1

PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Votre file - Votre référence

Our file - Notre référence

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Canada

**LONG RANGE ANTIFERROMAGNETIC EXCHANGE
COUPLING IN DINUCLEAR COPPER(II) COMPLEXES CONTAINING
1,4-DICYANAMIDOBENZENE DIANION BRIDGING LIGANDS**

by

LINNUS L. CHERUIYOT, B.Ed(Sc.), M.Sc.

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Doctor of Philosophy

Department of Chemistry

Carleton University

Ottawa, Ontario

December, 1994

© copyright

1994, Linnus L. Cheruiyot

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

THE AUTHOR HAS GRANTED AN
IRREVOCABLE NON-EXCLUSIVE
LICENCE ALLOWING THE NATIONAL
LIBRARY OF CANADA TO
REPRODUCE, LOAN, DISTRIBUTE OR
SELL COPIES OF HIS/HER THESIS BY
ANY MEANS AND IN ANY FORM OR
FORMAT, MAKING THIS THESIS
AVAILABLE TO INTERESTED
PERSONS.

L'AUTEUR A ACCORDE UNE LICENCE
IRREVOCABLE ET NON EXCLUSIVE
PERMETTANT A LA BIBLIOTHEQUE
NATIONALE DU CANADA DE
REPRODUIRE, PRETER, DISTRIBUER
OU VENDRE DES COPIES DE SA
THESE DE QUELQUE MANIERE ET
SOUS QUELQUE FORME QUE CE SOIT
POUR METTRE DES EXEMPLAIRES DE
CETTE THESE A LA DISPOSITION DES
PERSONNE INTERESSEES.

THE AUTHOR RETAINS OWNERSHIP
OF THE COPYRIGHT IN HIS/HER
THESIS. NEITHER THE THESIS NOR
SUBSTANTIAL EXTRACTS FROM IT
MAY BE PRINTED OR OTHERWISE
REPRODUCED WITHOUT HIS/HER
PERMISSION.

L'AUTEUR CONSERVE LA PROPRIETE
DU DROIT D'AUTEUR QUI PROTEGE
SA THESE. NI LA THESE NI DES
EXTRAITS SUBSTANTIELS DE CELLE-
CI NE DOIVENT ETRE IMPRIMES OU
AUTREMENT REPRODUITS SANS SON
AUTORISATION.

ISBN 0-315-98472-4

Canada

Name LINUS L. CHERUYOT

Dissertation Abstracts International is arranged by broad, general subject categories. Please select the one subject which most nearly describes the content of your dissertation. Enter the corresponding four-digit code in the spaces provided.

INORGANIC CHEMISTRY

SUBJECT TERM

0488

U·M·I

SUBJECT CODE

Subject Categories

THE HUMANITIES AND SOCIAL SCIENCES

COMMUNICATIONS AND THE ARTS

Architecture 0729
Art History 0377
Cinema 0900
Dance 0378
Fine Arts 0357
Information Science 0723
Journalism 0391
Library Science 0399
Mass Communications 0708
Music 0413
Speech Communication 0459
Theater 0465

EDUCATION

General 0515
Administration 0514
Adult and Continuing 0516
Agricultural 0517
Art 0273
Bilingual and Multicultural 0282
Business 0688
Community College 0275
Curriculum and Instruction 0727
Early Childhood 0518
Elementary 0524
Finance 0277
Guidance and Counseling 0519
Health 0680
Higher 0745
History of 0520
Home Economics 0278
Industrial 0521
Language and Literature 0279
Mathematics 0280
Music 0522
Philosophy of 0998
Physical 0523

Psychology 0525
Reading 0535
Religious 0527
Sciences 0714
Secondary 0532
Social Sciences 0534
Sociology of 0340
Special 0529
Teacher Training 0530
Technology 0710
Tests and Measurements 0288
Vocational 0747

LANGUAGE, LITERATURE AND LINGUISTICS

Language 0679
General 0289
Ancient 0290
Linguistics 0291
Modern 0401
Literature 0294
General 0295
Classical 0297
Comparative 0298
Medieval 0316
Modern 0591
African 0305
American 0352
Asian 0355
Canadian (English) 0593
Canadian (French) 0311
English 0312
Germanic 0315
Latin American 0313
Middle Eastern 0314
Romance 0314
Slavic and East European 0314

PHILOSOPHY, RELIGION AND THEOLOGY

Philosophy 0422
Religion 0318
General 0321
Biblical Studies 0319
Clergy 0320
History of 0322
Philosophy of 0469
Theology 0323

SOCIAL SCIENCES

American Studies 0323
Anthropology 0324
Archaeology 0326
Cultural 0327
Physical 0310
Business Administration 0272
General 0770
Accounting 0454
Banking 0338
Management 0385
Marketing 0501
Canadian Studies 0503
Economics 0505
General 0508
Agricultural 0509
Commerce-Business 0510
Finance 0511
History 0358
Labor 0366
Theory 0351
Folklore 0366
Geography 0351
Gerontology 0578
History 0578
General 0578

Ancient 0579
Medieval 0581
Modern 0582
Black 0328
African 0331
Asia, Australia and Oceania 0332
Canadian 0334
European 0335
Latin American 0336
Middle Eastern 0333
United States 0337
History of Science 0585
Law 0398
Political Science 0615
General 0616
International Law and Relations 0617
Public Administration 0814
Recreation 0452
Social Work 0626
Sociology 0627
General 0938
Criminology and Penology 0631
Demography 0628
Ethnic and Racial Studies 0629
Individual and Family Studies 0630
Industrial and Labor Relations 0700
Public and Social Welfare 0344
Social Structure and Development 0709
Theory and Methods 0999
Transportation 0453
Urban and Regional Planning 0453
Women's Studies 0453

THE SCIENCES AND ENGINEERING

BIOLOGICAL SCIENCES

Agriculture 0473
General 0285
Agronomy 0475
Animal Culture and Nutrition 0476
Animal Pathology 0359
Food Science and Technology 0478
Forestry and Wildlife 0479
Plant Culture 0480
Plant Pathology 0817
Plant Physiology 0777
Range Management 0746
Biology 0306
General 0287
Anatomy 0308
Biostatistics 0309
Botany 0379
Cell 0329
Ecology 0353
Entomology 0369
Genetics 0793
Limnology 0410
Microbiology 0307
Molecular 0317
Neuroscience 0416
Oceanography 0433
Physiology 0821
Radiation 0778
Veterinary Science 0472
Zoology 0786
Biophysics 0760
General 0425
Medical 0996

EARTH SCIENCES

Biogeochemistry 0425
Geochemistry 0996

Geodesy 0370
Geology 0372
Geophysics 0373
Hydrology 0388
Mineralogy 0411
Paleobotany 0345
Paleoecology 0426
Paleontology 0418
Paleozoology 0985
Palynology 0427
Physical Geography 0368
Physical Oceanography 0415

HEALTH AND ENVIRONMENTAL SCIENCES

Environmental Sciences 0768
Health Sciences 0566
General 0300
Audiology 0992
Chemotherapy 0567
Dentistry 0350
Education 0769
Hospital Management 0758
Human Development 0982
Immunology 0564
Medicine and Surgery 0347
Mental Health 0569
Nursing 0570
Nutrition 0380
Obstetrics and Gynecology 0354
Occupational Health and Therapy 0381
Ophthalmology 0571
Pathology 0419
Pharmacology 0572
Pharmacy 0382
Physical Therapy 0573
Public Health 0574
Radiology 0575
Recreation 0575

Speech Pathology 0460
Toxicology 0383
Home Economics 0386

PHYSICAL SCIENCES

Pure Sciences 0485
Chemistry 0749
General 0486
Agricultural 0487
Analytical 0488
Biochemistry 0738
Inorganic 0490
Nuclear 0491
Organic 0494
Pharmaceutical 0495
Physical 0754
Polymer 0405
Radiation 0605
Mathematics 0986
Physics 0606
General 0608
Acoustics 0748
Astronomy and Astrophysics 0607
Atmospheric Science 0798
Atomic 0759
Electronics and Electricity 0609
Elementary Particles and High Energy 0752
Fluid and Plasma 0610
Molecular 0756
Nuclear 0611
Optics 0463
Radiation 0346
Solid State 0984
Statistics 0346
Applied Sciences 0984
Applied Mechanics 0984
Computer Science 0984

Engineering 0537
General 0538
Aerospace 0539
Agricultural 0540
Automotive 0541
Biomedical 0542
Chemical 0543
Civil 0544
Electronics and Electrical 0348
Heat and Thermodynamics 0545
Hydraulic 0546
Industrial 0547
Marine 0794
Materials Science 0548
Mechanical 0743
Metallurgy 0551
Mining 0552
Nuclear 0549
Packaging 0765
Petroleum 0554
Sanitary and Municipal 0790
System Science 0428
Geotechnology 0796
Operations Research 0795
Plastics Technology 0994
Textile Technology 0994

PSYCHOLOGY

General 0621
Behavior 0384
Clinical 0622
Developmental 0620
Experimental 0623
Industrial 0624
Personality 0625
Physiological 0989
Psychobiology 0349
Psychometrics 0632
Social 0451

The undersigned hereby recommend to
the Faculty of Graduate Studies and Research
acceptance of the thesis,

**“LONG RANGE ANTIFERROMAGNETIC EXCHANGE
COUPLING IN DINUCLEAR COPPER(II) COMPLEXES CONTAINING
1,4-DICYANAMIDOBENZENE DIANION BRIDGING LIGANDS”**

submitted by

LINNUS L.CHERUIYOT, B.Ed(Sc.), M.Sc.

in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University

December, 1994

ABSTRACT

The fundamental understanding of exchange coupling propagated by multiatom bridges and new insights into the electron transfer pathways in novel magnetic and electronic materials is important to the experimentalist and theoretician alike. This thesis explores the effect of metal magnetic orbitals on the antiferromagnetic superexchange and in addition, models the coordination sphere of copper in Cu(DCNQI)₂ molecular metals. To achieve these goals copper(II) complexes have been designed and synthesized.

