [6, 7]. Such differences can often be explained by the factors listed above. Perhaps these factors are even more significant when a solid surface is present because the surface can be
considered a very large, multifunctional, charged ligand (increasing the potential significance of, for example, stereochemical effects).

Whether these types of ligand-induced differences can explain the sorption behavior of Cu(II) on amorphous SiO$_2$ (am-SiO$_2$) in the presence of bipy, as first studied by Bourg et al. [8], is a question of considerable interest. Bourg et al. [8] suggested that Cu(II)-bipy complexes bond to the am-SiO$_2$ surface through Cu(II) and that the affinity of Cu(II)-bipy complexes for the am-SiO$_2$ surface can be larger than the affinity of Cu(II) for am-SiO$_2$ (Chapter 5 gives a more detailed discussion on the hypothesis that had been put forward to explain these differences in affinity). Another question of interest, is whether this type of ligand-induced difference, if it exists, also affects the sorption of Cu(II) on other oxide surfaces, for example, γ-Al$_2$O$_3$.

To answer these questions, it is necessary to find out whether Cu(II)-bipy complexes also have higher affinity for the γ-Al$_2$O$_3$ surface than does Cu(II). If uptake measurements demonstrate that bipy also enhances Cu sorption on γ-Al$_2$O$_3$, then it strengthens the hypothesis that the same factor is responsible for increasing Cu(II) sorption on oxide surfaces in general. If, however, uptake measurements demonstrate the opposite, that is, if Cu(II)-bipy complexes have lower affinity for γ-Al$_2$O$_3$ than does Cu(II), then it would be necessary to find out what factors cause the difference in sorption behavior on the two oxides. This would entail using techniques that give speciation information for both Cu(II) and bipy on the two oxide surfaces and give bonding mode information for Cu(II) sorption in the presence and absence of bipy. X-ray Absorption Fine Structure (XAFS) spectroscopy, a technique which gives quantitative information on distances between Cu(II) and its coordinating ligands, as well as distances between Cu(II) and the substrate cations (Si or Al), can provide the necessary information on bonding mode in many cases [9] and is, therefore, a principal tool in this work.

As described earlier, the approach of this thesis is to break down the problem into "simple" pieces. Chapters 2 and 3 focus on the sorption mode of Cu(II) on am-SiO$_2$ and γ-Al$_2$O$_3$, respectively. These two chapters give baseline information on the bonding strength of free Cu(II) with these surfaces, the type of Cu(II) sorption complexes, and the pH dependence of Cu(II) sorption. Chapter 4 presents infrared and uptake studies of bipy sorption on am-SiO$_2$ and γ-Al$_2$O$_3$. Infrared studies of bipy adsorbed on am-SiO$_2$ and γ-Al$_2$O$_3$ in the presence of Cu(II) are also presented. These results help to elucidate the role of bipy in the sorption of Cu(II)-bipy complexes.
Chapter 5 presents results of Cu(II) and bipy sorption on the am-SiO₂ surface. The effects of bipy-to-Cu(II) ratio, concentration, and ionic strength on Cu(II)-bipy sorption were studied. Electron paramagnetic resonance was used to help elucidate the speciation of Cu(II), for example, whether Cu(II) is bonded to any bipy, while XAFS, as described earlier, gives information on the bonding mode and complex geometry.

Chapter 6 presents results of Cu(II) and bipy sorption on γ-Al₂O₃. The differences between Cu(II) sorption on am-SiO₂ and γ-Al₂O₃, as found in Chapter 2 and 3, are found to manifest themselves in the sorption of Cu(II)-bipy complexes as well.
CHAPTER II

XAFS Spectroscopy Study of Cu(II) Sorption on Amorphous SiO₂ and γ-Al₂O₃: Effect of Substrate and Time on Sorption Complexes

2.1. INTRODUCTION

The sorption of metal cations on oxide surfaces is a major factor in controlling their mobility in aquatic systems. As more macroscopic information on sorption processes is gathered, there is an increasing need to relate macroscopic observations, such as cation uptake as a function of solution pH, to molecular-scale sorption mechanisms in order to develop surface chemical principles that can be used to predict macroscopic sorption behavior as a function of different system variables. For example, if weakly bound to a particle surface as a fully solvated outer-sphere complex, the cation should be more mobile than if present in a multinuclear surface complex or a precipitate phase. Mechanistic information of this type for various sorbate-sorbent systems has been provided by spectroscopic and imaging methods, for example, X-ray absorption fine structure (XAFS) [10-18], electron paramagnetic resonance (EPR) [19-32], and transmission electron microscopy [18, 33]. However, spectroscopic studies that involve systematic comparison of the effect of substrates on the geometry of sorption complexes for a given cation have focused on intermediate to high surface concentration ranges, where multinuclear complexes and precipitates dominate [11, 12, 14, 17, 18, 34, 35]. Thus, there is relatively little knowledge about the type of sorption complexes formed under conditions in which monomeric, or dimeric surface complexes are predicted to predominate. Information about this coverage range is important because this is likely to be the concentration range in many natural environmental settings. For example, the number of surface ligands coordinated to an adsorbed metal cation M, and the affinity of these surface ligands for M, will influence the cation's mobility and bioavailability in soils. Furthermore, macroscopic uptake and spectroscopic data over wide concentration ranges are essential for definition of sorption reactions and robust quasi-thermodynamic models [36-38].

XAFS spectroscopy studies have suggested that multinuclear surface complexes and clusters most likely "grow" from smaller, isolated surface complexes as surface coverage increases [11]. To more accurately predict possible changes in polymerization of metal-ion complexes at oxide-aqueous solution interfaces, including the formation of
precipitates, as a function of surface coverage and time, it is necessary to understand the effects of different substrates in promoting these changes. For example, do substrates that seem to promote the formation of multinuclear complexes or precipitates bind strongly or weakly to cation monomers? Another question prompted by the XAFS study of O'Day et al. [17] on the mechanism of Co(II) sorption on α-SiO2 and TiO2 (rutile) is what are the effects on sorption products of structural mismatch between surface cation-oxygen polyhedra and the coordination polyhedra of the solution species? To more fully understand surface reactivity and the transformation or growth of surface clusters, we need to compare the types of sorption complexes formed on different metal-oxide surfaces at both low and high surface coverages of a given metal cation and as a function of contact time between aqueous solution and substrate.

In this paper, we report XAFS results for Cu(II) adsorbed on am-SiO2 (amorphous silica) and γ-Al2O3 (γ-alumina). Our main objectives are to determine the structure and mode of sorption of Cu(II) complexes on these two metal oxides at Cu(II) coverages where monomeric or small inner-sphere or outer-sphere sorption complexes should dominate. We shall also attempt to correlate molecular-level data with macroscopic uptake of Cu(II) on these two solids. This study is part of a larger investigation of the co-adsorption of Cu(II) and an organic ligand, 2,2'-bipyridine, on metal-oxide surfaces using both solution chemistry and spectroscopic methods, including XAFS, Fourier-Transform infrared (FTIR), and EPR spectroscopies.

2.1.1. Choice of Systems

Cu(II) was chosen as the sorbate ion in this study because it is present as a trace metal in most natural settings, and may reach higher concentrations as a result of contamination from, for example, acid mine drainage, untreated industrial waste waters, or landfill leachates. Cu is essential for life at low concentrations, but may be toxic at high concentrations. For example, Cu deficiency in wheat may cause reduced grain yield [39]; however, it can inhibit aquatic plant growth at concentrations < 0.03 mg liter⁻¹ [40]. Recent work has indicated that the concentration of Cu is a major regulatory parameter for methane oxidation in methanotrophs [41], a group of bacteria that plays an important role in oxidizing methane to CO2. Methanotrophs can oxidize hazardous organic pollutants, for example, halogenated solvents such as trichloroethylene (TCE), and the availability of Cu affects the efficiency of this process [41]. An understanding of Cu speciation in natural environments and its utilization by microorganisms will help us predict the response of methanotrophs and other microbial populations to environmental perturbations.
Copper is also important for catalysis, both in industry and in abiotic transformations of organic pollutants in heterogeneous systems. Cu supported on silica is used as a catalyst for steam reforming of methanol, methanol dehydrogenation, ester hydrogenolysis, and the liquid phase hydrolysis of acrylonitrile to acrylamide [42]. In aquatic systems, metal cations such as Cu(II) are among the most effective metal catalysts in the hydrolysis of organic compounds [43]. This is because metals like Cu(II) can polarize hydrolyzable groups, causing the groups to become vulnerable to nucleophilic attack.

The substrates chosen for this study were am-SiO₂ and γ-Al₂O₃. The oxides of Al and Si are ubiquitous in geological environments. Oxides and hydroxides of Al are important components of soils, both as individual minerals in tropical environments, and as coatings on aluminosilicate clay minerals in temperate climate zones; whereas α-SiO₂ (quartz) is an important aquifer material. Macroscopically, γ-Al₂O₃ can serve as an analog for aluminum hydroxide, amorphous aluminum oxide gel in natural environment, and aluminol layers in clays.

The structures and surface properties of am-SiO₂ and γ-Al₂O₃ differ significantly. All Si sites in am-SiO₂ are tetrahedral, thus ionizable hydroxyl sites on the surface (generically, SiOH) are all bound to SiO₄ tetrahedra. Aluminum is present in both tetrahedral and octahedral sites in γ-Al₂O₃ [44, 45], thus AlOH sites may be bound in AlO₄ tetrahedra, AlO₆ octahedra, or in sites bridging tetrahedra and octahedra. The surface of am-SiO₂ is a very acidic. Its PZNPC (point of zero net proton charge) is typically between 2 and 3 [46-48], thus, other than at low pH, the predominant ionized surface sites are negative. On the other hand, γ-Al₂O₃ is amphoteric, with a PZNPC between 8 and 9 [49, 50], and the predominant ionized surface sites are positive at low pH and negative at high pH, relative to the PZNPC.

2.2. PREVIOUS WORK

There have been a number of studies of Cu(II) sorption on α-SiO₂ [51, 52], am-SiO₂ [8, 24, 28, 29, 53-55], and γ-Al₂O₃ [25, 29, 51, 56-58], as well as oxyhydroxides and clays containing AlOH groups [23, 27, 30, 59]. There are three general conclusions from these previous studies. (1) Most found that Cu(II) forms inner-sphere complexes with oxide surfaces. (2) At sufficiently low concentrations, Cu(II) forms mononuclear complexes, with monodentate or bidentate coordination to the surface. (3) To a first approximation, Cu(II) bonding on Al-oxide or hydroxide phases is stronger than on SiO₂.

9
Evidence supporting the first and second conclusions comes from electron paramagnetic resonance studies. For example, McBride et al. [30] used EPR to study Cu(II) on oriented gibbsite surfaces and found that at low pH, monomeric square planar Cu(II) adsorbs on the surface with the symmetry axis aligned perpendicular to the gibbsite (001) faces. EPR results also suggest that Cu(II) is equatorially coordinated to at least one hydroxyl or structural oxygen atom on the gibbsite surface. One bonding arrangement that can satisfy both these results (symmetry axis of Cu(II) perpendicular to the gibbsite surface and bonding through the equatorial oxygen) is to have the Cu(II) bonded to edge steps on the (001) face. In their experiments, the amount of monomeric Cu(II) on gibbsite films was very small, probably less than 0.05 μmol m⁻².

In a detailed study of Cu(II) sorption on γ-Al₂O₃, Rudin and Motschi [60] utilized electron nuclear double resonance (ENDOR) and found evidence for the formation of inner-sphere Cu(II) surface complexes of predominantly tetragonal geometry. They estimated the Cu-O-equatorial (Oeq) and Cu-O-axial (Oax) bonds to be 2.0 Å and 2.6 Å, respectively. Moreover, they concluded that Cu(II) bonds to two AlO⁻ groups through equatorial bonds. Simulation of the spectra is complicated because not all parameters needed for the simulation are well known, including the number of interacting nuclei from the surface and spin delocalization [61].

The third generalization, that Cu(II) binding is stronger on alumina than on silica, is supported primarily by arguments based on the EPR studies of the adsorbed Cu(II) [31] and pH dependence of uptake on the two oxides [8, 27, 51, 52, 56, 62].

As discussed earlier, the PZNPC of γ-Al₂O₃ is between 8 and 9 [49, 50]. Generally, the range of pH for 50% sorption of Cu(II) on γ-Al₂O₃ [51, 56] or amorphous alumina [27] is 5 ≤ pH ≤ 6, well below the PZNPC of alumina, indicating that Cu(II) is able to specifically adsorb on surfaces containing AlOH groups, against electrostatic repulsion. The PZNPC of am-SiO₂ is usually around 2 to 3 [46-48]. Yet, the range of pH for 50% sorption of Cu(II) on surfaces containing SiOH groups is 5 ≤ pH ≤ 7.3 [8, 51, 52, 62], where the silica surface is negative. While this does not necessarily indicate that the bonding between Cu(II) and SiOH is weak, it is puzzling that the pH of Cu(II) sorption on silica is not lower, since electrostatic attraction between the negatively charged surface and the positively charged Cu(II) should have made the free energy of sorption on silica more favorable than the free energy of sorption on alumina.
Based on their EPR results for Cu(II) adsorbed on aluminum hydroxides and oxyhydroxides, as well as a comparison with the results of other studies, Clark and McBride [31] suggested that Cu(II) bonds to SiOH groups weakly, perhaps through the axial ligand position. EPR spectroscopy has been used in a variety of experiments to investigate the stereochemistry and ligand environments of Cu(II). Based on a comparative study of the effects of different ligands on the EPR parameters of Cu(II), Kivelson and Neiman [63] concluded that as the covalency of the bond between Cu(II) and the coordinating ligands increases, the parallel g-factor, $g_\parallel$, decreases and the hyperfine splitting $A_\parallel$ increases. Later, Motschi [29] was able to establish an empirically derived, quantitative relationship between $g_\parallel$ and the thermodynamic stability constants for aqueous complexation and sorption reactions of Cu(II), which is given by:

$$\log K = 84 (2.44 - g_\parallel)$$  \hspace{1cm} (2.1)

where 2.44 is the $g_\parallel$ value for Cu(H$_2$O)$_6^{2+}$, and $K$ is the stability constant for the ligand exchange reaction Cu(H$_2$O)$_6^{2+} + L = CuL(H_2O)_5^{2+} + H_2O$. This relationship indicates that as $g_\parallel$ decreases, the stability of the Cu(II)-ligand complex increases. Clark and McBride's suggestion [31] was based on the relative $g_\parallel$ and $A_\parallel$ parameters for Cu(II) adsorbed on different oxides. Table 2.1 gives a summary of EPR results of studies which examined the binding of Cu(II) to SiOH and AIOH groups. Generally, $g_\parallel$ and $A_\parallel$ parameters for Cu(II) adsorbed on surfaces containing AIOH groups are smaller and larger, respectively, than those for Cu(II) adsorbed on surfaces containing SiOH groups. The smaller $g_\parallel$ for Cu(II) on surfaces containing AIOH suggests that AIOH is able to bind to Cu(II) more strongly.

The above hypothesis that Cu(II) binds with different strengths on different oxide adsorbents can be tested further by XAFS spectroscopy. For example, the distance between the Cu adion and an Al or Si atom in the substrate surface ($R_{Cu-(Al,Si)}$) can be used to distinguish inner-sphere from outer-sphere complexes. If $R_{Cu-(Al,Si)}$ is too short to allow a water molecule to intervene between the Cu and the surface site, then Cu must be bonded directly to a surface functional group in an inner-sphere mode. Furthermore, $R_{Cu-Al}$ and $R_{Cu-Si}$ can be used in modeling to determine whether Cu(II) is bonded to the surface in a monodentate or bidentate mode. This can help in determining whether bonding between Cu(II) and AIOH is stronger than bonding between Cu(II) and SiOH.
Table 2.1. Summary of EPR parameters of Cu(II) sorption on surfaces containing SiOH and AIOH groups. Often, the samples may have two different set of $g_\parallel$ and $A_\parallel$ values, indicating the presence of at least two different species on the surface.

Note: if sorption density of Cu(II) is available, it is listed in the bracket immediately below the substrate name in units of μmol m$^{-2}$.

Note: average accuracy of $g_\parallel$ is ±0.01, average accuracy of $A_\parallel$ is ±5 × 10$^{-4}$ cm$^{-1}$ [29].

Note: am-alumina = non-crystalline alumina

<table>
<thead>
<tr>
<th>Surfaces containing AIOH groups</th>
<th>Surfaces containing SiOH groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate</td>
<td>$g_\parallel$</td>
</tr>
<tr>
<td>am-alumina (0.09)</td>
<td>2.32</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$ (0.25)</td>
<td>2.357</td>
</tr>
<tr>
<td>am-alumina (0.54)</td>
<td>2.31-2.32</td>
</tr>
<tr>
<td>am-alumina (0.86)</td>
<td>2.34</td>
</tr>
<tr>
<td>boehmite</td>
<td>2.36-2.37</td>
</tr>
<tr>
<td>gibbsite</td>
<td>2.35</td>
</tr>
</tbody>
</table>

* Detection of giso means the surface complex is mobile in the time-scale of the EPR technique, which is often interpreted as non-specifically adsorbed Cu(II).

# Dipolar broadening indicates that Cu atoms are not in magnetically isolated sites, i.e., polymeric species or precipitates have formed.
2.3. EXPERIMENTAL

2.3.1. Uptake Studies and Sample Preparation

A 0.1 M Cu(NO₃)₂ solution standard from Orion was used as the source of Cu(II). Product specifications and further communication with Orion indicate no additional nitric acid was added to this solution. γ-Al₂O₃ and am-SiO₂ solids were obtained from Degussa under the brand name Aluminum Oxide C and Aerosil 200, respectively. Degussa reports the BET surface areas of these two oxides as 100±15 m²g⁻¹ and 200±25 m²g⁻¹, respectively. However, Schindler et al. [53] determined the surface area of aerosil 200 to be 160 m² g⁻¹. For the purpose of calculating sorption densities in this work, surface area values used for γ-Al₂O₃ and am-SiO₂ are 100 m²g⁻¹ and 160 m²g⁻¹, respectively.

All uptake experiments were performed in a N₂-flooded glove-box. Water used in the sample preparation was Milli-Q doubly-deionized grade. It was boiled under N₂ or sparged with N₂ before being brought into the glove-box.

For pH adjustments, two sources of 0.05 N or 0.1 N NaOH were used: one was prepared from JT Baker "Low-CO₂ dilut-it" volumetric NaOH concentrate; the other was Titrister NaOH from EM Science. Both types of NaOH were estimated to contain ≤ 0.7 x 10⁻³ M CO₂ by their respective manufacturers. Additionally, titration experiments by Van Geen et al. [64] in a separate study confirmed that the CO₂ content of the NaOH concentrate from JT Baker is ≤ 0.7 x 10⁻³ M.

All samples studied in this investigation were prepared by equilibrating 1000 or 2000 m² liter⁻¹ of solid (in the case of am-SiO₂, 6.25 or 12.5 g liter⁻¹; and for γ-Al₂O₃, 10.0 or 20.0 g liter⁻¹) in a background electrolyte of 0.1 M NaNO₃ with selected Cu(II) concentrations. Typical experiments were conducted as follows: the solid was introduced into 19.8 ml of 0.1 M NaNO₃ background electrolyte in a polypropylene centrifuge tube. The mixture was equilibrated for 12-24 hours; mixing was maintained during this period by rotating the centrifuge tube on an end-over-end rotator. The pH of the slurry was measured the following day and adjusted to approximately 4.3 before addition of Cu(II), so as to prevent Cu(II) hydrolysis in the solution before sorption. Cu(II) solution from a 0.01 M stock was then added to the slurry in aliquots of 50 µl or less, maintaining a high rate of stirring on a magnetic stir-plate at all times. After complete addition of Cu(II) solutions, pH was adjusted to the desired values using 0.1 or 0.05 N nitric acid or sodium hydroxide. The samples were then equilibrated for approximately 12-24 hours on an end-over-end rotator. Final pH were measured the next day, at the end of equilibration. The slurry was
then centrifuged until greater than 80% of liquid was removed. Final Cu(II) concentrations in the supernatant were determined by atomic absorption, primarily in graphite-furnace mode, and in several cases on the same samples in flame mode to check for reproducibility and accuracy. Because of differences in sensitivity of different wavelengths to dilute concentrations in AA analysis, our analyses were occasionally made using different wavelengths in both AA modes. This procedure minimized the need for diluting samples, which is a significant source of error in AA analysis.

Samples used for XAFS data collection were all prepared at a pH where greater than 73% of the initial Cu(II) adsorbs on the solids. The combination of high uptake and centrifugation to remove most of the solution minimizes unwanted XAFS contributions from Cu dissolved in the aqueous phase. However, for each sample, Cu K-edge XAFS spectra of the supernatants showed that the Cu absorption edge was too small to interfere with the XAFS spectra of the sorbed Cu.

Sorption samples are named according to the substrate, preceded by the abbreviation Cu/ and followed by the surface Cu concentrations in units of μmol m\(^{-2}\) in brackets. For example, Cu/SiO\(_2\) (0.05) designates a sample with Cu adsorbed on am-SiO\(_2\) with the final sorption density of 0.05 μmol Cu per m\(^2\) of am-SiO\(_2\).

2.3.2. XAFS Data Collection

The resulting wet pastes after centrifugation were mounted in 1-2 mm thick Teflon sample holders sealed with 10 mil Mylar windows for XAFS data collection. Spectra were collected in fluorescence-yield mode, with the sample at 45° to the incident X-ray beam, using either a Stern-Heald-type detector with Soller slits [65] and a Ni filter to minimize elastically scattered X-rays, or a 13-element Ge detector. XAFS data for model compounds were collected in transmission mode. Sources, verification, and XAFS analysis of model compounds are described in Chapter 3. Samples collected in transmission mode were put in 1 mm-thick aluminum frame sample holders protected with Mylar windows, with the sample at 90° to the incident X-ray beam.

XAFS data were collected at the Stanford Synchrotron Radiation Laboratory on wiggler beam lines IV-2 and IV-3 with the storage ring operating at 3.0 GeV and 20-100 mA. A Si(220) double-crystal monochromator was used. Data for all except one sample were measured in unfocused mode. Harmonics were removed by (1) detuning the second monochromator crystal by 50-70% at 10 keV or (2) insertion of a platinum harmonic rejection mirror downstream from the monochromator, in which case no detuning of the
monochromator was necessary. Internal energy calibration was performed using a Cu-metal foil for all the fluorescence samples, with the first inflection point of the K-absorption edge of the Cu foil assigned as 8,980.3 eV. Data were typically collected over the energy range from 8,700 eV to 10,000 eV, with a step size of 0.2 eV in the edge region (8960-9015 eV). When converting data from energy to k-space \( k^2=2m_e(E-E_0)/h^2 \), where \( m_e \) is the mass of the electron, \( E \) is the energy, \( E_0 \) is the energy at \( k=0 \), and \( h \) is the Planck’s constant), \( E_0 \) was defined as 9,000 eV for all samples. Typically, two to three XAFS scans were collected for model compounds and 12 to 24 XAFS scans were collected for sorption samples, all to k-values of 15-16 Å\(^{-1} \), except for low concentration samples, where spectra were collected to \( k = 13 \) Å\(^{-1} \). Individual scans at the beginning and end of XAFS data collection for each sample were examined to determine whether there was any change in the sample with time. All samples except for Cu/SiO\(_2\) (0.03) and Cu/SiO\(_2\) (0.05) showed no detectable changes in the XAFS spectra over time.

EXAFS (Extended X-ray Absorption Fine Structure) data were reduced using the EXAFSPAK software package [66], with phase-shift and amplitude functions derived from model compounds and from theoretical multiple-scattering calculations using FEFF version 6.01a or above [67, 68]. Final fitting of the spectra was done on the normalized, background-subtracted raw data using all shells simultaneously.

Changes in the spectra of Cu/SiO\(_2\) (0.05) as a function of contact time were observed. This sample was prepared and the XAFS spectra were measured in 1993. In preparing this sample, am-SiO\(_2\) was equilibrated with 106 μM Cu(NO\(_3\))\(_2\) solution for 12 hours at a temperature of approximately 26-27°C, then centrifuged and loaded wet into an XAFS sample holder as described above (see Table 2.2 for details). XAFS data were collected using a 13-element Ge detector, with the sample holder in air. XAFS scans for the 1993 sample were collected after two different total contact times, with total contact time defined as the experimental equilibration time between solid and Cu(NO\(_3\))\(_2\) solution prior to centrifugation plus the time in which the sample was in the form of a wet paste after centrifugation and during XAFS data collection. The first data set was collected after a total contact time of approximately 21 to 29 hours (this data set was designated Cu/SiO\(_2\) (0.05)\(_{\text{short}}\)) and the second data set was collected after a total contact time of approximately 79 to 92 hours (this data set was designated Cu/SiO\(_2\) (0.05)\(_{\text{long}}\)). Between the two experiments, the sample holder was wrapped in wet Kimwipes and placed in a Zip-lock bag.
A fresh sample was made and XAFS data collected in 1995 to check for reproducibility of the XAFS spectra as a function of total contact time. In this experiment, variables like the total Cu(II) concentration, pH of equilibration, amount of surface area of am-SiO₂, and ionic strength were chosen as close as possible to those used in the preparation of 1993 Cu/SiO₂ (0.05) sample (see Table 2.2). The 1995 Cu/SiO₂ sample differed from the 1993 sample in the following ways: am-SiO₂ was equilibrated with the Cu(II) solution for 31 hours (rather than 12 hours) at a temperature of 21°C (rather than 26-27°C) before centrifugation and preparation of the XAFS sample. These differences in contact time and equilibration temperature resulted in slightly lower Cu(II) sorption on the surface of the 1995 sample, resulting in a surface coverage of 0.03 μmol m⁻². The error in surface coverage is estimated to be ±0.005 μmol m⁻², so the XAFS work on the 1995 sample is considered a repeat experiment of the 1993 sample. XAFS spectra for Cu/SiO₂ (0.03) were collected with a Lytle fluorescence detector. The sample chamber was continuously flushed with He gas during data collection and consequently the sample holder was not exposed to air. One XAFS scan of this sample was collected after a total contact time of approximately 37.5 hours (this data set is designated Cu/SiO₂ (0.03)short). An additional 20 XAFS scans of this sample were collected over a time-span of approximately 79 to 96 hours total contact time (this data set is designated Cu/SiO₂ (0.03)long). This difference in contact time resulted in differences in the XANES spectra of Cu/SiO₂ (0.03) for the two contact times which are discussed below.

Table 2.2. Experimental conditions for XAFS sorption samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>initial pH</th>
<th>final pH</th>
<th>initial Cu conc.</th>
<th>final Cu conc.</th>
<th>% Cu Uptake</th>
<th>total contact time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Al₂O₃ (=0.007)</td>
<td>4.26</td>
<td>5.71</td>
<td>9.67 μM</td>
<td>&lt; 2.5 μM</td>
<td>&gt;73%</td>
<td>≈ 80-90</td>
</tr>
<tr>
<td>Cu/Al₂O₃ (=0.04)</td>
<td>4.32</td>
<td>5.80</td>
<td>50 μM</td>
<td>&lt; 10.0 μM</td>
<td>&gt;80%</td>
<td>≈ 90-100</td>
</tr>
<tr>
<td>Cu/Al₂O₃ (0.05)</td>
<td>4.53</td>
<td>5.93</td>
<td>103 μM</td>
<td>1.86 μM</td>
<td>98.2%</td>
<td>156-166</td>
</tr>
<tr>
<td>Cu/SiO₂ (0.03)long</td>
<td>4.38</td>
<td>6.65</td>
<td>106 μM</td>
<td>17.5 μM</td>
<td>83.4%</td>
<td>79-96</td>
</tr>
<tr>
<td>Cu/SiO₂ (0.05)short</td>
<td>4.64</td>
<td>6.60</td>
<td>98.8 μM</td>
<td>0.3 μM</td>
<td>99.7%</td>
<td>21-29</td>
</tr>
<tr>
<td>Cu/SiO₂ (0.05)long</td>
<td>4.64</td>
<td>6.60</td>
<td>98.8 μM</td>
<td>0.3 μM</td>
<td>99.7%</td>
<td>79-92</td>
</tr>
</tbody>
</table>
2.4. RESULTS

2.4.1. Uptake Measurements

Figure 2.1 shows Cu(II) uptake on γ-Al₂O₃ and am-SiO₂ as a function of pH. Cu(II) uptake on γ-Al₂O₃ occurs at lower pH than Cu(II) uptake on am-SiO₂ for equivalent solid surface areas and Cu(II) concentration. Table 2.2 summarizes conditions and results for uptake experiments used to produce the XAFS samples.

![Figure 2.1](image)

Figure 2.1. Cu uptake on am-SiO₂ and γ-Al₂O₃ as a function of pH compared with reported pH ranges of the point of zero charge for am-SiO₂ and γ-Al₂O₃. Cu(II) uptake on γ-Al₂O₃: solid circles; Cu(II) uptake on am-SiO₂: empty circles. Solution conditions: 0.0001 M Cu(NO₃)₂, 0.1 M NaNO₃, 2000 m² liter⁻¹ solid.

Sorption of Cu may involve simple adsorption, but formation of multimeric sorption complexes and/or precipitates is also possible. We made a preliminary assessment of the possibility of precipitation of hydroxides, oxides, hydroxide nitrates, and silicates by calculating the degree of saturation of the aqueous phase at both initial and final experimental conditions. For example, for dioptase, the solubility equilibrium equation can be written as

\[
\text{CuSiO}_3 \cdot \text{H}_2\text{O} \ (s) \rightleftharpoons \text{Cu}^{2+} + \text{SiO}_3^{2-} + \text{H}_2\text{O} \quad K_{s0} = -15.75 \quad (2.2)
\]

Ion activity product (IAP) = \{Cu²⁺\}\{SiO₃²⁻\} \quad (2.3)
For $\text{IAP} < K_{s0}, = K_{s0},$ and $> K_{s0},$ the solution is, respectively, undersaturated, in equilibrium, and oversaturated with respect to the particular solid phase [69]. The degree of saturation, $\log (\text{IAP}/K_{s0})$, before and after equilibration was calculated using the speciation program, HYDRAQL [70] and thermodynamic data from Baes and Mesmer [71] for Cu(II) and silicate hydrolysis constants and the Davies equation for approximate activity coefficients. Table 2.3 shows a summary of the $K_{s0}$ values used for the calculation of the four solid precipitates discussed below.

While some Cu silicates are known, thermodynamic data are available only for dioptase ($\text{Cu}_6(\text{Si}_6\text{O}_{18}).6\text{H}_2\text{O}$) [72]. Williams et al. [73] found that for silica with specific surface area 160 to 200 m$^2$ g$^{-1}$, measured solubility range from 0.001 to 0.002 M. The concentration of silica in our experiments was probably lower than this, because equilibrium times never exceeded 48 hours, a time frame much shorter than in the Williams et al. study. Using 0.002 M as an upper limit for total dissolved silicic acid in every case, none of our solutions, either before or after equilibration, were supersaturated with respect to dioptase.

The only solid copper hydroxy nitrate for which some solubility data are available is $\text{Cu(OH)}_{1.5}(\text{NO}_3)_{0.5}$ [74]. Calculations show that all the samples had solution conditions more than an order of magnitude undersaturated with respect to this solid.

For $\text{Cu(OH)}_2$ and CuO, values of $\log (\text{IAP}/K_{s0})$ calculated for both initial and final experimental conditions are summarized in Figure 2.2. All initial solutions were undersaturated with respect to $\text{Cu(OH)}_2$ and CuO. After equilibration, all samples were also undersaturated with respect to both solids, except for $\text{Cu/SiO}_2$ (0.03). This sample was undersaturated with respect to $\text{Cu(OH)}_2$ but slightly supersaturated with respect to CuO.

2.4.2. XAFS Results

The stability constant between $\text{NO}_3^-$ and Cu(II) is $10^{0.4-10^{0.5}}$ [75, 76]. At the conditions of our experiments, it is possible that up to 30% of the Cu(II) is coordinated to one $\text{NO}_3^-$, resulting in at least two species in solution. XAFS, however, cannot easily differentiate nitrogen from oxygen, except by differences in Cu-O and Cu-N distances, and this complexation does not seem to cause any difference in the XAFS spectra of the samples.
Table 2.3. Solubility product $K_{sp}$ for Cu precipitates that might form in the experiments.

(a) Dioptase $(\text{Cu}_6(\text{Si}_6\text{O}_{18}).6\text{H}_2\text{O})$

\[
\text{CuSiO}_3\cdot\text{H}_2\text{O} (s) \rightleftharpoons \text{Cu}^{2+} + \text{SiO}_3^{2-} + \text{H}_2\text{O} \quad \log K_{sp} = -15.75
\]

(b) Cu Hydroxy Nitrate $(\text{Cu(OH)}_{1.5}(\text{NO}_3)_{0.5})$

\[
2(\text{Cu(OH)}_{1.5}(\text{NO}_3)_{0.5}) (s) + 3\text{H}^+ \rightleftharpoons 2\text{Cu}^{2+} + \text{NO}_3^- \quad \log K_{sp} = 35.63
\]

(c) Cu(II) Oxide $(\text{CuO})$

\[
\text{CuO} (s) + 2\text{H}^+ \rightleftharpoons \text{Cu}^{2+} + \text{H}_2\text{O} \quad \log K_{sp} = 7.62
\]

(d) Cu Hydroxide $(\text{Cu(OH)}_2)$

\[
(\text{Cu(OH)}_2) (s) + 2\text{H}^+ \rightleftharpoons \text{Cu}^{2+} + 2\text{H}_2\text{O} \quad \log K_{sp} = 8.66
\]

Note: at least two solubility products for Cu(OH)$_2$ are available. $\log K_{sp}$ = 10.31 as reported by Gulens et al. [77] and $\log K_{sp}$ = 8.66 (IUPAC data base, [78]). The value from IUPAC was used for the Cu(OH)$_2$ precipitation calculations.
Figure 2.2. Relative degrees of saturation, log (IAP/Ks0) of initial and final solution conditions of XAFS samples with respect to (a) Cu(OH)₂ and (b) CuO precipitation. Solid circles: initial saturation index. Empty circles: final saturation index.
For the purpose of comparing surface species on am-SiO₂ and γ-Al₂O₃, only XAFS results for these samples that were obtained after a contact time of ≥ 80 hours are used. XAFS spectra collected at ≤ 80 hours contact time are discussed later in this section.