Two mononuclear complexes, [Cu(dien)-(2,3-Cl₂pcyd)][CF₃SO₃] (1), [Cu(bpii)-(2,3-Cl₂pcyd)₂] (2) and six dinuclear complexes [{Cu(dien)}₂-(μ-Dicyd)][CF₃SO₃]₂ (3), [{Cu(dien)}₂-(μ-Me₂Dicyd)][CF₃SO₃]₂ (4), [{Cu(dien)}₂-(μ-Cl₂Dicyd)][CF₃SO₃]₂ (5), [{Cu(bpii)}₂-(μ-Dicyd)] (6), [{Cu(bpii)}₂-(μ-Me₂Dicyd)] (7), [{Cu(bpii)}₂-(μ-Cl₂Dicyd)] (8), where pcyd = cyanamidobenzene, Dicyd²⁻ = 1,4-dicyanamidobenzene, Me₂Dicyd²⁻ = 1,4-dicyanamido-2,5-dimethylbenzene, Cl₂Dicyd²⁻ = 1,4-dicyanamido-2,5-dichlorobenzene, dien = diethylenetriamine and bpii = 1,3-bis (2'-pyridylimino)-isoindolinato have been synthesized and characterized by elemental analysis, IR and UV-vis and ESR spectroscopies. In addition, temperature dependent magnetic susceptibility measurements of the complexes 3 - 8 from 5 to 300 K are reported. The data for 4, 5, 7 and 8 have been fitted to a dimer model with a modified Bleaney-Bowers expression which takes into account intramolecular antiferromagnetic exchange, temperature independent paramagnetism and the presence of a paramagnetic impurity. The fits for 4,

5, 7 and 8 derived antiferromagnetic exchange constants $-2J = 21.2, 90, 9.8$ and 70 cm^{-1} respectively (where the Hamiltonian is of the form $H = -2J \mathbf{S}_a \cdot \mathbf{S}_b$). For 6 an approach to maximum in χ_m with decreasing temperature gave an estimated $-J < 70 \text{ cm}^{-1}$. Only complex 3, showed Curie-Weiss behavior. This is far weaker antiferromagnetic exchange compared to that observed for dinuclear Ru(III) complexes incorporating the Dicyd²⁻ bridging ligands and is attributed to both a symmetry and energy mismatch between Cu(II) σ^* magnetic orbitals and π HOMO superexchange pathway of the bridging ligand. The Coffmann and Buettner's limit function is broached using the magnetic data for the copper complexes. For a distance of $13.2 \text{ \AA}$ between the Cu(II) ions the limit function predicts $2J = -6.50 \times 10^{-4} \text{ cm}^{-1}$ and is not in agreement with the magnetic data observed for the systems in this study and shows that a favorable superexchange pathway exists in these systems which propagates magnetic exchange interactions between the copper ions

The X-band ESR spectra of polycrystalline, undoped, powdered samples of the dinuclear copper complexes 4 - 8 show features characteristic of an axial g tensor with $g_{\parallel} > g_{\perp} > 2.0$ and indicates that the unpaired electron is located in a dx^2-y^2 orbital. Solution ESR spectra of the complexes 1 - 8 have been obtained in various solvents. The room temperature spectra of the complexes 3, 4 and 5 in degassed DMF solution are very similar. For complex 5, the estimated hyperfine splitting $A_{iso} = 41.7 \times 10^{-4} \text{ cm}^{-1}$ is approximately one-half that of the monomer complex 1 for which $A_{iso} = 80.6 \times 10^{-4} \text{ cm}^{-1}$ as expected for an exchange coupled system. Only a weak radical Dicyd²⁻ resonance was observed for the complexes 6, 7 and 8 in DMF at 295 or 77 K.

In addition, the heteronuclear complexes, $[\text{Cu}(\text{bpil})-(\mu\text{-Dicyd})\text{-Ru}(\text{NH}_3)_5][\text{PF}_6]_2$ (**9**) and $[\text{Cu}(\text{bpil})-(\mu\text{-Cl}_2\text{Dicyd})\text{-Ru}(\text{NH}_3)_5][\text{PF}_6]_2$ (**10**) have been synthesized and characterized by elemental analysis, IR and UV-vis-NIR spectroscopy and cyclic voltammetry. Variable temperature dependent magnetic susceptibility measurements of **9** shows that the magnetic behavior follows the Curie-Weiss law. This behavior is unexpected and it is proposed that the same symmetry magnetic orbitals are required to overlap simultaneously with the bridging ligand π_{nb} HOMO and thus, provide a superexchange pathway for exchange coupling..

Finally, the synthesis of a new tridentate ligand, $\text{N}[(\text{CH}_2)_4\text{CN}]_3$ is reported. This ligand has been fully characterized by elemental analysis, IR and NMR spectroscopy and FAB mass spectrometry.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the many people who offered help and advice throughout the lifetime of this research work. First and foremost, I wish to thank my thesis supervisor, Dr. Robert Crutchley for his continuous assistance, encouragement, constructive discussions and invaluable criticisms. Thanks are also extended to Dr. John Greedan and his coworkers at McMaster University, Hamilton who performed the magnetic measurements and Dr. Laurence Thompson and coworkers at Memorial University, St. John's, Newfoundland for the ESR measurements and for allowing me to use his ESR spectrometer during my short visit to St. John's.

Thanks are due to Karl Diedrich for his friendship and for his assistance in the synthesis of the tridentate ligand; Keith Bourque for running the NMR spectra, Robert Kehle, Tony O'Neill and Dave Raffler for technical assistance.

I wish to extend my deepest thanks to my two friends and fellow colleagues, Ali Rezvani and Mark Naklicki for their advice and support that helped to make the hard times much easier to bear and for making the coffee club a success.

Special thanks are extended for Manuel Aquino, Dave McDonald, and Robert Letcher for their help and support in settling down, when I arrived in Ottawa for the first time. Thanks also go to Chris Evans for reading the introduction of this thesis and for providing invaluable advice, Chris White for his help on the computer and to Weigang Zhang for his support.

I wish to extend my deepest thanks to all the members of staff of the Kenya High Commission, Ottawa and the entire Kenyan Community in Ottawa for making life away from home easier to bear.

Thanks and appreciation are also extended to my colleague, friend and roommate, Peter Githira for his advice, kindness and for standing by me when things went haywire.

I would like to thank the Canadian Bureau for International Education for a Commonwealth Scholarship to pursue studies in Canada, NSERC and Carleton University for research and operating grants and Moi University for granting a study leave.

Last, but by no means the least my sincere thanks and gratitude to my wife for gallantly bearing the duty of parenthood singly and to my two daughters for their patience with an absentee daddy, as well as to my mother, father, brothers, sisters and in-laws in Kenya for their support and to whom I am indebted.

DEDICATION

This Thesis is dedicated to my two daughters Doris Cheronno and Yvonne Chebet, to my wife Hellen Cheptoo and to my parents Anjelina and William Saina.

TABLE OF CONTENTS

	<u>Page</u>
Acceptance Sheet	ii
Abstract	iii
Acknowledgements	vi
Dedication	vii
Table of Contents	ix
List of Tables	xiv
List of Figures	xv
List of Appendices	xxi
List of Abbreviations	xxii
CHAPTER 1 INTRODUCTION	1
1.1 Background	1
1.2 Magnetic Exchange Interaction in Binuclear Copper(II) Complexes	7
1.2.1 Experimental Evaluation of Electron Exchange Constant	9
1.2.2 The Superexchange Mechanism	12
1.3 Theoretical Basis for Exchange Coupling	15
1.4 The Distance Dependence of Superexchange	19
1.5 Review of Metal-Cyanamide Coordination Chemistry	24
1.6 System Design and the Aims of the Thesis	28
1.6.1 Aims of the Thesis	31

CHAPTER 2	EXPERIMENTAL	<u>Page</u>
		34
2.1	Starting Materials	34
2.1.1	Reagents for Ligand Synthesis	34
2.1.2	Reagents for Metal Complex Syntheses	35
2.1.3	Solvents	36
2.1.4	Electrolyte and Chromatography	36
2.2	Syntheses of the Ligands	37
2.2.1	Preparation of 1,3-bis(2'-pyridylimino)isoindoline	37
2.2.2	Preparation of the Thallium Salt of 2,3-Dichloro-phenylcyanamide	37
2.2.3	Syntheses of 1,4-Dicyanamidobenzene Bridging Ligands	38
2.2.3.1	General Description	38
2.3	Syntheses of the Metal Complexes	40
2.3.1	Syntheses of Precursor and Monomer Copper(II) Complexes	40
2.3.2	Syntheses of Homonuclear Copper(II) Dimer Complexes	42
2.4	Preparation of Heteronuclear Dimer Complexes	45
2.4.1	Preparation of Mononuclear Pentaammineruthenium(III) Complexes	45
2.4.2	Preparation of Heteronuclear Dimer Complexes	47
2.5	Physical measurements	49
2.5.1	Infrared Spectra	49
2.5.2	Electronic Absorption Spectra	49
2.5.3	Cyclic Voltammetry	49
2.5.4	Magnetic Susceptibility Measurements	50
2.5.5	Electron Spin Resonance (ESR) Measurements	50
2.5.6	NMR Spectroscopy	51

	<u>Page</u>
2.5.7 Spectroelectrochemistry	52
2.5.8 Mass Spectrometry	52
2.5.9 Elemental Analysis	52
 CHAPTER 3 PHYSICAL CHARACTERIZATION AND RESULT DISCUSSION	 53
 3.1 Mononuclear and Homonuclear Dimer Copper(II) Complexes	 53
3.1.1 Infrared Spectroscopy	53
3.1.2 Electronic Absorption Spectroscopy	61
3.1.2.1 Diethylenetriaminecopper(II) Complexes	61
3.1.2.2 1,3-bis(2'-pyridylimino)isoindolinatocopper(II) Complexes	65
3.1.3 Cyclic Voltammetry	70
3.1.3.1 Bridging Ligands	70
3.1.3.2 Diethylenetriaminecopper(II) Complexes	72
3.1.3.3 1,3-(2'-pyridylimino)isoindolinatocopper(II) Complexes	74
3.1.4 Variable Temperature Magnetic Susceptibility	77
3.2 Heteronuclear Complexes	85
3.2.1 Infrared Spectroscopy	85
3.2.2 Electronic Absorption Spectroscopy	88
3.2.3 Cyclic Voltammetry	93
3.2.4 Variable Temperature Magnetic Susceptibility	98

	<u>Page</u>
CHAPTER 4 ELECTRON SPIN RESONANCE SPECTROSCOPY OF COPPER(II) COMPLEXES	102
4.1 Background	102
4.2 The g -values and the Hyperfine Coupling Constant, A	104
4.3 Monomer Complexes of the Cu(II) ion	105
4.3.1 Powder ESR Data	109
4.4 Binuclear Copper(II) Complexes	110
4.5 ESR fine structure: The Case of Exchange Coupled Systems	112
4.6 Determinations of the ESR Parameters g and A	114
4.7 Results and Discussion	115
4.7.1 Polycrystalline Powdered X-band ESR Spectra of Copper(II) Complexes	115
4.7.2 Solution X-band ESR Spectra of Copper(II) Complexes	121
 CHAPTER 5 MAGNETIC EXCHANGE COUPLING: Coupling Mechanism and the Effect of Energy and Symmetry	 135
5.1 Background	135
5.2 Homonuclear Cu(II) Dimer Complexes	136
5.3 Heteronuclear Dimer Complexes	145
5.4 Failure of the Coffmann and Buettner Limit Function	145

	<u>Page</u>
CHAPTER 6 MODELING OF THE Cu(DCNQI) ₂ MOLECULAR METALS	148
6.1 Introduction	148
6.2 Design of a Tridentate Ligand	154
6.3 Synthesis of the Tridentate Ligand, N[(CH ₂) ₄ CN] ₃	157
6.4 Synthesis of Metal Complexes	161
 CHAPTER 7 CONCLUSIONS AND FUTURE STUDIES	 167
 APPENDIX	 171
 REFERENCES	 179

LIST OF TABLES

<u>Table</u>	<u>Description</u>	<u>Page</u>
1.1	Magnetic Coupling Data for Ligand-Bridged Copper(II) Complexes	21
3.1	Characteristic $\nu(\text{NCN})$ for the free Ligands, Dinuclear Cu(II) and Ru(III) complexes	54
3.2	IR Data $\nu(\text{NCN})$ of Pcyd anion-metal complexes	55
3.3	Visible Electronic Absorption Data for Diethylenetriaminecopper(II) complexes and $[\text{Cu}(\text{bpy})(2,3\text{-Cl}_2\text{Pcyd})][\text{PF}_6]$	62
3.4	Electronic Absorption Data for Cu(II) complexes containing bpil as terminal ligand	66
3.5	Electrochemical Data of Free 1,4-Dicyanamidobenzene Dianion Derivatives and Copper(II) complexes	76
3.6	Summary of Magnetic Susceptibility Data	78
3.7	Infrared Data and Electronic Absorption Data of Mononuclear Precursor Complexes and $[\text{Ru}(\text{III})\text{-Cu}(\text{II})]$ Complexes	90
3.8	Redox Potentials for the Free Dicyd ²⁻ ligands, the mononuclear Ru(III) complexes, dinuclear Ru(III) complex and the Ru(III)-Cu(II) complexes in acetonitrile	95
4.1	ESR Data of the Cu(II) Monomer and Dimer complexes	126

LIST OF FIGURES

<u>Figures</u>	<u>Description</u>	<u>Page</u>
1.1	The Plot of the Inverse of Molar Magnetic Susceptibility and Generalized Temperature Dependencies	11
1.2	Potential Energy Configuration Diagram	16
1.3	Plot of Log J vs. the Distance, R between Paramagnetic Centers	22
1.4	Resonance Stabilised Phenylcyanamide and π -Symmetry Molecular Orbitals	26
3.1	Infrared Spectrum of $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{Pcyd})][\text{NO}_3]$	56
3.2	Infrared Spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Dicyd})][\text{CF}_3\text{SO}_3]_2$	56
3.3	Infrared Spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$	57
3.4	Infrared Spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$	57
3.5	Infrared Spectrum of $[\text{Cu}(\text{bpil})(2,3\text{-Cl}_2\text{Pcyd})]$	59
3.6	Infrared Spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Dicyd})]$	59
3.7	Infrared Spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Me}_2\text{Dicyd})]$	60
3.8	Infrared Spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Cl}_2\text{Dicyd})]$	60

3.9	UV-vis Absorption Spectrum of $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{Pcyd})][\text{NO}_3]$	63
3.10	UV-vis Absorption Spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$	63
3.11	UV-vis Solid State Absorption Spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$	64
3.12	Electronic Absorption Spectrum of $[\text{Cu}(\text{bpil})(2,3\text{-Cl}_2\text{Pcyd})]$	67
3.13	Electronic Absorption Spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Me}_2\text{Dicyd})]$	68
3.14	UV-vis Solid State Absorption Spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Dicyd})]$	69
3.15	Cyclic Voltammogram of $(\text{AsPh}_4)_2[\text{Cl}_2\text{Dicyd}]$ in 2-methoxyethanol	71
3.16	Cyclic Voltammogram of $(\text{AsPh}_4)_2[\text{Cl}_2\text{Dicyd}]$ in 1,2-dichloroethane	71
3.17	Cyclic Voltammogram of $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{Pcyd})][\text{NO}_3]$	72
3.18	Cyclic Voltammograms of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$ in 2-methoxyethanol	73
3.19	Cyclic Voltammograms of $[\text{Cu}(\text{bpil})(2,3\text{-Cl}_2\text{Pcyd})]$ in 1,2-dichloroethane	75
3.20	Cyclic Voltammogram of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Me}_2\text{Dicyd})]$ in 1,2-dichloroethane	75
3.21	Molar magnetic Susceptibility of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$	80
3.22	Molar Magnetic Susceptibility of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$	81
3.23	Molar Magnetic Susceptibility of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Dicyd})]$	82
3.24	Molar Magnetic Susceptibility of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Me}_2\text{Dicyd})]$	83
3.25	Molar Magnetic Susceptibility of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Cl}_2\text{Dicyd})]$	84
3.26	IR Spectrum of $[(\text{NH}_3)_5\text{Ru}(\text{DicydH})][\text{PF}_6]_2$	86

3.27	IR Spectrum of $[(\text{bpil})\text{Cu}(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$	86
3.28	IR Spectrum of $[(\text{bpil})\text{Cu}(\mu\text{-Cl}_2\text{Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$	87
3.29	UV-vis-NIR Spectrum of $[\text{NH}_3)_5\text{RuDicydH}][\text{PF}_6]_2$	91
3.30	UV-vis-NIR Spectrum of $[\text{Cu}(\text{bpil})(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$	91
3.31	UV-vis-NIR Spectrum of $[\text{Cu}(\text{bpil})(\mu\text{-Cl}_2\text{Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$	92
3.32	Cyclic Voltammograms of $[\text{Cu}(\text{bpil})(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$	96
3.33	Cyclic Voltammogram of $[\text{Cu}(\text{bpil})(\mu\text{-Cl}_2\text{Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$	97
3.34	Molar Magnetic susceptibility of $[\text{Cu}(\text{bpil})(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$	100
3.35	Plot of $1/\chi_m$ versus temperature of $[\text{Cu}(\text{bpil})(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$	101
4.1	Site geometries and d orbital splittings for Copper(II) in Octahedral and Tetragonal environments	106
4.2	Dipolar-induced zero field splitting of binuclear cupric spin triplet at three metal-metal separations	111
4.3	X-band ESR spectrum of $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{Pcyd})][\text{NO}_3]$ at 295 K (solid state)	117
4.4	X-band ESR spectrum of $[\text{Cu}(\text{bpil})(2,3\text{-Cl}_2\text{Pcyd})]$ at 295 K (solid state)	117
4.5	X-band ESR spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$ at 77 K (solid state)	118
4.6	X-band ESR spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$ at 77 K (solid state)	118

4.7	X-band ESR spectrum of [$\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Me}_2\text{Dicyd})$] at 77 K (solid state)	119
4.8	X-band ESR spectrum of [$\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Me}_2\text{Dicyd})$] at 77 K (solid state)	119
4.9	X-band ESR spectrum of [$\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Cl}_2\text{Dicyd})$] at 77 K (solid state)	120
4.10	X-band ESR spectrum of $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{Pcyd})][\text{NO}_3]$ in DMF at 295 K and 77 K	123
4.11	X-band ESR spectrum of [$\{\text{Cu}(\text{dien})\}_2(2,3\text{-Cl}_2\text{Pcyd})][\text{NO}_3]$ in DMSO at 295 K	124
4.12	X-band ESR spectrum of $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{Pcyd})][\text{NO}_3]$ in acetonitrile at 295 K	124
4.13	X-band ESR spectrum of $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{Pcyd})]$ in DMF at 295 K	125
4.14	X-band ESR spectrum of [$\{\text{Cu}(\text{dien})\}_2(\mu\text{-Dicyd})\]^{2+}$ in DMF at 295 K and 77 K	128
4.15	X-band ESR spectrum of [$\{\text{Cu}(\text{dien})\}_2(\mu\text{-Dicyd})\]^{2+}$ in DMSO at 295 K	129
4.16	X-band ESR spectrum of [$\{\text{Cu}(\text{dien})\}_2(\mu\text{-Dicyd})\]^{2+}$ in acetonitrile at 295 K	129
4.17	X-band ESR spectrum of [$\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})\]^{2+}$ in DMF at 295 K and 77 K	130