Figure 2.3 shows XANES (X-ray Absorption Near-edge Structure) spectra and second derivatives of the XANES spectra of sorption samples and some model compounds. Sorption samples have X-ray absorption edges characteristic of divalent Cu(II), indicating the oxidation state of Cu on the surface is the same as in aqueous solution. Sorption samples have XANES spectra and derivatives different from those of Cu(NO₃)₂ aqueous solution and Cu(OH)₂ (s). Cu/SiO₂ (0.03)ₐₙₙ and Cu/SiO₂ (0.05)ₐₙₙ have XANES and second derivative spectra similar to those of copper acetate monohydrate, a model compound with isolated dimeric Cu units. Figure 2.4 shows EXAFS and Fourier Transforms (FT) of sorption samples compared with those of model compounds. Quantitative results of EXAFS analysis are given in Table 2.4.

The main EXAFS contributions of all samples are from oxygen atoms at approximately 1.95 Å. Varying both coordination number and Debye-Waller factor, σ², for the first shell in the least-squares fitting led to a coordination number close to 4 for this first shell of oxygens. Debye-Waller factors for axial oxygen atoms are large and no reliable numbers for their coordination number or distances could be obtained. Most samples have features in the FT indicating second neighbors, probably Cu or substrate cation (Al or Si). As found in the model compound study described in Chapter 3, most of the samples have contributions from multiple scattering among Cu and its equatorial oxygens.

For three of the sorption samples on γ-Al₂O₃, Cu/Al₂O₃ (≈ 0.007), Cu/Al₂O₃ (≈ 0.04), and Cu/Al₂O₃ (0.05), filtering and back transforming of the second-shell feature in the FT showed that most of the amplitude is at about k = 6.5 Å⁻¹ (see Figure 2.5 (a) to (c) for experimental data and non-linear least-square fit). This amplitude envelope is characteristic of a light backscatterer like Al or oxygen. Final fitting of the raw data showed that the best fit is with one shell of oxygen at about 1.95 Å, one shell of Al at about 2.8 Å, and a Cu→Oₑq→Oₑq multiple scattering path at ≈ 3.9 Å, which is approximately twice the distance of the Cu-Oₑq shell (≈ 1.95 Å).

For Cu/SiO₂ (0.03), XANES and second derivative spectra of this sample are similar to those of Cu(II) acetate monohydrate, a crystalline model compound with isolated
**Figure 2.3.** (a) Normalized X-ray absorption edges of sorption samples and some model compounds. (b) Second derivatives of XANES features of sorption samples and some model compounds. Note the differences between sorption samples and Cu(NO₃)₂ solution and solid Cu(OH)₂. Spectrum for CuAl₂O₃ (0.04) is similar to that of CuAl₂O₃ (0.05) and is not shown. Note the significant difference between Cu(II) sorbed on am-SiO₂ and Cu(II) sorbed on γ-Al₂O₃, for example, in the differences of the positions of the first inflection points of the edges, which are the zero-points in the second derivatives.
Figure 2.4. (a) Normalized, background-subtracted EXAFS spectra weighted by $k^3$ of Cu(II) sorbed on am-SiO$_2$ and $\gamma$-Al$_2$O$_3$ compared to spectra for copper nitrate solution (10 mM, pH 4.9), crystalline copper acetate monohydrate and Cu(OH)$_2$(s). (b) Radial structure functions (RSFs) produced by forward Fourier transforms of spectra of sorption samples and model compounds shown in (a). The Fourier transforms are not corrected for backscatterer phase shift ($\Delta$). Spectrum for Cu/Al$_2$O$_3$ (=0.04) is similar to that of Cu/Al$_2$O$_3$ (0.05) and is not shown.
Table 2.4. EXAFS results of Cu/SiO₂ and Cu/Al₂O₃. Cu-O-O MS refers to Cu--equatorial oxygen--equatorial oxygen multiple scattering path. N = coordination number, R = distance of the atoms, and σ² = Debye-Waller factor. * denotes parameters fixed during final fitting. Estimated standard deviations of the least square fitting routine are given in parentheses below the actual values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu-O</th>
<th>Cu-Cu</th>
<th>Cu-O-O MS</th>
<th>Cu-Al or Cu-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>R(Å)</td>
<td>σ²(Å²)</td>
<td>N</td>
</tr>
<tr>
<td>Cu/Al₂O₃ (0.007)</td>
<td>3.3</td>
<td>1.94</td>
<td>0.0024</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>(0.4)</td>
<td>(0.004)</td>
<td>(0.0009)</td>
<td>(5.3)</td>
</tr>
<tr>
<td>Cu/Al₂O₃ (=0.04)</td>
<td>3.9</td>
<td>1.94</td>
<td>0.0032</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>(0.2)</td>
<td>(0.004)</td>
<td>(0.0005)</td>
<td>(3.8)</td>
</tr>
<tr>
<td>Cu/Al₂O₃ (0.05)</td>
<td>4.2</td>
<td>1.95</td>
<td>0.0044</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>(0.2)</td>
<td>(0.003)</td>
<td>(0.0003)</td>
<td>(2.1)</td>
</tr>
<tr>
<td>Cu/SiO₂ (0.03)long</td>
<td>3.8</td>
<td>1.97</td>
<td>0.0028</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>(0.3)</td>
<td>(0.005)</td>
<td>(0.0005)</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Cu/SiO₂ (0.05)short</td>
<td>4.2</td>
<td>1.94</td>
<td>0.0047</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>(0.3)</td>
<td>(0.005)</td>
<td>(0.0005)</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Cu/SiO₂ (0.05)long</td>
<td>4.4</td>
<td>1.95</td>
<td>0.0047</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>(0.3)</td>
<td>(0.005)</td>
<td>(0.0006)</td>
<td>(0.1)</td>
</tr>
</tbody>
</table>
Figure 2.5. (a-c) Sample Cu/Al₂O₃ (0.05) (a) Experimental EXAFS spectrum (solid) and non-linear least squares fit (dashed). (b) Radial structure functions (RSFs) (solid) and non-linear least square fit (dashed). The labels indicate approximate positions of the backscatterers. The label Cu-O-O MS indicates a peak in the RSFs which is attributed to Cu→equatorial oxygen→equatorial oxygen multiple scattering. (c) Filtered experimental EXAFS spectrum (solid) and non-linear least-squares fits (dashed) of second RSF peak (labeled Al in (b)). The filtered spectrum has maximum amplitude envelope at approximately $k = 6.5 - 7 \text{ Å}^{-1}$, typical of a lighter element like Al. The fit of the filtered spectrum is not perfect because there are overlaps among the RSF peaks and the filtering process cannot isolate them completely.
Figure 2.5. (d-f) Cu/SiO$_2$ (0.05)$_{\text{long}}$. (d) Experimental EXAFS spectrum (solid) and non-linear least squares fit (dashed). (e) RSFs (solid) and non-linear least squares fit (dashed). (f) Filtered experimental EXAFS spectrum (solid) and non-linear least-squares fits (dashed) of second RSF peak (labeled Cu in (e)). The filtered spectrum has maximum amplitude envelope at approximately $k = 9.5$ Å$^{-1}$, typical of a heavier element like Cu.
centrosymmetric dimeric acetate-bridged units of Cu(II), with a Cu-Cu distance of 2.62 Å. These similarities lend evidence that dimeric hydroxo- or oxo-bridged Cu(II) units are present on the surface of am-SiO₂, even though the surface concentration is only 0.03 μmol m⁻². EXAFS analysis of this sample shows that it is possible to fit the second-shell feature with either an oxygen or a Cu at approximately 2.6 Å. This is because the photoelectron backscattered by oxygen is about 2π out of phase with that of a Cu backscatterer, both at 2.6 Å distance from the central Cu. However, if the second-shell feature were fit with an oxygen, it would result in an unrealistically low Debye-Waller factor (≈0.0001 Å⁻² for two axial oxygens). In other words, even though the quality of the fit looks reasonable visually and statistically, it is not a result that makes physical sense. Another procedure useful for checking the identity of the second-neighbor backscatterer is to filter and to back-transform the second shell feature in the FT. This procedure shows that the amplitude envelope of the second shell has its maximum at k≈9.5 Å⁻¹, which is characteristic of a heavier element like Cu (see Figure 2.5 (d) to (f)). Thus the second neighbor at approximately 2.6 Å is more likely to be Cu than oxygen, which agrees with our interpretation of the XANES spectra.

Two different quantitative comparisons were made to evaluate the changes in the EXAFS spectra of Cu/SiO₂ (0.05). In the first comparison, all the spectra collected during a total contact time of 21-29 hours were averaged together, designated Cu/SiO₂ (0.05)short in Table 2.4, and compared to the average of all the spectra collected during a total contact time of 79-92 hours, designated Cu/SiO₂ (0.05)long. This procedure allowed us to take advantage of the better data quality obtainable through data averaging. Even though the data were changing with time, the change from 21 to 29 hours was much less than the change from 29 to 79 hours. These two sets of data were analyzed using the same Debye-Waller factors for the Cu(II) shell. Approximately 0.5 Cu second neighbors at a distance of 2.59 Å were found for Cu/SiO₂ (0.05)short, and approximately 0.8 Cu second neighbors at 2.58Å were found for Cu/SiO₂ (0.05)long. Estimates of the precision of least-squares fitting (from EXAFSPAK) for the second-shell coordination numbers are ±0.1 atoms in both cases. The difference in coordination number between Cu/SiO₂ (0.05)short and Cu/SiO₂ (0.05)long is 0.3, which is larger than the ±2σ confidence limit of the least-squares fit. Since precision is the important statistical parameter when comparing results at different time periods for one sample, the difference in coordination number between these two periods (≤ 30 hours contact time and ≥ 79 hours contact time) is statistically significant.
To further evaluate the changes in the coordination environment of Cu/SiO$_2$ (0.05) with time, each scan in the data set was separately processed and analyzed. Qualitative comparison of raw XANES and its derivative is especially useful because very little mathematical manipulation was done in plotting the XANES and derivatives, except for background subtraction, smoothing, and taking the derivatives. Figure 2.6 shows five representative XANES and second derivative spectra collected for Cu/SiO$_2$ (0.05) at different total contact times, indicating a large change of the XANES and second derivative spectra with time.

To obtain a quantitative estimate of the change in species with time, it is desirable to analyze the EXAFS and XANES quantitatively to discern whether there is any trend in the coordination number of the second-shell Cu(II). Unfortunately, it is not possible to obtain a reliable coordination number in the second-shell from a single spectral scan. The best that could be done in this case was to average every two spectral scans that are closest in time, and to fit the EXAFS of the average of two scans. The Debye-Waller factor, $\sigma^2$, for the second shell was fixed at 0.007 Å$^{-2}$ in the analysis of each spectrum. Figure 2.7 shows the coordination number of the second copper shell as a function of time. Because of the significant noise due to the small number of scans that were averaged, the coordination number obtained contains significant error. Nevertheless, there is a general upward trend of the number of Cu(II) in the second shell. Since the number of second-shell Cu(II) is $< 1$, Cu(II) complexes on the surface are most likely a mixture of monomeric and dimeric species. As time increases, the number of second-shell Cu(II) increases, indicating that the fraction of dimeric species increases.

Quantitative analysis of the Cu K-XANES spectra of the sorption samples was accomplished by fitting the spectra to a linear combination of component spectra, using the method described by Pickering et al. [79]. Since the quality of the data is better for the XANES region, it is possible to analyze single spectral scans. Three different components were assumed in the fit: dimeric Cu(II), monomeric Cu(II) in aqueous solution, and monomeric Cu(II) species bonded to an oxide surface. The model for the dimeric species was Cu acetate monohydrate, and the model for monomeric species in aqueous solution was a 0.01 M Cu(NO$_3$)$_2$ at pH 3. Earlier analysis shows that Cu/Al$_2$O$_3$ (0.05) consists of monomeric Cu(II) species bonded to the surface in a monodentate or bidentate fashion. Therefore, the edge spectrum of Cu/Al$_2$O$_3$ (0.05) was assumed to be a "model" of monomeric Cu(II) adsorbed on an oxide surface. Figure 2.8 (a) shows results from fitting individual XANES spectra for the 1993 data, while Figure 2.8(b) shows results from fitting the second derivatives of individual scans for the 1993 data. Both sets of fits show
Figure 2.6. (a) Normalized X-ray absorption edges of Cu/SiO$_2$ (0.05) as a function of time and the XANES of some Cu(II) model compounds. (b) Derivatives of XANES features of Cu/SiO$_2$ (0.05) as a function of time and the derivative spectra of some Cu(II) model compounds. Note that at short total contact time, there are two maxima in the derivatives (~8989 eV and ~8992 eV) and as time increases, the maximum at ~8992 eV decreases significantly.
that, within experimental errors, the contribution of dimeric species to the overall XANES spectra increases with time, while the contribution of monomeric species adsorbed on an oxide surface decreases with time, and the contribution of solution phase monomeric species to the spectra is negligible. These results agree with the change in the second-shell coordination number of Cu(II) as a function of time as obtained from fitting the EXAFS.

As mentioned earlier, XAFS data on freshly prepared Cu/SiO₂ (0.03) samples were collected again in 1995. Figures 2.8(c) and 2.8(d) show analyses of the individual XANES spectra of Cu/SiO₂ (0.03) as a function of time. There are again trends of increasing dimeric species and decreasing monomeric species bonded to the am-SiO₂ surface as a function of time.

Figure 2.7. Change in coordination number in the second copper shell of Cu/SiO₂ (0.05) as a function of time using coordination numbers obtained by quantitative analysis of EXAFS of the average of every two scans.
Figure 2.8. Trends in dimeric versus monomeric Cu(II) species on the am-SiO₂ surface as a function of time resulting from an analysis of the edges and derivatives as a sum of component of species. (a) Cu/SiO₂ (0.05), results of fitting the edges. (b) Cu/SiO₂ (0.05), results of fitting the derivatives. Note that the general trends are the same as those obtained by fitting the edges. Both sets of fits show that the contribution of dimeric Cu(II) species to the overall XANES spectra increases with time, while the contribution of monomeric Cu(II) species adsorbed on the oxide surface decreases with time. The contribution of solution phase monomeric Cu(II) species, using the Cu(NO₃)₂ solution as a model, to the spectra is negligible. (c) Cu/SiO₂ (0.03), results of fitting the edges. (d) Cu/SiO₂ (0.03), results of fitting the derivatives.
Figure 2.8. (c)

% dimeric Cu
% monomeric Cu
% CuNO₃ soln

Total from datfit of edges
time (hours)
DISCUSSION

2.5.1. Cu(II)-Surface Interaction based on Polyhedral Approach

We can use quantitative results from XAFS analysis of our sorption samples, combined with the polyhedral approach [15, 80] discussed below, to derive plausible models of Cu(II) surface complexes. Equatorial oxygen-oxygen distances in a distorted Cu(II)O$_6$ octahedron are approximately 2.8 Å, while O-O edge distances of AlO$_6$ octahedra in γ-Al$_2$O$_3$ range from 2.69 to 2.90 Å (the O-O edge distance of AlO$_4$ tetrahedra in γ-Al$_2$O$_3$ is about 2.90 Å) [45]. Using this structural information, the molecular visualization and modeling program Cerius (version 1.6 to 2.0) was employed to visualize and to constrain possible types of Cu(II) sorption complexes on the am-SiO$_2$ and γ-Al$_2$O$_3$ surfaces.

Based on this modeling, if Cu(II)O$_6$ \(^1\) bonds to oxygens or hydroxyl groups on the γ-Al$_2$O$_3$ surface in corner-sharing, monodentate mode (Figure 2.9a), it would have Cu-Al second-neighbor distances ranging from 2.8 to 3.8 Å. The range of possible monodentate Cu-Al distances is large because Cu can bond through either an equatorial or axial oxygen. Furthermore, it is quite possible that the angle between the distorted Cu(II)O$_6$ octahedron and the surface will vary from complex to complex. If Cu(II)O$_6$ bonds to an Al(O,OH)$_6$ octahedron in edge-sharing, bidentate mode (Figure 2.9b), it would have Cu-Al second-neighbor distances ranging from 2.7 to 2.8 Å. If Cu(II)O$_6$ bonds to an Al(O,OH)$_4$ tetrahedron in edge-sharing, bidentate mode, it would have a Cu-Al second-neighbor distance of approximately 2.1 Å. If Cu(II)O$_6$ bonds to two oxygen on different Al(O,OH)$_6$ octahedra, that is, in corner-sharing, bidentate mode, it would have Cu-Al second neighbor distances ranging from 3.2 to 3.7 Å (Figure 2.9c). A tridentate bonding geometry had been determined to be likely for Co(II) on γ-Al$_2$O$_3$ by Chisholm-Brause [81]. In this bonding configuration, Co(II) could simultaneously bond to one oxygen at the corner of an AlO$_4$ tetrahedron and to two adjacent (bridging) oxygen atoms on AlO$_6$ octahedra, resulting in the face of the Co(II)O$_6$ octahedron being parallel to the surface. Because the Cu(II)O$_6$ octahedron is normally distorted, it does not have three edges of similar lengths on one face, and our modeling results indicate that such a tridentate bonding to the surface would

---

\(^1\) The ligand can be O, OH, or H$_2$O, and we will use O to represent these possible ligands throughout the rest of this chapter.
cause considerable strain in the Cu(II) distorted octahedron. Thus it is a very unlikely attachment geometry.

The surface of \(\gamma\)-Al\(_2\)O\(_3\) depicted in Figure 2.11(a) shows both AlO\(_4\) tetrahedra and AlO\(_6\) octahedra. However, this surface is likely to undergo significant reconstruction when it reacts with water, as suggested in our separate FTIR study of water and hydroxyl vibrational frequencies on the surface of hydrated \(\gamma\)-Al\(_2\)O\(_3\), which indicates the surface has converted to a mixture of gibbsite and bayerite [82], both of which have only Al(O,OH)\(_6\) octahedra and no AlO\(_4\) tetrahedra. This suggested reconstruction is also supported by other evidence cited in Bargar et al. [83]. Thus it is unlikely that Cu(II) is bonded to AlO\(_4\) tetrahedra on the surface of \(\gamma\)-Al\(_2\)O\(_3\) in contact with water. Therefore Cu-Al distances for Cu(II)O\(_6\) bonded to an Al(O,OH)\(_6\) octahedron on the wet \(\gamma\)-Al\(_2\)O\(_3\) surface are predicted to be between \(\approx 2.7\) and \(2.8\) Å for edge-shared bidentate bonding to one Al(O,OH)\(_6\) octahedron, \(\approx 2.8\) to \(3.8\) Å for monodentate (corner-shared) bonding, and \(3.2 - 3.7\) Å for bidentate bonding to the apices of two adjacent Al(O,OH)\(_6\) octahedra (referred to as bridging bidentate bonding). XAFS can distinguish between Cu-Al distances that differ by \(\approx 0.04\) Å for different samples [84] and \(\approx 0.01\) Å for the same sample. If we find Cu-Al distances very close to \(2.8\) Å, however, it will be difficult to make bonding assignments, as this distance represents the maximum expected value for bidentate bonding and the minimum expected value for monodentate bonding. Otherwise, XAFS should be useful in differentiating monodentate vs. bidentate complexes on the hydrated \(\gamma\)-Al\(_2\)O\(_3\) surface.

For the Cu/Al\(_2\)O\(_3\) (0.007), Cu/Al\(_2\)O\(_3\) (0.04), and Cu/Al\(_2\)O\(_3\) (0.05) sorption samples, we find Cu-Al distances of 2.83, 2.82, and 2.83 Å, respectively. These distances are at the borderline between corner-shared, monodentate and edge-shared, bidentate bonding. Therefore, we cannot definitively conclude which sorption mode is the dominant one on the \(\gamma\)-Al\(_2\)O\(_3\) surface. However, even if Cu(II) binds in a monodentate mode, the Cu-Al distance found is at the low end of monodentate bonding, and the Cu(II)O\(_6\) distorted octahedron has to be tilted fairly significantly towards the surface as shown in Figure 2.11(a), indicating that Cu(II) is still strongly bonded to oxygens or hydroxyls on the \(\gamma\)-Al\(_2\)O\(_3\) surface. There is even the possibility of two types of bonds to the surface - an inner-sphere bond to an AlOH group through Cu(II), and a hydrogen bond from one of the water molecules in the coordination sphere of Cu(II) to an oxygen on the surface. Such bonding attachments have been suggested by Ottaviani et al. [25], based on their EPR study of Cu(OH)\(_4\)\(^{2-}\) sorbed on alumina.
Figure 2.9. CuO$_6$ distorted octahedron adsorbed on Al(O,OH)$_6$ octahedron, and the resulting characteristic Cu-Al distances.
Corner-sharing
Monodentate:

Cu-Si = 2.6 - 3.5 Å

Edge-sharing
Bidentate:

Cu-Si = 2.2 - 2.4 Å

Corner-sharing
Bidentate:

Cu-Si = 3.0 - 3.5 Å

Figure 2.10. CuO$_6$ distorted octahedron adsorbed on SiO$_4$ tetrahedron, and the resulting characteristic Cu-Si distances.
For the am-SiO$_2$ surface, O-O edge distances of SiO$_4$ tetrahedra range from 2.58 to 2.67 Å, assuming individual SiO$_4$ tetrahedra in am-SiO$_2$ are similar in size to tetrahedra in α-SiO$_2$ (quartz). Based on this assumption, if Cu(II) bonds to a SiO$_4$ tetrahedron on the am-SiO$_2$ surface in a corner-shared mode (monodentate) (Figure 2.10a), it would have Cu-Si distances ranging from $\approx 2.6$ to 3.5 Å. If Cu(II) bonds to a SiO$_4$ tetrahedron in an edge-shared, bidentate mode (Figure 2.10b), it would have Cu-Si second-neighbor distances ranging from $\approx 2.2$ to 2.4 Å. If a monomeric Cu(II) bonds to the surface in a corner-shared, bridging bidentate mode (Figure 2.10c), then each Cu(II) should have two Si second neighbors at distances in the range 3.0 to 3.5 Å that are different, which should be detectable by XAFS spectroscopy (see, e.g., [15, 81, 84]).

For Cu/SiO$_2$ (0.03) and Cu/SiO$_2$ (0.05), after a contact time of $\approx 80$ hours, an observed Cu-Si distance of $\approx 3.0$ Å indicates that Cu(II) is bonded to the am-SiO$_2$ surface in either corner-shared, monodentate or bridging bidentate mode. As mentioned earlier, Cu(II) bonded in bridging bidentate mode should have two different Cu-Si distances, which should be distinguishable by XAFS spectroscopy. The finding of only one Cu-Si distance, therefore, suggests that Cu(II) on the surface is sorbed in a monodentate mode.

The presence of Cu(II) second neighbors indicates that the dominant surface species is dimeric, the formation of which is discussed later. If the Cu(II) dimer lies parallel to the surface (each distorted Cu(II)O$_6$ octahedron is bonded to one oxygen on the surface), then each Cu would have one Si second neighbor. If the Cu(II) dimer is perpendicular to the surface (only one Cu(II) in the dimer is directly bonded to the am-SiO$_2$ surface), then each Cu would have 0.5 - 1.0 Si second neighbor. Quantitative analysis of the EXAFS indicates that each Cu(II) in the dimer has approximately one (1±0.4) Si second neighbor, which is permissive for either arrangement. It is worth noting, however, that if the Cu(II) dimers lie parallel to the am-SiO$_2$ surface, then each Cu(II) in the dimer can bond to the surface only in a monodentate mode. Figure 2.11(b) shows one possible way such a dimer can be oriented on the surface.

In summary, Cu(II) is directly bonded to oxygen atoms on the γ-Al$_2$O$_3$ and am-SiO$_2$ surfaces, forming inner-sphere complexes. The Cu-Al distance is consistent with
Figure 2.11. (a) Illustration of possible structures of Cu(II) complexes on γ-Al₂O₃, with an edge-shared, bidentate complex on the left, and a corner-shared, monodentate complex on the right. The γ-Al₂O₃ (111) surface is used in this illustration, where both Al(O,OH)₆ octahedra (gray) and Al(O,OH)₄ tetrahedra (white) are present. (b) Illustration of possible arrangements of a Cu(II) dimer on the am-SiO₂ surface (the α-SiO₂ (100) surface is used in this drawing). In this illustration, the Cu(II) dimer is shown parallel to the surface, and Cu(II) is bonded in a monodentate mode to the surface.
formation of edge-shared, bidentate surface complexes or strongly bound monodentate complexes or a mixture of the two. At the Cu concentrations studied, Cu(II) on γ-Al2O3 is monomeric. For Cu(II) on am-SiO2, edge-shared bidentate bonding can definitely be ruled out based on the Cu-Si distance found (≈ 3.0 Å), which is most consistent with a monodentate sorption mode. However, we cannot definitively rule out bridging bidentate bonding as a possible mode of Cu(II) sorption on am-SiO2 surface. The distorted Cu(II)O6 octahedron sorbed in monodentate mode is not tilted toward the surface, in contrast with Cu(II) sorbed in a monodentate mode on γ-Al2O3. The Cu(II) on the surface is predominantly dimeric at a total contact time ≥ 80 hours.

2.5.2. Structural Mismatch and Dimer Formation

The absence of edge-shared, bidentate bonding between Cu(II)O6 and SiO4 tetrahedron is not unexpected. The significant difference between the equatorial edge O-O distances in the distorted Cu(II)O6 octahedron (2.8 Å) and the SiO4 tetrahedron (=2.6 Å) should cause considerable strain if Cu(II)O6 were to bond in a bidentate mode to the SiO4 tetrahedron on the am-SiO2 surface. Consequently, monodentate or bridging bidentate bonding between Cu(II) and an SiO4 tetrahedron, as indicated by the present study, should be more energetically favorable than edge-shared bidentate bonding. In contrast, the equatorial O-O distances in the distorted Cu(II)O6 octahedron and the O-O edge distances in the Al(O, OH)6 octahedron are similar (2.8 vs. 2.7-2.9 Å), so Cu(II)O6 can bond to Al(O,OH)6 octahedra in either bidentate or monodentate modes without much strain.

Besides stereochemical constraints, electrostatic effects should also play an important role in determining the type of surface complexes formed. Electrostatic repulsion between Si(IV) and Cu(II) should be larger than that between Al(III) and Cu(II). Consequently Cu(II) should prefer a bonding mode in which it is further away from the SiO4 tetrahedron than the Al(O,OH)6 octahedron, resulting in weaker bonding between Cu(II) and the oxygens or hydroxyls of SiO4 tetrahedra on the am-SiO2 surface relative to Cu(II)-(O,OH) bonds on the γ-Al2O3 surface.

The structural differences between am-SiO2 and γ-Al2O3 should correlate with systematic differences in pH_{ads} of Cu(II) observed by earlier workers. Cu(II) uptake on γ-Al2O3 generally occurs at lower pH than on am-SiO2, indicating the ability of Cu(II) ions to displace protons from the surface, and the possibility of stronger bonding between Cu(II) and AlOH groups. This reasoning is in agreement with the finding of stronger bonding between Cu(II) and γ-Al2O3 surface.
The weaker bonding between Cu(II) and SiO₄ resulting from the structural mismatch discussed above may facilitate diffusion of Cu(II) on the am-SiO₂ surface, resulting in the formation of dimers on am-SiO₂. On the γ-Al₂O₃ surface, breakage of the stronger bond between Cu(II) and the Al(O,OH)₆ octahedron should require more energy, which contributes to the stability of monomeric surface Cu(II) complexes on the γ-Al₂O₃ surface.

Another possible physical cause of Cu(II) dimerization is hydrolysis reactions on the surface. James et al. [85] suggested that metal ion sorption on surfaces occurs via a mechanism in which adsorption of the free aquated metal ion is followed by surface hydrolysis of the metal ion. The principal cationic hydrolysis product of Cu(II) is the dimeric species Cu₂(OH)₂²⁺ [71, see p.420]. A likely hydrolysis reaction producing this species is

\[ 2\text{Cu(II)} + 2\text{OH}^- = \text{Cu}_2(\text{OH})_2^{2+} \] (2.4)

Towle et al. [18] showed that an oxide surface cannot promote the growth of a neutral precipitate, or a reaction that does not involve a net change of charge. However, as shown below, mathematically the apparent equilibrium constant for the hydrolysis reaction (2.4) is larger on a negative surface, indicating that a reaction that results in a net decrease in positive charge is more likely to occur on a solid surface with negative charge. Following the approach of Towle et al. [18], the intrinsic equilibrium constant for reaction (2.4) in aqueous solution is:

\[ K = (a_{aq} \text{Cu(II)})^2 \cdot (a_{surf} \text{OH}^-)^2 \] (2.5)

where \(a_{aq}\) is the activity of the ion in the aqueous phase. The activity \(a_{surf}\) of an ion on the surface is:

\[ a_{surf} = a_{aq} \exp(-zF\Psi_{surf}) \] (2.6)

where \(z\) is the charge of the ion, \(F\) is Faraday's constant, and \(\Psi_{surf}\) is the electric field potential at the surface. The apparent equilibrium constant \(K'\) for the hydrolysis reaction (2.4) on a solid surface is therefore:

\[ K' = (a_{surf} \text{Cu(II)})^2 \cdot (a_{surf} \text{OH}^-)^2 = [a_{aq} \text{Cu(II)} \exp(-2F\Psi_{surf})]^2 [a_{aq} \text{OH}^- \exp(F\Psi_{surf})]^2 \]

\[ \Rightarrow K' = K \exp(-2F\Psi_{surf}) \] (2.7)
On a negatively charged surface such as am-SiO$_2$ at pH 6-7, $\Psi_{\text{surf}}$ is negative and consequently $(-2F\Psi_{\text{surf}}) > 0$, $\exp(-2F\Psi_{\text{surf}}) > 1$, and $K' > K$, that is, the apparent equilibrium constant for hydrolysis reaction (2.4) on a negative solid surface is larger than the intrinsic equilibrium constant for this reaction in the aqueous phase (the extent to which $K' > K$, will depend on $\Psi_{\text{surf}}$). In other words, if a particular reaction, whether it is hydrolysis and/or dimerization, has the effect of decreasing the net positive charge on the surface, then that reaction is more likely to occur on a negatively charged surface than in the aqueous phase.

In reaction (2.4), the hydrolysis product is a dimer. Our XAFS results indicate that at after a total contact time $> 80$ hours, a significant proportion of the Cu(II) sorption complexes on the negatively charged am-SiO$_2$ surface is dimers. Therefore, it is not unreasonable to postulate that the dimers on am-SiO$_2$ are hydrolysis products. Unfortunately XAFS does not provide information on the charge of the species nor on the number of hydrogens attached to oxygens. Thus other methods are required to determine whether the surface species formed are Cu$_2$(OH)$_2^{2+}$ or Cu(II) dimers with some other stoichiometry. Other information that can be useful is the exact structure of Cu$_2$(OH)$_2^{2+}$ in aqueous solution, which can potentially be obtained through XAFS. A comparison of the XAFS of the surface dimer to aqueous Cu$_2$(OH)$_2^{2+}$ would also provide useful information.

**2.5.2.1. Detailed Structure of the Cu(II) Dimers on am-SiO$_2$**

Four possible arrangements of Cu(II) dimeric units have been reported in the literature (see [86] for summary). The exact type of dimer structure affects the reactivity of Cu(II) on the surface significantly, which in turn helps determine the effectiveness of Cu(II) in catalysis or the bioavailability of Cu(II) in aquatic environments. We present a brief discussion of the four possible arrangements and the likely candidates for Cu(II) dimers on am-SiO$_2$.

The four types of dimer arrangements are shown in Figure 2.12. The first type of arrangement is referred to as planar monobridged dimer, where the two Cu(II) ions essentially lie "flat". Each Cu(II) ion can be coordinated by 4 to 6 ligands, with one of the ligands bridging the two Cu(II) ions. The second type is called planar double bridged dimer; this arrangement is essentially the same as the first type, but there are two ligand bridges between the Cu(II) ions. Copper in this structure can also be coordinated to 4 to 6 ligands. If this arrangement grows linearly, it will form part of the structure in Cu(OH)$_2$. 
Normalized Cu K-XANES and the second derivative of the XANES spectrum of Cu(II) on am-SiO₂ are distinctly different from those of solid Cu(OH)₂, suggesting that the surface dimers may have a very different structure than in Cu(OH)₂. Furthermore, Cu-Cu distances in Cu/SiO₂ (0.03) and Cu/SiO₂ (0.05) are ≈2.6 Å, which are shorter than those in Cu(OH)₂ by ≈0.35 Å, which confirms that the dimers on am-SiO₂ are distinctly different from the arrangement in Cu(OH)₂. The third possibility, corner-sharing between two Cu(II)-containing square pyramids, can be ruled out, because the Cu-Cu distance in this arrangement should be greater than 3.0 Å. This distance is much greater than the ≈2.6 Å Cu-Cu distance found in the sorption samples. The fourth arrangement also contains square-pyramidal Cu(II) ions. In this arrangement, each Cu(II) ion is bonded to 5 ligands, with the other Cu(II) ion sitting in the position of a 6th ligand. Among these four possible arrangements, the first, second, and fourth are possible, even though the second arrangement may not be very likely.

XANES and second derivative spectral features of Cu(II) dimers on am-SiO₂ are almost identical to those of Cu(II) acetate monohydrate, the most well-known compound having the fourth type of geometry described above. The Cu(II) ion in copper acetate monohydrate is coordinated to 5 oxygens, with two oxygens at an average distance of 1.99 Å, with two are at an average of 1.95 Å, and with the axial oxygen (oxygen associated with the water molecule) at 2.16 Å. The similarity in XANES and second derivative spectra suggests that the structure of the Cu(II) surface complexes on am-SiO₂ is similar to square pyramidal dimeric units in Cu(II) acetate monohydrate. This is important because direct metal-metal bonding in the square pyramidal structure is known to cause the Cu(II) ions to be kinetically unsuitable for any involvement in redox processes [86]. Furthermore, some authors have suggested that multinuclear metal-ion complexes grow from isolated, adsorbed metal adions [11, 12]. If Cu(OH)₂-like multinuclear complexes or precipitates were to grow from these Cu dimers with short Cu-Cu distances, then considerable structural rearrangement would have to occur because of the large difference between the Cu-Cu distance in the dimers and the Cu-Cu distance in a poloymeric structure compatible with that of Cu(OH)₂.
(a) Planar monobridged  
$X = \text{Cl}^-$ and $\text{OH}^-$

(b) Planar double bridged  
$X = \text{OH}^-$, $\text{Cl}_2$, and $\text{Br}^-$

(c) Square pyramidal  
$X = \text{O}$ or $\text{Cl}^-$, $\text{Br}^-$  
Cu-Cu distance $> 3.0$ Å

(d) Square pyramidal  
$X = \text{O}$; $Y = \text{C}$

**Figure 2.12.** Types of possible Cu(II) dimer arrangements. Modified from Figure 30, reference [86].
2.5.3. Observed Changes in the XAFS Spectra of Cu/SiO\(_2\) Samples as a Function of Time

There are several possible explanations for the change in XAFS spectra observed for Cu/SiO\(_2\) (0.03) and Cu/SiO\(_2\) (0.05) after different total contact times. One class of factors is experimental conditions during XAFS data collection. Another possibility is that the changes seen are due to dimerization on the surface with increasing contact time between the solution and the surface.