4.18	X-band ESR spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})]^{2+}$ in DMSO at 295 K	131
4.19	X-band ESR spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})]^{2+}$ in acetonitrile at 295 K	131
4.20	X-band ESR spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})]^{2+}$ in DMF at 295 K and 77 K	132
4.21	X-band ESR spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})]^{2+}$ in DMF at 295 K	133
4.22	X-band ESR spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Cl}_2\text{Dicyd})]^{2+}$ in acetonitrile at 77 K	133
4.23	X-band ESR spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Me}_2\text{Dicyd})]^{2+}$ in DMF at 295 K	134
4.24	X-band ESR spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})]^{2+}$ in undegassed DMF at 295 K	134
5.1	Frontier orbitals of Dicyd^{2+} from EHMO calculations	139
5.2	Interaction of Ru(III) π -orbitals and the bridging ligands HOMO and SHOMO	141
5.3	Interaction of Cu(II) σ^* d -orbitals and the bridging ligands π SHOMO	143
6.1	Electronic Absorption spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})]^{2+}$ in methanol	156

6.2	Alchemy III 3D molecular modeling of $\text{N}[(\text{CH}_2)_4\text{CN}]_2\text{Cu}$	156
6.3	(a) IR spectrum and (b) ^1H NMR (CDCl_3 , 200 MHz) of $\text{Cl}[(\text{CH}_2)_4\text{CN}]$	162
6.4	IR spectrum of $\text{ClHN}[(\text{CH}_2)_4\text{CN}]_3$	163
6.5	IR spectrum of $\text{N}[(\text{CH}_2)_4\text{CN}]_3$	163
6.6	^1H NMR spectrum of $\text{ClHN}[(\text{CH}_2)_4\text{CN}]_3$ in CD_3OD	164
6.7	^1H NMR spectrum of $\text{N}[(\text{CH}_2)_4\text{CN}]_3$ in CDCl_3	165
6.8	FAB MS spectrum of $\text{ClHN}[(\text{CH}_2)_4\text{CN}]_3$	166

LIST OF APPENDICES

<u>Appendix</u>	<u>Description</u>	<u>Page</u>
A.1	IR Spectrum of $\text{ClH}_3\text{N}(\text{CH}_2)_4\text{CN}$	171
A.2	IR Spectrum of $\text{H}_2\text{N}(\text{CH}_2)_4\text{CN}$	172
A.3	IR Spectrum of $\text{ClH}_2\text{N}[(\text{CH}_2)_4\text{CN}]_2$	173
A.4	IR Spectrum of $\text{HN}[(\text{CH}_2)_4\text{CN}]_2$	173
A.5	200 MHz ^1H NMR Spectrum of $\text{ClH}_3\text{N}(\text{CH}_2)_4\text{CN}$ in d_4 -methanol	174
A.6	400 MHz ^1H NMR Spectrum of $\text{ClH}_2\text{N}[(\text{CH}_2)_4\text{CN}]_2$ in d_4 -methanol	175
A.7	FAB MS Spectrum of $\text{ClH}_3\text{N}(\text{CH}_2)_4\text{CN}$	176
A.8	FAB MS Spectrum of $\text{ClH}_2\text{N}[(\text{CH}_2)_4\text{CN}]_2$	177
A.9	Letter of Permission to adapt some Figures from the American Chemical Society	178

ABBREVIATIONS

Me	methyl
dien	diethylenetriamine
bpil	1,3-bis(2'-pyridylimino)isoindoline
TBAH	tetrabutylammonium hexafluorophosphate
DCNQI	N,N'-dicyano-1,4-benzoquinonediimine
TCNQ	7,7,8,8-tetracyanoquinonediimethane
TTF	tetrathiafulvalene
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
SHOMO	second highest occupied molecular orbital

CHAPTER 1

INTRODUCTION

1.1 Background

Increasing interest has been devoted to the study of exchange interactions between transition-metal ions through extended bridging groups by both inorganic and bioinorganic chemists during the last few years[1]. Indeed, the study of polymetallic complexes in which coupling between metals is propagated via a bridging molecule has clear application to the design of novel magnetic and electronic solid state materials and to the role of polymetallic sites in biological processes[1,2]. In exchange coupled systems, the role of the intervening bridging medium can't be underscored and it is now well known that not only single-atom but also multi-atom bridges can propagate magnetic exchange interactions between paramagnetic metal ions[3].

Exchange coupling through multi-atom bridges can occur in at least four types of complexes[3]; 1) Polynuclear transition metal complexes with unsaturated bridges; 2) Polynuclear transition metal complexes with saturated bridges; 3) Transition metal complexes with a paramagnetic ligand; 4) Organic biradicals that are bridged by transition metal moieties. In these coupled polynuclear systems, the magnetic properties can be totally different from the magnetic properties of the monomer. If both ions have an unpaired electron (e.g. Cu(II) ions),

then the molecular state of lowest energy is either a spin singlet or a spin triplet. In the former case, the interaction is said to be antiferromagnetic, in the latter case ferromagnetic. Kahn[4] has shown that by careful selection of the bridging and terminal ligands, a very large antiferromagnetic interaction can be achieved, even if the metal ions are far away from each other.

The inorganic chemist has always been interested in coupled polynuclear compounds. This is because there are several justifications that can be given for studying magnetic exchange interactions in metal complexes with extended bridges. On the one hand, there is the theoretically interesting question as to whether there is a distance-dependent limit to magnetic exchange interactions. How far apart can two paramagnetic metal ions be and what are the requirements of the intervening electron density to establish an appreciable magnetic exchange interaction? This distance-dependent limit to magnetic exchange interactions will be addressed by this thesis in due regard to the limit function proposed by Coffmann and Buettner[5].

The study of magnetic exchange interactions propagated by multi-atom bridges could also potentially give some insight into pathways of electron transfer in biological electron transport chains. A particularly fruitful diagnostic application of magnetic susceptibility to biochemical preparations is in the study of metalloenzymes with sites of metal clusters. These types of enzymes generally participate in various electron transfer processes, with both metals participating in the mechanism. Perhaps the most thoroughly documented example of magnetic coupling in a metalloenzyme is ferredoxin. Palmer et al. have reported anomalous magnetic behavior in Spinach ferredoxins[6,7] and proposed a structure involving two iron(III) ions

bridged by sulfurs[8]. Antiferromagnetic coupling has also been observed in hemerythrin. The first indication of magnetic interactions was the observation of diamagnetic Fe(III) at very low temperatures in hemerythrin[9].

Another type of magnetic coupling in metallobiomolecules consists of paramagnetic centers so strongly coupled that the excited spin states are not populated at room temperature. With such systems, only a lower limit of the magnetic exchange parameter may be estimated. Oxyhemocyanin has magnetic behavior that is consistent with very strong antiferromagnetic coupling; values have been estimated to be $-J > 625 \text{ cm}^{-1}$ (where $H = -J S_a S_b$)[10]. The hemocyanin model predicts a dioxygen molecule bridging the two metal ions[11]. Laccase also shows very strong coupling estimated at $-J \geq 300 \text{ cm}^{-1}$ [12]. The laccase enzyme has four copper(II) ions, only two of which are coupled[13]. The types of copper in laccase are sketched below:

scheme 1.1

There could also be a practical side to the study of magnetic exchange interactions propagated by extended bridges. In the past few years there has been rapid development in the syntheses and characterization of unusual magnetic or electronic solid state materials[14]. One of the greatest challenges in the sector of molecular materials is the synthesis of molecular ferromagnets. A particularly interesting example is the bimetallic complex, $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ with $\text{pbaOH} = 2\text{-hydroxy-1,3-propylenebis(oxamato)}$ which was synthesized by Kahn et al.[15]. In this complex, the bimetallic units with antiparallel alignment of spins of different magnitude (Mn(II) with $S = 5/2$ and Cu(II) with $S = 1/2$) are coupled. The spins of different units then couple ferromagnetically, resulting in a ferrimagnet[16]. In 1973, the crystalline 1:1 charge-transfer(CT) complex formed by the donor tetrathiafulvalene (TTF) and the acceptor tetracyanoquinonediimethane (TCNQ) that exhibited metallic behavior, ($\sigma_{\pi} = 500 \text{ S cm}^{-1}$, $\sigma_{\text{max}} = 10^4 \text{ S cm}^{-1}$ at 59 K) was isolated[17]. This discovery initiated a major research effort which led to the syntheses of other conductors, the notable ones being the radical anion salts of $\text{N,N}'\text{-dicyanoquinonediimine}$ (DCNQI) reported by Aumuller and Hünig[18].

These salts are built up by segregated stacks of dianions (very similar to TCNQ) and stacks of metal ions as counterions. A striking feature of these materials is the occurrence of metallic conductivity in the copper ion salt $(\text{Me}_2\text{DCNQI})_2\text{Cu}$ down to the lowest temperature reached (0.45 K)[18,19]. They show a conductivity of 1000 S cm^{-1} at ambient temperature and extremely high conductivity of $500,000 \text{ S cm}^{-1}$ at 3.5 K[18,19]. The conductivity is pseudo-three dimensional with a value as high as 100 S cm^{-1} at room temperature,

perpendicular to the stacking axis, with the N-C-N bridges providing a channel for conduction in this direction. X-ray photoelectron spectroscopy indicates that the copper atoms are present in the mixed valent state with an average oxidation state of +1.3[19]. This was proposed to arise from the admixture of the $3d$ orbitals on copper with the $p\pi$ conduction band of the Me_2DCNQI ligands[18,19,20 ,21,22]. The crystal structure data of $(\text{Me}_2\text{DCNQI})_2\text{Cu}$ reveals that each metal is tetrahedrally coordinated to four DCNQI ligands by strong Cu-N interactions ($d = 1.99 \text{ \AA}$) and the acceptor forms one dimensional columns with an intrastack distance of $3.2 \text{ \AA}$ [18].

Recently, in an effort to model the coordination environment in $(\text{Me}_2\text{DCNQI})_2\text{Cu}$ molecular metals, Crutchley et al.[23] reported the synthesis and characterization of five- and four-coordinate mononuclear copper(II) complexes of 2,2'-bipyridine and phenylcyanamide anion ligands. In another investigation on the effect of magnetic exchange interaction by very extended multiatom bridges, Aquino et al. [24,25,26] successfully synthesized binuclear Ru(III) complexes containing 1,4-dicyanamidobenzene dianion (Dicyd^{2-}) and its derivatives as the bridging ligands. These complexes have an intradimer separation of $13.2 \text{ \AA}$ and exhibit strong antiferromagnetic exchange coupling i.e ($100 \leq |2J| \leq 800 \text{ cm}^{-1}$ $H = -2JS_a S_b$). This magnitude of magnetic exchange interaction between two paramagnetic centers propagated by very extended multiatom bridges is unprecedented and must be attributed to a favorable superexchange pathway (see section 1.2.2 for definition of superexchange).

As mentioned earlier copper metal ions play a major role, both in biological processes and in solid state materials and this has been the driving force for many investigators to model the "active sites" in metalloproteins or the building blocks in the crystal structures of novel solid state materials with complexes possessing suitable magnetic or electronic properties. As a continuation of the work initiated by Aquino et al.[23,24,25,25], four-coordinate dinuclear copper(II) complexes containing the same bridging ligands as the Ru(III) complexes have been designed and synthesized. The fundamental understanding of exchange coupling propagated by multiatom bridges and new insights into the electron transfer pathways in these materials are among the goals of this thesis.

This thesis, therefore deals with magnetic exchange coupling in dinuclear copper(II) complexes containing very extended multiatom bridges. The Cu(II) ions in these complexes are bridged by 1,4-dicyanamidebenzene dianion derivatives. A comparison between the temperature dependent magnetic susceptibility of these complexes and their Ru(III) analogues[24,25,26] explores the effect of the nature of the metal magnetic orbitals on the magnitude of antiferromagnetic superexchange. In addition, the dinuclear Cu(II) complexes model the coordination sphere of copper in Cu(DCNQI)₂ molecular metals[18,19,20] and provide insight into the mechanism of conductivity found in these novel solid state materials.

As a prelude to a discussion of the main systems of this thesis, a more detailed treatment of magnetic exchange interaction in binuclear copper complexes, and superexchange mechanisms in general will be given.

1.2 Magnetic Exchange Interaction in Binuclear Copper(II) Complexes

Transition metal complexes containing more than one metal atom with unpaired electrons can generally be classified according to their magnetic behavior into three main groups depending on the strength of the metal-metal interaction[27].

- (i) The non interacting type
- (ii) The strongly interacting type and
- (iii) The weakly interacting type

The weakly interacting metal ions are of interest as the low-lying excited states of different spin can be populated at thermal energies ($\leq 1000 \text{ cm}^{-1}$). The resulting magnetic behavior will be antiferromagnetic or ferromagnetic, depending on whether the low spin (spins paired) or high spin (spins parallel) state is the ground state, respectively[27].

For a system composed of metal A with spin S_a and metal B with spin S_b which are bridged by an organic molecule L,

the general isotropic exchange Hamiltonian for such a system may be written as

$$H = -2J S_a S_b \quad (1.2)$$

where the exchange coupling constant J is positive if the spins are parallel and negative if they are paired.

If two metal ions with $S = 1/2$ e.g., Cu(II) are antiferromagnetically coupled, a singlet ground state and an excited triplet state are created which are separated in energy by $-2J$

Ferromagnetic coupling results in the formation of a triplet ground state and excited singlet state

whether a singlet or triplet ground state is formed depends on the relative magnitude of ferromagnetic(J_F) and antiferromagnetic(J_{AF}) terms and

$$2J = J_F - J_{AF} \quad (1.5)$$

J_F represents the overall spin pairing energy and J_{AF} is the energy released as a result of the coupling of the spins. Experimentally $2J$ can be evaluated by variable temperature magnetic susceptibility measurements.

1.2.1 Experimental Evaluation of the Electron Exchange Constant J

The magnetic properties of a compound are evaluated by measuring its magnetic susceptibility as a function of temperature. In a magnetic field H , one mole of any compound acquires a molar magnetic moment M_m given by

$$M_m = \chi_m H \quad (1.6)$$

Pierre Curie[28] derived an empirical equation for magnetic susceptibility of a paramagnetic sample as inversely proportional to the temperature.

$$\chi_m = C/T \quad (1.7)$$

The Curie constant for the spin only magnetic susceptibility is

$$C = [Ng^2\beta^2 S(S+1)] / 3k \quad (1.8)$$

where N is the avogadro number, g is the Zeeman factor, β is the Bohr magneton, k is the Boltzmann constant and S the spin quantum number.

A weak magnetic interaction between neighbouring spins may be described by replacing the temperature parameter in Equation 1.7 with a $T - \Theta$ term, giving the Curie-Weiss law [29].

$$\chi_m = C / (T - \Theta) \quad (1.9)$$

where χ_m is the molar magnetic susceptibility and has units of emu mole⁻¹ and the Weiss constant Θ has the units of Kelvin. A plot of magnetic susceptibility for a system that obeys the Curie-Weiss law yields the straight solid line as shown in Fig. 1.1(a). The intercept of the line with temperature axis gives both the sign and magnitude of the Weiss constant. A positive value for Θ [lower dashed line in Fig. 1.1(a)] is caused by ferromagnetic spin interactions, while a negative value [upper dashed line Figure 1.1(a)] is caused by antiferromagnetic spin interactions[29]. Fig 1.1(b) shows the three most common types of magnetic behavior namely paramagnetic, antiferromagnetic and ferromagnetic. The temperature at which the maximum occurs for antiferromagnetic systems is called the Neel temperature (T_N) while for ferromagnetic systems, the temperature at which the deviation from paramagnetic behavior occurs is called the Curie temperature (T_C). The simplest model for analysis of susceptibility data for $S = 1/2$ spin coupled binuclear copper complexes is the so-called Bleaney-Bowers equation [30]

$$\chi_m = (2Ng^2 \beta^2 / 3kT) [1 - (1/3) \exp(-2J/kT)]^{-1} + TIP \quad (1.10)$$

where g is the powder averaged g value, β is the Bohr magneton and TIP , the temperature independent paramagnetism. Typical values of TIP terms for 3d metals range from

Figure 1.1 (a) The plot of inverse of the molar magnetic susceptibility ($1/\chi_m$) versus temperature (b) Generalized temperature dependencies of (i) ferromagnetic (ii) paramagnetic (iii) antiferromagnetic behavior

60×10^{-6} emu mole⁻¹ for copper(II) to 400×10^{-6} emu mole⁻¹ for cobalt(II)[31]. The literature is abundant in examples of the application of equation 1.10, particularly in Cu(II) complexes, and a few of these are given in Table 1.1. One characteristic feature of all these examples is the presence of a bridging moiety between two Cu(II) ions. The mechanism by which a bridging moiety propagates the magnetic exchange interaction is referred to as superexchange and a discussion on the superexchange mechanism follows.

1.2.2 The Superexchange Mechanism

There is much current interest in the study of electron transfer or energy transfer between centers linked by a bridge. The mechanism of coupling between two metal centers linked by a bridge is referred to as superexchange. Mediation by ligands or bridging groups is conveniently considered in terms of electron and hole superexchange formalisms[32]. The former mechanism involves imparting to the ground states of the reactants and products some metal-to-ligand charge transfer (MLCT) excited state characters. By contrast, the hole superexchange mechanism involves mixing of ligand-to-metal charge transfer (LMCT) excited states.

Depending on the nature of the metal centers and of the ligands either the electron-or the hole-conduction mechanism may predominate. The electron conduction pathway will be favored when the energies of the metal orbitals are close to that of the ligand LUMO. On the

other hand, when the metal orbitals are closer to that of the ligand π highest occupied molecular orbitals (HOMO), the hole-conduction pathway is favored.

In the ligand mediated electron exchange mechanisms (hole conduction pathway) called superexchange, the LMCT excited states are involved,

The mixing of the LMCT excited state with the ground state therefore stabilizes a ground state in which electrons are antiparallel. The optimization of superexchange requires that the magnetic orbitals overlap simultaneously with a single ligand molecular orbital, the superexchange pathway. To overlap effectively, magnetic orbitals must have the same symmetry and be as close in energy as possible to the ligand molecular orbital. The interaction will result in an LMCT transition whose energy is a measure of the gap between magnetic orbitals and the superexchange pathway[33] and whose oscillator strength is a measure of the electronic interaction [33,34,35]. The energy gap (ΔE) between magnetic orbitals and the bridging ligand can be estimated by equation 1.12[36]

$$\Delta E = E_{OP} - \lambda \quad (1.12)$$

where E_{OP} is the energy of the LMCT at the maximum and λ is a correction to compensate for the change in inner and outer coordination configurations resulting from a transition into an

excited vibrational level. In terms of the energy requirements, the ligand mediated electron exchange mechanism is the most appropriate for explaining magnetic exchange interaction in exchange coupled systems containing extended multiatom bridges. The magnetic behavior of the dinuclear copper(II) systems will be rationalized by invoking this mechanism.