The following experimental factors could have caused changes in the sample. These include the possibility of CO\(_2\) in the atmosphere reacting with sorbed Cu(II), the gradual loss of water through the Mylar covering, and the X-ray beam itself. Possible changes caused by the X-ray beam seem to be an unlikely cause, based on past experience in XAFS studies of other wet sorption samples (e.g., [15, 17, 83]) in which no changes in the XANES spectra have been observed as a function of time. However, we cannot absolutely rule out this factor as potentially causing the observed increase in the proportion of dimeric species.

The possible diffusion of CO\(_2\) into the sample is not a likely cause of the increase in Cu(II) dimers with time as explained below. The sample paste was sealed in Mylar tape, which was reported to have a CO\(_2\) permeability constant of 7.6 x 10\(^{-10}\) [87] to 4.9 x 10\(^{-9}\) cm\(^3\) (STP) s\(^{-1}\) cm\(^{-2}\) cm atm\(^{-1}\) [88]. Using these values, the maximum amount of CO\(_2\) that could diffuse through the Mylar tape during data collection is estimated to be 10\(^{-9}\) moles\(^{*}\), which is less than the available Cu(II) by more than three orders of magnitude. Thus we do not expect the formation of Cu(II) carbonate to a significant extent. Furthermore, when XAFS data for Cu/SiO\(_2\) (0.03) were collected in 1995, the atmosphere in the sample chamber was controlled by constant flushing with He gas. Yet dimeric Cu(II) species were still found in this experiment, which indicates that diffusion of CO\(_2\) and formation of Cu carbonate species were probably not the causes of dimer formation.

One other potential experimental cause of Cu(II) dimer formation is the loss of water from the sample paste, and the potential corresponding change in pH and/or double-

* Mylar window area = 1cm\(^2\), Mylar thickness = 0.025 cm, time of data collection 65000 seconds, and assuming partial pressure of CO\(_2\) = 10\(^{-3.5}\) atm outside the sample cell, and partial pressure of CO\(_2\) to be negligible inside the cell.
layer interaction between the am-SiO₂ particles. Polymerization ofCu(II) ions might occur if Cu(II) was losing its waters of hydration or if Cu(II) played some role in binding adjacent SiO₂ particles together. The permeability of H₂O through Mylar tape is 6 x 10⁻⁸ [87] to 1.4 x 10⁻⁶ cm³ (STP) s⁻¹ cm⁻² cm atm⁻¹ [89]. Using these values, the maximum amount of H₂O that could diffuse through the Mylar tape during data collection is approximately 10⁻⁶ moles, which is approximately 10⁻⁴ to 10⁻³ times the water content in the sample cell. The loss of such a small amount of water should result in a negligible change in pH. It seems likely that this potential small loss of water on the double-layer interaction should also be negligible.

One possible cause for the observed increase in Cu(II) dimerization is that Cu(II) ions may initially adsorb on am-SiO₂ as monomeric species and diffuse over time on the am-SiO₂ surface to form dimers. Diffusion and dimerization of ions has been observed for Cr(III) adsorbed on hematite by scanning tunneling microscopy [90]. Because of the large difference in water exchange rate of aquated Cu(II) (> 10⁸ s⁻¹) and aquated Cr(III) (= 5 x 10⁻⁷ s⁻¹) [91], the diffusion rate of Cu(II) on an oxide surface is anticipated to be greater than that of Cr(III), assuming that ligand exchange rate in solution is a guide to surface diffusion rates. However, surface diffusion must also involve the breaking and reforming of O-H bonds on the oxide surface, and the energy required for this should be smaller on the am-SiO₂ surface than on the γ-Al₂O₃ surface or the hematite surface, based on consideration of the relative strengths of the Si-O, Al-O, and Fe(III)-O bonds. Thus the dimerization of Cu(II) on the am-SiO₂ surface through a surface diffusion mechanism is not unrealistic.
2.6. CONCLUSIONS

At low surface coverages (0.03-0.05 μmol m⁻²), Cu(II) adsorbs on am-SiO₂ at higher pH than on γ-Al₂O₃. XAFS results show that monomeric species are formed on γ-Al₂O₃, with the Cu-Al distance on γ-Al₂O₃ shorter than the Cu-Si distance on am-SiO₂, suggesting stronger interaction between Cu(II) and AlOH surface functional groups than between Cu(II) and SiOH surface functional groups. Dimeric species are formed on am-SiO₂, even at coverage as low as 0.03 μmol m⁻². The XAFS data for Cu(II) on am-SiO₂ at low coverage was observed to change from spectrum to spectrum with increasing total contact time. Quantitative analysis of the XAFS spectra indicates that the proportion of dimeric Cu(II) species increased during the time-span of data collection. This result has potential implications for future studies of metal cation sorption on surfaces and on the role of kinetics in possible oligomerization reactions on oxide surfaces. Further studies are necessary to determine the exact cause of the increase in dimeric Cu(II) species as function of time.
CHAPTER III

XAFS Study of the Sorption of Copper(II) on Amorphous SiO₂, γ-Al₂O₃, and Anatase at High Sorption Density

3.1. INTRODUCTION

Sorption of metal cations on solid surfaces is important in a variety of contexts, including the mobility of contaminant metal cations in groundwater, the segregation of these metal ions during waste water treatment, and the preparation of industrial catalysts. When multinuclear surface complexes, precipitates, or co-precipitates rather than monomeric complexes of the metal cation form on a mineral surface or catalyst support, the mobility of the cation or the properties of a catalyst may be dramatically changed. This study examines the sorption of aqueous Cu(II) on amorphous SiO₂, γ-Al₂O₃, and anatase (α-TiO₂) at high sorption densities using X-ray absorption fine structure (XAFS) spectroscopy with the objective of determining the effect of these different sorbents on the nature of the Cu(II) sorption complexes. It is part of a larger study of Cu(II) sorption on these oxide surfaces that examines the effect of sorbent type (Chapter 2) and the effect of the organic ligand 2,2' bipyridine (Chapter 5 and 6) on Cu(II) sorption.

Recent X-ray absorption fine structure (XAFS spectroscopy studies of Co(II) and Ni(II) sorption complexes on oxide and clay surfaces have shown that at less than monolayer surface coverages of the metal cation and under solution conditions that are undersaturated with respect to multinuclear cation species or precipitates, metal cations form multinuclear complexes, precipitates, and coprecipitates on these sorbents [11, 14, 16-18, 35, 92]. More specifically, Co(OH)₂-like multinuclear complexes [11, 17, 35] were found on γ-Al₂O₃, α-SiO₂, and kaolinite; a Ni(II)-Al(III)-hydroxide co-precipitate was found on clays and aluminum hydroxide [16, 92]; a Co(II)-Al(III)-hydroxide co-precipitate was found on α-Al₂O₃ [18]; and a Cr(III)-oxyhydroxide precipitate (γ-CrOOH) was found on silica [14]. These precipitates or co-precipitates have structures similar to their hydroxides or oxyhydroxides or to mixed-cation hydroxides (where one of the two types of cations is derived from the sorbate and the other is derived from the sorbent), but the metalₐₗₐₜₐₜₐₗₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜₐₜедьн
Two previous studies of Cu(II) sorption on mineral surfaces, however, suggest that the Cu-Cu distance in Cu(II) dimer sorption complexes can be as much as \( \approx 0.35 \) Å shorter than the Cu-Cu distances in Cu(OH)\(_2\). These results are from a REFLEXAFS (reflection extended X-ray absorption fine structure) spectroscopy and X-ray photoelectron spectroscopy (XPS) study of Cu(II) sorbed on the (0001) surface of muscovite [93], and our earlier study of Cu(II) sorption on amorphous SiO\(_2\) (am-SiO\(_2\)) and \( \gamma \)-Al\(_2\)O\(_3\) (Chapter 2). The difference between the average Cu-Cu distance found in these studies and that in Cu(OH)\(_2\) is significantly larger than the reported differences between Ni-Ni or Co-Co distances in Co(II) and Ni(II) surface sorption complexes and their respective hydroxides [11, 14, 16-18, 35, 92]. These large differences suggest that the geometric arrangement in the hydroxo-bridged Cu(II) dimers is different from the local arrangement in Cu(OH)\(_2\).

A possible reason for this difference may be related to the greater stability of CuO vs. Cu(OH)\(_2\). Cu(II) oxide (CuO), also known as tenorite, is the more stable phase compared to Cu(OH)\(_2\). However, Cu(OH)\(_2\) is the phase that is commonly precipitated from aqueous solution. Schindler et al. [94, 95] showed that this apparent contradiction is because the surface energy of CuO is larger than that of Cu(OH)\(_2\). Consequently, Cu(OH)\(_2\) would become the more stable phase when the particle sizes of CuO and Cu(OH)\(_2\) are small enough such that surface energy is an important contribution to the free energy. With time, however, the precipitated Cu(II) phase grows, and Cu(OH)\(_2\) converts to CuO. Because the kinetics of precipitation in the presence and absence of a solid surface may be significantly different, a CuO-like phase, rather than a Cu(OH)\(_2\)-like phase, may form.

The type of solid sorbent may also have significant effect on the sizes of multinuclear surface complexes and/or precipitates. For example, in our previous study of Cu(II) sorption on am-SiO\(_2\) and \( \gamma \)-Al\(_2\)O\(_3\) at similar low surface coverages (Chapter 2), dimeric Cu(II) species formed on am-SiO\(_2\), while Cu(II) surface complexes on \( \gamma \)-Al\(_2\)O\(_3\) were found to be monomeric. In addition, previous XAFS studies of Co(II) sorption complexes on kaolinite, \( \alpha \)-SiO\(_2\), \( \gamma \)-Al\(_2\)O\(_3\), and rutile at similar sorption densities indicate that the Co(II) cluster sizes on the different sorbents are significantly different [11, 17]. These results suggest that the sorbent plays a significant role in affecting the type of sorption complexes formed.

Further evidence for this substrate effect comes from macroscopic uptake experiments. In their study of the sorption of several trace metals on \( \gamma \)-Al\(_2\)O\(_3\), \( \gamma \)-FeOOH, and \( \alpha \)-SiO\(_2\), Benjamin and Leckie [51] concluded that in the system Cu/\( \alpha \)-SiO\(_2\), Cu(II)
forms a CuO-type solid precipitate, either in the bulk phase or on the surface of α-SiO₂, at a surface concentration as low as 0.005 μmol m⁻². No precipitate formation was suggested for Cu(II) sorbed on γ-Al₂O₃ and γ-FeOOH at similar sorbate to sorbent ratios. This conclusion is based on the observation that the pH of Cu(II) sorption on α-SiO₂ decreases when total Cu(II) concentration increases, i.e., sorption is enhanced by increasing Cu(II) concentration. This result suggests that Cu(II) forms precipitates and/or multinuclear complexes on the silica surface more readily.

If Cu(II) forms precipitates and/or multinuclear complexes more readily on silica surface, then the size of these precipitates and/or multinuclear complexes on silica is potentially larger than those on the γ-Al₂O₃ and γ-FeOOH surfaces. When the surface cluster size becomes sufficiently large, CuO would become more stable than Cu(OH)₂. These macroscopic results suggest that CuO-like precipitates may form on some oxides that favor large Cu(II) surface clusters, whereas Cu(OH)₂-like precipitates may form on other oxides that favor small Cu(II) surface clusters.

One objective of the present study is to determine whether surface multinuclear complexes or precipitates that are formed when Cu(II) adsorbs on oxide surfaces from aqueous solution have a structure similar to that of Cu(OH)₂, CuO, or another Cu(II) phase. A second objective of the project is to determine the effect of substrates, more specifically, the effect three different oxides substrates, am-SiO₂, γ-Al₂O₃, and anatase (a-TiO₂), on the relative sizes and structure of Cu(II) multinuclear complexes or precipitates.

As part of this study, it was necessary to investigate Cu(II)-containing model compounds in detail using XAFS spectroscopy to determine: (1) which backscattering atoms surrounding Cu(II) can be detected and whether their distances can be determined accurately; (2) the range of σ² values for these backscattering atoms; and (3) multiple-scattering paths that tend to be significant for the local environment typical of Cu(II). This type of information is essential in guiding our quantitative analysis of Cu(II) sorption products on oxide surfaces. In the present investigation, we have studied CuO, Cu(OH)₂, dioptase, and Cu(II) acetate monohydrate in detail to provide this information. We have also investigated contributions to the EXAFS frequencies from backscattering of atoms that are ≥ 3.2 Å from Cu, which was not examined in a previous study [96], and which turn out to contribute significantly to the EXAFS.
3.2. EXPERIMENTAL

3.2.1. Uptake Measurements and Sorption Sample Preparation

Solution uptake experiments and XAFS measurements are similar to those described in Chapter 2, except that the Cu(II) concentration used was 0.0016 M. Sorption samples are named according to the substrate, preceded by the abbreviation Cu/, and followed by the surface Cu concentrations in units of μmol m⁻² in brackets. For example, Cu/am-SiO₂ (0.73) designates a sample with Cu adsorbed on am-SiO₂ with the final sorption density of 0.73 μmol Cu per m² of am-SiO₂.

3.2.2. Sources and Verification of Model Compounds

Model compounds for two varieties of crystalline Cu(II) hydroxy silicate, dioptase (Cu₆(Si₆O₁₈)·6H₂O) and shattuckite (Cu₅(SiO₃)₄(OH))₂), used in this study are natural samples from Guchab, Otavi District, Southwest Africa, and Ajo, Arizona, respectively. Three other synthetic model compounds, CuO (mineral name tenorite), Cu(OH)₂ (mineral name spertiniite), and Cu(II) acetate monohydrate ((CH₃CO₂)₂Cu·H₂O) were obtained from Aldrich Chemical Company. Their respective product specifications are CuO: 99.9999%, Aldrich product # 20,313-0; Cu(OH)₂: stabilized, technical grade, Aldrich product # 29,978-7; Cu(II) acetate monohydrate: 99.99+%, Aldrich product # 22,960-1. Both copper(II) oxide and copper(II) hydroxide are referred to by their formulas in this paper.

The identity of these phases was verified by powder X-ray diffraction using a Rigaku diffractometer and Cu Kα radiation. The model compound Cu(OH)₂ has broad XRD peaks, suggesting small particle size or structural disorder. This model compound was treated initially as an unknown during XAFS analysis and the XAFS-derived distances and coordination numbers indicate that the local environment around Cu(II) in Cu(OH)₂ is consistent with that predicted from x-ray crystallography.

Chrysocolla, an amorphous Cu(II) hydroxy silicate, from Inspiration, Gila County, Arizona, was also examined using XAFS spectroscopy. It was crushed in a porcelain mortar, cleaned of visible and magnetic impurities, and size-separated by screening to obtain particles in the -48 +65 mesh (Tyler) range [97]. The clean material contained 28.5% Cu [97]. Comparison of X-ray diffraction and infrared absorption spectra with those reported for chrysocolla verify its identity [97]. Because it is amorphous,
chrysocolla was not used as a model compound. Similarly, shattuckite was not used as a XAFS standard because it has three significantly different Cu sites. The XAFS spectra of chrysocolla and shattuckite were used for qualitative comparison with the spectra of sorption samples to determine whether any Cu(II) hydroxy silicate similar to these phases precipitated in our experiments.

3.3. RESULTS AND DISCUSSION--XAFS STUDY OF MODEL COMPOUNDS

Figure 3.1 shows the XANES spectra and second derivatives of the model compounds studied. Figure 3.2 shows EXAFS spectra and the corresponding partial radial distribution functions (partial RDFs) for the model compounds, as well as fits to these spectra using phase and amplitude parameters calculated using FEFF version 6.01a or FEFF 6.10. Table 3.1 shows a comparison of the interatomic distance obtained from quantitative least-squares fitting of the EXAFS data to those calculated based on crystallographic information. In general, the fit to the experimental data are very good and the interatomic distances obtained agree well. As shown in Table 1, however, the first and second neighbors in some of the model compounds can be detected, while they are not detectable in others. The following discussion examines these fits and relates them to the structures of these model compounds in order to obtain information on the types of neighbors surrounding the Cu(II) central absorber.

3.3.1. Detection of Equatorial and Axial Oxygens in the First Coordination Sphere of Cu

Because of the Jahn-Teller effect, the first coordination shell of Cu(II) is generally a distorted octahedron, with four short bonds to equatorial ligands and two longer bonds to axial ligands. In the four model compounds examined in this study, these first-shell ligands are all oxygens. In the fitting of the EXAFS spectra of these model compounds, the four equatorial oxygens were found to contribute significantly, comprising the main EXAFS oscillations in the spectra. Contributions of the axial oxygens to the EXAFS frequencies, however, are generally minimal due to their very large Debye-Waller factors ($\sigma^2 > 0.02 \, \text{Å}^2$). Additionally, their distances also generally cannot be determined accurately ($> 0.2 \, \text{Å}$ relative to the correct values).
Figure 3.1. (a) Normalized X-ray absorption edges of model compounds. (b) Derivatives of XANES features of some model compounds.
Figure 3.2. (a) Normalized, background-subtracted EXAFS spectra (weighted by $k^3$) of model compounds. (b) Partial radial distribution functions of the corresponding EXAFS spectra. The partial RDFs are not corrected for backscatterer phase shift ($\Delta$). For both (a) and (b): solid lines indicate experimental data and dashed lines indicate non-linear least square fit to the data.
Table 3.1. Results of least square fits of Cu K-EXAFS of model compounds compared to the reported structures. MS, MS3, and MS4 designate Cu→Oeq→Oeq, 3 legged
Table 3.1 (cont). Results of least square fits of model compounds compared to the reported structures.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Reported Structure</th>
<th>Fit Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>R (Å)</td>
</tr>
<tr>
<td>Z(<em>{\text{a}})-Z(</em>{\text{b}})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(II) Acetate Monohydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-O(_{\text{eq}})</td>
<td>4</td>
<td>1.95-1.99</td>
</tr>
<tr>
<td>Cu-O(_{\text{ax}})</td>
<td>1</td>
<td>2.16</td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>1</td>
<td>2.62</td>
</tr>
<tr>
<td>Cu-C</td>
<td>4</td>
<td>2.82-2.91</td>
</tr>
<tr>
<td>Cu-O</td>
<td>4</td>
<td>3.06-3.17</td>
</tr>
<tr>
<td>Cu-MS</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

The only model compound for which the axial oxygen distance could be determined accurately was CuO. From a structural standpoint, this is not unexpected. The structure of CuO is fairly packed, with each oxygen coordinated to six Cu atoms. Each axial oxygen ligand of a Cu atom is held firmly in its position by five other Cu atoms and should have relatively small disorder, hence a small Debye-Waller factor (\(\sigma^2\)), and can be detected by EXAFS. Furthermore, both of the axial oxygens of Cu in CuO are at the same distance from the Cu central absorber (2.78 Å), and their EXAFS frequencies constructively interfere, which enhances their contribution to the overall EXAFS of CuO. In comparison, Cu(OH)\(_2\) has two axial oxygens at different distances (2.36 and 2.92 Å\(^1\)). Additionally, both of these oxygen atoms are coordinated to only three to four Cu atoms and are not held as strongly as the oxygens in CuO. Therefore, they have large \(\sigma^2\) values, and their distances cannot be determined accurately. In dioptase and Cu(II) acetate monohydrate, the axial oxygens of Cu atoms are part of water molecules in the structures that are not bonded to other atoms, and thus are not held strongly, resulting in large \(\sigma^2\) values and a negligible contribution to their respective EXAFS spectra.

\(^1\) The oxygen at 2.92 Å is so far away that it is often considered not directly ligated to Cu, and so the Cu atoms in Cu(OH)\(_2\) is then considered five-coordinated, having square pyramidal geometry. For ease of comparison between different model compounds, we will continue to designate Cu(II) in Cu(OH)\(_2\) to be having distorted octahedral geometry, bearing in mind the weak coordination of the sixth ligand.
3.3.2. Detection of Second-Neighbor and More-Distant Cu Atoms

3.3.2.1. Second shell Cu atoms

Quantitative least-squares fitting of the EXAFS spectra of Cu(OH)$_2$ and dioptase indicates that backscattering from the Cu atoms at 2.95 Å contributes significantly to EXAFS frequencies of these two samples, while backscattering from the other second-shell Cu atoms that are slightly further away (3.34 Å for Cu(OH)$_2$, and 3.15 Å for dioptase) is negligible, due to their large Debye-Waller factors. These findings can be explained post priori by considering the oxygen atoms linking two different Cu(II) ions. For simplicity, Cu(II) ions that are linked by two equatorial oxygens, i.e., sharing an edge formed by two equatorial oxygens, are designated equatorial edge-shared Cu(II), while Cu(II) ions that are linked by one equatorial oxygen and one axial oxygen, are designated axial edge-shared. In Cu(OH)$_2$ and dioptase, the second-shell Cu(II) ions at 2.95 Å are equatorial edge-shared Cu(II) ions. Consequently, they should be held more tightly by the equatorial oxygens and have relatively small $\sigma^2$ values. Thus their distances can be accurately determined. On the other hand, the four second-shell Cu(II) ions at 3.34 Å in Cu(OH)$_2$ and the two second-shell Cu(II) ions at 3.15 Å in dioptase are axial edge-shared Cu(II) ions which are less tightly bound and have large $\sigma^2$ values, rendering their contribution to the overall EXAFS insignificant.

In CuO, two distinct Cu atoms at 2.90 and 3.08 Å were needed to fit the EXAFS spectrum, and the two-peak feature at $R = 2.2$ to 3.2 Å in the partial RDF (uncorrected for phase shift) arise from interference of these two Cu shells. This is because no purely edge-shared Cu atoms are present in CuO—all the shared edges are either axial edges for both Cu(II)O$_6$ distorted octahedra, or an equatorial edge for one distorted octahedron but an axial edge for the adjacent distorted octahedron. The well-packed structure of this mineral results in these second-shell Cu atoms being held strongly, making a significant contribution to the EXAFS spectra. Thus the Cu-Cu (second neighbor) distances in CuO can be determined accurately.

3.3.2.2. Fourth-shell Cu atoms

The distorted edge-shared Cu(II)O$_6$ octahedra in CuO are linked together in two alternating chains. Consequently, each Cu atom has four fourth-shell Cu neighbors at twice the distance of the second-shell Cu neighbors. The Cu atoms in dioptase and Cu(II) acetate monohydrate do not have fourth-shell Cu neighbors. In Cu(OH)$_2$, equatorial edge-sharing CuO$_6$ octahedra form chains along the [100] direction, and every Cu atom has two

56
Cu fourth-shell neighbors at 5.90 Å, which is twice the distance of the Cu second shell neighbors (2.95 Å).

The linear or near-linear arrangement of Cu atoms in Cu(OH)₂ and CuO causes "forward-scattering" or focusing paths which can increase the EXAFS scattering amplitude relative to that predicted by single-scattering theory [84]. In CuO, the peak at approximately 5.5 Å in the phase-shift uncorrected partial RDF can be fitted by Cu→Cu single scattering at 5.80 Å, and 3-legged Cu→Cu→Cu and 4 legged Cu→Cu→Cu→Cu multiple-scattering paths at approximately the same distance. The Cu-Cu (fourth neighbor) distance of the Cu atoms (5.80 Å) in this shell can be determined to an accuracy of ±0.04 Å. In the case of Cu(OH)₂, the peak at R = 5-6 Å in the phase-shift uncorrected partial RDF can also be fitted by a combination of single- and multiple- scattering paths. However, in this case, when the distances of all three paths are varied, the minimum in the least-square fit gives a Cu-Cu (fourth neighbor) distance of 5.80 Å, which is approximately 0.1 Å shorter than the actual Cu-Cu distance and slightly more than the normal error expected in EXAFS analysis.

3.3.3. Si second neighbors

One model compound, dioptase, has four Si second neighbors around Cu atoms at distances of 3.09, 3.14, 3.18, 3.28 Å, respectively. In fitting the second-shell Si distances of Cu(II), we have grouped the 3.14 and 3.18 Å shells together (fitting them as one shell with a coordination number of 2). As shown in Table 3.1, this approach results in two Si shells at 3.17 Å and 3.32 Å. The Si second-neighbor shell at 3.09 Å, however, cannot be fit. Our results generally agrees with those from McKeown's XAFS study of dioptase [96].

3.3.4. Cu→Oeq→Oeq Multiple Scattering

In three model compounds Cu(OH)₂, CuO, and Cu(II) acetate monohydrate, multiple-scattering path among the first-shell equatorial oxygens (Oeq), i.e., the Cu→Oeq→Oeq path, makes a non-negligible contribution to the EXAFS frequencies. The contribution of this path is not large (=1-2%), and it generally does not appear as a single, well-resolved peak in the partial RDF (due to overlapping with other shells, for example, Cu at ≈ 3 Å). However, including this path in the overall fit generally improves the EXAFS fit at low k-values and the fit of the partial RDF between 3 and 4 Å (uncorrected for phase shift).
3.4. RESULTS--SORPTION SAMPLES

3.4.1. Solution Uptake Results

Figure 3.3 shows Cu(II) uptake on γ-Al₂O₃ and am-SiO₂ as a function of pH and total Cu(II) concentrations. As Cu(II) concentration in solution increases, the pH of sorption (pHₐds) of Cu(II) on am-SiO₂ seems to decrease. However, this conclusion is based on only one of the points in the uptake curves. If it is true, however, the decrease in pHₐds as Cu(II) concentration increases is the same trend that Benjamin and Leckie found for Cu(II) sorption on α-SiO₂ [51], and indicates the possibility of precipitate formation on am-SiO₂. On the other hand, as total Cu(II) concentration increases, pHₐds on γ-Al₂O₃ increases.

![Figure 3.3. Cu uptake on am-SiO₂ and γ-Al₂O₃ as a function of total Cu(II) concentration and pH. Background electrolyte is 0.1M NaNO₃ in all samples. The two set of experiments for Cu(II) sorption on γ-Al₂O₃ were conducted at slightly different temperature. Data set for 1.5 mM and 0.1 mM ΣCu were collected at approximately 26-27°C and 21°C respectively.](image)

3.4.2. XAFS Results--Sorption Samples

Table 3.2 summarizes conditions and results for uptake experiments used to produce XAFS samples. Preliminary assessment of the possibility of precipitation of hydroxides, oxides, hydroxide nitrates, and dioptase by calculating the degree of saturation of the aqueous phase at both initial and final experimental conditions, was carried out using procedures same as those discussed in Chapter 2. All samples are undersaturated with
respect to dioptase and Cu(II) hydroxy nitrate. Values of log (IAP/K_{so}) calculated for Cu(OH)_2 and CuO, at both initial and final experimental conditions are summarized in Figure 3.4.

### Table 3.2. Experimental conditions for XAFS sorption samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>initial pH</th>
<th>final pH</th>
<th>initial Cu concentration</th>
<th>final Cu concentration</th>
<th>% Cu Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/γ-Al_2O_3 (0.60)</td>
<td>4.49</td>
<td>6.01</td>
<td>1.23 mM</td>
<td>66.8 μM</td>
<td>94.4%</td>
</tr>
<tr>
<td>Cu/γ-Al_2O_3 (0.98)</td>
<td>4.32</td>
<td>6.46</td>
<td>1.95 mM</td>
<td>28.4 μM</td>
<td>98.4%</td>
</tr>
<tr>
<td>Cu/a-TiO_2 (0.95)</td>
<td>3.60</td>
<td>5.95</td>
<td>0.887 mM</td>
<td>5.15 μM</td>
<td>99.4%</td>
</tr>
<tr>
<td>Cu/am-SiO_2 (0.56)</td>
<td>4.36</td>
<td>6.33</td>
<td>1.28 mM</td>
<td>142 μM</td>
<td>88.5%</td>
</tr>
<tr>
<td>Cu/am-SiO_2 (0.73)</td>
<td>4.63</td>
<td>6.36</td>
<td>1.60 mM</td>
<td>131 μM</td>
<td>91.3%</td>
</tr>
</tbody>
</table>

Normalized Cu X-ray absorption K-edges and their second derivatives for sorption samples, as well as some model compounds, are shown in Figure 3.5. Normalized, background-subtracted EXAFS spectra and corresponding partial RDF of sorption samples are shown in Figure 3.6. Results of quantitative analysis of EXAFS data are shown in Table 3.3. XANES and EXAFS of sorption samples are distinctly different from those of CuO, chrysocolla, shattuckite, and dioptase, indicating these species did not precipitate in the samples, or they form a very minor fraction of the total Cu(II) species.

#### 3.4.2.1. Cu/SiO_2

Qualitative and quantitative results show XAFS spectra for Cu/SiO_2 (0.56) and Cu/SiO_2 (0.73) are similar to each other, and these two sets of XAFS data will be discussed at the same time. Qualitative comparison of XANES and EXAFS features shows that sorption samples have features similar, but not identical to those of Cu(OH)_2, and different from those of CuO.
Figure 3.4. (a) Relative degrees of saturation, log (IAP/Ks₀) of initial and final solution conditions of XAFS samples with respect to Cu(OH)₂ precipitation. Empty circles: initial saturation index. Solid circles: final saturation index. (b) Relative degrees of saturation, log (IAP/Ks₀) of initial and final solution conditions of XAFS samples with respect to CuO precipitation. Empty circles: initial saturation index. Solid circles: final saturation index.
Figure 3.5. (a) Normalized X-ray absorption edges of sorption samples and some model compounds. (b) Derivatives of XANES features of sorption samples and some model compounds.
Figure 3.6. (a) Normalized, background-subtracted EXAFS spectra (weighted by $k^3$) of Cu sorbed to $\gamma$-Al$_2$O$_3$, a-TiO$_2$ and am-SiO$_2$ compared to the spectrum of Cu(NO$_3$)$_2$ aqueous solution. (b) Partial radial distribution functions of the corresponding EXAFS spectra. The partial RDFs are not corrected for backscatterer phase shift ($\Delta$).
Table 3.3. Results of quantitative analysis of EXAFS data. * denotes parameters fixed during fitting.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu-O N</th>
<th>Cu-O R, Å</th>
<th>Cu-O σ²(Å²)</th>
<th>Cu-Al or -Si or -Ti N</th>
<th>Cu-Al or -Si or -Ti R, Å</th>
<th>Cu-Al or -Si or -Ti σ²(Å²)</th>
<th>Cu-Cu N</th>
<th>Cu-Cu R, Å</th>
<th>Cu-Cu σ²(Å²)</th>
<th>Cu-Cu N</th>
<th>Cu-Cu R, Å</th>
<th>Cu-Cu σ²(Å²)</th>
<th>Cu-other N</th>
<th>Cu-other R, Å</th>
<th>Cu-other σ²(Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/γ-Al₂O₃ (0.60)</td>
<td>4</td>
<td>1.95</td>
<td>0.0040</td>
<td>0.8</td>
<td>2.85</td>
<td>0.008</td>
<td>0.3</td>
<td>2.94</td>
<td>0.007</td>
<td>0.3</td>
<td>2.94</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu/γ-Al₂O₃ (0.98)</td>
<td>4</td>
<td>1.95</td>
<td>0.0049</td>
<td></td>
<td></td>
<td></td>
<td>0.7</td>
<td>2.97</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu/a-TiO₂ (0.95)</td>
<td>4</td>
<td>1.95</td>
<td>0.0039</td>
<td>0.5</td>
<td>2.94</td>
<td>0.0057</td>
<td>1.1</td>
<td>3.01</td>
<td>0.013</td>
<td>0.5</td>
<td>3.90</td>
<td>0.005</td>
<td>0.2 Ti</td>
<td>3.70</td>
<td>0.005</td>
</tr>
<tr>
<td>Cu/am-SiO₂ (0.56)</td>
<td>4</td>
<td>1.95</td>
<td>0.0035</td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td>2.96</td>
<td>0.007</td>
<td>1.2</td>
<td>Cu</td>
<td>5.72</td>
<td>0.007</td>
<td>0.2-1.0 Cu</td>
<td>3.29</td>
</tr>
<tr>
<td>Cu/am-SiO₂ (0.73)</td>
<td>4</td>
<td>1.94</td>
<td>0.0033</td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td>2.95</td>
<td>0.007</td>
<td>1.0</td>
<td>Cu</td>
<td>5.73</td>
<td>0.007</td>
<td>0.4-1.1 Cu</td>
<td>3.30</td>
</tr>
</tbody>
</table>
Each sample has a total of three separate shells of Cu neighbors. Two Cu second neighbors at 2.95 Å are found, which is the same as the number of Cu second neighbors at this distance in Cu(OH)$_2$. Comparison of the second peak in the partial RDF of the sorption samples to that of Cu(OH)$_2$ indicates asymmetries in the second shell are more significant in the sorption samples. Quantitative analysis shows that this is due to Cu second neighbors at approximately 3.34 Å, which overlaps the Cu shell at 2.95 Å. The coordination number of Cu second neighbors at approximately 3.3 Å cannot be determined accurately, and ranges from 0.2 to 1.1. The feature at approximately $R \approx 5-6$ Å in the phase-shift uncorrected partial RDF is fitted with approximately one Cu neighbor at approximately 5.72 Å. This distance is much shorter than the X-ray diffraction distance of 5.89 Å in Cu(OH)$_2$. However, as noted earlier, even in crystalline Cu(OH)$_2$, the distance $R$ of fourth-shell Cu is determined only up to ±0.1 Å accuracy, so perhaps the finding of Cu neighbors at 5.72 Å rather than 5.89 Å in the sorption sample is not significant.

3.4.2.2. Cu/γ-Al$_2$O$_3$

Qualitatively, the XANES and EXAFS spectra of these sorption samples are different from those of Cu(OH)$_2$, as well as those of the other model compounds mentioned above. For Cu/γ-Al$_2$O$_3$ (0.60), 0.3 copper second neighbors at a distance of 2.94 Å were found. This Cu-Cu distance is very close to that of 2.95 Å in Cu(OH)$_2$. It is necessary to include aluminum second neighbors in the fit, and approximately one Al second neighbor was found at 2.85 Å.

For the higher concentration sample, Cu/γ-Al$_2$O$_3$ (0.98), 0.7 copper second neighbors at 2.97 Å were fit. Including one Al second neighbor in the fit decreased the statistical error only by a small amount, indicating contribution of the Al atom to the spectrum is not significant.

3.4.2.3. Cu/a-TiO$_2$

For Cu(II) on a-TiO$_2$, two shells of Cu atoms and two shells of Ti atoms were found in the EXAFS analysis. Approximately one Cu second neighbor was found at 3.01 Å; the Cu-Cu distance being approximately 0.06 Å longer than that in Cu(OH)$_2$ or those in the Cu/SiO$_2$ and Cu/γ-Al$_2$O$_3$ samples. Additionally, approximately 0.5 Ti second neighbors at a distance 2.94 Å were found. The Fourier transform of the EXAFS spectrum shows a feature at approximately 3.8 Å, and quantitative analysis shows that two shells, one at 3.7 Å and one at 3.9 Å, contribute to this feature. However, interference
between the 3.70 and 3.90 Å shells results in poor fitting, and the distances of these two shells have errors in the range of 0.1 to 0.2 Å, which is larger than the 0.03 Å error normally estimated for EXAFS data analysis of second neighbor distance [84]. There are also large errors in the coordination number of Cu and Ti neighbors in these two shells. Additionally, the coordination number and \( \sigma^2 \) values of the 3.7 and 3.9 Å shells cannot be varied simultaneously, supporting the observation of significant correlation between these two shells.

3.5. DISCUSSION

3.5.1. Cu/am-SiO\(_2\) Samples

For the two samples of Cu(II) adsorbed on am-SiO\(_2\), the EXAFS-derived Cu-Cu distances (2.95 Å, 3.30 Å, and 5.72 Å) are very close to those in Cu(OH)\(_2\). The detection of Cu at 2.95 Å and 5.72 Å indicates the growth of linear chains of Cu. The number of second-shell Cu neighbors in the sorption sample is the same as that in Cu(OH)\(_2\), while the number of fourth-shell Cu neighbors (=1) in the sorption sample is fewer than that in Cu(OH)\(_2\) (=2). Since the number of second neighbors at 5.72 Å is only 1.0-1.2, the minimum number of Cu in the chain would be four. The detection of Cu at 3.3 Å in the sorption samples indicates the growth of a two-dimensional structure. Unfortunately, it is difficult to detect Cu neighbors in different corrugated layers in a Cu(OH)\(_2\)-like structure, and we cannot determine whether the multinuclear complexes and/or precipitates have three-dimensional structure. The coordination number and distances obtained, and the similarities of the XANES features to those of Cu(OH)\(_2\), however, indicate that a Cu(OH)\(_2\)-like multinuclear complex or precipitate has formed, at least in its two-dimensional structure.

These samples were undersaturated with respect to Cu(OH)\(_2\) and CuO at the beginning and end of the uptake experiments, and still undersaturated with respect to Cu(OH)\(_2\) at the end of equilibration, but oversaturated with respect to CuO. Therefore, the growth of some multinuclear complexes and/or precipitates is not unexpected. Furthermore, the formation of a precipitate phase is consistent with the trend of a decrease in the pH of sorption (pH\(_{ads}\)) as total Cu(II) concentration increases on the surface. As already pointed out, however, the structure of these precipitates are similar to that of Cu(OH)\(_2\) rather than that of CuO. This finding suggests that the cluster sizes of these precipitates are still small enough that Cu(OH)\(_2\) is the more stable phase formed.
An earlier study found Cu(II) dimers formed on am-SiO₂ surface with Cu-Cu distance of 2.6 Å (Chapter 2). However, in this study, where the Cu surface coverage is approximately 10 times higher, the Cu-Cu distance in multinuclear complexes formed on am-SiO₂ is 2.95 Å. Least square fitting results do not indicate the presence of any Cu-Cu correlation at 2.6 Å, which could mean that dimeric Cu species does not exist at this higher surface coverages, or they form such a minority of the total species that they cannot be detected. The pH of preparation for the higher surface coverage samples in this study (pH = 6.3) is slightly lower than the pH of preparation for the lower surface coverage samples in the earlier study (pH = 6.6), which may also be a factor in affecting the structure of the surface complexes. Future experiments at coverages in between these two studies, i.e., at Cu surface coverages 0.05 μmol m⁻² < Γ < 0.6 μmol m⁻², and at similar pH, may yield some interesting information.

3.5.2. Cu/γ-Al₂O₃ Samples

For the lower concentration Cu(II) sorbed on γ-Al₂O₃ sample, Cu/γ-Al₂O₃ (0.60), least square fitting of the EXAFS data indicates that presence of approximately one Al second neighbor at 2.85 Å. This indicates that the Cu(II) surface complexes is directly bonded to AlOH groups in bidentate or monodentate mode, based on modeling and visualization of surface complexes described in Chapter 2. XAFS analysis also indicates that there are approximately 0.3 Cu second neighbors at 2.94 Å in this sample. The small number of Cu second neighbors indicates that Cu(II) on the surface is either a combination of monomeric and dimeric species, or mostly monomeric coexisting with a small number of multinuclear species. The formation of dimeric or multinuclear species is not predicted based on solution equilibrium since the aqueous solution in equilibrium with the solid is undersaturated with respect to both Cu(OH)₂ and CuO at the beginning and end of the experiment.

The higher concentration Cu(II) on γ-Al₂O₃ sample, Cu/γ-Al₂O₃ (0.98), is undersaturated with respect to Cu(OH)₂ at the beginning and end of the experiment. It is also undersaturated with respect to CuO at the beginning of equilibration, but oversaturated with respect to CuO at the end. XAFS analysis shows the presence of approximately 0.7 Cu second neighbors at 2.97 Å. This may indicate an increase in the proportion of dimeric or multinuclear complexes, versus monomeric species, compared to the lower concentration Cu/γ-Al₂O₃ sample. It is also possible that a small coprecipitate or precipitate, with Cu-Cu distance closer to that in Cu(OH)₂ than CuO, was formed in this sample. Another point worth noting is that if dimers were formed on γ-Al₂O₃, then the
Cu-Cu distance of 2.94 Å is much longer than the Cu-Cu distance observed for dimers that form at much lower surface coverages on am-SiO₂ (Chapter 2), indicating that the dimensions of surface dimers formed are possibly constrained by the structure of the underlying surface structure or by differences in pH of equilibration. The pH of equilibration of this sample (pH = 6.46), however, is not significantly different from the pH of equilibration of the lower coverage Cu/am-SiO₂ samples (pH = 6.60), suggesting that pH is probably not the factor responsible for the differences in the Cu-Cu distance in the dimers.

3.5.3. Cu/a-TiO₂ Sample

For Cu(II) on a-TiO₂, the finding of one Cu second neighbors at 3.01 Å indicates that the surface complexes are predominantly dimeric. The Cu-Cu distance in these dimers is longer than the Cu-Cu distances in CuO or Cu(OH)₂, in the dimers found on γ-Al₂O₃ at similar surface coverages, and in the dimers formed on am-SiO₂ at much lower surface coverages (Chapter 2). This result supports the hypothesis that the substrate has a significant effect on the structure of the sorption complexes formed. The small number of Ti second neighbors (0.5) found at 2.94 Å suggest that at least some of the Cu(II) is bonded directly to a Ti(IV)O₆ distorted octahedron.

3.5.4. Summary and Comparison of to Other Studies

In summary, no CuO-like precipitate was found in any of the sorption samples. The structure of the surface complexes on am-SiO₂ is Cu(OH)₂-like. For Cu/γ-Al₂O₃ and Cu/a-TiO₂ samples, dimeric species or mixtures of precipitates (or coprecipitates) and monomeric species form when Cu(II) adsorbs on the surfaces. The Cu-Cu distance found is similar to that in Cu(OH)₂ for Cu/am-SiO₂ and Cu/γ-Al₂O₃ samples, but is longer than that of Cu(OH)₂ for Cu/a-TiO₂ samples.

Earlier studies by Schéidegger et al. [16, 92] and Towle et al. [18] found the formation of mixed-cation coprecipitates when Co(II) adsorbs on clay minerals, gibbsite, and α-Al₂O₃. In this study, we cannot rule out Cu(II)-Al(III) mixed cation coprecipitates in the Cu/γ-Al₂O₃ samples. However, the small number of Cu second neighbors found (0.3-0.7) at the surface coverages studied indicates that there are still some monomeric species on the surface. For Cu(II) adsorbed on am-SiO₂, it is unlikely that Cu(II) and Si(IV) can form a mixed hydroxide, since Si hydroxide is not a stable phase. We have looked for evidence of formation of Cu(II) silicate species by comparing XAFS spectra of
our samples with the spectra of chrysocolla, diopside, and shattuckite. The differences between the XAFS spectra of the sorption samples and these silicates suggest that Cu(II) silicates are not formed under the conditions of our study.

At similar surface Cu(II) concentrations on the three solids, the number of Cu second neighbors in Cu sorption complexes on γ-Al₂O₃ and a-TiO₂ is significantly smaller than on am-SiO₂, indicating that the cluster size of Cu(II) on am-SiO₂ is significantly larger than those on the other two sorbents. Overall, the finding of larger cluster sizes on am-SiO₂ may suggests that the am-SiO₂ surface promotes the formation of a more ordered arrangement of Cu(OH)₂-like multinuclear complexes or precipitates. Comparison of results from this study with those for Co(II) sorption on ξ-SiO₂ [17], γ-Al₂O₃ [11, 81], r-TiO₂ (rutile) [11, 17] shows that the trends in cluster size observed for Cu(II) sorption complexes are similar to those for Co(II) sorption complexes. Our findings indicate that the type of substrate has a significant effect on the size and type of sorption complexes formed.

3.6. CONCLUSIONS

XAFS analysis of Cu(II) sorbed on am-SiO₂ at 0.56 and 0.73 μmol m⁻² indicates that a Cu(OH)₂-like multinuclear complex or precipitate formed, which agrees with the observed trend of a decrease in pHₐds, as total Cu(II) concentration increases, on am-SiO₂. Sorbed Cu(II) on γ-Al₂O₃, at sorption densities of 0.60 and 0.98 μmol m⁻², is present as a mixture of monomeric, dimeric, and perhaps a small number of multinuclear species. Sorbed Cu(II) on a-TiO₂ is present predominantly as dimeric Cu species. At similar coverages, Cu(II) cluster sizes on am-SiO₂ are significantly larger than those on γ-Al₂O₃ or a-TiO₂, indicating that the substrate has an important effect on the type of Cu(II) sorption complex formed. Another objective of the present study is to determine whether surface multinuclear complexes or precipitates that are formed when Cu(II) adsorbs on oxide surfaces from aqueous solution have a structure similar to that of Cu(OH)₂, CuO, or another Cu(II) phase. The XAFS derived Cu-Cu second neighbor distances for Cu(II) sorbed on all three oxides are closer to that in Cu(OH)₂ than CuO. Qualitative comparison shows that XAFS spectra of Cu(II) sorbed on γ-Al₂O and a-TiO₂ are distinctly different from those of CuO and Cu(OH)₂, while XAFS spectrum of Cu(II) sorbed on am-SiO₂ is different from that of CuO but similar to that of Cu(OH)₂. Therefore both quantitative and qualitative results indicate that the surface multinuclear complexes or precipitates have a structure similar to that of Cu(OH)₂.
CHAPTER IV

Infrared Studies of Sorption of 2,2'-Bipyridine on Amorphous SiO₂ and γ-Al₂O₃ in the Presence and Absence of Copper(II)

4.1. INTRODUCTION

This chapter summarizes some infrared and uptake studies of sorption of 2,2'-bipyridine (bipy) on amorphous SiO₂ (am-SiO₂) and γ-Al₂O₃ in the presence and absence of Cu (II). In the first part of the study, the "parent" binary bipy/solid system is examined by (1) uptake measurements, which give information on the macroscopic uptake behavior of free bipy and (2) Fourier Transform Infrared spectroscopy (FTIR), which provides microscopic-scale information on the sorption mode of free bipy on am-SiO₂ and γ-Al₂O₃. There are several ways bipy can adsorb on oxides such as am-SiO₂ and γ-Al₂O₃ in the absence of Cu(II). These include physisorption, formation of hydrogen bonds with the surface, or chemisorption. In the case of chemisorption, bipy should form a coordinative bond with Lewis acid centers on the surface, since bipy is a weak Lewis base. Knowledge of the sorption mode of bipy would provide insight on the affinity and strength of bonding of bipy to the two oxides in the absence of Cu(II), which is important in our understanding of the ternary system, where both bipy and Cu(II) adsorb on oxide surfaces.

Figure 4.1. The bipy molecule (C₁₀N₂H₈). Dark gray: nitrogen atoms, light gray: carbon atoms bonded to one hydrogen atom each.
In the second part of the study, FTIR was used to study bipy adsorbed on am-SiO$_2$ and γ-Al$_2$O$_3$ in the presence of Cu(II). Results of this part of the study will help determine (1) whether bipy on the surface is still bonded to Cu(II), and in either case, (2) whether bipy forms any direct coordinative bond (inner-sphere sorption) to the surface. Results of this part of the study will be combined with uptake and spectroscopic studies described in Chapter 5 and 6 to elucidate the composition and structure of surface ternary complexes in the Cu(II)/bipy/oxide surface system.

4.2. EXPERIMENTAL

4.2.1. Uptake Measurements and Sorption Sample Preparation

Sorption samples were prepared using methods generally similar to those described in Chapter 2 and 5, and the solids and solutions are the same as described therein. One difference, however, is that sorption experiments for the bipy uptake study were conducted in air, since precipitation of carbonate should not be a problem in the absence of Cu(II).

Sorption samples for spectroscopic studies were prepared in a nitrogen-flooded glove box, using procedures similar to those described in Chapter 2. The slurry containing the solid which had equilibrated with the solution was centrifuged until greater than 80% of the liquid was removed. The resulting wet pastes were dried in the antechamber of the glove-box which contained a beaker of water. The antechamber was pumped to approximately 382 torr (0.5 atmospheric pressure). Since this pressure is much higher than the vapor pressure of water (3.1 x 10^{-2} atm), and there is a continual source of vapor from the beaker of water, this method of drying should ensure that the solid is in equilibrium with an atmosphere saturated with water at least when it was first ready to be put into the infrared spectrometer.

4.2.2. Infrared Data Collection

The infrared spectra were collected on a Perkin-Elmer 1760X spectrometer. Most of the data, which were in the range of 800 cm$^{-1}$ to 4000 cm$^{-1}$, were collected using a narrow band MCT (Mercury Cadmium Telluride) detector manufactured by EG&G Judson. Some data in the range of 400 cm$^{-1}$ to 900 cm$^{-1}$ were collected with a FR-DTGS (Fast Recovery Deuterated Tri Glycerin Sulfate) detector manufactured by Perkin-Elmer. The DTGS detector is good from 400 cm$^{-1}$ to at least 4000 cm$^{-1}$, but it is not as sensitive as the MCT detector for frequencies above 750 cm$^{-1}$.
Sorption samples were recorded as diffuse reflectance spectra, using a diffuse reflectance accessory with the praying-mantis design manufactured by Harrick Scientific Corporation. Finely powdered KBr (Merck, IR spectroscopic grade) was used as a non-absorbing matrix. It was ground in an agate mortar and dried in a desiccator at 70°C under vacuum. Just before data collection, approximately 0.5 g of the dried KBr was mixed very gently with 18-22 mg of sorption sample in an agate mortar; gentle mixing was necessary to ensure that the mixture was not subjected to elevated pressures.

FTIR spectra for aqueous solutions with varying ratios of Cu(II) and bipy were collected in the transmission mode. The concentration of bipy in these aqueous solutions ranged from 40 mM to 200 mM. The window material used was calcium fluoride (CaF₂) and the thickness of the cell was 25 μm. Polypropylene spacers were used in the transmission sample holders for solution samples. Typically 2000 scans were collected and averaged. Data for the solution samples were collected only down to 1000 cm⁻¹ since this was the lower "cutoff" frequency of the CaF₂ window material. When collecting transmission data, a shuttle in the beam was used to allow for alternate collection of data from the sample and the background. In other words, at first one background scan was collected, then one scan of the sample was collected, ratioing out the background scan that had most recently been collected, and so forth. This "shuttling" method gives a more accurate background subtraction, but it could not be implemented when collecting diffuse-reflectance data.

During both transmission and diffuse reflectance IR data collection, the sample compartment in the spectrometer was purged with air which had been dried and cleaned in a CO₂ removal dryer (Carrier and Complete Protection Ltd.). For Diffuse-Reflectance Infrared Fourier Transform (DRIFT) data collection, a single-beam background spectrum of 10,000 scans was recorded after the sample compartment had been well-purged, with only the KBr powder in the sample container, and this spectrum was stored in the background file. Spectra of sorption samples were then recorded in the absorbance mode and were automatically ratioed to the background spectrum. For sorption samples, typically 10,000 scans were collected and averaged.

4.2.3. Infrared Data Analysis

After data collection, the absorbance data were converted to Kubelka-Munk units. The conversion to Kubelka-Munk units is the most widely accepted method to relate scattered radiation intensity to sample concentration [98, 99]. This conversion is necessary
because diffuse reflectance, or scattered radiation, does not follow the Beer-Lambert law as in the case of transmitted radiation.

The next step in the data analysis is to subtract spectra of other components—such as substrate, NO₃⁻, and H₂O, all of which have overlapping absorption frequencies with bipy—from the spectrum of the sorption sample. This subtraction step helps isolate absorption bands specifically related to the interaction of bipy with the oxide surface and/or Cu(II). A similar procedure has been used and described by Yost et al. [100] and Biber and Stumm [101].

The necessity to subtract the infrared absorption of the surface indicates that the surface should still have hydration water on it. The humidity in the air was approximately 70%, which suggests that the solids were coated by approximately five monolayers of water [102]. However, the infrared beam can potentially heat and dry the sample, and it is very difficult to know the temperature on the surface of the solids in the IR beam.

4.2.4. Sample Nomenclature

Bipy sorption samples containing no Cu(II) are named according to the substrate, preceded by the letter B. For example, BSiO₂ designates a sample with bipy adsorbed on am-SiO₂. Sorption samples prepared with Cu(II) present are named according to the substrate, the ratio of total bipy to total Cu(II) (bipytot/Cu(II)tot), which is also equals to the initial ratio of bipy to Cu(II) in the aqueous phase, before any sorption on the solid, and the final surface Cu concentration, or sorption density (Γ). For example, SiO₂ (bipytot/Cuptot = 2; Γ = 0.048 μmol m⁻²) designates a sample prepared with bipytot/Cuptot = 2 on an am-SiO₂ substrate with the final sorption density of Cu equal to 0.048 μmol m⁻².

4.3. RESULTS AND DISCUSSION

4.3.1. Uptake studies

Figure 4.2 shows bipy uptake on am-SiO₂, which is approximately constant at 15% for the pH range 3 < pH < 8. The concentration of bipy was 0.0002 M in this experiment, while solid concentration was 12.5 g liter⁻¹ (2000 m² liter⁻¹). Park et al. [55] found that, for a much higher bipy concentration (0.001 M), bipy sorption on silica gel is also approximately constant, at 27±2%, for the pH range 2 < pH < 8. It is not known whether the sorbate-to-sorbent ratio was higher or lower than in this study since these authors did not report the surface area of the solid they used.
4.2. Sorption of bipy on am-SiO₂. [bipy]=0.0002 M, [NaNO₃]=0.1 M, [solid]=12.5 g liter⁻¹.

4.3.2. FTIR Spectroscopy

Several sorption samples from the uptake study were also examined by FTIR. Frequencies of vibrational bands of bipy on am-SiO₂ and γ-Al₂O₃ compared with several known species in the literature are shown in Table 4.1. Detailed results and interpretive methods for each sample are described separately in sections 4.3.2.1-4.3.2.4. Here we will summarize some information on IR spectra of bipy that has been found by previous authors.

The IR absorption of bipy and metal-bipy complexes has been fairly well-studied. Strukl and Walter [103, 104], as well as Thornton and Watkins [105], have assigned vibrational modes to absorption bands in the IR spectra of bipy and metal-bipy complexes empirically by studying the effects of deuteration and halogen substitutions of the molecule on the IR spectra, as well as by comparing the spectra of bipy to the much more well-studied organic ligands pyridine and biphenyl. These empirical assignments were further substantiated by theoretical calculations of the vibrational frequencies, using the method of normal coordinate analysis [103, 104]. Because of the resonance structure of the aromatic bipy molecule, there is significant mixing between vibrational modes of the aromatic ring and hydrogen bending modes in the compound [103]. Therefore, assignments of the vibrational modes can be made only for the general type of vibrations, and not for individual bonds between atoms in the molecule. In other words, the IR vibrational bands
of bipy are assigned as ring stretches, H in plane bends, etc., instead of a more detailed level of assignment (e.g., stretching between carbon #1 and carbon #2, etc.) that is possible in simpler molecules.

When bipy is coordinated to a hydrogen ion or a metal cation, one of the important changes in its IR spectra is the appearance of new absorption bands. The new vibrational band at approximately 1605 cm\(^{-1}\), in particular, is often used as an indicator of the formation of coordinative bonds between Lewis acid centers on surfaces and bipy [106]. Other changes include shifts in most vibrational frequencies. The change in frequencies upon coordination with a hydrogen or metal cation is not systematic across the spectra, i.e., the change in frequency of some bands is more significant than for others.* Unfortunately as described earlier, it is not possible to assign vibrational bands to individual bonds, and consequently it is not possible to analyze the shifts in frequency for individual bonds.

Since vibrational bands of bipy with various known coordination environments are different, they can be used as a "finger-print" to help identify the type of sorption complexes in the sorption samples, where the environment of bipy is not known. The following sections discuss how this information is used to elucidate the coordination environment of bipy sorbed on am-SiO\(_2\) and \(\gamma\)-Al\(_2\)O\(_3\) prepared under different conditions.

4.3.2.1. Sample BSiO\(_2\)

Figure 4.3 shows the FTIR spectrum of this sample compared to that of bipy (aq). This sample has vibrational bands at 1427, 1467, 1566, and 1593 cm\(^{-1}\), which match those of physisorbed species (with bands at 1423, 1463, and 1563 cm\(^{-1}\)) found by Bagshaw and Cooney in their study of sorption of gas-phase bipy onto oxides [108]. The presence of physisorbed species is in agreement with the lack of pH dependence of bipy sorption on am-SiO\(_2\).

In the Bagshaw and Cooney study, there were also additional IR bands at 1434, 1488, 1590, and 1600 cm\(^{-1}\), as well as additional Raman bands at 1449, and 1576 cm\(^{-1}\),

* This is partly the result of general rules in inorganic chemistry: (1) when a Lewis base forms a bond with a Lewis acid, the immediate adjacent bonds in both the donor and acceptor molecules are lengthened. (2) This, however, causes the next adjacent bonds to be shortened slightly, which then causes the next-next adjacent bonds to be lengthened slightly, and so on and so forth [107].
which were interpreted by the authors as indicating the presence of hydrogen-bonded bipy on the surface. In the current study of sorption of aqueous bipy onto am-SiO₂, a band at 1593 cm⁻¹ was found, which gives some indication that hydrogen-bonded bipy may also be present in this system. The other IR bands which serve as indicators for hydrogen-bonded species, however, were not detected in our study. We also do not have Raman results to substantiate this interpretation. Therefore, the existence of hydrogen-bonded bipy in this sample cannot be confirmed unequivocally.

![FTIR spectra](image)

**Figure 4.3.** FTIR spectra of BSiO₂ and bipy in aqueous solution. The vibrational frequencies of the sorption sample are similar to those of bipy (aq).

### 4.3.2.2. Sample BAl₂O₃

Figure 4.4 shows the FTIR spectrum of this sample. The IR absorption intensity of this sample is very low, indicating that only a small amount of bipy is on the surface. In this sample, two bands that can be detected are at 1448 and 1497 cm⁻¹. These two bands do not match those of physisorbed bipy, or those of H-bonded bipy found in the Bagshaw and Cooney study [108]. Rather, they match those of bipy chemisorbed on γ-Al₂O₃ by forming a coordinative bond with Lewis acid centers on the surface, as can be seen in Table

75
4.1. This result indicates that bipy in BA1₂O₃ is probably also directly coordinated to Lewis acid centers on the surface. However, it is puzzling that the most distinctive lines at 1605 and 1617 cm⁻¹ were not detected for this sample. This is likely the result of interference of the broad water absorption band at approximately 1630 cm⁻¹, which extends to almost to 1580 cm⁻¹. Any bipy absorption near these frequencies are superimposed on a slope, making them hard to detect. Normally the water absorption band can be subtracted out fairly successfully, but because of the extremely strong absorption of water, a slight difference in surface hydration may result in incomplete subtraction of bulk water IR absorption [101].

![FTIR spectra of BA1₂O₃ and bipy (aq).](image)

**Figure 4.4.** FTIR spectra of BA1₂O₃ and bipy (aq). The sorption sample BA1₂O₃ has vibrational frequencies significantly different from those of bipy (aq).

Data in the 1000 to 1400 cm⁻¹ region should also be useful in confirming whether sorbed bipy is directly bonded to Lewis acid centers. However, absorption intensities in this region are low, and they were not detected for this sample.

The coordination of bipy to Lewis acid sites on γ-Al₂O₃ is not unexpected. Lewis acid sites are abundant on γ-Al₂O₃: on dehydrated alumina, for example, it had been
proposed that unsaturated Al(III) ions on the surface are high energy Lewis acid centers [108]. However, on hydrated alumina, the surface of alumina is hydroxylated, and there probably should not be bare Al(III) ions on the surface. On the hydrated alumina surface, the Lewis acid sites are probably those hydroxyl groups that are coordinated to two Al(III) cations, because the Al(III) ions strongly polarize the oxygen atoms in the hydroxyl groups, which in turn, make the hydroxyl groups lose protons more easily, i.e., more acidic [109].

Table 4.1. IR band positions (unit=cm⁻¹) for sorption samples BSiO₂ and BAl₂O₃, compared to those of physisorbed bipy, H-bond (hydrogen-bonded) bipy, and Lewis bipy (bipy coordinated to Lewis acid sites on γ-Al₂O₃ surface) found in the Bagshaw and Cooney study [108].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>IR Frequencies (cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1423</td>
<td>1423</td>
<td>1447</td>
<td>1427</td>
<td>1448</td>
</tr>
<tr>
<td>1463</td>
<td>1464</td>
<td>1496</td>
<td>1467</td>
<td>1497</td>
</tr>
<tr>
<td>1563</td>
<td>1566</td>
<td>1566</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1590</td>
<td></td>
<td>1593</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td></td>
<td>1605</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1617</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3.2.3. Sample Cu/bipy/Al₂O₃

For samples where both Cu(II) and bipy adsorb on the surface, the first goal is to determine whether bipy is physisorbed or coordinated to a metal cation. Transmission spectra of Cu(II) coordinated to one versus two bipy molecules in aqueous solution, Cu(II)-bipy₁ (aq) and Cu(II)-bipy₂ (aq) respectively, were collected for comparison and to aid in interpretation of the spectra of sorption samples, which are shown in Figures 4.5.
Figure 4.5. FTIR spectra of Cu(II)-bipy$_1$ (aq) (solid line) and Cu(II)-bipy$_2$ (aq) (dashed line), (a): in the frequency range 1400-1600 cm$^{-1}$, (b): in the frequency range 1000-1400 cm$^{-1}$.
As found in the Strukl and Walter study [104], bipy coordinated to Cu(II) has substantially different absorption bands than uncoordinated bipy. Frequencies of the vibrational bands of the sorption sample, Cu(II)-bipy complexes in aqueous solution, and two different species identified in the Bagshaw and Cooney study are summarized in Table 4.2.

IR spectra of sorption sample α-Al₂O₃ (bipy\(_{\text{tot}}/\text{Cu}_{\text{tot}} = 2; \Gamma = 0.4 \, \mu\text{mol m}^{-2}\) is shown in Figure 4.6. This sorption sample does not have IR bands that match those of physisorbed bipy or H-bonded bipy. This indicates that, within detection limits, these two species are not significant in the sample. Rather, the sorption sample has clear absorption bands a 1447, 1474, 1498, 1571, 1579, 1606, and 1614 cm\(^{-1}\), which are almost a one-to-one match to both bipy coordinated to Cu(II) or bipy coordinated to Lewis acid sites on γ-Al₂O₃. This indicates that bipy on the γ-Al₂O₃ surface is coordinated to a metal ion or a proton (e.g., from acidic sites on the γ-Al₂O₃ surface). Because of these similarities of the vibrational bands of bipy coordinated to Cu(II) and of bipy coordinated to Lewis acid centers on γ-Al₂O₃, the region 1400 to 1600 cm\(^{-1}\), which has the most intense absorption, is not useful in differentiating which species bipy is coordinated to.

To determine whether bipy on the surface is coordinated to Cu(II) or Lewis acid sites on the surface, it is more useful to examine data in the lower frequency region. Vibrational bands of the two different species of interest, are more different in the frequency region 1000 to 1400 cm\(^{-1}\). It was found that vibrational bands of the sorption sample, especially those from 1100 to 1200 cm\(^{-1}\), match those of aqueous Cu(II)-bipy\(_1\) or Cu(II)-bipy\(_2\) better than those of bipy coordinated to Lewis acid centers on γ-Al₂O₃. This result indicates that bipy on the surface is still bonded to Cu(II).

### 4.3.2.4. Samples Cu/bipy/am-SiO₂

Vibrational frequencies for sorption samples (bipy\(_{\text{tot}}/\text{Cu}_{\text{tot}} = 1; \Gamma = 0.8 \, \mu\text{mol m}^{-2}\) and SiO₂ (bipy\(_{\text{tot}}/\text{Cu}_{\text{tot}} = 2; \Gamma = 0.8 \, \mu\text{mol m}^{-2}\) are reported in Table 4.2. Their spectra are shown in Figure 4.6. As in the case of sample Al₂O₃ (bipy\(_{\text{tot}}/\text{Cu}_{\text{tot}} = 2; \Gamma = 0.4 \, \mu\text{mol m}^{-2}\), there are no bands that correspond with physisorbed or H-bonded bipy, indicating that these two species are not significant. Furthermore, there is almost a one-to-one match for the bands in the region 1400 to 1600 cm\(^{-1}\) to those of bipy coordinated to Cu(II) or those of bipy coordinated to Al(III) reported in the Bagshaw and Cooney study [108]. Data in the 1000 to 1400 cm\(^{-1}\) range are not available because am-SiO₂ absorption is extremely intense from 900 to 1300 cm\(^{-1}\). Even after spectral subtraction, we were not able to examine vibrational bands of bipy in this frequency region.
Figure 4.6(a). FTIR spectra of sorption samples in the frequency range 1400-1600 cm\(^{-1}\). (i) SiO\(_2\) (bipy\(_{\text{tot}}\)/Cu\(_{\text{tot}}\) = 1; \(\Gamma \approx 0.8\ \mu\text{mol m}^{-2}\))—shown in dashed line, (ii) SiO\(_2\) (bipy\(_{\text{tot}}\)/Cu\(_{\text{tot}}\) = 2; \(\Gamma \approx 0.8\ \mu\text{mol m}^{-2}\))—shown in solid line, and (iii) Al\(_2\)O\(_3\) (bipy\(_{\text{tot}}\)/Cu\(_{\text{tot}}\) = 2; \(\Gamma \approx 0.4\ \mu\text{mol m}^{-2}\)).

Figure 4.6(b). FTIR spectrum of Al\(_2\)O\(_3\) (bipy\(_{\text{tot}}\)/Cu\(_{\text{tot}}\) = 2; \(\Gamma \approx 0.4\ \mu\text{mol m}^{-2}\)) in the frequency range 1100-1300 cm\(^{-1}\).
Table 4.2. IR band positions (unit=cm$^{-1}$) for sorption samples SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=1; $\Gamma$ =0.8 $\mu$mol m$^{-2}$), SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=2; $\Gamma$ =0.8 $\mu$mol m$^{-2}$), and Al$_2$O$_3$ (bipy$_{tot}$/Cu$_{tot}$=2; $\Gamma$ =0.8 $\mu$mol m$^{-2}$), compared to those of Cubipy$_1$ (aq) and Cubipy$_2$ (aq), as well as those of physisorbed bipy and Lewis bipy (bipy coordinated to Lewis acid sites on $\gamma$-Al$_2$O$_3$ surface) found in the Bagshaw and Cooney study [108]. NG=values not given in [108]; NA=a peak around this position can be seen in the spectra, but its exact frequency cannot be resolved.

<table>
<thead>
<tr>
<th>physisorbed bipy source: [108]</th>
<th>Lewis bipy source: [108]</th>
<th>Cubipy$_1$ (aq)</th>
<th>Cubipy$_2$ (aq)</th>
<th>SiO$<em>2$ (bipy$</em>{tot}$/Cu$_{tot}$=1; $\Gamma$ =0.8 $\mu$mol m$^{-2}$)</th>
<th>SiO$<em>2$ (bipy$</em>{tot}$/Cu$_{tot}$=2; $\Gamma$ =0.8 $\mu$mol m$^{-2}$)</th>
<th>Al$<em>2$O$<em>3$ (bipy$</em>{tot}$/Cu$</em>{tot}$=2; $\Gamma$ =0.8 $\mu$mol m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG</td>
<td>1023</td>
<td>1023</td>
<td></td>
<td>1021</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NG</td>
<td>1037</td>
<td>1033</td>
<td></td>
<td>1030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1066</td>
<td>1065</td>
<td>1063</td>
<td></td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1091</td>
<td></td>
<td>1111</td>
<td>1108</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1150</td>
<td></td>
<td>1163</td>
<td>1163</td>
<td>1159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1164</td>
<td></td>
<td>1177</td>
<td>1177</td>
<td>1172</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1236</td>
<td></td>
<td>1252</td>
<td>1251</td>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1252</td>
<td></td>
<td>1315</td>
<td>1321</td>
<td>1318</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1423</td>
<td></td>
<td>1447</td>
<td>1449</td>
<td>1448</td>
<td>1447</td>
<td>1447</td>
</tr>
<tr>
<td>1463</td>
<td></td>
<td>1472</td>
<td>1478</td>
<td>1476</td>
<td>1475</td>
<td>1474</td>
</tr>
<tr>
<td>1496</td>
<td></td>
<td>1502</td>
<td>1500</td>
<td>1496</td>
<td>1496</td>
<td>1498</td>
</tr>
<tr>
<td>1563</td>
<td></td>
<td>1571</td>
<td>1572</td>
<td>1571</td>
<td>1570</td>
<td>1571</td>
</tr>
<tr>
<td>1582</td>
<td></td>
<td>1579</td>
<td>1579</td>
<td>1579</td>
<td>1578</td>
<td>1579</td>
</tr>
<tr>
<td>1605</td>
<td></td>
<td>1609</td>
<td>1608</td>
<td>1606</td>
<td>1605</td>
<td>1606</td>
</tr>
<tr>
<td>1617</td>
<td></td>
<td>1616</td>
<td>1616</td>
<td>1613</td>
<td>NA</td>
<td>1614</td>
</tr>
</tbody>
</table>
The data in the 1400 to 1600 cm\(^{-1}\) frequency region indicate that bipy on the surface is coordinated to a proton or a metal cation, which could be either Cu(II) or Lewis acid sites on the surface. IR results of free bipy sorption show that bipy is physisorbed or H-bonded to the am-SiO\(_2\) surface. In the presence of Cu(II), there is no reason to believe that Cu(II) could change the surface in such a way that direct bonding of bipy and Lewis acid sites on the surface would become possible. Therefore, bipy on the surface most likely is coordinated to Cu(II).