The strength of the exchange interaction, therefore depends primarily upon the symmetry and energy of the copper(II) ion ground state relative to the highest occupied molecular orbitals of the bridging moiety. For example, in binuclear copper(II) complexes bridged by oxalate, squarate and the dianions of 2,5-dihydroxybenzoquinones[37,38] as shown below the largest exchange interaction is found for the

μ -oxalate complex as expected on the basis of the Cu-Cu separation, but the next largest interaction is found for the dihydroxybenzoquinone complex and not the squarate complex. Apparently, the greater number of proper symmetry orbitals and their energy proximity to the copper(II) orbitals in the dihydroxybenzoquinone dianion accounts for the greater interaction as compared to the squarate orbitals[37,38]. The effects of energy and symmetry of the magnetic and the bridging ligand orbitals on the magnitude of exchange coupling becomes obvious in the following theoretical models proposed previously by various magnetochemists

1.3 Theoretical Basis for Exchange Coupling

Three theoretical models will be presented in this section. These include:

- (i) The Charge Transfer model
- (ii) The Hay-Thibeault-Hoffmann model
- (iii) The Kahn et al. model

The Charge Transfer Model

In this model, the description used by Anderson [39], in which the electron interaction results from the mixing of the charge transfer state F with the initial state I , is employed.

This mixing can only occur if the spins in state I are antiparallel and results in the stabilization energy J_{AF} . The potential energy-configuration diagram representing initial and final states is shown in Figure 1.2.

Figure 1.2 Potential energy configuration diagram

E'_{OP} is the charge transfer energy between initial and final states at the same nuclear configuration. H_{ab} is the resonance energy between the two states. H_{ab} , E'_{OP} and J_{AF} are related by the following expression [36]

$$J_{AF} = 2 |H_{ab}|^2 / E'_{OP} \quad (1.14)$$

The Hay-Thibeault-Hoffmann Model

For copper(II) complexes with electronic configuration d^9 and the unpaired electrons in predominantly dx^2-y^2 orbitals, Hay, Thibeault and Hoffmann[27] write the following linear combinations.

$$\Phi_1 \sim (dx^2 - y^2)^a + (dx^2 - y^2)^b \quad (1.15)$$

$$\Phi_2 \sim (dx^2 - y^2)^a - (dx^2 - y^2)^b$$

Using perturbation theory, Hoffmann and coworkers [27] have obtained the singlet-triplet splitting as being approximately

$$E_T - E_S = -2K_{ab} + (\varepsilon_1 - \varepsilon_2)^2 / (J_{aa} - J_{ab}) \quad (1.16)$$

where K_{ab} is the exchange integral, $J_{aa} - J_{ab}$ are the one- and two-center coulomb repulsion integrals, and ε_1 and ε_2 are the energies of the molecular orbitals Φ_1 and Φ_2 . The implications of equation 1.16 were previously summarized by Hatfield, W.E.[40] and emphasizes that the ground state will be a triplet when the exchange coupled molecular orbitals are equal and that the triplet state will be destabilized with respect to the singlet state when the energies of the symmetric and antisymmetric combinations become different.

The Kahn et al. model

The model proposed by Kahn, O. [41,42] shows that

$$J_{AF} = 2S[(\Delta - \delta)] \quad (1.17)$$

where S is the overlap integral between the magnetic orbitals and Δ is the energy gap between the two molecular orbitals in the A-B dimer constructed from the magnetic orbitals for the $S = 1$ state. Finally δ is the energy gap between Φ_A and Φ_B as shown below.

scheme 1.2

If the A-B dimer is symmetrical, the A and B fragments are identical and δ is zero. J_{AF} is reduced to equation 1.18,

$$J_{AF} = -2\Delta S \quad (1.18)$$

Thus, J_{AF} in absolute value depends on the overlap and energy gap between the magnetic orbitals. Δ is formally identical to $\varepsilon_1 - \varepsilon_2$ which appeared in equation 1.16. The conceptual difference between the Hay-Thibeault-Hoffman model[27,40] and the Kahn model[41,42] is that in the former orthogonal magnetic orbitals[O.M.O] are used while in the latter non-orthogonal magnetic orbitals[N.M.O] are used.

In summary, an orbital model may either be the basis of quantitative calculation or provide a frame for rationalizing experimental results, understanding the role of structural changes, and designing new coupled systems exhibiting expected magnetic properties. The Hay-Thibeault-Hoffmann formalism is particularly suited for quantitative calculations while all three models are appropriate when considering strategy for designing new systems, the Kahn model since it considers the antiferromagnetic component as arising essentially from the ground configuration is better suited in design strategy. The Kahn model was used extensively by Kahn et al. in proposing the strategy of strict orthogonality of the magnetic orbitals and the concept of tunable exchange in a given bridging network[43]. However, all these models are silent about the effect that the distance between paramagnetic centers has on the magnitude of antiferromagnetic exchange coupling. The distance dependence of superexchange is of continuing interest and was mentioned briefly in section 1.1 and will be highlighted again in section 1.4.

1.4 The Distance Dependence of Superexchange

The investigation of magnetic exchange is perhaps the area of most intense interest in magnetochemistry. Copper(II) in particular has been the object of very extensive magnetic investigation in dimeric systems and several interesting empirical relationships have been compiled from some of these studies. Hatfield, Hodgson, and coworkers[44] have shown that a systematic comparison of spin coupled dihydroxide bridged dimers shows a linear correlation

between the coupling constant J and the Cu-O-Cu bridging angle(θ). A similar correlation has also been proposed by Willett[45] for chloride bridged dimers, and by Hatfield for chloride bridged polymers [46]. More recently, Hatfield[47] has proposed that the ratio of the bridging angle to the internuclear distance(θ/R) has an effect on the sign and magnitude of the magnetic coupling in sulfur bridged copper(II) systems.

Most of the work done on magnetic exchange in complexes has implied that there is no direct influence of the internuclear distance on the magnitude of the magnetic coupling. Rather, it appears that the chemical nature of the bridge has a more profound effect on the efficiency of magnetic exchange. Coffmann and Buettner[5] more than a decade ago proposed that while the chemical nature of the bridging medium may very well determine the overall efficiency of the propagation of magnetic information, the magnitude of the internuclear distance will nevertheless impose a limit on the maximum magnitude of the magnetic coupling constant J . In Table 1.1 a summary of the J values and the metal-metal distances of various ligand bridged complexes of copper(II) are given.

Table 1.1 Magnetic Coupling Data for Ligand-Bridged Copper(II) Complexes

Complex ^a	M-M(Å)	$J(\text{cm}^{-1})$	Ref.
$[\text{Cu}_2(\text{Et}_3\text{dien})_2(\text{C}_2\text{O}_4)][\text{BPh}_4]_2$	5.410	-37	48
$[\text{Cu}_2(\text{dien})_2(\text{C}_2\text{O}_4)][\text{ClO}_4]_2$	5.488	$ J < 0.5$	48
$[\text{Cu}_2(\text{DMAEO})(\text{NCS})_2(\text{DMF})_2]$	5.153	-291	49
$[\text{Cu}_2(\text{Me}_3\text{dien})_2(\text{N}_3)_2][\text{BPh}_4]_2$	5.228	-6.50	50
$[\text{Cu}_2(\text{tren})_2(\text{BZD})][\text{NO}_3]_4$	12.270	$ J \sim 3.0$	51
$[\text{Cu}_2(\text{terpy})_2(\text{H}_2\text{O})_2(\text{C}_4\text{O}_4)][\text{ClO}_4]_2$	7.874	-3.6	52
$[\text{Cu}_2(\text{bpca})_2(\text{C}_5\text{O}_5)] \cdot 3\text{H}_2\text{O}$	6.824	-9.63	53
$[\text{Cu}_2(\text{bimp})(\text{H}_2\text{O})_2][\text{ClO}_4]_3$	4.090	$ J \leq 0.3$	54
$[\text{Cu}_2(\text{bimp})(\text{OCH}_3)][\text{ClO}_4]_2$	3.026	-47	54

^aAbbreviations: *dien* = diethylenetriamine, *Et₃dien* = 1,1',4,7,7'-pentaethyldiethylenetriamine; *Me₃dien* = 1,1',4,7,7'-pentamethyldiethylenetriamine; $\text{C}_2\text{O}_4^{2-}$ = Oxalate dianion; *tren* = 2,2',2''-triaminotriethylamine; *BZD* = Benzidine, N_3 = Azide; *terpy* = 2,2',2'',6 - terpyridine, $\text{C}_4\text{O}_4^{2-}$ = dianion of 3,4 - dihydroxycyclobutenedione(squarate dianion); *bpca* = bis(2-pyridylcarbonyl)amide anion; *bimp* = 2,6-bis[(bis(1-methylimidazol-2-yl)methylamino)methyl]-4-methylphenol anion; $\text{C}_5\text{O}_5^{2-}$ = 4,5-dihydroxy-4-cyclopentene-1,2,3-trione(croconate)
DMAEO =

Coffmann and Buettner[5], using the examples given in Table 1.1 and other examples in literature established an experimentally determined limit function for long range ferromagnetic and antiferromagnetic superexchange. In other words, they entered available data on a plot of $\text{Log } J$ vs. the distance, R in Å between paramagnetic centers. A straight line was then drawn such that all known systems fell to the left of this line. The resulting plot of $\text{Log } J$ vs R is reproduced below in Fig 1.3 (Note: Coffmann and Buettner used an isotropic exchange Hamiltonian defined as $H = +2J S_1 S_2$)

Figure 1.3 Plot of $\text{Log } J$ vs. the distance, R between Paramagnetic centers (Taken from Ref. 4 with permission)

From the straight line shown in Fig. 1.3, they proposed the following limit function for the distance dependence of antiferromagnetic exchange between metal ions bridged by an insulating medium.

$$2|J_{lim}| = 1.35 \times 10^7 \exp(-1.80R) \text{ cm}^{-1} \quad (1.19)$$

where R is the distance between paramagnetic centers in Å. The above relationship has held up fairly well with some exceptions[24,51,55,56]. A notable example in the Cu(II) family of complexes is $[\text{Cu}_2(\text{tren})_2(\text{BZD})][\text{NO}_3]_4$ [51], which despite of an internuclear distance of 12.270 Å exhibits significant magnetic coupling with $|J| \sim 3.0 \text{ cm}^{-1}$. Recently, Aquino et al.[24] reported the synthesis of dinuclear Ru(III) complexes containing 1,4-dicyanamidobenzene dianion bridging ligands with an internuclear distance of 13.2 Å. At this separation equation 1.19 predicts $|2J| = 6.5 \times 10^4 \text{ cm}^{-1}$. The experimental values obtained ($100 \leq |2J| \leq 800 \text{ cm}^{-1}$) are in total disagreement with the predicted value.