4.4. CONCLUSION

When Cu(II) is absent, sorption of bipy on am-SiO\(_2\) is relatively constant from 3 < pH < 8. The FTIR study of bipy sorption found that bipy is likely to adsorb on am-SiO\(_2\) and \(\gamma\)-Al\(_2\)O\(_3\) differently. On the am-SiO\(_2\) surface, physisorption of bipy is the dominant mode. There may also be some hydrogen-bonded bipy on the surface. On the \(\gamma\)-Al\(_2\)O\(_3\) surface, the observed vibrational bands suggest that bipy is chemisorbed to Lewis acid centers on the surface. For samples prepared with Cu(II) present, bipy on both am-SiO\(_2\) and \(\gamma\)-Al\(_2\)O\(_3\) surfaces is coordinately bonded to a Cu(II) ion. In the presence of Cu(II), no physisorbed bipy was detected on either oxide surface.
CHAPTER V

Solution and Spectroscopic Studies of Ternary Surface Complexes.  I. Sorption of Copper(II) and 2,2'-Bipyridine on Amorphous SiO₂

5.1. INTRODUCTION

This study examines the effect of a specific organic ligand, 2,2'-bipyridine (hereafter referred as bipy) (Figure 5.1) on the sorption behavior of aqueous Cu(II) [(Cu(H₂O)₆]²⁺] on amorphous silica (am-SiO₂) using a combination of macroscopic uptake measurements and spectroscopic techniques. This particular system serves as a simplified example of more complex natural aquatic systems in which metal-organic complexes interact with the surfaces of oxide particles. Such interactions are quite important in governing the behavior of contaminant ions such as Cu(II) in these systems. For example, up to 90% of the soluble copper in soils is complexed by organic molecules [110-112]. Such complexation affects solution speciation of contaminant ions, which in turn significantly affects their transport, toxicity, and bioavailability. Complexation of aqueous metal ions by organic ligands also affects industrial waste water treatment and recycling of metal, ore formation processes [113], the bioavailability of plant nutrients and the geochemical cycling of metal ions [114].

Metal-organic complexes sorbed on solid surfaces are also important in technological contexts. They play critical roles in froth flotation, metal corrosion, and catalysis [2]. In the preparation of supported heterogeneous catalysts, chemists have been able to produce metal particles with well-controlled sizes and structure by attaching metal complexes of certain composition to the support surfaces [115].

Given the importance of organic ligands in metal-ion sorption processes in these different contexts, it is essential to understand how they influence these processes at the molecular-level. Most studies of metal-ion sorption at mineral surfaces have been carried out in the presence of "innocent ligands" such as NO₃⁻ and ClO₄⁻ [2] that do not form strong complexes with the dissolved metal ions [2]. A number of macroscopic studies have been done on the interaction of aqueous metal ions with high molecular weight organic compounds such as humic acids, but the exact nature of the bonding, structure, and
sorption mechanisms of metal-humic acid complexes is poorly known largely because of their complexity. Because many naturally occurring organic molecules of this type have complex structures, it is necessary to study simple organic molecules to elucidate the properties of each functional group of the more complex organic substances. With this more general objective in mind, the focus of the present study is to determine the effect of bipy on the sorption mode of aqueous Cu(II) on am-SiO₂ surfaces at the molecular level.

The importance of Cu(II) and of surfaces containing SiOH type functional groups in natural environments has been discussed in Chapter 2. We chose to examine the effects of bipy on the sorption of Cu(II) on am-SiO₂ because bipy is a simple, yet important organic molecule that has been well studied and exhibits interesting effects on the adsorption of metal ions on am-SiO₂ and other oxides [8, 55, 116]. Previous studies of Cu(II)-bipy-oxide surface systems [8, 21, 22, 28, 29, 55, 60, 116] suggest that cation and ligand are associated in the sorption complex and that the complex is bonded to the surface through the Cu(II) ion. Investigations including spectroscopic methods have strengthened this hypothesis [21, 22, 28, 29, 60]. The present study uses a combination of room-temperature, *in situ* X-ray absorption fine structure (XAFS) and electron paramagnetic resonance (EPR) spectroscopies and macroscopic uptake measurements of Cu(II) on am-SiO₂ in the presence of bipy to investigate this system in more detail. The following chapter presents a parallel study of Cu(II)-bipy sorption complexes on γ-Al₂O₃ and explores differences between the two systems.

Bipy belongs to a class of organic compounds referred to as nitrogen-containing polycyclic aromatic compounds. Some compounds in this class, which are acutely toxic and have teratogenic activities, have been introduced into the environment. Bipy is the raw starting material for the synthesis of diquat and paraquat (Reglone® and Gramoxone®), which are important herbicides [117, 118]. Related, monocyclic compounds are also potentially dangerous contaminants. Pyridine and its derivatives, for example, are present naturally in the environment in trace amounts. They have also been introduced in localized areas at toxic concentrations through agricultural and industrial activities, in particular, the production of synthetic fossil fuel [119, 120]. The interaction of these ligands with metal cations can affect the fate and transport of both the ligands and the cations. Among these ligands, bipy has been most studied in the context of co-adsorption of metal cations and organic compounds on various metal oxides.
Figure 5.1. The bipy molecule (C$_{10}$N$_{2}$H$_{8}$). Dark gray: nitrogen atoms, light gray: carbon atoms bonded to one hydrogen atom each.

5.1.1. Previous Studies

A previous study of the sorption of Cu(II)-bipy complexes on the surface of aerosil-300 made by Degussa revealed that bipy dramatically shifts the pH of Cu(II) sorption on am-SiO$_2$ surfaces to lower values; i.e., bipy increases the sorption of Cu(II) on am-SiO$_2$ [8] while retaining the “cation-like” pH-dependence. By assuming the formation of type-A ternary complexes and negligible sorption of free bipy, Bourg et al.[8] were able to fit the uptake data. They and others suggested that increased affinity of Cu(II) for the am-SiO$_2$ surface in the presence of bipy might result from a change in the electronic structure of Cu(II) induced by the coordinated bipy molecule(s) [2, 8, 28] and/or a more negative free energy of sorption caused by additional interaction of the ligand with the solid surface [121].

Bourg et al. [8] suggested that Cu(II)-bipy may have a higher affinity for surface functional groups with oxygen donors than free Cu(II) because $\pi$-acceptor ligands, like bipy, can draw electron density from the d-orbitals of the metal ion, and therefore enhance the positive charge of the Cu(II) center [2, 8]. This hypothesis is based on the observation that for the analogous reactions in solution, Cu(II)-bipy$_1$ has higher affinity than free Cu(II) for oxalate and phthalate, which are ligands with oxygen donor functional groups [6]. However, the hypothesis is not supported by extended-Hückel-MO calculations [2].

Von Zelewsky and Bemtgen [28] studied the influence of a number of organic ligands on Cu(II) sorption on aerosil 300 using EPR. Uptake of Cu(II) as a function of pH was also estimated based on the amplitudes of the EPR spectra. Their results confirm that
bipy increases sorption of Cu(II) on aerosil 300. Furthermore, they interpreted the EPR results as indicating that when \( \text{bipy}_{\text{tot}} / \text{Cu(II)}_{\text{tot}} = 1 \) or 2, the surface complexes formed are \((=\text{SiO}^-)\text{Cu}\text{bipy}_1\) and \((=\text{SiO}^-)\text{Cu}\text{bipy}_2\), respectively. The surface complexes are \((=\text{SiO}^-)\text{Cu}\text{bipy}_2\) when \( \text{bipy}_{\text{tot}} / \text{Cu(II)}_{\text{tot}} \) increases to \( \geq 2 \). Von Zelewsky and Bemtgen [28] also estimated the stability of the Cu(II)-bipy-am-SiO\(_2\) complexes to be in the order: \([\text{Cu(II)-bipy}_1] \geq [\text{Cu(II)-bipy}_2] \geq [\text{Cu}^{2+}(\text{aq})] \). However, these stability estimates are not sufficient to distinguish among different modes of surface attachment of Cu(II) and Cu(II)-bipy complexes. In summary, EPR spectra indicate that the sorbed Cu(II) and bipy are bonded to each other and that the resulting surface complex is relatively immobile, thus adding weight to the hypothesis of an inner-sphere ternary complex with surface SiO\(^-\) groups.

There is further independent, relatively direct evidence—mostly from electron paramagnetic resonance (EPR) [22, 29], electron nuclear double resonance (ENDOR) [60], and electron spin echo envelope modulation (ESEEM) [61]—for the formation of inner-sphere complexes when Cu(II) sorbs on oxides other than silica in the presence of bipy and some other organic ligands. The nitrogen ENDOR results of Cu(II)/organic ligand/\(\gamma\)-Al\(_2\)O\(_3\) system [60] also provided evidence that, in the case of \( \text{bipy}_{\text{tot}} / \text{Cu(II)}_{\text{tot}} = 1 \), nitrogen donor atoms from the organic ligands are coordinated to the equatorial plane of Cu(II), i.e., ternary surface complexes were formed.

An alternative explanation for the increased sorption of Cu(II)-bipy, involving hydrophobic interaction of bipy with the surface, was first suggested by Schindler and Stumm [121]. Park et al [55] report uptake data that generally support bipy-induced enhancement of Cu(II) sorption. They find weak pH-dependence at low pH and increasing enhancement of Cu(II) sorption at higher bipy/Cu(II) ratios, and interpret these observations as evidence that hydrophobic expulsion or bonding contributes to the stability of the ternary surface complex.

5.1.2. Experimental Strategy

The predominant hypothesis adopted by previous investigators suggests that Cu(II) sorbs onto am-SiO\(_2\) from aqueous solutions dominated by Cu(II)-bipy\(_1\) or Cu(II)-bipy\(_2\) as one or more ternary, type A complexes bonded to the surface through the Cu(II) ion, perhaps augmented by hydrophobic bonding. A possible structure proposed by von Zelewsky and Bemtgen [28] is similar to those proposed on the basis of more definitive spectroscopic evidence for \(\gamma\)-Al\(_2\)O\(_3\) [60, 61]. In recent work on the system
Cu(II)/bipy/anatase, Ludwig and Schindler [116] have also considered the possibility of type B sorption complexes. We propose to test these possibilities for the Cu(II)/bipy/am-
SiO₂ system in several ways, including:

- (1) verifying that Cu(II) sorption is enhanced by bipy
- (2) determining the stoichiometry of bipy/Cu(II) on the surface
- (3) determining that Cu(II) and bipy are associated in the sorption complex.
- (4) determining the mode of sorption, in particular, whether the complex is inner-sphere or outer-sphere.
- (5) assuming the sorption complex is inner-sphere, determining if it is type A (bound to the surface through Cu(II) ions) or type B (bound to the surface through the bipy ligand).
- (6) determining if enhanced Cu(II) sorption is due to bipy-induced changes in the electronic structure of adsorbed Cu(II).

We have used a combination of macroscopic sorption measurements and FTIR and EPR spectroscopies to determine whether Cu and bipy adsorb independently or are bonded together as a Cu(II)-bipy surface complex. Direct measurement of the sorption densities of both Cu and bipy permit qualitative definition of the influence of bipy on Cu sorption and quantitative calculation of the average bipy/Cu ratio on the surface, and hence help to define the average composition of sorption complexes. The pH-dependence of Cu uptake will help to determine whether the sorbed Cu or Cu complex exhibits behavior more like a cation, a neutral complex, or an anion [2, 3]. If changes in ionic strength have little effect on uptake, inner-sphere behavior is suggested [3, 122, 123]. Analogy with salt effects on the solubilities and micelle formation of organic substances [124-126] suggests that added salts might either inhibit sorption, as in the case of simple inorganic adions [122, 123], or enhance sorption depending on the hydrophilic/hydrophobic balance (see definition, p267 in [126]) of the sorbing complex and the solid surface. The IR spectra of free aqueous bipy and bipy coordinated to Cu(II) are different (Chapter 3) thus IR spectra of the sorption complex can be used to determine whether the majority of sorbed bipy is free or bonded to Cu(II). Similarly, since the EPR parameters of “free” aqueous Cu(II) ion are different from those of Cu(II)-bipy [127, 128], EPR spectroscopy can help determine whether or not the sorbed copper and bipy are bonded or associated in a complex. This technique can also provide information about the coordination geometry of sorbed Cu(II) [129], and
hence about the structure of the sorption complex, because EPR spectra are sensitive to the different stereochemistries of Cu(II) complexes.

X-ray absorption fine structure (XAFS) spectroscopy can provide valuable information on the local structural environment of the Cu(II) center in Cu(II)/bipy/am-SiO₂ surface complexes. Most important in this context, quantitative interpretation of Cu-XAFS spectra may permit identification of silicon among second neighbor atoms in the coordination environment of sorbed Cu(II)—and the Cu-Si interatomic distance, R_{Cu-Si}. If R_{Cu-Si} is so short that neither bipy nor water of hydration can be present between Cu(II) and the Si atom, then we can conclude that Cu(II) forms a direct chemical bond with oxygen on the am-SiO₂ surface.

The hypothesis that bipy can draw electron density from Cu(II) and thus increase the affinity of Cu(II) for oxygen donor groups on the am-SiO₂ surface can also be tested with XAFS spectroscopy. If this hypothesis is true, then the Cu(II)-O\textsubscript{surface} bond should be stronger. Since stronger bonds generally have shorter bond lengths, the Cu(II)-O\textsubscript{surface} distance in the ligand-present system should be shorter than the Cu(II)-O\textsubscript{surface} distance in the ligand-free system. XAFS spectroscopy provides an average distance between Cu(II) and its first shell of oxygen and nitrogen neighbors; it is not capable of differentiating a Cu(II)-O\textsubscript{surface} distance from a Cu(II)-O\textsubscript{non-surface} or a Cu(II)-N distance, if these distances are within ≈0.04 Å of each other. If the Cu(II)-O\textsubscript{surface} bond is shorter in the ligand-present system than in the ligand-absent system, then on average, the distance between Cu(II) and its first-shell neighbors in the ligand-present system should be shorter than in the ligand-free system. These differences can only be considered statistically significant, however, if they are more than ≈0.04 Å apart. Depending on the geometry of the sorption complexes, a shortening in Cu(II)-O\textsubscript{surface} bond(s) might also lead to a shorter R_{Cu-Si} that can be detected by EXAFS. In addition, bipy can also potentially change the bonding geometry of Cu(II) to the surface by changing the bonding mode from monodentate to bidentate. In this case, the Cu-Si distance in the ligand-present and ligand-absent systems should be different, but the distance between Cu and its first shell neighbors should not change significantly.
5.2. EXPERIMENTAL

5.2.1. Materials and Reagents

A 0.1 M Cu(NO₃)₂ solution standard from Orion was used as the source of Cu(II). Product specifications and further communication with Orion indicate no additional nitric acid was added to this solution. Bipy was obtained from Fisher and was used as obtained. γ-Al₂O₃ and am-SiO₂ solids were obtained from Degussa under the brand name Aluminum Oxide C and Aerosil 200, respectively. Degussa reports the BET surface areas of these two oxides as 100±15 m²g⁻¹ and 200±25 m²g⁻¹, respectively. However, Schindler et al. [53] determined the surface area of aerosil 200 to be 160 m² g⁻¹. For the purpose of calculating sorption densities in this work, surface area values used for γ-Al₂O₃ and am-SiO₂ are 100 m²g⁻¹ and 160 m²g⁻¹, respectively. Water used in the sample preparation was Milli-Q doubly-deionized grade. It was boiled under nitrogen or sparged with nitrogen before use.

Typically, Cu-bipy stock solutions were prepared at a concentration of 0.01 M or 0.02 M Cu(II). A defined bipy to Cu(II) ratio was achieved by adding an appropriate amount of bipy to the Cu(II) solutions. The pH values of the stock solutions were not adjusted (at [Cu(II)] = 0.01 M, pH = 4.8 for bipy_{tot}/Cu(II)_{tot} = 1, and pH = 5.5 for bipy_{tot}/Cu(II)_{tot} = 2).

For pH adjustments during uptake experiments, two sources of 0.05 N or 0.1 N NaOH were used: one was prepared from JT Baker "Low-CO₂ dilut-it" volumetric NaOH concentrate; the other was Titrister NaOH from EM Science. Both types of NaOH were estimated to contain ≤ 0.7 x 10⁻³M CO₂ by their respective manufacturers. Additionally, titration experiments by Van Geen et al. [64] in a separate study confirmed that the CO₂ content of the NaOH concentrate from JT Baker is ≤ 0.7 x 10⁻³M.

5.2.2. Uptake Experiments-Procedure

Unless otherwise specified, all samples studied in this investigation were prepared by equilibrating 2000 m² liter⁻¹ (12.5 g liter⁻¹) of am-SiO₂ in a background electrolyte of 0.1 M NaNO₃ with selected Cu(II) concentrations. For some systems, sorption of Cu(II) and bipy at two different ionic strengths was studied, one at =0.1 M with NaNO₃ as the background electrolyte, and the other with no added NaNO₃ and an ionic strength of =0.0002 M to =0.0032 M, derived principally from the Cu(NO₃)₂ in solution.
All uptake experiments were performed in a nitrogen gas flooded glove-box. Typical experiments were conducted as follows: the solid was introduced into 16.8 to 19.8 ml of NaNO₃ background electrolyte in a polypropylene centrifuge tube. The mixture was equilibrated for 12-24 hours; mixing was maintained during this period by rotating the centrifuge tube on an end-over-end rotator. After this pre-equilibration, the pH of the slurry was measured before addition of Cu(II)-bipy solution from 0.01 M or 0.02 M stock solutions. The stock solution was then added to the slurry in aliquots of 100 µl or less, maintaining a high rate of stirring on a magnetic stir-plate at all times. The total volume of stock solution added ranged from 0.1 ml to 3.2 ml and did not cause a significant change in ionic strength. After complete addition of Cu(II) solutions, pH was adjusted to the desired values using 0.1 or 0.05 N nitric acid or sodium hydroxide added in 10-20 µl increments with intense stirring. Calculations with the speciation program HYDRAQL [70] based on stability constants for protonation and Na⁺ and Cu²⁺ complexation of bipy [130] indicate that when bipyₜₒₜ/Cu(II)ₜₒₜ = 1.0, Cu(II)-bipy₁ is the dominant species, (comprising 95% of total Cu(II)) at all pH values in this study. When bipyₜₒₜ/Cu(II)ₜₒₜ = 2, Cu(II)-bipy₂ is the dominant species (≈80%) at all pH values in this study, while Cu(II)-bipy₁ and Cu(II)-bipy₃ each comprises approximately 10% of the species.

The samples were then equilibrated for approximately 12-24 hours on an end-over-end rotator. Final pH's were measured at the end of the equilibration period. The slurry was then centrifuged until greater than 80% of liquid was removed. The amount of liquid removed was estimated by recording the weight difference between the slurry (before centrifugation) and the resulting paste (after centrifugation and removal of supernatant).

Sorption densities, Γ (x), and percent uptake of species x (where x represents Cu or bipy) were calculated from the initial and final total dissolved concentrations of Cu and bipy as follows:

Let $V_{stock} = volume$ of stock solution added,

$C_{stock}(x) = concentration$ of x in stock solution (verified by AA or UV measurements as appropriate as discussed in the analytical section),

$V_{tot} = total$ volume of slurry $= V_{background~electrolyte} + V_{stock} + V_{acid} + base, \quad (5.1)$

and let $C_{supernatant}(x) = concentration$ of x in supernatant (determined by AA or UV measurements);
then initial and final amounts of x in the aqueous phase are given by

\[ [x_{\text{init}}] = V_{\text{stock}} \cdot C_{\text{stock}}(x), \]  

(5.2)

and \([x_{\text{final}}] = V_{\text{tot}} \cdot C_{\text{supernatant}}(x) \]  

(5.3)

\[%x_{\text{ads}} = 100 \cdot \frac{[x_{\text{init}}] - [x_{\text{final}}]}{[x_{\text{init}}]} \]  

(5.4)

The surface concentration or sorption density of a species x in mol m\(^{-2}\) (\(\Gamma(x)\)) is calculated according to:

\[ \Gamma(x) = \frac{[x_{\text{init}}] \cdot \%x_{\text{ads}}}{\text{surface area}_{\text{BET}}(m^2g^{-1}) \cdot \text{solid conc.}(g \text{ liter}^{-1})} \]  

(5.5)

The average molar ratio of bipy to Cu(II) in the sorbed material is defined by the ratio of sorption densities:

\[ \frac{\text{bipy}_{\text{ads}}/\text{Cu(II)}_{\text{ads}}}{\Gamma(\text{bipy})/\Gamma(\text{Cu(II)})} = \frac{\%\text{bipy}_{\text{ads}}}{\%\text{Cu}_{\text{ads}}}. \]  

(5.6)

5.2.3. Uptake Experiments--Analytical Methods and Error

Final Cu(II) concentrations in the supernatant were determined by atomic absorption, primarily in graphite-furnace mode, and in several cases on the same samples in flame mode to check for reproducibility and accuracy. Measurements using the two different modes were reproducible. Because of differences in sensitivity of the two modes, and differences in sensitivity of different wavelengths to dilute concentrations in AA analysis, our analyses were occasionally made using different modes and wavelengths. This procedure minimized the need for diluting samples, which is a significant source of error in AA analysis.

The error in the sorption density and uptake of Cu(II) associated with the methods we used is approximately 6 to 8% [131] and is attributed largely to the amount of dilution required for the samples prior to AA measurements [131]. In this study, dilution was minimized, when appropriate, by using alternative wavelengths that are less sensitive by three orders of magnitude, or using flame-mode AA (instead of graphite-furnace mode AA), a method which is generally less sensitive than graphic-furnace mode AA. Consequently the error in \% Cu\(_{\text{ads}}\) in this study should probably be at the low end of the 6 to 8% estimate.

The concentration of bipy in solution was measured by its UV absorbance at approximately 300 nm. Because the absorption wavelengths of the different bipy species,
Cu(II)-bipy\textsubscript{n}, (where \( n = 1, 2, \text{ or } 3 \)) overlap, it was necessary for calibration and analysis to ensure that only one bipy species is in the solution to be measured. This was achieved by adding excess Cu(II) to the sample to achieve a Cu(II) concentration that is at least three times the maximum possible bipy concentration and adjusting the pH to approximately 4. HYDRAQL [70] calculations confirmed that Cu(II)-bipy\textsubscript{1} is the only bipy species under these conditions. In addition, experimental tests, by using known solutions as unknowns, showed that this procedure results in the correct answers.

The following reasoning was used to estimate the measurement error of bipy in the supernatant. The error in measurement of bipy in a solution is approximately 2-3\%, under conditions in which ionic strength of the background electrolyte is fixed. This value of 2-3\% was obtained by measuring a number of freshly made standard solutions as if they were "unknowns". The dilution required during measurement of bipy in the supernatant introduced an additional 1-2\% into the error. For example, the two pipettes most frequently used in the dilution procedure have errors of 0.8\% and 0.6\%, respectively, yielding a total error of at least 1.4\% in the dilution procedure. Other errors can come from slight differences in the background electrolyte concentration of the standard and the sample. It was found that background electrolyte, irrespective of whether it is Cl\textsuperscript{-}, ClO\textsubscript{4}\textsuperscript{-}, or NO\textsubscript{3}\textsuperscript{-}, interferes with the measurements of bipy concentration. This is because when the background electrolyte concentration is high, the tail of its absorption overlaps slightly with the absorption wavelength of bipy. Two methods were used simultaneously to minimize this interference, one was by subtracting out the UV absorption of a blank solution of similar background electrolyte composition. However, if there is any sorption of background electrolyte on the solid, then there is a slight difference between [NO\textsubscript{3}\textsuperscript{-}] in the samples and [NO\textsubscript{3}\textsuperscript{-}] in the standards which causes interference in the bipy measurement. The other method of minimizing interference was by subtracting out the reference wavelength which corresponds with the absorption wavelength of NO\textsubscript{3}\textsuperscript{-} in the analysis. Even though both methods were used, the interference from NO\textsubscript{3}\textsuperscript{-} could not be eliminated completely. For example, a 10\% sorption of NO\textsubscript{3}\textsuperscript{-} on the solid would introduce an additional 0.2-1\% error in bipy measurement. Taking all these factors into account, the error in measuring bipy concentration in the supernatant is approximately 5\%. Ludwig and Schindler [116] estimated that an error of ligand measurement of about 5\% corresponds to an adsorption error of 6 to 7\%. The error in \% bipy\textsubscript{ads} in this study is thus probably also in the range of 6-7\%. 

92
5.2.4. Sample Labeling

Sorption samples are named according to the substrate, and followed by the value of \( \text{bipy}_{\text{tot}}/\text{Cu(II)}_{\text{tot}} \), and the surface Cu concentration or sorption density (\( \Gamma \) in \( \mu \text{mol m}^{-2} \)) in parentheses. For example, \( \text{SiO}_2 \) (bipy\text{tot}/Cu(II)\text{tot} = 2; \( \Gamma = 0.05 \)) designates a sample prepared with bipy\text{tot}/Cu(II)\text{tot} = 2 on an am-SiO\text{2} substrate with the final sorption density of Cu = 0.05 \( \mu \text{mol m}^{-2} \). Cu rather than Cu(II) is used in this case to account for the possibility of reduction of Cu(II) to Cu(I) or Cu(0) upon sorption, although there is no experimental evidence for such reduction. In the following sections, Cu(II) coordinated to one or more bipy is generally referred to as Cu(II)-bipy.

5.2.5. EPR Data Collection

Samples for EPR data collection were prepared in the same manner as for XAFS measurements. EPR spectra for both in-situ (wet) and air-dried samples were collected at room temperature (RT) and at 77 K. EPR spectra were measured on a Bruker ER-220D spectrometer equipped with a X-band, rectangular cavity resonator operating in the TE\text{102} mode. The modulating frequency was always set at 100 kHz and the time constant at 500 msec. A microwave attenuation of 10 or 13 dB, corresponding, respectively, to microwave powers of 20 or 10 mW was used. Resonating microwave frequencies were 9.7-9.8 GHz for wet (RT) samples and 9.5 GHz for wet (77K), air-dried (RT), and air-dried (77 K) samples. Detailed information regarding spectrometer settings, in addition to conditions and temperature of the samples, is given in Figures 5.5.

To collect room temperature EPR data for wet sorption samples, the wet-pastes resulting from centrifugation were placed in a Suprasil tissue cell (manufacturer: Wilmad, part #: WG-806-A-Q). During data collection, the tissue cell was aligned to the magnetic component of the microwave, in order to reduce amount of microwave energy absorbed by water ("lossiness"), which is caused by the interaction between the electric component of the microwave field with the strong dipole of the water molecules in the sample. During data collection, sorption samples held at 77K and air-dried samples held at RT were put in cylindrical quartz tubes (Clear Fused Quartz EPR tubes supplied by Wilmad) with 4 mm o.d. and 3 mm i.d. Similarly, frozen aqueous solutions were also placed in quartz tubes of the same type.
5.2.6. XAFS--Data Collection

Samples used for XAFS data collection were prepared in the same manner as for uptake measurements, but at pH's where greater than 87% of the initial Cu(II) adsorbs. Table 5.1 shows initial and final pH, as well as Cu(II) concentrations, for the XAFS samples. Following centrifugation, sorption samples were mounted as wet pastes in 1-2 mm thick Teflon sample holders sealed with 10 mil Mylar windows so they could be studied in situ, to prevent alteration caused by drying or evacuation. They were further protected from atmospheric CO₂ and drying during storage and transport to SSRL by wrapping them in wet Kimwipes and storing them in a sealed ziplock plastic bag filled with nitrogen.

Data for two model compounds, each with Cu(II) bonded to one or two bipy, respectively, were collected. The model compound Cubipy₁(NO₂)₂ was donated by Dr. B. J. Hathaway. Details of its structure and characterization are given in [132]. The other model compound, [Cu(bipy)₂ClO₄]ClO₄, was prepared in our laboratory using methods described in [133]. The identity of the compound synthesized was verified by powder X-ray diffraction. We found a very good match between the experimental powder X-ray diffraction pattern and that calculated using the molecular modeling program Cerius 2.0. Additional details about the structure and properties of the second compound are given in [133, 134].

XAFS data for model compounds were collected in transmission mode. Samples used in the transmission XAFS experiments were mounted in 1 mm-thick aluminum frame sample holders protected with Mylar windows, with the sample at 90° to the incident X-ray beam. XAFS spectra for sorption samples and aqueous solutions were collected in fluorescence-yield mode, with the sample at 45° to the incident X-ray beam, using either a Stern-Heald-type detector with Soller slits [65] and a Ni filter to minimize elastically scattered X-rays, or a 13-element Ge array detector.

XAFS data were collected at the Stanford Synchrotron Radiation Laboratory on wiggler beam lines IV-2 and IV-3 with the storage ring operating at 3.0 GeV and 20-100 mA. A Si(220) double-crystal monochromator was used. Data for all samples were measured in unfocused mode. Harmonics were removed by (1) detuning the second monochromator crystal by 50-70% at 10 keV or (2) insertion of a platinum harmonic rejection mirror downstream from the monochromator, in which case no detuning of the monochromator was necessary. Internal energy calibration was performed using a Cu-
metal foil for all the fluorescence samples, with the first inflection point of the K-absorption edge of the Cu foil assigned as 8,980.3 eV. Data were typically collected over the energy range from 8,700 eV to 10,000 eV, with a step size of 0.2 eV in the edge region (8960-9015 eV). Typically, two to three XAFS scans were collected for model compounds and 12 to 24 XAFS scans were collected for sorption samples, all to k-values of 15-16 Å⁻¹, except for low concentration samples, where spectra were collected to k = 13 Å⁻¹. Individual scans at the beginning and end of XAFS data collection for each sample were examined to determine whether there was any change in the sample with time. All samples showed no detectable changes in the XAFS spectra over time.

5.2.7. XAFS--Data Analysis

EXAFS (Extended X-ray Absorption Fine Structure) data were analyzed using the EXAFSPAK software package [66]. When converting data from energy to k-space (k²=2mₑ(E-E₀)/h², where mₑ is the mass of the electron, E is the energy, E₀ is the energy at k=0, and h is the Planck's constant), E₀ was defined as 9,000 eV for all samples.

XANES features can be deconvoluted to separate absorption peaks corresponding to different bound-state transitions or multiple-scattering features. In actuality, rigorous deconvolution can be very complicated because of the large number of variables needed to account for each feature. Fortunately, because of the importance of Cu in diverse scientific fields, there have been some detailed XANES spectroscopy studies of Cu compounds [135-137], which provide some background information that helps in fitting the XANES spectra of the Cu(II)-bipy/am-SiO₂ sorption samples.

In fitting the XANES data, the only parameters fixed were edge-step, number of peaks, and the assumed peak shape (% Gaussian vs. % Lorentzian). These values were obtained either from other studies or through examination of the second derivative of each XANES spectrum. Pickering and George [137] carried out a detailed polarized XAFS study of single crystal cupric chloride dihydrate in which XAFS data of the crystal at different crystallographic orientations were collected. They determined that an edge-step energy of 9,010 eV resulted in the best fit of their data. For the purpose of consistency and ease of comparison between different samples, we fixed the Cu K-edge-step energy for all samples at 9,010 eV. In choosing the number of peaks necessary to fit the Cu K-XANES data, it is common to first examine the second derivatives to estimate how many peaks are necessary to fit the data [138, 139]. This procedure suggests that seven absorption peaks are needed to fit the XANES spectra of the sorption samples, and this number of peaks was
found to give a good fit to the data. Pickering and George [137] determined that the shape of the individual absorption peaks is best approximated by a pseudo-Voigt mixing parameter of 0.871 (87% Gaussian and 13% Lorentzian). We have assumed the same pseudo-Voigt mixing parameter for fitting the Cu K-XANES spectra of the sorption samples in this study.

Phase-shift and amplitude functions for the least-square fitting procedure used in EXAFS data analysis were derived from model compounds and from theoretical multiple-scattering calculations using FEFF version 6.01a or above [67, 68]. Final fitting of the spectra was done on the normalized, background-subtracted raw data using all shells simultaneously.

5.3. RESULTS

Cu(II)-bipy uptake on am-SiO₂ was studied as a function of pH, bipyₜₒₜ/Cu(II)ₜₒₜ, Cu(II) concentration (keeping bipyₜₒₜ/Cu(II)ₜₒₜ constant), and ionic strength. Results of these experiments are discussed below. Based on the uptake studies, four sorption samples prepared at different conditions were chosen for spectroscopic study, with the objective of assessing the effects of the surface concentration of the adsorbate and the ratio bipyₜₒₜ/Cu(II)ₜₒₜ on the type of surface complexes formed. The spectroscopic results for each sample are presented following the uptake results section.

5.3.1. Uptake Results

Figure 5.2 shows the uptake of Cu(II) and bipy, as well as bipyₐₜₐₕs/Cu(II)ₐₜₐₕs, on am-SiO₂ as a function of pH and the ratio, bipyₜₒₜ/Cu(II)ₜₒₜ when [Cu(II)] = 0.1 mM. Cu(II) uptake on am-SiO₂ is enhanced by bipy. Furthermore, as bipyₜₒₜ/Cu(II)ₜₒₜ increases, the enhancement in Cu(II) sorption increases. Both results agree with trends found in previous studies [8, 28], even though the sorbate to sorbent ratios in this study are different (one higher and one lower). The error in the value of bipyₐₜₐₕs/Cu(II)ₐₜₐₕs was calculated by assuming a 6% error in %bipyₐₜₐₕs, and a 6% error in %Cu(II)ₐₜₐₕs. This corresponds to a very large error in the value of bipyₐₜₐₕs/Cu(II)ₐₜₐₕs when %bipyₐₜₐₕs and %Cu(II)ₐₜₐₕs are small. In the higher pH, higher uptake region, the error in bipyₐₜₐₕs/Cu(II)ₐₜₐₕs is significantly smaller, and we can conclude that bipyₐₜₐₕs/Cu(II)ₐₜₐₕs approximately equals bipyₜₒₜ/Cu(II)ₜₒₜ.

Figure 5.3 shows the uptake data, %Cu(II)ₐₜₐₕs, %bipyₐₜₐₕs, and bipyₐₜₐₕs/Cu(II)ₐₜₐₕs at a sorbate concentration 16 times higher than that for the data in Figure 5.2, while the sorbent
concentration is the same. At this higher sorbate to sorbent ratio, bipy decreases Cu(II) sorption on am-SiO₂. Furthermore, as \( \frac{bipy_{\text{tot}}}{Cu(II)_{\text{tot}}} \) increases, the decrease in Cu(II) sorption becomes greater. In the higher pH, higher uptake region, we can conclude that \( \frac{bipy_{\text{ads}}}{Cu(II)_{\text{ads}}} \) approximately equals \( \frac{bipy_{\text{tot}}}{Cu(II)_{\text{tot}}} \).

Figure 5.4 shows effect of concentration on sorption of Cu(II) and bipy, and \( \frac{bipy_{\text{ads}}}{Cu(II)_{\text{ads}}} \), with \( \frac{bipy_{\text{tot}}}{Cu(II)_{\text{tot}}} = 2 \) in this set of experiments. As the ratio of sorbate to available sorbent surface area increases from 0.05 \( \mu \text{mol m}^{-2} \) to 0.8 \( \mu \text{mol m}^{-2} \), the maximum concentration of sorbed species on the surface (maximum \( \Gamma \)) increases correspondingly from 0.05 \( \mu \text{mol m}^{-2} \) to 0.8 \( \mu \text{mol m}^{-2} \). However, as the ratio of sorbate to available sorbent surface area increases from 0.8 \( \mu \text{mol m}^{-2} \) to 1.6 \( \mu \text{mol m}^{-2} \), maximum \( \Gamma \) remains at 0.8 \( \mu \text{mol m}^{-2} \), suggesting that an upper limit of sorption density has been reached. The ratio \( \frac{bipy_{\text{ads}}}{Cu(II)_{\text{ads}}} \) approximately equals \( \frac{bipy_{\text{tot}}}{Cu(II)_{\text{tot}}} \) at the various concentrations studied.

Figure 5.5 compares the sorption of Cu(II) and bipy and the resultant \( \frac{bipy_{\text{ads}}}{Cu(II)_{\text{ads}}} \) ratio for two ionic strengths, one approximately 0.1 M, with NaNO₃ as the background electrolyte, and the other approximately 0.0002 M to 0.0032 M, which was derived principally from the Cu(NO₃)₂ in solution with no added NaNO₃. Two systems were studied: one system has a sorbate-to-sorbent surface area ratio of 0.05 \( \mu \text{mol m}^{-2} \), with \( \frac{bipy_{\text{tot}}}{Cu(II)_{\text{tot}}} = 2 \). The second system has a sorbate-to-sorbent surface area ratio of 0.8 \( \mu \text{mol m}^{-2} \), with \( \frac{bipy_{\text{tot}}}{Cu(II)_{\text{tot}}} = 1.0 \). There is no statistically significant ionic strength effect on Cu(II) or bipy sorption, and also no effect of ionic strength on the resultant \( \frac{bipy_{\text{ads}}}{Cu(II)_{\text{ads}}} \) in either system.
Figure 5.2. Uptake of Cu(II) and bipy, and the ratio bipy_{ads}/Cu(II)_{ads} on am-SiO₂ (12.5 g liter⁻¹) as a function of pH and the bipy-to-Cu(II) ratio for ΣCu = 0.1 mM, NaNO₃ = 0.1 M.
**Figure 5.3.** Uptake of Cu(II) and bipy, and the ratio bipy_{ads}/Cu(II)_{ads} on am-SiO₂ (12.5 g liter⁻¹) as a function of pH and the bipy-to-Cu(II) ratio for ΣCu = 1.6 mM, NaNO₃ = 0.1 M.
Figure 5.4. Effect of concentration and pH on Cu(II) and bipy sorption, and the ratio bipy$_{ads}$/Cu(II)$_{ads}$, for bipy$_{tot}$/Cu(II)$_{tot}$=2. As the sorbate-to-solid ratio increases, an upper limit of sorption density seems to have been reached, with the maximum sorption density on the surface of $\approx 0.8$ µmol m$^{-2}$. 

(a) Cu uptake

(b) bipy uptake

(c) bipy$_{ads}$/Cu(II)$_{ads}$
Figure 5.5. Effect of ionic strength (IS) and pH on Cu(II) and bipy sorption, and the resultant bipy$_{ads}$/Cu(II)$_{ads}$ ratio for the following systems: [Cu(II)]=0.0001 M, [bipy]=0.0002 M, [solid]=12.5 g liter$^{-1}$ (Figures 5.5 (a) to (c)) and [Cu(II)]=0.0016 M, [bipy]=0.0016 M, [solid]=12.5 gliter$^{-1}$ (Figures 5.5 (d) to (f)).
Figure 5.5. Effect of ionic strength (IS) and pH on Cu(II) and bipy sorption, and the resultant bipy_{ads}/Cu(II)_{ads} ratio for the following systems: [Cu(II)]=0.0016 M, [bipy]=0.0016 M, [solid]=12.5 gliter^{-1} (Figures 5.5 (d) to (f)).
### 5.3.2. Spectroscopic Results

Several sorption samples from the uptake study were chosen for spectroscopic studies (Table 5.1). We will describe results of our EPR and XAFS experiments separately. Results common to most samples are described first, followed by detailed results specific to each sample.

#### Table 5.1. Experimental conditions for XAFS sorption samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>final pH</th>
<th>initial Cu conc. (M)</th>
<th>final Cu conc. (M)</th>
<th>% Cu uptake</th>
<th>bipy$<em>{tot}$/Cu$</em>{tot}$</th>
<th>bipy$<em>{ads}$/Cu$</em>{ads}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$<em>2$ (bipy$</em>{tot}$/Cu$_{tot}$ = 1, ( \Gamma = 0.05 \mu$mol m$^{-2}$)</td>
<td>6.73</td>
<td>9.94 x 10$^{-5}$</td>
<td>4.05 x 10$^{-6}$</td>
<td>95.9%</td>
<td>1</td>
<td>0.98</td>
</tr>
<tr>
<td>SiO$<em>2$ (bipy$</em>{tot}$/Cu$_{tot}$ = 1, ( \Gamma = 0.8 \mu$mol m$^{-2}$)</td>
<td>8.16</td>
<td>1.53 x 10$^{-3}$</td>
<td>&lt; 10$^{-6}$</td>
<td>&gt; 99%</td>
<td>1</td>
<td>≈1</td>
</tr>
<tr>
<td>SiO$<em>2$ (bipy$</em>{tot}$/Cu$_{tot}$ = 1, ( \Gamma = 0.04 \mu$mol m$^{-2}$)</td>
<td>6.14</td>
<td>1.98 x 10$^{-4}$</td>
<td>&lt; 10$^{-6}$</td>
<td>&gt; 99%</td>
<td>2</td>
<td>≈2</td>
</tr>
<tr>
<td>SiO$<em>2$ (bipy$</em>{tot}$/Cu$_{tot}$ = 1, ( \Gamma = 0.77 \mu$mol m$^{-2}$)</td>
<td>8.98</td>
<td>1.42 x 10$^{-3}$</td>
<td>1.81 x 10$^{-4}$</td>
<td>87.2</td>
<td>2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

#### 5.3.2.1. EPR Results

Figure 5.6 shows EPR spectra of sorption samples and Table 5.2 summarizes EPR parameters derived from these spectra as well as parameters reported in other studies. The following general conclusions can be drawn from the EPR spectra for all the sorption samples in this study:

1. Even when wet at RT, the EPR spectra are anisotropic, indicating that the surface complexes are immobile on the time-scale of the technique, which is approximately 10$^{-11}$ to 10$^{-10}$ seconds.

2. All the spectra are of the "axial type" [32], with spectral parameters \( g_{||} \geq g_{\perp} \), which is consistent with the presence of tetragonal or square-planar Cu(II) on the surfaces.
The $g_{||}$ and $A_{||}$ parameters for all the sorption samples prepared in the presence of bipy are different from those of free Cu(II) (aq) or Cu(II) adsorbed on am-SiO$_2$ prepared in the absence of bipy.

Since multinuclear complexes and/or precipitates of metal ions produce very broad or undetectable spectra, while isolated metal ions produce the normal paramagnetic spectra, the EPR data for the sorption samples indicate that Cu(II) ions on the surface occupy magnetically isolated sites.

If more than one species is present on the surface, they should appear as different lines in the EPR spectra. The EPR spectra in this study therefore indicate that predominantly one species is present in each system.

More detailed analysis of the samples made with bipy$_{tot}$/Cu(II)$_{tot}$ = 1 (the first three samples in Table 5.2) shows that the $g_{||}$ and $A_{||}$ parameters for these samples are close to those of Cu(II)-bipy$_1$. This result provides evidence that Cu(II) on the surface is still complexed with one bipy. Data for sample SiO$_2$ (bipy$_{tot}$/Cu(II)$_{tot}$=1, $\Gamma$=0.05 $\mu$mol m$^{-2}$) had to be collected at low temperature (77K) because the low concentration of Cu(II) in the sample resulted in very poor data quality at RT. The $g$ parameters of this sample are similar to those of the higher concentration sample (0.8 $\mu$mol m$^{-2}$) prepared with the same bipy$_{tot}$/Cu(II)$_{tot}$, suggesting that the structure of the surface complexes is constant in the concentration range 0.05-0.8 $\mu$mol m$^{-2}$, if we assume freezing has no significant effect on the sample.

For sorption samples prepared with bipy$_{tot}$/Cu(II)$_{tot}$ = 2, EPR spectra yielded less definitive information because detailed EPR parameters of Cu(II)-bipy$_2$ in aqueous solution is not available. This is because Cu(II)-bipy$_2$ (aq) disproportionates into Cu(II)-bipy$_1$ and Cu(II)-bipy$_3$ at 77K [128], and it is necessary to collect EPR data at a temperature where the aqueous solution is frozen to obtain its $g_{||}$, $g_{\perp}$, and $A_{||}$ parameters.

EPR data also yielded some information on the effect of drying on the samples. When possible, EPR spectra were collected in-situ (wet, RT). Data for the SiO$_2$ (bipy$_{tot}$/Cu(II)$_{tot}$=1, $\Gamma$=0.8 $\mu$mol m$^{-2}$) sample were collected with the sample as a wet paste and, separately, an air-dried paste. Drying the sample in air apparently did not cause significant changes in the measured EPR spectra.
Figure 5.6. EPR spectra of sorption and aqueous samples. (a) Wet paste, RT samples: (i) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=1, $\Gamma$=0.8 $\mu$mol m$^{-2}$). Microwave frequency: 9.747 GHz. (ii) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=2, $\Gamma$=0.77 $\mu$mol m$^{-2}$). Microwave frequency: 9.769 GHz; microwave power: 13.0 dB, gain $1.25 \times 10^4$. (b) Dried samples at RT or wet samples at 77K: (iii) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=1, $\Gamma$=0.8 $\mu$mol m$^{-2}$). Microwave frequency: 9.48 GHz; microwave power: 13.0 dB, gain $2.50 \times 10^4$. (iv) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=1, $\Gamma$=0.05 $\mu$mol m$^{-2}$). Microwave frequency: 9.504 GHz; microwave power: 13.0 dB, gain $1.25 \times 10^4$. (v) 1.0 mM Cu(ClO$_4$)$_2$ aqueous solution. Microwave frequency: 9.5 GHz; microwave power: 13.0 dB, gain $2.0 \times 10^4$. 

Figure 5.6.
Table 5.2. Spectral parameters derived from EPR data. Errors in $g_{\parallel}$, $g_{\perp}$, and $A_{\parallel}$ are those estimated for samples in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conditions</th>
<th>$g_{\parallel}$</th>
<th>$g_{\perp}$</th>
<th>$A_{\parallel} \times 10^4$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Adsorbed Species:</strong></td>
<td></td>
<td>($\pm 0.001$)</td>
<td>($\pm 0.002$)</td>
<td>($\pm 5 \text{ cm}^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>SiO$<em>2$ (bipy$</em>{\text{tot}}$/Cu$_{\text{tot}}$=1, $\Gamma$=0.8 $\mu$mol m$^{-2}$)</td>
<td>wet paste, RT</td>
<td>2.293</td>
<td>2.066</td>
<td>166</td>
<td>this study</td>
</tr>
<tr>
<td>SiO$<em>2$ (bipy$</em>{\text{tot}}$/Cu$_{\text{tot}}$=1, $\Gamma$=0.8 $\mu$mol m$^{-2}$)</td>
<td>air-dried, RT</td>
<td>2.292</td>
<td>2.071</td>
<td>171</td>
<td>this study</td>
</tr>
<tr>
<td>SiO$<em>2$ (bipy$</em>{\text{tot}}$/Cu$_{\text{tot}}$=1, $\Gamma$=0.05 $\mu$mol m$^{-2}$)</td>
<td>frozen wet paste (77 K)</td>
<td>2.296</td>
<td>2.066</td>
<td>172</td>
<td>this study</td>
</tr>
<tr>
<td>SiO$<em>2$ (bipy$</em>{\text{tot}}$/Cu$_{\text{tot}}$=2, $\Gamma$=0.77 $\mu$mol m$^{-2}$)</td>
<td>wet paste, RT</td>
<td>2.259</td>
<td>2.077</td>
<td>148</td>
<td>this study</td>
</tr>
<tr>
<td>Cu(II) on aerosil 300</td>
<td>--</td>
<td>2.380</td>
<td>2.085</td>
<td>128</td>
<td>[28]</td>
</tr>
<tr>
<td>SiO$<em>2$ (bipy$</em>{\text{tot}}$/Cu$_{\text{tot}}$=1)</td>
<td>--</td>
<td>2.290</td>
<td>2.067</td>
<td>165</td>
<td>[28]</td>
</tr>
<tr>
<td>SiO$<em>2$ (bipy$</em>{\text{tot}}$/Cu$_{\text{tot}}$=2)</td>
<td>--</td>
<td>2.259</td>
<td>2.073</td>
<td>150</td>
<td>[28]</td>
</tr>
<tr>
<td><strong>Solution species:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(H$_2$O)$_6$ (aq)</td>
<td>77 K</td>
<td>2.416</td>
<td>2.094</td>
<td>144</td>
<td>this study</td>
</tr>
<tr>
<td>Cu(H$_2$O)$_6$ (aq)</td>
<td>77 K</td>
<td>2.39</td>
<td>2.07</td>
<td>142</td>
<td>[140]</td>
</tr>
<tr>
<td>Cu(H$_2$O)$_6$ (aq)</td>
<td>77 K</td>
<td>2.448</td>
<td>2.115</td>
<td>137</td>
<td>[28]</td>
</tr>
<tr>
<td>Cu(bipy)$_1$ (aq)</td>
<td>77 K</td>
<td>2.315</td>
<td>2.072</td>
<td>165</td>
<td>[127]</td>
</tr>
<tr>
<td>Cu(bipy)$_2$ (aq)</td>
<td>77 K</td>
<td>2.227</td>
<td>2.082</td>
<td>129</td>
<td>[127]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.285</td>
<td></td>
<td>165</td>
<td></td>
</tr>
</tbody>
</table>
5.3.2.2. XAFS--XANES Results

The following general conclusions can be drawn from the XANES spectra for all the sorption samples:

1. The edge positions of all sorption samples are characteristic of those of Cu(II), indicating no reduction of Cu(II) to Cu(I) or Cu(0) when it adsorbs on am-SiO$_2$.

2. Cu K-edge structures and their second derivatives (Figure 5.7) of all Cu(II) sorption samples prepared in the presence of bipy are different from those of Cu(II) (aq) or Cu adsorbed on am-SiO$_2$ prepared in the absence of bipy, indicating that the electronic structure of the surface species is significantly different from that of Cu(II)(aq) or Cu adsorbed on am-SiO$_2$ in the absence of bipy.

3. Cu K-edge structures (Figure 5.8a) of all Cu(II) sorption samples are different from those of aqueous Cu(II)-bipy complexes, indicating that the surface complexes have different electronic structures from those of aqueous Cu(II)-bipy complexes. The differences between the sorption complexes and Cu(II)-bipy complexes in solution can be seen even more clearly in the second derivatives of the spectra (Figure 5.8b). Quantitatively, the XANES spectra of the sorption samples have larger amplitude in the 8,982-8,990 eV region than aqueous Cu(II)-bipy. Figure 5.9 shows the deconvolution of the XANES spectra of SiO$_2$ (bipy$_{tot}$/Cu(II)$_{tot}$ = 1; $\Gamma$ =0.8 $\mu$mol m$^{-2}$) and Cu(II)-bipy$_1$ (aq) to illustrate the differences between sorbed and aqueous Cu(II) species. Specifically, the sorption sample has much larger absorption at 8,983 eV and 8,988 eV, two energies that are normally assigned to the 1s$\rightarrow$3d and the 1s$\rightarrow$4p transitions, respectively [135-137]. The increase in intensity in the 1s$\rightarrow$3d transition is probably due to the Cu(II) complex becoming even more noncentrosymmetric, thus allowing more p-d mixing in Cu(II) energy levels and conferring more dipole-allowed character to the d-orbital.

5.3.2.3. XAFS--EXAFS Results

Figures 5.10 and 5.11 show normalized, background-subtracted EXAFS spectra and the corresponding Fourier transforms of Cu(II)-bipy/am-SiO$_2$ sorption samples, Cu(NO$_3$)$_2$ aqueous solution, Cu(II)-bipy complexes in aqueous solution, and Cu(II)-containing crystalline model compounds. Model compounds with specific numbers of bipy ligands coordinated to Cu(II) have characteristic features, which are useful for a qualitative estimate of the surface Cu(II) species. For example, a second weaker frequency at
Figure 5.7. Normalized Cu K-XANES spectra and second derivatives of sorption samples prepared in the presence and absence of bipy, and Cu(II) (aq). For both (a) and (b): (i) Cu(NO$_3$)$_2$ solution, (ii) sample prepared in the absence of bipy, Cu/SiO$_2$ (0.05 μmol m$^{-2}$), (iii) sample prepared in the absence of bipy, Cu/SiO$_2$ (0.8 μmol m$^{-2}$), (iv) SiO$_2$ (bipy$_{\text{tot}}$/Cu$_{\text{tot}}$=1, Γ=0.05 μmol m$^{-2}$), (v) SiO$_2$ (bipy$_{\text{tot}}$/Cu$_{\text{tot}}$=1, Γ=0.8 μmol m$^{-2}$), (vi) SiO$_2$ (bipy$_{\text{tot}}$/Cu$_{\text{tot}}$=2, Γ=0.04 μmol m$^{-2}$), (vii) SiO$_2$ (bipy$_{\text{tot}}$/Cu$_{\text{tot}}$=2, Γ=0.77 μmol m$^{-2}$). All sorption samples prepared in the presence of bipy have features significantly different from those prepared in the absence of bipy, and from Cu(II) (aq).
Figure 5.8. Normalized Cu K-XANES spectra (8a) and second derivatives (8b) of sorption samples, compared to Cu(II)-bipy complexes in solution and crystalline model compounds. For both (a) and (b): (i) crystalline Cu(bipy)$_1$(NO$_2$)$_2$ model compound, (ii) Cu(II)-bipy$_1$ (aq), (iii) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=1, $\Gamma$=0.05 $\mu$mol m$^{-2}$), (iv) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=1, $\Gamma$=0.8 $\mu$mol m$^{-2}$), (v) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=2, $\Gamma$=0.04 $\mu$mol m$^{-2}$), (vi) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=2, $\Gamma$=0.77 $\mu$mol m$^{-2}$), (vii) Cu(II)-bipy$_2$ (aq), (viii) crystalline Cu(bipy$_2$)ClO$_4$ClO$_4$ model compound. Model compound and aqueous solution of Cu(II)-bipy$_2$ have a small absorption feature at approximately 9005 eV (marked with arrows in Fig. 5.8a), so are sorption samples prepared with bipy$_{tot}$/Cu(II)$_{tot}$ = 2.
Figure 5.9. Deconvolution of Cu K-XANES spectrum of sorption sample SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$ = 1; $\Gamma$=0.8 $\mu$mol m$^{-2}$) and Cu K-XANES spectrum of Cu(II)-bipy$_1$ (aq).
Figure 5.10. Normalized, background-subtracted Cu K-EXAFS spectra (Fig. 5.10a) and the corresponding Fourier transforms (Fig. 5.10b), of sorption samples prepared in the presence and absence of bipy, and Cu(II) (aq). For both (a) and (b): (i) Cu(NO₃)₂ solution, (ii) sample prepared in the absence of bipy, Cu/SiO₂ (0.05 μmol m⁻²), (iii) sample prepared in the absence of bipy, Cu/SiO₂ (0.8 μmol m⁻²), (iv) SiO₂ (bipyₜ₀₂/Cuₜ₀₂=1, Γ=0.05 μmol m⁻²), (v) SiO₂ (bipyₜ₀₂/Cuₜ₀₂=1, Γ=0.8 μmol m⁻²), (vi) SiO₂ (bipyₜ₀₂/Cuₜ₀₂=2, Γ=0.04 μmol m⁻²), (vii) SiO₂ (bipyₜ₀₂/Cuₜ₀₂=2, Γ=0.77 μmol m⁻²). Note that samples prepared in the absence of bipy have distinct peaks in the phase-shift uncorrected RDFs (at approximately 2.0 Å and 2.7 Å, for (ii) and (iii) respectively) that are absent in samples prepared in the presence of bipy.
Figure 5.11. Normalized, background-subtracted Cu K-EXAFS spectra (Fig. 5.11a) and the corresponding Fourier transforms (Fig. 5.11b) of sorption samples prepared in the presence of bipy, and Cu(II)-bipy complexes in aqueous solution and crystalline model compounds. For both (a) and (b): (i) crystalline Cu(bipy)$_1$(NO$_2$)$_2$ model compound, (ii) Cu(II)-bipy$_1$ (aq), (iii) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=1, Γ=0.05 μmol m$^{-2}$), (iv) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=1, Γ=0.8 μmol m$^{-2}$), (v) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=2, Γ=0.04 μmol m$^{-2}$), (vi) SiO$_2$ (bipy$_{tot}$/Cu$_{tot}$=2, Γ=0.77 μmol m$^{-2}$), (vii) Cu(II)-bipy$_2$ (aq), (viii) crystalline [Cu(bipy$_2$)ClO$_4$]ClO$_4$ model compound. The arrows in Fig. 5.11(a) point out the visible differences in EXAFS of sorption samples prepared with bipy$_{tot}$/Cu(II)$_{tot}$=1 from that of Cu(II)-bipy$_1$ (aq).
k \approx 5 \text{ Å}^{-1} \text{ is characteristic of model compounds with one bipy (Cubipy}_1(\text{NO}_2)_2 \text{ and Cu(II)-bipy}_1 \text{ (aq), while the second frequency at } k \approx 5 \text{ Å}^{-1} \text{ is significantly more pronounced for model compounds with two bipy. Qualitative comparison of the EXAFS spectra of sorption samples prepared with bipy}_\text{tot}/\text{Cu(II)}_\text{tot} = n \text{ to those of model compounds indicates that they are more similar to those of Cu(II)-bipy}_n \text{ than to those of other complexes.}

Quantitative analysis of the EXAFS spectra yields estimates of the number and interatomic distances of first and, in favorable cases, more distant neighbor atoms in the vicinity of the Cu(II) ion. As can be seen in Figures 5.10 and 5.11, the Fourier transforms of Cu(II) prepared in the presence of bipy are complicated, due to the large number of atoms (mostly carbon in the organic ligand) surrounding the Cu center. To successfully analyze the spectra of the sorption samples, it was first necessary to analyze those of the model compounds to understand which scattering paths contribute significantly to EXAFS spectra of Cu(II) coordinated with bipy.

Analysis of the model compounds indicate that the major oscillation in the EXAFS comes from first-shell equatorial nitrogens and/or oxygens. The next significant contributions come from single scattering of the second shell carbon atoms at approximately 2.8 to 3.0 Å (fitted with two separate components, see Figure 5.12). For third and fourth shell carbon atoms, multiple scattering paths, for example, Cu→N1→C3 as illustrated in Figure 5.12d are more important than single scattering paths. Figure 5.12a to 5.12c show fits to the EXAFS and FT, and components of the fit, to the model compound Cubipy}_1(\text{NO}_2)_2 \text{ including single and multiple scattering paths.}

Table 5.3 summarizes results of fitting the model compounds and sorption samples. In general, the first-shell coordination of Cu(II) in all sorption samples is the same as that in the solution samples, with four oxygen and/or nitrogen atoms at approximately 1.95 Å from the Cu atom. In several cases discussed in detail below, second-neighbor Si atoms were observed.

In fitting the sorption samples, single- and multiple-scattering paths arising from the bipy ligand(s) are fitted first, then contributions from silicon atoms from the surface, if any, are included in the fit. For the two samples prepared with bipy}_\text{tot}/\text{Cu(II)}_\text{tot} = 1, quantitative analysis shows that there is approximately one Si second neighbor at approximately 3.2 Å from Cu(II). A least-squares gradient search routine in EXAFSPAK was used to help determine the coordination number (N) and distance (R) of the Si shell.
Figure 5.12. (a) Solid line: experimental Cu K-EXAFS spectrum of Cubipy(NO$_2$)$_2$, dashed line: fit of Cu K-EXAFS spectrum of Cubipy(NO$_2$)$_2$. (b) Solid line: forward Fourier transform (uncorrected for phase shift) of experimental data of Cubipy(NO$_2$)$_2$; dashed line: fit of FT of Cubipy(NO$_2$)$_2$. (c) $\chi$ components of the fit. (d) Structure of individual units in the Cubipy(NO$_2$)$_2$ crystal; these units are bound by van der Waals forces in the crystal. In each of these unit, the Cu(II) metal ion is six-coordinated: with 2 oxygens from NO$_2$, and two nitrogens from bipy at the equatorial positions, as well as 2 oxygens from NO$_2$ at the axial positions. The important type of scattering paths, corresponding to the $\chi$ components in (c), are shown.
This procedure also confirmed that the coordination and distance found correspond to a true least-squares minimum. For the two samples prepared with bipy$_{\text{tot}}$/Cu(II)$_{\text{tot}}$ = 2, EXAFS analysis was not able to show conclusively the presence of or the distance to Si second-neighbors.

Figure 5.13. Least-squares gradient search profile for the coordination number (N) and distance (R) (Figure 5.13a and 5.13b respectively) of Si second neighbors fitted in the EXAFS data of SiO$_2$ (bipy$_{\text{tot}}$/Cu$_{\text{tot}}$ = 1; Γ=0.8 μmol m$^{-2}$).

5.4. DISCUSSION

5.4.1. Composition and Structure of the Surface Complexes

Uptake experiments show that bipy enhances Cu(II) sorption onto am-SiO$_2$ at our lowest Cu concentration (ΣCu = 0.1 mM), and that bipy inhibits Cu(II) sorption at ΣCu = 1.6 mM, for solution bipy$_{\text{tot}}$/Cu(II)$_{\text{tot}}$ ratios of 1 and 2.

In order to determine the composition and structure of the surface complexes, it is necessary to combine results from the macroscopic uptake measurements and spectroscopic techniques. Table 5.4 summarizes results from the four sorption samples selected for spectroscopic studies. In a later section, we present our interpretation of the EPR and XAFS results and the bonding mode of the surface complexes thus derived for samples prepared with different bipy$_{\text{tot}}$/Cu(II)$_{\text{tot}}$. Here we will first focus on determining the composition of the surface complexes (objectives 2 and 3 in the Experimental Strategy section) using results that are common to most samples and mass action considerations.
Table 5.3. Results of quantitative EXAFS analysis. *Parameter fixed during the fit. MS = multiple scattering path.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>R</th>
<th>σ²</th>
<th>ΔE</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sorption samples with bipy</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂ (bipy\textsubscript{tot}/Cu\textsubscript{tot} = 1, Γ=0.8 μmol m⁻²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-(N and O)</td>
<td>4.2</td>
<td>1.94</td>
<td>0.0051</td>
<td>-0.03</td>
<td>this study</td>
</tr>
<tr>
<td>Cu-C</td>
<td>2.4</td>
<td>2.86</td>
<td>0.0030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C5 MS</td>
<td>4.5</td>
<td>3.11</td>
<td>0.0009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C4 MS</td>
<td>6.7</td>
<td>4.18</td>
<td>0.0070</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C3 MS</td>
<td>32.0</td>
<td>4.68</td>
<td>0.0197</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Si</td>
<td>1.4</td>
<td>3.22</td>
<td>0.0070</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂ (bipy\textsubscript{tot}/Cu\textsubscript{tot} = 1; Γ=0.048 μmol m⁻²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-(N and O)</td>
<td>4.4</td>
<td>1.96</td>
<td>0.0047</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Cu-C</td>
<td>2.0</td>
<td>3.00</td>
<td>0.0058</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C5 MS</td>
<td>4.6</td>
<td>3.08</td>
<td>0.0030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C4 MS</td>
<td>15.1</td>
<td>4.22</td>
<td>0.0040</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C3 MS</td>
<td>18.9</td>
<td>4.77</td>
<td>0.0030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Si</td>
<td>0.6</td>
<td>3.20</td>
<td>0.0007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂ (bipy\textsubscript{tot}/Cu\textsubscript{tot} = 2, Γ=0.77 μmol m⁻²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-(N and O)</td>
<td>5.2</td>
<td>1.98</td>
<td>0.0062</td>
<td>-0.67</td>
<td></td>
</tr>
<tr>
<td>Cu-C</td>
<td>4.0</td>
<td>2.86</td>
<td>0.0051</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C5 MS</td>
<td>8.1</td>
<td>3.14</td>
<td>0.0030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C4 MS</td>
<td>17.6</td>
<td>4.21</td>
<td>0.0030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C3 MS</td>
<td>13.4</td>
<td>4.75</td>
<td>0.0025</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂ (bipy\textsubscript{tot}/Cu\textsubscript{tot} = 2, Γ=0.04 μmol m⁻²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-(N and O)</td>
<td>5.1</td>
<td>1.98</td>
<td>0.0052</td>
<td>-0.87</td>
<td></td>
</tr>
<tr>
<td>Cu-C</td>
<td>4.0</td>
<td>2.86</td>
<td>0.025</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C5 MS</td>
<td>7.4</td>
<td>3.08</td>
<td>0.0041</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C4 MS</td>
<td>40.9</td>
<td>4.20</td>
<td>0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C3 MS</td>
<td>17.2</td>
<td>4.71</td>
<td>0.0065</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Model Compound</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cubipy\textsubscript{1}(NO\textsubscript{2})\textsubscript{2}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-O</td>
<td>2</td>
<td>1.97</td>
<td>0.0041</td>
<td>4.3</td>
<td>this study</td>
</tr>
<tr>
<td>Cu-N</td>
<td>2</td>
<td>2.02</td>
<td>0.0047</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-C</td>
<td>4</td>
<td>2.90</td>
<td>0.0048</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C5 MS</td>
<td>7.3</td>
<td>3.14</td>
<td>0.0092</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C4 MS</td>
<td>29.5</td>
<td>4.24</td>
<td>0.011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-N1-C3 MS</td>
<td>7.0</td>
<td>4.76</td>
<td>0.0013</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.3 (cont). Results of quantitative EXAFS analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>R</th>
<th>$\sigma^2$</th>
<th>$\Delta E$</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption Samples without bipy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu/SiO$_2$ (0.030 $\mu$mol m$^{-2}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>chapter 2</td>
</tr>
<tr>
<td>Cu-O</td>
<td>3.8</td>
<td>1.97</td>
<td>0.0028</td>
<td>-10.1</td>
<td></td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>0.9</td>
<td>2.58</td>
<td>*0.007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Si</td>
<td>1.0</td>
<td>2.98</td>
<td>*0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu/SiO$_2$ (0.73 $\mu$mol m$^{-2}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>chapter 3</td>
</tr>
<tr>
<td>Cu-O</td>
<td>*4</td>
<td>1.94</td>
<td>0.0033</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>2.0</td>
<td>2.95</td>
<td>*0.0070</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>0.4-1.1</td>
<td>3.30</td>
<td>0.0045</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>1.0</td>
<td>5.73</td>
<td>*0.0070</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4. Summary of spectroscopic results for sorption samples.

<table>
<thead>
<tr>
<th>Sample --&gt;</th>
<th>SiO$<em>2$ (bipy$</em>{tot}$/Cu$_{tot}$=1, $\Gamma$=0.05 $\mu$mol m$^{-2}$)</th>
<th>SiO$<em>2$ (bipy$</em>{tot}$/Cu$_{tot}$=1, $\Gamma$=0.8 $\mu$mol m$^{-2}$)</th>
<th>SiO$<em>2$ (bipy$</em>{tot}$/Cu$_{tot}$=2, $\Gamma$=0.04 $\mu$mol m$^{-2}$)</th>
<th>SiO$<em>2$ (bipy$</em>{tot}$/Cu$_{tot}$=2, $\Gamma$=0.77 $\mu$mol m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methods of study</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>final pH</td>
<td>6.73</td>
<td>8.16</td>
<td>6.14</td>
<td>8.98</td>
</tr>
<tr>
<td>bipy$<em>{tot}$/Cu$</em>{tot}$</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>bipy$<em>{ads}$/Cu$</em>{ads}$</td>
<td>0.98</td>
<td>$\approx$1</td>
<td>$\approx$2</td>
<td>1.8</td>
</tr>
<tr>
<td>IR</td>
<td>bipy bonded to Cu</td>
<td>bipy bonded to Cu</td>
<td>bipy bonded to Cu</td>
<td>bipy bonded to Cu</td>
</tr>
<tr>
<td>surface species from EPR</td>
<td>Cu(II)-bipy$_1$</td>
<td>Cu(II)-bipy$_1$</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>geometry from EPR</td>
<td>tetragonal</td>
<td>tetragonal</td>
<td>--</td>
<td>tetragonal</td>
</tr>
<tr>
<td>mobility from EPR (wet samples)</td>
<td>--</td>
<td>immobile</td>
<td>--</td>
<td>immobile</td>
</tr>
<tr>
<td>inferred electronic structure from EPR</td>
<td>different from Cu(II)-bipy$_1$, Cu(II) (aq), and Cu/SiO$_2$</td>
<td>different from Cu(II)-bipy$_1$, Cu(II) (aq), and Cu/SiO$_2$</td>
<td>--</td>
<td>different from Cu(II)-bipy$_1$, Cu(II) (aq), and Cu/SiO$_2$</td>
</tr>
<tr>
<td>inferred electronic str.fr XANES</td>
<td>similar to conclusions from EPR</td>
<td>similar to conclusions from EPR</td>
<td>similar to conclusions from EPR</td>
<td>similar to conclusions from EPR</td>
</tr>
<tr>
<td>EXAFS</td>
<td>0.6 Si @ 3.20 Å</td>
<td>1.4 Si @ 3.22 Å</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
In the aqueous phase, most, if not all, of the bipy is bonded to Cu(II) when 
\( \text{bipy}_{\text{tot}} / \text{Cu}(\text{II})_{\text{tot}} = n \) (\( n = 1 \) or 2), and the dominant species in solution is Cu-bipy\(_n\) (aq). Upon sorption to the am-SiO\(_2\) surface, some bipy could potentially dissociate from Cu(II) and bond to the surface directly. Additionally, any bipy bound to Cu(II) on the surface could be in either Cu(II)-bipy\(_1\), Cu(II)-bipy\(_2\), or Cu(II)-bipy\(_3\) complexes. The sorption equilibrium from the aqueous phase to the am-SiO\(_2\) surface, disregarding the details of bonding to the surface for the moment, can thus be written as:

\[
\text{Cu(II)-bipy}_n(aq) = \text{surface}\{\alpha \text{ bipy} + \beta \text{ Cu(II)-bipy}_1 + \gamma \text{ Cu(II)-bipy}_2 + \delta \text{ Cu(II)-bipy}_3\}
\]

(5.7)

where \( \alpha \) and \( \beta \) \( \leq n \), \( \gamma \leq n/2 \), \( \delta \leq n/3 \), and their values can be constrained further from spectroscopic results.