The breakdown of Equation 1.19 for Ru(III) complexes arises from the difference in the nature and properties of the electron exchange pathway as compared with that of the Cu(II) complexes used to derive the Coffmann-Buettner relationship. For Cu(II) the odd electron resides in a mostly σ symmetry d -orbital and exchange would occur via the σ bonding framework of the bridging ligand which are of high energy (difference $> 3\text{eV}$) and the bridging ligand can be classified as an insulating medium. For Ru(III) complexes, the electron exchange

pathway occurs via Ru(III) πd -orbitals and the π symmetry HOMO of the bridging Dicyd²⁻ ligand and thus, the bridging ligand can be classified as a semi-conducting medium [24].

To further address the subject of distance dependence and the Coffmann-Buettner relationship copper(II) complexes containing the 1,4-dicyanamidobenzene bridging ligands have been prepared and the magnitude of the antiferromagnetic exchange coupling constant, J determined. The results are compared to those obtained for the Ru(III) complexes[24] and the Coffmann-Buettner relationship broached to establish agreement or disagreement with the data obtained. The data are finally rationalized by proposing a suitable pathway for superexchange.

1.5 Review of Metal-Cyanamide Coordination Chemistry

The coordination chemistry of the cyanamide anion group have received little attention to date mainly because free cyanamides tend to polymerize[57]. The Phenylcyanamides are more stable and using these ligands, Hollebone et al.[58] reported the first phenylcyanamide complexes $[ML_4]^{2-}$ ($M = Co, Ni, Cu, Zn$; $L = 2,4,6$ -trichloro or 2-chlorophenylcyanamide ion). Eighteen years later, pentaammineruthenium(III) complexes of neutral and anionic 2,3-dichlorophenylcyanamide were reported[57].

Since this re-introduction of the cyanamide ligand, a substantial body of work by Crutchley and coworkers[23,24,25,26,33,34,57,59] and by Brodie and coworkers[60,61] has been performed. The phenylcyanamide anion (Pcyd⁻) ligands are pseudohalides and resonance stabilized π systems. Two pairs of non-bonding electrons can be delocalized in these systems

(see Fig. 1.5)[57,59,60]. These ligands are strong σ and π -donors and prefer coordination to π -acid metal ions[62,63].

The first step in the study of the coordination chemistry of the cyanamide group began with the syntheses of mononuclear complexes incorporating the phenylcyanamide anion (pcyd). The complexes, pentaammineruthenium(III)phenylcyanamide[57], 2,2'-bipyridinecopper(II)-bis(phenylcyanamide)[23], bis(2,2'-bipyridine)copper(II)phenylcyanamide and 1,3-bis(2'-pyridylimino)isoindolatonickel(II)phenylcyanamide[64], (2,2',2''-terpyridine)palladium(II)-phenylcyanamide[65], bis(bipyridine)ruthenium(III)phenylcyanamide[66], have all been synthesized and characterized.

The crystal structure of the complex $[(bpy)_2Cu(2,3-Cl_2pcyd)][PF_6]$ [23], shows that the coordination sphere around Cu(II) is a distorted square pyramid made of nitrogen donor atoms in which the phenylcyanamide ligand occupies a basal coordination site while for the complex $[(bpy)Cu(2,3-Cl_2pcyd)_2]$ [23], the coordination geometry is a distorted square planar. In both complexes, the anionic cyanamide group of $2,3-Cl_2pcyd^-$ ligand is nearly coplanar with the phenyl ring due to a strong π -coupling and coordination to copper(II) via the cyano nitrogen. Crystal structure data, LMCT band intensity and electrochemical data are consistent with a mostly σ -bonding interaction between Cu(II) and the cyanamide anion group. However, there is also a partially allowed $p\pi \rightarrow dx^2-y^2$ transition which supports an electronic interaction between Cu(II) and DCNQI necessary to form a mixed-valence state in $Cu(DCNQI)_2$ molecular metals [20].

(a)

(b)

Figure 1.4 (a) Resonance stabilized phenylcyanamide anion ligand.

(b) π -symmetry molecular orbitals (π_{nb1} is orthogonal to π_{nb2}) resulting from the delocalization of two-bonding electron pairs as in resonance form B. The size of atomic orbitals approximate their contribution to the molecular orbital.

In addition, the crystal structure data of $[\text{Ni}(\text{bpil})-(2\text{-Cl-pcyd})]$ where bpil^- is the tridentate ligand 1,3-bis(2'-pyridylimino)isoindolinato[64], shows that the nickel ion is in a tetragonally distorted tetrahedral coordination sphere, the Ni-NCN bond is bent and the plane of the phenylcyanamide ligand is at approximately right angles to the best plane of the tridentate ligand bpil^- .

The phenylcyanamide anion and the phenyldicyanamide dianion ligands are planar[67] and this is suggested to arise from π coupling between cyanamide and phenyl ring groups. For a significant number of phenylcyanamide transition metal complexes, crystal structures have shown the retention of planarity upon cyanamide ligand coordination[23,24,32,57,60,61,68]. In the X-ray crystal structures of $[\{(\text{NH}_3)_3\text{Ru}\}_2(\mu\text{-Dicyd})][\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3]_4$ [24] and $\text{trans-}[\{(\text{NH}_3)_4\text{PyRu}\}_2(\mu\text{-Dicyd})][\text{PF}_6]_4$ [68], the planarity of the dicyanamide bridging group is maintained and the separation between the Ru(III) ions is approximately 13 Å. As a crystal structure of one of the dinuclear copper complexes is not available at this time, the above information will be important in arriving at a proposed superexchange pathway to be given later.

The successful synthesis of the above mentioned complexes has provided an impetus to design and synthesize other complexes, in particular dinuclear complexes. As a part of these efforts, the goal of this research was to design and synthesize dinuclear copper(II) complexes incorporating the 1,4-dicyanamidobenzene dianion(Dicyd^{2-}) as the bridging ligand. The dinuclear copper(II) complexes could be used to investigate the attenuation or enhancement of

superexchange observed in Ru(III) complexes, by simply changing the nature of the metal ion. The second goal was to design complexes that could model the $\text{Cu}(\text{DCNQI})_2$ molecular metals[18,19,20,21]. In this endeavour the coordination chemistry unveiled for the phenylcyanamide complexes described above will be used as a basis for understanding the structural, spectroscopic and magnetic properties of the mononuclear and dinuclear copper(II) complexes of this study. In the next section, before we elaborate on the aims of this thesis, the rationale used in choosing the terminal and bridging ligands will be presented.

1.6 System Design and the Aims of the Thesis

The fulfilment of the objectives set for this thesis requires the design and synthesis of suitable dinuclear copper(II) complexes. The bridging ligands and the co-ligands required to build the said complexes must meet some criteria. The criteria required for a bridging ligand have been reviewed previously[69] and only a few pertinent ones will be highlighted. For optimization of magnetic exchange coupling, the metal magnetic orbitals and the bridging ligand orbitals must be well matched both in energy and symmetry. In this context, the energies of the ligand orbitals and the metal magnetic orbitals must be comparable. The ligand of choice should therefore, have suitable redox properties. In addition, the bridging ligand should have the following criteria:

1. **Planarity** - The Dicyd^{2-} ligands must be planar to have a continuous π_{orb} HOMO that interacts simultaneously with both metal ions.

2. **Tunability** - For any given co-ligand, the properties of the bridging ligand can be investigated by varying the substituents on the phenyl ring or any other moiety (e.g. from electron withdrawing to electron donating).

The bridging ligands which meet the above mentioned criteria and have been used previously in the syntheses of dinuclear Ru(III) complexes[24,69] are the 1,4-dicyanamidobenzene dianion (Dicyd²⁻) ligands. The Dicyd²⁻ shown below is the 2e⁻ reduction product of DCNQI used in the synthesis of Cu(DCNQI)₂ molecular metals[18,19,20].

The Dicyd²⁻ ligand can be oxidised twice as shown below at potentials which are dependent on the nature of the substituents on the phenyl ring[18,19, 20,24].

As mentioned in the preceding section 1.1, one of the research goals was to model the coordination environment about copper(II) in $\text{Cu}(\text{DCNQI})_2$ molecular metals[18,19,20]. In order to achieve this goal, suitable nitrogen-based tridentate co-ligands had to be chosen. The co-ligands of choice are diethylenetriamine (dien) and 1,3-bis(2'-pyridylimino)isoindoline(bpii), respectively. The former ligand is readily available while the latter ligand can be prepared in high yields with relative ease. The structures of these ligands are shown below:

1,3-bis(2'-pyridylimino)isoindolinato(bpil⁻)

Diethylenetriamine(dien)

Having given the types of bridging and co-ligands used in the system design, the aims of the thesis will now be elaborated.

1.6.1 Aims of the Thesis

1. To synthesize and characterize monomer complexes containing a phenylcyanamide ligand

(a)

(b)

2. To synthesize and characterize a series of dimer copper(II) complexes containing 1,4-dicyanamidobenzene dianion bridging ligands.

(a) Dication copper(II) complexes

(b) Neutral copper(II) complexes

3. To investigate magnetic exchange coupling in the dinuclear copper(II) complexes both in the solid state by temperature dependent magnetic susceptibility studies and in solution by electron spin resonance spectroscopy.
4. To synthesize and characterize heterodinuclear Ru(III)-Cu(II) complexes.

5. To investigate magnetic exchange coupling in the heterodinuclear complexes by temperature dependent magnetic susceptibility studies.
6. Conclusions concerning the importance of symmetry and energy on the extent of magnetic exchange
7. Design and synthesis of a tridentate ligand.

CHAPTER 2

EXPERIMENTAL

2.1 Starting Materials

2.1.1 Reagents for Ligand Syntheses

Ammonium thiocyanate (reagent grade, Fisher scientific Co.), benzoyl chloride (99%, reagent grade, Aldrich), lead acetate trihydrate (reagent grade, Anachemia), 1,4-phenylenediamine (97%, Aldrich), 2,5-dimethyl-1,4-phenylenediamine (97%, Aldrich), 2,5-dichloro-1,4-phenylenediamine (97%, Aldrich), sodium hydroxide (lab grade, Anachemia), tetraphenylarsonium chloride hydrate (97%, Aldrich), glacial acetic acid (99.7%, reagent grade, Anachemia), 2-aminopyridine (99%, Aldrich), anhydrous calcium chloride (reagent grade, Anachemia), phthalonitrile (reagent grade, Eastman-Kodak), 2,3-dichloroaniline (99%, Aldrich), thallium acetate (99.99%, Aldrich), 5-chlorovaleronitrile (98%, Aldrich), 5-bromovaleronitrile (98%, Aldrich), 1,2,2,6,6-pentamethylpiperidine (97%, Aldrich), and ammonia gas (anhydrous, 99.99+%, Aldrich) were used without further purification.

2.1.2 Reagents for Metal Complex Syntheses

Cupric bromide (reagent grade, Anachemia), copper metal turnings (Fisher Scientific Co.), copper triflate hexahydrate (Prepared by digesting copper metal turnings, in triflic acid), triflic acid (99%, Aldrich), cupric nitrate (analytical grade, Baker), triethylamine (99%, Aldrich), nitric acid (reagent grade, Anachemia), diethylenetriamine (99%, Aldrich), ruthenium(III) chloride hydrate (Aldrich), hydrazine monohydrate (98%, Aldrich), ammonium hexafluorophosphate (99.99%, Aldrich), ammonium hexafluorophosphate (prepared from ammonia and hexafluorophosphoric acid), tetrabutylammonium bromide (99%, Aldrich), hydrochloric acid (36.5 - 38%, reagent grade, Anachemia), sulfuric acid (95-98%, reagent grade, Anachemia) and sodium chloride (99+%, reagent grade, anachemia) were used as received. Zinc/mercury amalgam was first prepared by first cleaning zinc metal (mossy, reagent grade, Anachemia) with 1M HCl and then treating with a saturated solution of mercurous chloride (reagent grade, Anachemia).

Chloropentaammineruthenium(III) Chloride

$[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was prepared from $\text{RuCl}_3 \cdot \text{XH}_2\text{O}$, hydrazine monohydrate and concentrated HCl according to the method of Clarke[70].

Aquopentaammineruthenium(II) hexafluorophosphate

$[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{PF}_6)_2$ was prepared from $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ by reduction with Zn/Hg amalgam according to the method reported by Sullivan et al.[71]

2.1.3 Solvents

Acetonitrile (HPLC grade, Caledon Labs), chloroform (spectro grade, Caledon Labs), 2-methoxyethanol (MET, 99+%, Aldrich), N,N'-dimethylformamide (DMF, glass distilled, Anachemia), N,N'-dimethylformamide (DMF, spectro grade, Caledon Labs), methanol (spectro grade, Caledon Labs), methanol (absolute, Consolidated Alcohols Ltd.), ethanol (Absolute, Consolidated Alcohols Ltd.), 1,2-dichloroethane (spectro grade, caledon Labs), methyl-2-pyrrolidinone (MPD, HPLC grade, Aldrich), acetone (spectro grade, Caledon Labs Ltd.), dimethyl sulphoxide (Fisher Scientific), n-hexanes (spectro grade, Caledon Labs), acetone (spectro grade, Caledon Labs), Acetonitrile (99.99%, anhydrous, Aldrich) were used as received. Solvents for EPR measurements were freeze - pump - thaw - degassed before use.

2.1.4 Electrolyte and Chromatography

Tetrabutylammonium hexafluorophosphate (98%, Aldrich) was recrystallized twice from ethanol and dried in vacuo at 118 °C for 18 h. CM-sephadex C25 cation exchange resin (bead size 40-125 microns, Sigma) was used as received.

2.2 Syntheses of the Ligands

2.2.1 Preparation of 1,3-bis(2'-pyridylimino)isoindoline(bpii)

The ligand was prepared using the method described previously by Siegl[72,73]. 2-aminopyridine (9.0 g, 60 mmol), phthalonitrile (3.84 g, 30 mmol), anhydrous calcium chloride (0.33 g, 3.0 mmol), and 100 ml of 2-methoxyethanol were combined together and refluxed with stirring for 48 h. A dark green solution was formed, which on cooling yielded a green-yellow precipitate. The crude product was recrystallized from a chloroform/hexane solvent mixture. In order to improve the yield, the filtrate obtained from the reaction mixture was concentrated and on cooling in fridge, more ligand was formed.

Final yield: 5.28 g (60%).

2.2.2 Preparation of the Thallium salt of 2,3-Dichloro-phenylcyanamide, Tl(2,3-Cl₂Pcyd)

The preparation of the neutral ligand and its thallium salt have been described elsewhere[57,59].

2.2.3 Syntheses of 1,4-Dicyanamidobenzene Bridging Ligands

2.2.3.1 General Description

The preparation of 1,4-dicyanamidebenzene ligand and derivatives have been reported previously[24,25,26 ,69,74]. These references contain the detailed synthetic procedures and no further attempt will be made to describe them. However, a summary of the main intermediates will be given in scheme 2.1 and are discussed below. 1,4-phenylenediamine was reacted with ammonium thiocyanate to form A which upon heating in base gave the thiourea derivative B. B was desulfurised with lead(II) acetate with gentle heating to produce the dicyanamide dianion C in situ. The dianion C was then protonated with acetic acid and precipitated out as D. During the reaction, the temperature must be maintained between 60-70 °C to avoid dimerization. The dimer formation can be detected by IR. A strong band at about 1680 cm⁻¹ is present due to $\nu(\text{C}=\text{N})$ of the dimer E.

scheme 2.1

2.3 Syntheses of the Metal Complexes

2.3.1. Syntheses of Precursor and Monomer Copper(II) Complexes

Diethylenetriaminecopper(II)-(2,3-dichlorophenylcyanamido)-nitrate,

The precursor complex $[\text{Cu}(\text{dien})\text{NO}_3][\text{NO}_3]$ was prepared by using the method described by Krestl et al.[75]. Benzaldehyde (2.1 ml, 20 mmol) was mixed with 1 ml (10 mmol) of diethylenetriamine and the resulting mixture was dissolved in methanol (50 ml). Copper nitrate trihydrate (2.416 g, 10mmol) was added to this solution and the mixture was refluxed for 1 h. After cooling for 12 h to room temperature, blue needles separated from the solution. They were isolated by filtration and dried in vacuo.

Yield 2.10 g (72%).

$[\text{Cu}(\text{dien}(\text{NO}_3))][\text{NO}_3]$ (0.50 g), and $[\text{Ti}][2,3\text{-Cl}_2\text{pcyd}]$ (0.67 g) were placed in methanol and the mixture refluxed for 5 h. The blue-green reaction mixture was cooled overnight at -15°C then filtered. The filtrate was then concentrated to 30 mL and the product forced out of solution by the addition of ether. Recrystallization from 1:1 methanol/ether at -15°C gave blue-green needles. Yield: 0.43 g (60%).

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{N}_6\text{O}_3\text{Cl}_2\text{Cu}$: C, 31.87; H, 3.86; N, 20.26. Found C, 31.75; H, 3.78; N, 19.88.

1,3-bis(2'-pyridylimino)isoindolinatocopper(II)-(2,3-dichlorophenylcyanamido),

Cu(bpii)(2,3-Cl₂pcyd)

Cu(bpii)X (X = Br, CF₃SO₃) was prepared from 1,3-bis(2'-pyridylimino)-isoindolinato(bpii⁻) and the CuX₂.nH₂O (X = Br, CF₃SO₃) using established procedure[76]. For Cu(bpii)Br, Anal. Calcd for C₁₈H₁₂N₅CuBr: C, 48.96; H, 2.70; N, 15.86. Found: C, 48.49; H, 2.82; N, 15.73. The Cu(bpii)PF₆ precursor complex was prepared from Cu(bpii)CF₃SO₃ and tetrabutylammonium hexafluorophosphate (TBAH) in acetone.

[Cu(bpii)(CF₃SO₃)](0.50 g) and [Ti](2,3-Cl₂pcyd) (0.44 g) were placed in 2-methoxyethanol and the mixture refluxed for 2 h. The hot deep green-yellow solution was filtered and the filtrate reduced to 20 mL. Cooling the solution precipitated the crude yellow product. Recrystallization by ether diffusion into 1,2-dichloroethane solution gave pale yellow needles. Yield: 0.32 g (52%).

Anal. Calcd for C₂₅H₁₅N₇Cl