Uptake measurements have shown that the ratio of bipy to Cu(II) sorbed is very close to the ratio in the predominant aqueous complex in the ambient solution, i.e., \( \text{bipy}_{\text{ads}} / \text{Cu}(\text{II})_{\text{ads}} = n \) when the predominant aqueous complex is Cu(II)-bipy\(_n\). Therefore, the following relation can be written when all the bipy in the system is adsorbed:

\[
\alpha + \beta + 2\gamma + 3\delta = n
\]

(5.8)

Results from spectroscopic studies can now be used to constrain the values of \( \alpha \), \( \beta \), \( \gamma \), and \( \delta \). A separate infrared (IR) spectroscopy study (Chapter 3) provided additional evidence that most, if not all, of the sorbed bipy is coordinated to Cu(II). In other words, there is no free bipy, and \( \alpha = 0 \) for \( n = 1 \) or 2. To determine the other coefficients for the case of \( \text{bipy}_{\text{tot}} / \text{Cu}(\text{II})_{\text{tot}} = 1 \) is relatively straightforward: EPR results indicate that Cu(II)-bipy\(_1\) is the predominant Cu(II) species on the surface and the other Cu(II) species are negligible. Consequently, \( \beta = 1 \), and \( \gamma \) and \( \delta \) are negligible. When \( \text{bipy}_{\text{tot}} / \text{Cu}(\text{II})_{\text{tot}} = 2 \), determining the surface species is more complicated because EPR results did not reveal the predominant Cu(II) species on the am-SiO\(_2\) surface. EPR results, however, do show that there is only one predominant species on the surface. Through uptake and IR studies we can show that:

\[
\beta + 2\gamma + 3\delta = 2
\]

(5.9)

If there is only one species on the surface, then only one of the variables \( \beta \), \( \gamma \), or \( \delta \) can be non-zero and its value has to be equaled to 1. The only way to satisfy equation (2) with this requirement is to have \( \gamma = 1 \), and the surface species is therefore Cu(II)-bipy\(_2\). Together, uptake, IR, and EPR results confirm that Cu(II) and bipy are mutually bonded
on the surface, and the predominant sorbed species is Cu(II)-bipy\textsubscript{n} (n = 1 when bipy\textsubscript{tot}/Cu(II)\textsubscript{tot} = 1 and n = 2 when bipy\textsubscript{tot}/Cu(II)\textsubscript{tot} = 2).

To determine the mode of bonding of Cu(II)-bipy\textsubscript{n} to the surface (objectives (4) and (5) in the Experimental Strategy section), it is necessary to combine both EPR and XAFS results. The strength of the evidence varies among samples, and the data, arguments, and explanations are reviewed in the following paragraphs.

5.4.1.1. Bonding mode of Cu(II)-bipy\textsubscript{1} on am-SiO\textsubscript{2} surface

EPR results indicate that the surface Cu(II) complexes are relatively immobile, i.e., Cu(II) are not "tumbling around", which suggests that inner-sphere complexes have formed [141]. The consistently lower g\textsubscript{||} parameter of the sorption samples (g\textsubscript{||} = 2.292-2.296) compared to that of Cu(II)-bipy\textsubscript{1}(aq) (g\textsubscript{||} = 2.315), indicates that Cu(II) on the surface experience a stronger equatorial ligand field, i.e., more covalent bonding [32, 63] than Cu(II)-bipy\textsubscript{1} (aq). This suggests that the Cu(II) is coordinated to the surface through equatorial bonds and the surface oxygen(s) or hydroxyl (SiOH) group(s) produce stronger ligand field than water molecule(s).

The EPR results are in general agreement with the XANES results, which indicate that the electronic structure of the Cu(II) in surface complexes is different from that of Cu(II)-bipy in aqueous complexes, thus suggesting relatively strong interaction between Cu(II) and the surface.

Addressing objective (5) in the Experimental Strategy section, we found direct evidence of a Si second neighbor at an average Cu-Si distance of 3.24 Å, which is too close to include a water of hydration between the Cu(II) metal center and the am-SiO\textsubscript{2} surface in any feasible bonding geometry. This finding provides evidence that the Cu(II) in the surface complex is bonded directly to SiO\textsuperscript{-} groups, i.e., the surface complex is inner-sphere, and it is a type-A ternary complex. Using distances found in quantitative analysis of EXAFS, the molecular modeling code Cerius 2 was used to model and visualize the surface complex (more details are in Chapter 2). This modeling suggests that the Cu-Si distance derived from our EXAFS spectra is consistent with Cu(II) bonded to an oxygen of an SiO\textsubscript{4} tetrahedron in monodentate fashion (Figure 5.14).
Figure 5.14. Schematic drawing of possible arrangement of Cu(II)-bipy₁ bonded to a SiO₄ tetrahedron in a monodentate mode.

5.4.1.2. Bonding mode of Cu(II)-bipy₂ on am-SiO₂ surface

For these samples, EXAFS analysis failed to reveal the presence of Si second neighbors. However, XANES results indicate that the electronic structure of the Cu(II) in surface complexes is different from that of Cu(II)-bipy₂ in aqueous solution, indicating that the local environment of the surface complexes is significantly different from Cu(II)-bipy₂ in aqueous solution, thus suggesting relatively strong interaction with the surface. This observation, together with the inferred immobility of the Cu from the EPR results, suggests that the predominant sorption complex comprises Cu(II)-bipy₂ bonded to the surface.

In summary, for samples prepared with bipyₜₒₜ/Cu(II)ₜₒₜ = 1 or 2, infrared, EPR, and XAFS spectroscopies suggest that Cu(II) is bonded to bipy. Furthermore, the IR results indicate that all the bipy is bonded to Cu(II) (see Chapter 3). XAFS and EPR results suggest that the complex is mononuclear in terms of Cu, is bonded to the surface through the Cu(II), and forms a relatively strong, inner-sphere, probably monodentate complex with surface sites. Together, these observations support the hypothesis that a true ternary, Type A complex is formed.
5.4.2. The Influence of bipy on Cu(II) sorption on am-SiO₂

For Cu(II)-bipy sorbed on am-SiO₂ with bipy_{tot}/Cu(II)_{tot} = 1, the Cu-first shell distance, i.e., the average Cu-N and Cu-O distances, is approximately 0.02 to 0.03 Å shorter than the equivalent Cu-first shell distance in the aqueous Cu(II)-bipy₁ complex. In other words, the average Cu-first-shell bond in the Cu(II)-bipy₁ sorption complex is slightly stronger than in aqueous Cu(II)-bipy₁. Similarly, the average first-shell distance for Cu(II) sorbed on am-SiO₂ in the absence of bipy is also 0.01-0.03 Å shorter than that in the simple hexaaquo Cu(II) complex, so the increase in Cu-first shell bond strength is not attributable to bipy, but suggests that the surface ligands are slightly stronger ligands than water molecules.

Bourg et al. [8] suggested that bipy, being a π-acceptor ligand, can withdraw electron density from Cu(II), resulting in higher affinity of Cu(II) for surface oxygen donors. Since EXAFS analysis does not provide any direct information about the electron density of Cu(II), we cannot totally rule out this hypothesis as a possible explanation for the enhancement in sorption at low sorbate-to-sorbent ratio. Increased Cu-surface bond strength, however, should be reflected in a decreased Cu-O and Cu-Si distance, but the EXAFS-derived Cu-O distance in the presence of bipy is similar to that in the absence of bipy. Furthermore, the EXAFS-derived Cu-Si distance in the sorbed Cu(II)-bipy₁ complex is slightly longer than that for sorbed Cu(II). This might be interpreted as evidence that the sorbed Cu(II)-bipy₁ is tilted away from the surface at a larger angle than sorbed Cu(II). In summary, we cannot provide a explanation, in terms of bond lengths, that can account for the increased affinity of Cu(II)-bipy₁ relative to Cu(II) for the am-SiO₂ surface. The apparent lack of a decreased Cu-surface bond length and inferred higher bond strength, suggests instead that hydrophobic expulsion or bonding, may be a more likely explanation for the increase of Cu(II) sorption in the presence of bipy at low sorbate to sorbent ratio.

Sorption enhancement by hydrophobic bonding can be interpreted in quasi-thermodynamic terms. The free energy of sorption comprises several contributions including at least: (1) the bond energy of sorption, (2) long-range electrostatic interaction (attraction or repulsion) with charged surfaces, (3) changes in solvation energy resulting from changes in the hydration shell of both the sorbate and the surface when the sorbate moves from solution to the surface, which applies to both hydrophilic and hydrophobic compounds. In other words,
\[ \Delta G_{\text{sorption}} = \Delta G_{\text{bond energy}} + \Delta G_{\text{electrostatic}} + \Delta G_{\text{solvation}} \] (5.10)

The bond energy term is always nil, or negative if a true bond forms. The electrostatic term is favorable for sorption of positively charged species, like the Cu(II)-bipy\textsubscript{n} complexes on a negative surface like am-SiO\textsubscript{2} for all pH > pH\textsubscript{pzc} (point of zero charge). The solvation term is invariably positive for the simple aquo cations like Cu(II), but is reduced by complexing that reduces the charge density of the adion.

When Cu(II) is coordinated by uncharged organic ligands like bipy, the absolute charge of the complex is unchanged, but the charge density is reduced because the entity is larger and the bipy shields the charge on the Cu(II) ion. The normally positive \( \Delta G_{\text{solvation}} \) of the resultant complex becomes smaller or less positive resulting in a more favorable free energy of sorption. The solvation contribution to \( \Delta G_{\text{sorption}} \) should logically include the energy associated with changes in the structure and entropy of the water in the vicinity of the ligand and the surface when the ligand sorbs, i.e., a hydrophobic bonding [142] contribution. For neutral bidentate ligands, for example, bipy and 1,10-phenanthroline (phen), coordination to a metal cation produces metal-ligand complexes that are positively charged, with an exposed hydrophobic side on the outside. The resulting interaction between these complexes and water is thus simultaneously both ion-dipole and hydrophobic in nature. Overall, then, the Cu(II)-bipy\textsubscript{n} complexes are more hydrophobic than free Cu(II). Therefore \( \Delta G_{\text{solvation}} \) should be more favorable for removal of Cu(II)-bipy\textsubscript{1} than removal of Cu(H\textsubscript{2}O)\textsubscript{6} from the bulk aqueous phase. In addition, considering that the dielectric constant of water near the solid surface is low, \( \Delta G_{\text{solvation}} \) should be more favorable for the existence of a larger, lower charge density, surface bound complex like surface-Cu(II)-bipy\textsubscript{1} than a smaller, higher charge density, surface bound complex like surface-Cu(II). Thus, comparison between Cu(II)-bipy\textsubscript{1} and Cu(H\textsubscript{2}O)\textsubscript{6}, both free in bulk water (initial state) and bound on surface (final state) result in enhancement of Cu(II) sorption in the presence of bipy at low sorbate-to-sorbent ratio.

The contribution of hydrophobic effects to the increased Cu(II) sorption in the presence of bipy is consistent with known properties of bipy. Bipy has a limited solubility in water (0.037 mol liter\textsuperscript{-1}) [143], suggesting that it might be hydrophobic. A \textsuperscript{1}H Nuclear Magnetic Resonance (NMR) study of bipy [144] concluded that bipy self-associates in aqueous solution, forming stacks of dimers, trimers, and tetramers, which provides evidence that bipy behaves in similar manner to other hydrophobic molecules. When bipy is bonded to Zn(II), the Zn(II)-bipy\textsubscript{1} complexes still form stacks in aqueous solution, even though the extent of self-association is significantly less than free bipy [144]. Since both
Zn(II) and Cu(II) are transition metals that have some similar properties, it is likely that the Cu(II)-bipy complex would also have some hydrophobic properties.

The increased Cu(II) sorption in the presence of bipy is also consistent with enhanced Cu(II) sorption on aerosil-300 in the presence of bipy, phen, and 2,2',6',2''-terpyridine (terpy) [28], but decreased Cu(II) sorption in the presence of ethylenediamine (en) [28, 54]. Ethylenediamine is a relatively small ligand compared to bipy, phen, and terpy, with the number of carbon atoms in these four ligands being 2, 10, 12, and 15, respectively (the number of nitrogen atoms in bipy, phen, and en is two, whereas terpy has three nitrogen atoms). Therefore, the hydrophobic character of en should be smaller and $\Delta G_{solvation}$ should be less favorable for Cu-en sorption.

For samples prepared with $\text{bipy}_{\text{tot}}/\text{Cu(II)}_{\text{tot}} = 2$, XAFS and EPR results suggest that Cu(II)-bipy$_2$ is likely to bond to the surface in an inner-sphere mode, yet we were unable to detect Si among second neighbors around Cu. This suggests either that the XAFS frequencies due to second-neighbor carbon and second-neighbor silicon overlap significantly or that the Cu-Si distance is much longer than observed for Cu(II), as discussed earlier. The increased enhancement in sorption as the ratio $\text{bipy}_{\text{tot}}/\text{Cu(II)}_{\text{tot}}$ increases is probably due to the even greater hydrophobic character of the resultant complex as more bipy increasingly shields the central Cu(II) ion.

5.4.3. Site Limitation

The fact that at high sorbate-to-am-SiO$_2$ ratio (see Figure 5.4) no additional sorption occurs suggests saturation of surface sites. If this interpretation is correct, our observation supports the suggestion that the Cu-bipy complexes are bonded through Cu(II), because "salting out" or hydrophobic bonding alone might be expected to be independent of specific sites. The maximum loading of approximately 0.8 $\mu\text{mol m}^{-2}$ Cu(II)-bipy$_2$ on the surface corresponds to one Cu(II)-bipy$_2$ complex per 2.13 nm$^2$. Assuming that Cu(II)-bipy$_2$ complexes are uniformly distributed on the surface, then a distance between Cu atoms on the surface should be approximately 14.6 Å. The "size" of the Cu(II)-bipy$_2$ complex depends partly on its stereochemistry and the orientation of the two bipy molecules with respect to one another. In aqueous solution, most of the Cu(II)-bipy$_2$ complexes have a cis-distorted octahedral geometry [145]. The size of this complex is probably similar to cis-distorted [Cu(II)(bipy)$_2$(NO$_2$)]NO$_3$ [133, 146], which has dimensions of approximately 9.6 Å x 7.3 Å x 6.9 Å. Each cis-distorted octahedral Cu(II)-bipy$_2$ complex will thus occupy an area of approximately 70 Å$^2$. On the other
hand, if the Cu(II)-bipy2 complex on the surface is close to tetragonal, i.e., the two bipy molecules are not twisted out of plane as much as in aqueous Cu(II)-bipy2, then the x and y dimension of this tetragonal complex are approximately 9.3 Å and 9 Å, respectively, and the z-dimension is approximately 6.3 Å. Each tetragonal Cu(II)-bipy2 will thus occupy an area of approximately 80 Å².

In summary, each Cu(II)-bipy2 complex, can "cover" a surface area of approximately 70-80 Å². Assuming that each Cu(II)-bipy2 complex occupies the upper limit of this surface area (80 Å²), with Cu(II) in the center of this area, and that the complexes are uniformly distributed on the surface, then the separation between the edges of sorbed Cu(II)-bipy2 complexes is approximately 5.6 Å (the Cu(II)-Cu(II) separation should be ≈ 14.6 Å). The O-H distance in a water molecule is 0.96 Å, and the distance between two water molecules should be approximately 2.7 Å, which is the distance of hydrogen bonding. We do not know exactly the distance of water molecules from the "outside" of the Cu(II)-bipy2 complex, but if we allow the water molecules to stagger as shown in Figure 5.15, and assuming the distance between the edge of the Cu(II)-bipy2 complex and a water molecule to be ≈ 1.3-1.5 Å, then a distance of 5.6 Å between two adjacent Cu(II)-bipy2 complexes should be sufficient to accommodate two water molecules between the complexes. This arrangement would allow each sorbed Cu(II)-bipy2 complex to maintain its innermost waters of solvation while forming a monolayer on the surface.

![Figure 5.15](image-url). Schematic drawing of the relative sizes of the various sorbate molecules on the am-SiO₂ surface.
5.5. CONCLUSIONS

Evidence from macroscopic uptake studies and from XAFS, EPR, and FTIR spectroscopic measurements allows us to determine the composition and structure of ternary surface complexes. Uptake experiments show that at a bipy/Cu(II) solution ratio of 1 or 2, bipy enhances Cu sorption onto am-SiO$_2$ at our lower concentration, $\Sigma$Cu = 0.1 mM, but inhibits Cu sorption at $\Sigma$Cu = 1.6 mM. The enhancement and/or inhibition is more pronounced at higher bipy-to-Cu(II) ratios. The ratio of bipy to Cu(II) sorbed is very close to the ratio in the predominant aqueous complex in the ambient solution, i.e., $\text{bipy}_{\text{ads}}$/Cu(II)$_{\text{ads}}$ = $n$ when the predominant aqueous complex is Cu(II)-bipy$_n$. A maximum sorption density is reached at about 0.8 $\mu$mol m$^{-2}$ of Cu(II)-bipy$_2$ on the am-SiO$_2$ surface which corresponds to one monolayer of Cu(II)-bipy$_2$ on the surface. The sorbed Cu(II)-bipy$_2$ complexes probably maintain a layer of waters of solvation around their edges.

Infrared, EPR, and XAFS spectroscopies suggest that Cu(II) and bipy are mutually bonded. XAFS and EPR results suggest that the complex is mononuclear in terms of Cu, is bonded to the surface through the Cu(II), and forms a relatively strong, inner-sphere, probably monodentate complex with surface sites. Together, these observations support the hypothesis that a true ternary, Type A complex is formed.

XAFS results show that the Cu-surface bond length and inferred bond strength, in the presence of bipy, are comparable to those in the absence of bipy. This result suggests that the increased affinity of Cu(II) for the am-SiO$_2$ surface in the presence of bipy is not due to changes in Cu(II)-surface bond strength, but is due to contributions of hydrophobic expulsion or bonding to the free energy of sorption. Future studies on ternary surface complexes should examine this effect.

Acknowledgments

Gratitude is expressed to Uma Sundaram for providing EPR spectrum of Cu(ClO$_4$)$_2$ (aq).
CHAPTER VI

Solution and Spectroscopic Studies of Ternary Surface Complexes. I. Sorption of Copper(II) and 2,2'-Bipyridine on $\gamma$-Al$_2$O$_3$

6.1. INTRODUCTION

This study examines the effect of a specific organic ligand, 2,2'-bipyridine (bipy), on the sorption of Cu(II) on $\gamma$-Al$_2$O$_3$ using a combination of macroscopic uptake measurements and spectroscopic techniques, primarily X-ray absorption fine structure (XAFS) spectroscopy. In Chapter 5, the effect of bipy on Cu(II) sorption on am-SiO$_2$ was examined. Chapter 5 and Chapter 6, together, allow us to address the effect of substrate on sorption of Cu(II)-organic complexes.

In ternary systems, substrates can be expected to have significant effect on the sorption of metal-organic complexes for a variety of reasons. In binary systems, substrates can affect the type of metal-cation sorption complexes formed on mineral surfaces, for example, a single adion may sorb as an outer-sphere complex on one oxide and as an inner-sphere complex on a second, reflecting stronger bonding or more negative free energy of sorption on the second oxide. One of the reasons that metal-organic complexes may sorb differently on different substrates may be that the substrates have different affinities for the individual components of the metal-organic complexes. Alternatively, different substrates may interact differently with the "whole" metal-organic complexes.

Understanding the effect of substrates on the sorption of metal-organic complexes is important both scientifically and for technological applications. Even for simpler ternary systems without solid surfaces, such as metal cations in the presence of two different organic ligands in aqueous solution, our knowledge of the factors that stabilize or destabilize ternary complexes is not yet complete [6, 7]. With solid surfaces present, predicting whether ternary surface complexes form, and their structure and bonding, is even more complicated. This is so because our understanding of the structure of the surface itself is incomplete, as is our knowledge of the factors and general principles governing the structure, binding strength, and thermodynamic stability of even binary...
sorption complexes formed when a ligand or metal ion react with a surface. These areas are still under active investigation.

In previous studies, we (Chapter 5) and others [8, 28, 55] found that bipy can increase or decrease Cu(II) sorption on am-SiO₂, depending on the relative ratio of sorbate and sorbent. In the current study we examine the effect of bipy on Cu(II) sorption on γ-Al₂O₃, including whether it also enhances Cu(II) sorption at particular concentrations, and whether similar types of surface complexes are formed on am-SiO₂ and γ-Al₂O₃. Am-SiO₂ and γ-Al₂O₃ were chosen as the minerals to study the influence of substrates on Cu(II) sorption because they have very different surface properties. The surface of am-SiO₂ is a very acidic. Its PZNPC (point of zero net proton charge) is usually around 2 to 3 [46-48], thus, except at extremely low pH, the predominant ionized surface sites are negative. On the other hand, γ-Al₂O₃ is amphoteric, with a PZNPC between 8 and 9 [49, 50], and the predominant ionized surface sites are positive at low pH and negative at high pH, relative to the PZNPC. The different surface charge of the oxides would affect the sorption of charged species significantly.

Another significant differences in surface properties are the reactive groups on the surfaces of these two oxides. All Si sites in am-SiO₂ are tetrahedral, thus ionizable hydroxyl sites on the surface (generically, SiOH) are all bound in SiO₄ tetrahedra. Al is present in both tetrahedral and octahedral sites in γ-Al₂O₃ [44, 45] thus AlOH sites may be bound in AlO₄ tetrahedra, AlO₆ octahedra, or in sites bridging tetrahedra and octahedra. Hydroxyl groups or oxygen on the exposed sides of AlO₆ octahedra, AlO₄ tetrahedra, and SiO₄ tetrahedra have different basicity [147], and may react with metal-organic complexes differently.

6.2. BACKGROUND

In this discussion, γ-Al₂O₃ and am-SiO₂ refer to Aluminum Oxide C and aerosil-200, both from Degussa. For discussion of other studies, the product brand names of the oxides will be used whenever such information is available. If no information is available on the exact source of oxides used, the generic terms silica and alumina will be used.

Examination of experimental investigations of Cu(II)-organic complexes sorbed on silica and alumina suggests that these two oxides have different affinities for these complexes. Hathaway [21], Von Zelewsky and Bemtgen [28], Motschi [29], and McBride
have used primarily EPR to investigate Cu-organic complexes on oxides and hydroxides. For quite a few of the ligands, the surface complexes are immobile in the time-scale of the EPR technique (10^{-10} \text{ sec}), suggesting a specifically sorbed species. Table 6.1 shows a summary of EPR parameters from previous studies of Cu(II)-organic complexes sorbed on oxides and oxyhydroxides, focusing on systems where the ratio of total ligand ($L_{\text{tot}}$) to total Cu(II) ($\text{Cu(II)}_{\text{tot}}$) equals one ($L_{\text{tot}}/\text{Cu(II)}_{\text{tot}} = 1$).

The results from the von Zelewsky and Bemtgen study on silica [28] and the Motschi study on $\gamma$-Al$_2$O$_3$ [29], as presented in Table 6.1, are particularly suitable for comparison because some of the organic ligands used are the same, and because concentrations of sorbates and sorbents are similar. These two studies are the focus of the discussion in the next several paragraphs. In the von Zelewsky and Bemtgen study, the solid used was aerosil 300 from Degussa, at a concentration of 40 g liter$^{-1}$, total Cu(II) was $10^{-3}$ M, while $L_{\text{tot}}/\text{Cu(II)}_{\text{tot}}$ (where $L$ = organic ligand) was varied. Aerosil 300 has a specific surface area of 300±30 m$^2$g$^{-1}$ [48], therefore the available surface area per volume was 12,000 m$^2$ liter$^{-1}$. The pH range under investigation was $0 \leq \text{pH} \leq 7$. In the Motschi study, the solid used was Aluminum Oxide C from Degussa, with a solid concentration of 40 g liter$^{-1}$, total Cu(II) was in the range of 1 to 4 x $10^{-3}$ M, while $L_{\text{tot}}/\text{Cu(II)}_{\text{tot}}$ was varied. Aluminum Oxide C has a surface area per unit weight of 100±15 m$^2$g$^{-1}$ [48], giving an available surface area per volume of 4000 m$^2$ liter$^{-1}$. The EPR samples were prepared in the pH range $8 \leq \text{pH} \leq 10$. Because the experimental pH ranges in the two studies differ significantly, speciation of Cu(II) and the ligand in the aqueous phase, and speciation of the solid surface may also differ significantly, so comparison of otherwise nearly identical systems may be difficult. Our own calculations using HYDRAQL [70] showed that the speciation of Cu(II)-bipy complexes is fairly constant from $3 \leq \text{pH} \leq 10$. However, Takimoto and Miura [22] suggested that Cu(II)-bipy$_1$ hydrolyzes at pH > 8, which would indicate different Cu(II) species are dominant in the different pH ranges in the Motschi study [29], and the von Zelewsky and Bemtgen study [28].

Focusing first on the EPR results of systems with $L_{\text{tot}}/\text{Cu(II)}_{\text{tot}} = 1$, as summarized in Table 6.1, the authors interpreted that Cu(II)-L$_1$ adsorbed in inner-sphere mode is the dominant species on both aerosil 300 and $\gamma$-Al$_2$O$_3$. The hyperfine parameters ($A_{||}$) of Cu(II)-en$_1$ (1,2-ethylenediamine), Cu(II)-phen$_1$ (1,10-phenantroline), Cu(II)-bipy$_1$, and Cu(II)(H$_2$O)$_6$ complexes on $\gamma$-Al$_2$O$_3$ are larger than those of the corresponding
Table 6.1. Summary of EPR parameters of Cu(II)-organic sorption complexes on oxides and oxyhydroxides from previous studies. Only complexes with solution ligand to metal ratio of 1:1 are presented in this table since data for this ratio are available for both aerosil-300 and γ-Al₂O₃. In other words, the dominant species in aqueous solution is Cu(H₂O)₄L, where L are nitrilotriacetate (NTA), 1,2-ethylenediamine (en), 1,10-phenantroline (phen), a-picollinate (a-pic), 2,2'-bipyridine (bipy), glycinate (Gly). Error estimates for data from [29] are g∥: ±0.01, A₁∥: ±5 cm⁻¹; error estimates for data from other sources are not available. For more detail discussion on the conditions of sample preparation, and the comparison of sorption of Cu(H₂O)₂(bipy)₂, please see text. The last three rows of data are Cu(II)-Gly complexes on gibbsite and boehmite.

<table>
<thead>
<tr>
<th>ligand (L)</th>
<th>γ-Al₂O₃</th>
<th>aerosil-300</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g∥</td>
<td>A₁∥ (10⁻⁴ cm⁻¹)</td>
</tr>
<tr>
<td>OH₂OH₂</td>
<td>2.357</td>
<td>148 [29]</td>
</tr>
<tr>
<td>NTA</td>
<td>2.334</td>
<td>155 [29]</td>
</tr>
<tr>
<td>en</td>
<td>2.255</td>
<td>184 [29]</td>
</tr>
<tr>
<td>phen</td>
<td>2.288</td>
<td>171 [29]</td>
</tr>
<tr>
<td>α-pic</td>
<td>2.300</td>
<td>170 [29]</td>
</tr>
<tr>
<td>bipy</td>
<td>2.295</td>
<td>177 [29]</td>
</tr>
<tr>
<td>bipy</td>
<td>2.265</td>
<td>172 [29]</td>
</tr>
<tr>
<td>Gly</td>
<td>2.283</td>
<td>176 [29]</td>
</tr>
<tr>
<td>Gly/gibbsite</td>
<td>=2.29</td>
<td>172 [148]</td>
</tr>
</tbody>
</table>

For more detail discussion on the conditions of sample preparation, and the comparison of sorption of Cu(H₂O)₂(bipy)₂, please see text. The last three rows of data are Cu(II)-Gly complexes on gibbsite and boehmite.
complexes on aerosil-300 by 12-20 x 10⁻⁴ cm⁻¹. This difference is larger than the error of measurement (5 x 10⁻⁴ cm⁻¹), or differences that might arise between laboratories. In general, larger $A_{||}$ indicates higher covalency of the ligand, or stronger bonding between the ligands and the Cu(II) [32, 63]. In this case, the larger $A_{||}$ for Cu(II)-L₁ on the γ-Al₂O₃ surface suggests slightly stronger bonding between Cu(II)-L₁ and γ-Al₂O₃ surface than the bonding between Cu(II)-L₁ and aerosil 300 surface.

For systems with $L_{tot}/Cu(II)_{tot} = 2$, comparison of EPR results is complicated by the different methods used in sample preparation in the two studies. Von Zelewsky and Bemtgen added solutions which have pre-defined $L_{tot}/Cu(II)_{tot}$ to aerosil 300 solids and allowed the mixtures to equilibrate. They found that the $g_{||}$ and $A_{||}$ parameters of Cu(II) complexes on aerosil 300 prepared with $L_{tot}/Cu(II)_{tot} = 2$ (where $L$ = bipy, phen, en, or α-pic (α-picolinate )), are different from those prepared with $L_{tot}/Cu(II)_{tot} = 1$ [28]. Von Zelewsky and Bemtgen interpreted these results as indicating that Cu(II)-bipy₂, Cu(II)-phen₂, and Cu(II)-en₂ bond to aerosil 300 in an inner-sphere mode, while the uncharged Cu(II)-α-pic₂ bonds to the surface through a hydrogen bond. In the Motschi study, apparently the γ-Al₂O₃ surface which already had Cu(II)-L₁ adsorbed on it was further reacted with excess ligands to determine whether Cu(II)-L₂ complexes can form on the surface. The author found that "treating the complex (≡AlO)₂Cu(II)L with an excess of the ligand L does not lead to a complex (≡AlO)₂Cu(II)L₂" [29]. The author, however, did not indicate what type of complexes were formed as a result of the experiment or whether there was any change in the complex at all. Thermodynamically, the sequence of addition of the various components should not affect the final products, but kinetically, this could be important. The particular method of sample preparation, therefore, does not allow us to conclude whether Cu(II)-L₂ does not adsorb on the γ-Al₂O₃ surface, or merely that Cu(II)-L₁ that is already on the surface does not react further with excess ligands in the time allowed. In summary, we can't say whether or not bond strength is affected by the substrate for Cu(II)-L₂ complexes, but that, if it proves true that Cu(II)-L₂ does not form (even given enough time) on alumina, then am-SiO₂ and γ-Al₂O₃ differ significantly in their influence on the complex.

An earlier study by Takimoto and Miura [22] on Cu(II)-bipy sorption on alumina and silica-alumina mixtures may offer some additional information on the type of complexes formed on alumina surfaces. However, it is necessary to be cautious in the comparison because the Takimoto and Miura experiment was conducted using methanol as
solvent; the speciation of Cu(II)-bipy complexes, as well as the surface properties, might be very different in methanol compared to those in aqueous systems. In this study, the authors also studied the pH dependence of EPR signals of Cu(II)-bipy complexes in aqueous solutions and used these results to aid their interpretation of EPR data of sorption samples. They suggested that EPR results of aqueous samples indicate Cu(II)-bipy complexes hydrolyze at pH > 8, i.e., one or two of the water molecules in the coordination sphere of Cu(II) are replaced by OH-.

In methanol, Takimoto and Miura found that when \( \text{bipy}_{\text{tot}}/\text{Cu(II)}_{\text{tot}} = 1 \), the EPR spectrum of the surface complexes on alumina can be deconvoluted into three components, indicating the presence of three different chemical species [22]. The species with the lowest g\( _\parallel \) value was interpreted as a Cu(II)-bipy1 complex coordinated to two surface OH groups, due to the similarity of its g\( _\parallel \) parameter to that of the Cu(II)-bipy1 complex in aqueous solution at pH > 12.5. The species with the intermediate g\( _\parallel \) value was interpreted as Cu(II)-bipy1 coordinated to one surface OH group, by comparison of its g\( _\parallel \) parameter with that of the Cu(II)-bipy1 complex in aqueous solution in the pH range 8 to 11. The species with the highest g\( _\parallel \) value was unassigned. This unassigned species is probably not Cu(II)-bipy2 because Cu(II)-bipy2 should have lower g\( _\parallel \) than Cu(II)-bipy1. In summary, two of the surface Cu(II) species are Cu(II)-bipy1, each coordinating to a different number of surface functional groups. When \( \text{bipy}_{\text{tot}}/\text{Cu(II)}_{\text{tot}} = 2 \), Takimoto and Miura interpreted the EPR spectrum of the surface complexes on alumina to be similar to those of the surface complexes that form with \( \text{bipy}_{\text{tot}}/\text{Cu(II)}_{\text{tot}} = 1 \). This result indicates that even though \( \text{bipy}_{\text{tot}}/\text{Cu(II)}_{\text{tot}} = 2 \), Cu(II)-bipy2 does not form on the surface, but rather, two of the three surface Cu(II) species have only one bipy coordinated to it. If the predominant species in methanol solution was Cu(II)-bipy2, then the result may suggest that one bipy is dissociated from Cu(II)-bipy2 when it adsorbs on alumina surfaces. If this is indeed what is happening, then the sorption of Cu(II)-bipy2 on alumina is different from the sorption of Cu(II)-bipy2 on am-SiO2, where the entire complex apparently adsorbs intact, as found in earlier studies by others [28] and in Chapter 5.

In summary, for the four or five ligands examined in the previous studies discussed above, there is ample evidence that both Cu(II)-L and Cu(II)-L\(_2\) sorption complexes can form on the silica surface under appropriate conditions (Chapter 5 and [28]). There is also evidence that Cu(II)-L surface complexes form on alumina from Cu(II)-L solutions, but there is tentative evidence that sorption onto alumina from solutions containing
predominantly Cu(II)-L₂ complexes yields Cu(II)-L₁ complexes [22, 29]. Since the trend seems to be true for a few ligands, both negatively charged (Cu(II)-α-pic₂) and positively charged metal complexes (Cu(II)-bipy₂, Cu(II)-phen₂, and Cu(II)-en₂), it has implications for the sorption of Cu(II)-organic complexes in general. Unfortunately we cannot conclude safely whether Cu(II)-L₂ indeed does not adsorb on alumina surface because experiments with alumina were conducted using slightly different methods or an entirely different solvent and pH.

In this study, the objectives are to: (1) determine whether Cu(II)-bipy₂ complexes can adsorb on γ-Al₂O₃; (2) determine whether bipy also increases sorption of Cu(II) on γ-Al₂O₃ at low sorbate to sorbent ratio; (3) determine whether the strength of the interaction between Cu(II)-bipy complexes and γ-Al₂O₃ relative to that of the interaction between Cu(II) complexes and am-SiO₂ surface.

6.3. EXPERIMENTAL

Experimental details have been described in Chapter 5.

6.4. RESULTS

6.4.1. Uptake Results

Figure 6.1 shows uptake of Cu(II) and bipy on γ-Al₂O₃ as a function of pH and ratio of bipytot/Cu(II)tot. From these independent uptake measurements, ratios of bipy to Cu(II) on the surface (bipyads/Cu(II)ads) were calculated and are also shown in Figure 6.1. For the system with bipytot/Cu(II)tot = 2, the experiments were conducted on two different time scales. One has an equilibration time of approximately 24 hours. The other has an equilibration time of approximately 1 hour. For both systems with bipytot/Cu(II)tot = 1 or 2, irrespective of time scale, Cu(II) uptake on γ-Al₂O₃ is decreased by bipy. Furthermore, as bipytot/Cu(II)tot increases, the decrease in Cu(II) sorption is more significant. The experiments with an equilibration time of 1 hour has less Cu(II) sorption than the experiments with 24 hours equilibration time in the low pH region. This is perhaps because sorption has not gone to completion in the short equilibration time. At the low pH region, the pH of the system seemed to be buffered, i.e., large amounts of base was necessary to titrate the samples to ca. pH 4 or 5. Data in that pH range have large uncertainties, perhaps because of dissolution of γ-Al₂O₃ at low pH, thus interfering with the sorption process.
Figure 6.1. Uptake of Cu(II) and bipy on γ-Al₂O₃ as a function of concentration and bipy to Cu(II) ratio. From these independent uptake measurements, ratios of bipy to Cu(II) on the surface were calculated and are also shown. [Cu(II)]=0.0001 M, [NaNO₃]=0.1 M, [solid]=20.0 g liter⁻¹.
For all systems, it was found that bipy$_{ads}$/Cu(II)$_{ads}$ is significantly smaller than bipy$_{tot}$/Cu(II)$_{tot}$. As discussed in Chapter 5, when % Cu(II) adsorbed is low (below 10 or 20%), the errors in bipy$_{ads}$/Cu(II)$_{ads}$ are very large. The low % Cu(II) adsorbed coincides with the low pH region, and because of the large errors in bipy$_{ads}$/Cu(II)$_{ads}$, their values cannot be determined accurately. For bipy$_{tot}$/Cu(II)$_{tot}$ = 1 and considering only samples with % Cu(II) adsorbed $\geq$ 10%, bipy$_{ads}$/Cu(II)$_{ads}$ is approximately 0.6 in the pH range 6 $\leq$ pH $< 9$, and drops to approximately 0.4 when pH $\approx$ 9. For bipy$_{tot}$/Cu(II)$_{tot}$ = 2 and considering only samples with % Cu(II) adsorbed $\geq$ 10%, then bipy$_{ads}$/Cu(II)$_{ads}$ is approximately 0.6 to 0.8 in the pH range 6 $\leq$ pH $\leq 9$, and drops to approximately 0.4 when pH $\approx$ 9.

Figure 6.2 shows the effect of concentration on sorption of Cu(II) and bipy, and bipy$_{ads}$/Cu(II)$_{ads}$, with bipy$_{tot}$/Cu(II)$_{tot}$ fixed at two. As sorbate-to-sorbent ratio increases, the decrease in Cu(II) sorption in the presence of bipy is even more significant. For the lowest sorbate-to-sorbent samples in this study, bipy$_{ads}$/Cu(II)$_{ads}$ ranges from 0.4 to 0.9. As sorbate-to-sorbent ratio increases, bipy$_{ads}$/Cu(II)$_{ads}$ seems to be increasing. At the highest sorbate-to-sorbent ratio, bipy$_{ads}$/Cu(II)$_{ads}$ is approximately 1.4.

The effect of ionic strength was studied in one system with low sorbate-to-sorbent ratio and bipy$_{tot}$/Cu(II)$_{tot}$ = 2, and Figure 6.3 shows results of this study. Two different ionic strengths were investigated, one at approximately 0.1 M, with NaNO$_3$ as the background electrolyte, and the other with no added NaNO$_3$, resulting in an ionic strength of $\approx$0.0002 M which was derived from the dilute Cu(NO$_3$)$_2$ solution. At the low pH, low uptake region and the high pH, high uptake region, ionic strength effect seems to be negligible. Unfortunately, there is quite a bit of scatter in the data in the relatively sharp adsorption edge, and the effect of ionic strength on sorption in that pH range cannot be ascertained.

6.4.2. Spectroscopic Results

Several sorption samples from the uptake study were chosen for spectroscopic studies. We will describe results of our EPR and XAFS experiments separately. Results common to most samples are described first, followed by detailed results specific to each sample.
Figure 6.2. Effect of concentration on Cu(II) and bipy sorption, keeping bipy$_{tot}$/Cu(II)$_{tot}$=2 in the all systems. [NaNO$_3$]=0.1 M, [solid]=20.0 g liter$^{-1}$ except where indicated.
Figure 6.3. Effect of ionic strength on Cu(II) and bipy sorption, as well as the resultant bipy$_{ads}$/Cu(II)$_{ads}$ ratio. [Cu(II)]=0.0001 M, [bipy]=0.0002 M, [solid]=20.0 g liter$^{-1}$. 
6.4.2.1. EPR Results

Figure 6.4 shows EPR spectrum of Al₂O₃ (bipyₜₒₜ/Cuₜₒₜ= 1, Γ = 0.05 μmol m⁻²). Because of the poor data quality due to low concentration and the presence of water, it is not possible to obtain reliable values of g∥ and A∥ from this sample. The following general conclusions can be drawn from the EPR spectrum:

(1) Even when wet at RT, the EPR spectrum is anisotropic, indicating that the surface complexes are immobile on the time-scale of the technique, which is approximately 10⁻¹¹ to 10⁻¹⁰ seconds.

(2) The spectrum is of the "axial type" [32], with spectral parameters g∥ ≥ g⊥, which is consistent with the presence of tetragonal or square-planar Cu(II) on the surfaces.

(3) It seems likely that this spectrum can be deconvoluted into two or three spectra, suggesting that there are multiple species on the surface.

(4) Since multinuclear complexes and/or precipitates of metal ions produce very broad or undetectable spectra, while isolated metal ions produce the normal paramagnetic spectra, the EPR data for the sorption samples indicate that Cu(II) ions on the surface occupy magnetically isolated sites.

\[
\text{Al}_2\text{O}_3 \ (\text{bipy}_{\text{tot}}\text{Cu(II)}_{\text{tot}}=1, \ \Gamma=0.05 \ \mu\text{molm}^{-2})
\]

Figure 6.4. EPR spectrum of Al₂O₃ (bipyₜₒₜ/Cuₜₒₜ = 1.0; Γ = 0.05 μmol m⁻²). Data collected on wet paste at RT. Microwave frequency: 9.848 GHz; microwave power: 13.0 dB, gain 1.25 x 10⁴.
6.4.2.2. XAFS--XANES Results

The following general conclusions can be drawn from the XANES spectra for all the sorption samples:

(1) The edge positions of all sorption samples are characteristic of those of Cu(II), indicating no reduction of Cu(II) to Cu(I) or Cu(0) when it adsorbs on γ-Al₂O₃.

(2) Cu K-edge structures and their second derivatives (Figure 6.5) of all Cu(II) sorption samples prepared in the presence of bipy are different from those of Cu(II) (aq) or Cu adsorbed on γ-Al₂O₃ prepared in the absence of bipy, indicating that the electronic structure of the surface species is significantly different from that of Cu(II)(aq) or Cu adsorbed on γ-Al₂O₃ in the absence of bipy.

(3) Cu K-edge structures (Figure 6.5) of all Cu(II) sorption samples are different from those of aqueous Cu(II)-bipy complexes, indicating that the surface complexes have different electronic structures from those of aqueous Cu(II)-bipy complexes. The differences between the sorption complexes and Cu(II)-bipy complexes in solution can be seen even more clearly in the second derivatives of the spectra (Fig. 8b). Quantitatively, the XANES spectra of the sorption samples have larger amplitude in the 8,982-8,990 eV region than aqueous Cu(II)-bipy. Specifically, the sorption sample has much larger absorption at 8,983 eV and 8,988 eV, two energies that are normally assigned to the 1s→3d and the 1s→4p transitions, respectively [135-137]. The increase in intensity in the 1s→3d transition is probably due to the Cu(II) complex becoming even more noncentrosymmetric, thus allowing more p-d mixing in Cu(II) energy levels and conferring more dipole-allowed character to the d-orbital.

6.4.2.3. XAFS--EXAFS Results

Figures 6.6 shows normalized, background-subtracted EXAFS spectra and the corresponding Fourier transforms of Cu(II)-bipy/γ-Al₂O₃ sorption samples, Cu(NO₃)₂ aqueous solution, Cu(II)-bipy complexes in aqueous solution, and Cu(II)-containing crystalline model compounds. As discussed in Chapter 5, a second weaker frequency at k \( \approx 5 \, \text{Å}^{-1} \) is characteristic of model compounds with one bipy (Cubipy(NO₂)₂ and Cu(II)-bipy₁ (aq)), while the second frequency at k \( \approx 5 \, \text{Å}^{-1} \) is significantly more pronounced for model compounds with two bipy. Qualitative comparison of the EXAFS spectra of
Figure 6.5. Normalized Cu K-XANES spectra (Figure 6.5a) and second derivatives (Figure 6.5b) of (i) Cu(NO₃)₂ solution, (ii) sample prepared in the absence of bipy, Cu/Al₂O₃ (0.05 µmol m⁻²), (iii) Cu(II)-bipy₁ (aq), (iv) Al₂O₃ (bipy⁻⁰⁻/Cu⁺⁻=1, Γ=0.05 µmol m⁻²), (v) Al₂O₃ (bipy⁻⁰⁻/Cu⁺⁻=2, Γ=0.05 µmol m⁻²), (vi) Al₂O₃ (bipy⁻¹⁻/Cu⁺⁻=2, Γ=0.4 µmol m⁻²), (vii) Cu(II)-bipy₂ (aq), (viii) SiO₂ (bipy⁻¹⁻/Cu⁺⁻=2, Γ=0.05 µmol m⁻²). Note that sorption samples prepared in the presence of bipy have XANES different from sorption sample prepared in the absence of bipy, e.g., in the feature marked by * at approximately 9010 eV. Sorption samples of Cu(II)-bipy on γ-Al₂O₃ prepared with bipy⁻¹⁻/Cu⁺⁻=2 do not have the pronounced absorption feature at ≈ 9005 eV typical of samples containing Cu(II)-bipy₂ (marked by arrows in Fig. 6.5a).
Figure 6.6. Normalized, background-subtracted Cu K-EXAFS spectra (Figure 6.6a) and the corresponding Fourier transforms (Figure 6.6b) of (i) Cu(NO₃)₂ solution, (ii) sample prepared in the absence of bipy, Cu/Al₂O₃ (0.05 μmol m⁻²), (iii) Cu(II)-bipy₁ (aq), (iv) Al₂O₃ (bipyₜₒₜ/Cuₜₒₜ=1, Γ=0.05 μmol m⁻²), (v) Al₂O₃ (bipyₜₒₜ/Cuₜₒₜ=2, Γ=0.05 μmol m⁻²), (vi) Al₂O₃ (bipyₜₒₜ/Cuₜₒₜ=2, Γ=0.4 μmol m⁻²), (vii) Cu(II)-bipy₂ (aq), (viii) SiO₂ (bipyₜₒₜ/Cuₜₒₜ=2, Γ=0.05 μmol m⁻²). Sorption samples of Cu(II)-bipy on γ-Al₂O₃ that are prepared with bipyₜₒₜ/Cu(II)ₜₒₜ = 2 do not have the pronounced feature at ≈ 5 Å⁻¹ typical of samples containing Cu(II)-bipy₂. Rather, all sorption samples, for bipyₜₒₜ/Cu(II)ₜₒₜ=1 or 2, have a second weak frequency at ≈ 5 Å⁻¹ that is typical of samples containing Cu(II)-bipy₁.
sorption samples to those of model compounds indicates that sorption samples have features more similar to those of Cu(II)-bipy₁.

Several points are worth noting in the quantitative fitting of the EXAFS of these two samples. Only one carbon second neighbor is present at approximately 2.9 Å, which suggests that only 50% of the Cu(II) in this sample is coordinated to bipy. Alternatively, there could be significant interference of other components in the fit with the backscattering path of these carbon atoms. Inclusion of an Al second neighbor improves the fit. However, deconvolution of the various components of the fit shows that there is significant cancellation between the backscattering path of the carbon atoms at 2.9 Å and the aluminum atom at approximately 2.7-2.8 Å. This raises a question about the validity of including Al in the fit. The data analysis code, EXAFSPAK, which was used in this study allows for the generation of search profiles for the coordination number (N), distance (R), and Debye-Waller factor(σ²) of individual component in the fit. Using this option, a search profile for Al second neighbor was generated. This search profile indicates that if an Al second neighbor does exist, then the most likely location is at approximately 2.7 to 2.8 Å.

### 6.5. DISCUSSION

#### 6.5.1. Composition and Structure of the Surface Complexes

We will first focus on determining the composition of the surface complexes using mass action considerations similar to those discussed in Chapter 5, but focusing on the speciation of Cu(II). In the aqueous phase, most, if not all, of the Cu(II) is bonded to bipy when \( \frac{\text{bipy}_{\text{tot}}}{\text{Cu(II)}_{\text{tot}}} = n \) (\( n = 1 \) or 2), and the dominant species in solution is \( \text{Cu(II)}\text{-bipy}_n^{(aq)} \). Upon sorption to the \( \gamma\text{-Al}_2\text{O}_3 \) surface, some bipy could potentially dissociate from Cu(II). The sorption equilibrium for Cu from the aqueous phase to the \( \gamma\text{-Al}_2\text{O}_3 \) surface, disregarding the details of bonding to the surface for the moment, can thus be written as:

\[
\text{Cu(II)}\text{-bipy}_n^{(aq)} = \text{surface[}\tau\text{Cu(II)} + \varphi\text{Cu(II)}\text{-bipy}_1 + \kappa\text{Cu(II)}\text{-bipy}_2 + \lambda\text{Cu(II)}\text{-bipy}_3]\]

\[(6.1)\]

where \( \tau, \varphi, \kappa, \) and \( \lambda \leq 1, \)

\[
\tau + \varphi + \kappa + \lambda = 1
\]

\[(6.2)\]

when all the Cu(II) in the system is adsorbed on the surface.
Uptake measurements have shown that the bipy$_{ads}$Cu(II)$_{ads}$ are non-integers which are $\leq 1$ indicating that some bipy dissociates from Cu(II) during sorption. Therefore, there must be some Cu(II) that is unbound to bipy on the surface, and $\tau \neq 0$. A separate infrared (IR) spectroscopy study (Chapter 4) provided additional evidence that most, if not all, of the sorbed bipy is coordinated to Cu(II). Consequently, there must also be some bipy-bound Cu(II) species on the surface, and $\varphi$, $\kappa$, or $\lambda$ is therefore $\neq 0$, and $\tau$ is $< 1$.

It is not possible to determine the other coefficients in eq. (6.1) based on the information available. However, EXAFS spectra for the sorption samples are qualitatively most similar to those of Cu(II)-bipy$_1$ containing aqueous solution or model compound, suggesting that the surface species has significant proportion of Cu(II)-bipy$_1$, and that the coefficients $\kappa$ and $\lambda$ may be negligible. In summary, for samples prepared with bipy$_{tot}$/Cu(II)$_{tot} = 1$ or 2, uptake measurements, mass action considerations, and IR results indicate that there are both bipy-bound and free Cu(II) on the $\gamma$-Al$_2$O$_3$ surface. The EPR spectrum for sample Al$_2$O$_3$ (bipy$_{tot}$/Cu$_{tot}$= 1, $\Gamma = 0.047$ $\mu$mol m$^{-2}$) indicates the presence of multiple species, supporting the conclusion of at least two types of Cu(II) on the surface.

XANES results indicate that the electronic structure of the Cu(II) in surface complexes is different from that of Cu(II)-bipy in aqueous solution, indicating that the local environment of the surface complexes is significantly different from Cu(II)-bipy in aqueous solution, thus suggesting relatively strong interaction with the surface. This observation, together with the inferred immobility of the Cu from the EPR results, suggests that the sorption complexes comprise of Cu(II) and Cu(II)-bipy$_n$ bonded to the surface. However, EXAFS analysis failed to conclusively reveal the presence of Al second neighbors and the exact bonding mode cannot be determined.

6.5.2. Comparison of Cu(II)-bipy Sorption on Different Oxides

There are several significant differences between sorption of Cu(II) on $\gamma$-Al$_2$O$_3$ and am-SiO$_2$. In the presence of bipy, at low sorbate-to-sorbent ratio, the Cu(II) sorption edge on am-SiO$_2$ is shifted to lower pH, i.e., bipy increases the sorption of Cu(II) on am-SiO$_2$ (Chapter 5) and aerosil 300 [8, 28, 55]. However, in the presence of bipy, at sorbate to sorbent ratios similar to those investigated in (Chapter 5), the Cu(II) sorption edge on $\gamma$-Al$_2$O$_3$ was shifted to higher pH, i.e., bipy decreases sorption of Cu(II) on $\gamma$-Al$_2$O$_3$. The effect of bipy on Cu(II) sorption is even larger when we consider that in the absence of
bipy, the Cu(II) sorption edge on γ-Al₂O₃ is at lower pH than the Cu(II) sorption edge on am-SiO₂ (Chapter 2).

Calculations of \( \text{bipy}_{\text{ads}}/\text{Cu(II)}_{\text{ads}} \) on the oxide surfaces show that when \( \frac{\text{bipy}_{\text{tot}}}{\text{Cu(II)}_{\text{tot}}} = 1 \), \( \frac{\text{bipy}_{\text{ads}}}{\text{Cu(II)}_{\text{ads}}} = 1 \) on am-SiO₂, while \( \frac{\text{bipy}_{\text{ads}}}{\text{Cu(II)}_{\text{ads}}} \) ranges from 0.4 to 0.6 on γ-Al₂O₃. When \( \frac{\text{bipy}_{\text{tot}}}{\text{Cu(II)}_{\text{tot}}} = 2 \), \( \frac{\text{bipy}_{\text{ads}}}{\text{Cu(II)}_{\text{ads}}} = 2 \) on am-SiO₂, and \( \frac{\text{bipy}_{\text{ads}}}{\text{Cu(II)}_{\text{ads}}} \) ranges from 0.6 to 1.4 on γ-Al₂O₃. In other words, \( \frac{\text{bipy}_{\text{ads}}}{\text{Cu(II)}_{\text{ads}}} \) for sorption of Cu(II)-bipy complexes on am-SiO₂, while \( \frac{\text{bipy}_{\text{ads}}}{\text{Cu(II)}_{\text{ads}}} \) ranges from 0.6 to 1.4 on γ-Al₂O₃. These differences suggest that Cu(II)-bipy complexes can adsorb intact on am-SiO₂ over much of the pH range of practical interest (4 ≤ pH ≤ 9), while dissociation of Cu(II)-bipy complexes occurs when they adsorb on γ-Al₂O₃. The degree of dissociation of Cu(II)-bipy complexes depends on pH, \( \frac{\text{bipy}_{\text{tot}}}{\text{Cu(II)}_{\text{tot}}} \), and the sorbate-to-sorbent ratio, i.e., the relative abundance of the various components in this system.

Spectroscopic studies show that Cu(II)-bipy₁ and Cu(II)-bipy₂ both adsorb on the am-SiO₂ surface. Quantitative EXAFS analysis shows that Cu(II)-bipy₁ complex adsorbs in an inner-sphere, monodentate mode on am-SiO₂. While the exact speciation of the surface complexes on γ-Al₂O₃ is not known, their EXAFS are qualitatively similar to those of Cu(II)-bipy₁ or a mixture of Cu(II)-bipy₁ and Cu(II) uncomplexed by bipy. One sample in this study, Al₂O₃ (bipyₜₒₜₜ/Cuₜₒₜ = 2; \( \Gamma = 0.44 \mu\text{mol m}^{-2} \)), was prepared at a pH value (9.8) very close to the pH of preparation of a sorption sample of Cu(II)-bipy on am-SiO₂ (SiO₂ (bipyₜₒₜₜ/Cuₜₒₜ = 2; \( \Gamma = 0.77 \mu\text{mol m}^{-2} \)), which was 9.0. This indicates pH is probably not the factor that causes formation of Cu(II)-bipy₁ sorption complexes on am-SiO₂ and dissociation of Cu(II)-bipy₂ on γ-Al₂O₃.

Ludwig and Schindler studied the influence of bipy on Cu(II) sorption on a-TiO₂ (anatase) [116]. The presence of bipy decreases the sorption of Cu(II) onto a-TiO₂. From the % bipy_ads and % Cu(II)_ads in the Ludwig and Schindler study, we can calculate bipy_ads/Cu(II)_ads in the Cu(II)/bipy/a-TiO₂ system. Figure 6.7 shows the pH dependence of bipy_ads/Cu(II)_ads in the a-TiO₂ system compared to bipy_ads/Cu(II)_ads in this study. In the a-TiO₂ system, when bipyₜₒₜₜ/Cu(II)ₜₒₜ = 1, bipy_ads/Cu(II)_ads increases from 0.2 at pH 4 to approximately 1.0 at pH 8. Above pH 9, bipy_ads/Cu(II)_ads starts to decrease. When bipyₜₒₜₜ/Cu(II)ₜₒₜ = 2, and above pH 6, bipy_ads/Cu(II)_ads ranges from 1.1 to 2. Below pH 6, errors in bipy_ads/Cu(II)_ads are large, partly because of the reasons described in Chapter 5,
and also partly because the data points were transcribed from the paper of Ludwig and Schindler. Results of the present study indicate that the Cu(II)/bipy/γ-Al₂O₃ ternary system behaves in a qualitatively similar fashion to the Cu(II)/bipy/a-TiO₂ ternary system.

(a)  
\[ \gamma\text{-Al}_2\text{O}_3 \text{ (this study)} \]
[Cu(II)] = 0.1 mM, [bipy] = 0.1 mM,  
[solid] = 20.0 g liter⁻¹;  
solid surface area per unit weight = 100 m² g⁻¹.

+ a-TiO₂ (Ludwig and Schindler, 1995)  
[Cu(II)] = 8.41 x 10⁻⁴ M, [bipy] = 8.22 x 10⁻⁴ M,  
[solid] = 9.4 g liter⁻¹;  
solid surface area per unit weight = 90 m² g⁻¹.

(b)  
\[ \gamma\text{-Al}_2\text{O}_3 \text{ (this study)} \]
[Cu(II)] = 1.5 mM, [bipy] = 3.0 mM,  
[solid] = 10.0 g liter⁻¹;  
solid surface area per unit weight = 100 m² g⁻¹.

+ a-TiO₂ (Ludwig and Schindler, 1995)  
[Cu(II)] = 8.24 x 10⁻⁴ M, [bipy] = 1.61 x 10⁻³ M,  
[solid] = 9.1 g liter⁻¹;  
solid surface area per unit weight = 90 m² g⁻¹.

Figure 6.7. Comparison of bipy_{ads}/Cu(II)_{ads} on γ-Al₂O₃ and a-TiO₂ (anatase).  
[NaNO₃] = 0.1 M in both studies. Figure 6.7 (a). Systems with bipy_{tot}/Cu(II)_{tot} = 1.  
Figure 6.7 (b). Systems with bipy_{tot}/Cu(II)_{tot} = 2.
While the trend of $\text{bipy}_{\text{ads}}/\text{Cu(II)}_{\text{ads}}$ may seem to be complicated, Ludwig and Schindler were able to model their results satisfactorily by allowing for the formation of a number of surface species including Cu(II) complexed to the a-TiO$_2$ surface (but not to bipy), Cu(II)-bipy$_1$ complexed to the a-TiO$_2$ surface, and Cu(OH)$_2$ precipitates. In order for surface functional groups on a-TiO$_2$ to substitute for bipy in the Cu(II) coordination sphere, the equilibrium constant between the surface functional groups and Cu(II) has to be large [116]. In other words, at least some of the surface functional groups on a-TiO$_2$ have larger affinities than bipy for Cu(II).

Results from Chapter 3 indicate that the a-TiO$_2$ surface can bind free Cu(II) strongly, so the suggestion of a large affinity of the a-TiO$_2$ surface for Cu(II) is not unreasonable. Results from Chapter 2 indicate that $\gamma$-Al$_2$O$_3$ binds Cu(II) more strongly than am-SiO$_2$. The stronger binding of Cu(II) on the $\gamma$-Al$_2$O$_3$ and a-TiO$_2$ surfaces, relative to am-SiO$_2$, is one possible explanation for the dissociation of some bipy from the coordination sphere of Cu(II) during sorption on these two solid surfaces. Conversely, because the am-SiO$_2$ surface does not have as high an affinity for Cu(II) as these two other solids, Cu(II)-bipy complexes adsorb on am-SiO$_2$ without dissociation.

This explanation, even though plausible, does not explain why Cu(II) cannot be simultaneously coordinated to both bipy and a strongly binding functional group on the $\gamma$-Al$_2$O$_3$ and a-TiO$_2$ surfaces. It is possible that the surface functional groups on both solids act as very large ligands, and for steric hindrance reasons, Cu(II) cannot be coordinated to both the surface functional group(s) and bipy.

A previous study by Takimoto et al. [149] of the sorption of Cu(II)-bipy complexes, from a methanol solution onto calcium hydroxide pretreated at 300°C or higher in vacuo, found that the surface Cu(II) is not coordinated to bipy. The resulting surface complexes have an EPR spectrum similar to that of cupric sulfate in methanol solution and to that of cupric sulfate adsorbed on heat-pretreated Ca(OH)$_2$ surfaces. Takimoto et al. suggested that when the calcium hydroxide was pretreated at or above 300°C for 3 hours in vacuum, the solid becomes calcium oxide. They further suggested that $\text{O}^{2-}$ ions on the calcium oxide surface, which are more basic than the hydroxyl groups on the calcium hydroxide surface, bonds strongly with Cu(II). These authors hypothesized that Cu(II) on the surface takes on a tetrahedral geometry, and the bipy molecule is expelled from the coordination sphere of Cu(II) as a result.
It is possible that the binding of Cu(II)-bipy complexes to γ-Al₂O₃ surface is stronger than that between Cu(II)-bipy complexes and am-SiO₂ surface. The proposed strong binding of Cu(II) to some functional groups on γ-Al₂O₃ is also consistent with the trend of increasing bipy_ads/Cu(II)ads as sorbate-to-sorbent ratio increases. The amount of Cu(II) complexed by different ligands, including the γ-Al₂O₃ surface, bipy, and OH⁻, is the result of the relative ratio of the various components. It is possible that there is only a limited number of highly reactive functional groups on γ-Al₂O₃. When the sorbate-to-sorbent ratio is small, the surface functional groups are able to compete with bipy for Cu(II) and the resultant bipy_ads/Cu(II)ads is ≤1, for bipy_tot/Cu(II)tot = 1 or 2. When the sorbate-to-sorbent ratio is large, the most reactive surface functional groups are already consumed, and the less reactive surface functional groups may bind Cu(II)-bipy complexes without causing the dissociation of bipy. This explanation is consistent with the finding that bipy_ads/Cu(II)ads = 1.4 at the highest sorbate to sorbent ratio studied.

Another possibility that may explain the sorption behavior of Cu(II) on γ-Al₂O₃ is the dissolution of γ-Al₂O₃. Dissolved Al(III) could potentially complex with bipy, competing with Cu(II) for bipy ligands, resulting in bipy_ads/Cu(II)ads < bipy_tot/Cu(II)tot. Unfortunately, the exact stability constants of Al(III) complexes with bipy are not known, so a direct comparison of the stability constant(s) of Cu(II)-bipy complexes and Al(III)-bipy complexes is not possible. General chemical principles, however, may offer a guide. Al(III) is a very hard acid, while bipy is a borderline soft ligand, which generally does not form strong complexes with hard acids [150]. Complexation of bipy by dissolved Al(III), or in other words, competition of Al(III) with Cu(II) for bipy, is probably negligible in this system.

Another way that dissolution of γ-Al₂O₃ might affect the sorption of Cu(II) and bipy is the availability of dissolved Al(III) to reprecipitate as Al(OH)₃ or to form a mixed Cu-Al-hydroxide coprecipitate phase. The incorporation of Cu(II) into Al(OH)₃ or into a coprecipitate phase may only occur if Cu(II) is not complexed with bipy, resulting in the loss of bipy from Cu(II) and, therefore, bipy_ads/Cu(II)ads < bipy_tot/Cu(II)tot. The dissolution of γ-Al₂O₃ should have been negligible under the pH and time scale (24 hours) of this study, according to results of dissolution studies conducted previously [151]. This negligible dissolution would mean that there is not much Al(III) for any reprecipitation or coprecipitation reactions. Furthermore, previous studies which found evidence for the formation of mixed metal-Al coprecipitate phases were conducted in the absence of organic
ligands [16, 18, 92]. More importantly, these previous studies found that the mixed metal-Al coprecipitates generally have structures similar to the hydroxides of the sorbed metal cations. In quantitative EXAFS analysis of coprecipitates, the sorbed metal cation has second neighbors of its own type (e.g., Cu second neighbors would be detected if a Cu-Al-hydroxide coprecipitate comprised a significant fraction of the surface species). In this study, XAFS does not show the presence of any Cu(II) second neighbors. EPR spectra of these samples also indicate the absence of any dipolar broadening, which would be present if there were any Cu second neighbors. Even if a mixed Cu-Al-hydroxide coprecipitate does form in this system, it would probably constitute a small fraction of the overall Cu(II) species on the γ-Al₂O₃ surface and cannot explain adequately the sorption behavior of Cu(II) and bipy on γ-Al₂O₃.

The reprecipitation or coprecipitation explanation also cannot explain the dissociation of Cu(II)-bipy₂ on alumina observed by Takimoto and Miura [22]. The solvent used in their experiment was methanol, which should provide a much smaller amount of OH⁻ ions for reprecipitation or coprecipitation. Lastly, the dissolution and reprecipitation idea cannot explain the sorption of Cu(II) and bipy on a-TiO₂, because a-TiO₂ is a very insoluble solid. The stronger bonding of Cu(II) on a-TiO₂ and γ-Al₂O₃, relative to am-SiO₂, however, is consistent with all the known experimental results.

6.6. CONCLUSIONS

Uptake measurements as a function of pH and bipy to Cu(II) ratio show that bipy decreases Cu(II) sorption onto γ-Al₂O₃ at all Cu(II) concentrations studied (from ΣCu = 0.1 mM to ΣCu = 1.6 mM). The inhibition is more pronounced at higher bipytot/Cu(II)tot ratios in the solution. The ratio bipyads/Cu(II)ads is a non-integer smaller than bipytot/Cu(II)tot in the aqueous solution. This suggests that some bipy dissociates from Cu(II) during sorption. This is in contrast to the Cu(II)/bipy/am-SiO₂ system, where evidence indicates that bipy does not dissociate from Cu(II) during sorption.

Based on uptake and spectroscopic measurements, as well as mass action considerations, there are both bipy-bound and free Cu(II) on the γ-Al₂O₃ surface, whether the dominant species in solution is Cu(II)-bipy₁ or Cu(II)-bipy₂. XANES results indicate that the electronic structure of the Cu(II) surface complexes is different from that of Cu(II)-bipy in aqueous solution, indicating that the local environment of the surface complexes is significantly different from Cu(II)-bipy in aqueous solution, thus suggesting relatively
strong interaction with the surface. This observation, together with the inferred immobility of the Cu(II) from the EPR results, suggests that the sorption complexes comprise of Cu(II) and Cu(II)-bipyₙ bonded to the surface. However, EXAFS analysis failed to conclusively reveal the presence of Al second neighbors, and the exact bonding mode cannot be determined.

Macroscopically, the influence of bipy sorption on am-SiO₂ and γ-Al₂O₃ are significantly different. Bipy decreases Cu(II) sorption on γ-Al₂O₃ at all concentrations, while it increases Cu(II) sorption on am-SiO₂ at low concentrations. Previous study (Chapter 5) suggests that hydrophobic effect is a factor that helps increase Cu(II) sorption on am-SiO₂. There are several reasons that may help explain the decrease in Cu(II) sorption on γ-Al₂O₃ in the presence of bipy. Among them are: (1) the hydrophobic effect may not as significant (e.g., if the γ-Al₂O₃ surface is more hydrophilic) or (2) the electrostatic repulsion between the positively charged γ-Al₂O₃ surface and the positively charged Cu(II)-bipy complexes may be large enough that the overall free energy of sorption is not favorable.

On the molecular scale, the composition of the Cu(II)-bipy surface complexes adsorbed on γ-Al₂O₃ is different than of those on am-SiO₂. Some uptake measurements and modeling studies conducted by Ludwig and Schindler [116] for the Cu(II)/bipy/a-TiO₂ system suggest that the composition of surface Cu(II)-bipy complexes on a-TiO₂ is similar to that found on γ-Al₂O₃ in this study. The similarity between Cu(II)-bipy on γ-Al₂O₃ and a-TiO₂, and the differences between Cu(II)-bipy on γ-Al₂O₃ and am-SiO₂, can perhaps be explained by differences in bonding strength. Studies of Cu(II) sorption in the absence of bipy suggests that Cu(II) bonding to the γ-Al₂O₃ and a-TiO₂ surfaces is stronger than that between Cu(II) and am-SiO₂ surfaces (Chapter 2 and 3). It is possible that bonding between Cu(II)-bipy complexes and the γ-Al₂O₃ and a-TiO₂ surfaces is also stronger than that on am-SiO₂. However, further work is necessary to conclusively support this hypothesis.
REFERENCES


[82] S. Cheah, P. Persson, G. E. Brown, Jr., and G. A. Parks, “Infrared studies of sorption of 2,2'-bipyridine on amorphous SiO₂ and γ-Al₂O₃ in the presence and absence of copper(II),” to be submitted to *J. Colloid Interface Sci.*


[130] W. A. E. McBryde, A Critical Review of Equilibrium Data for Proton- and Metal Complexes of 1,10-Phenanthonoline, 2,2'-Bipyridyl and Related Compounds, vol. 17,


[139] M. Peterson, Stanford University, personal communication, 1996.


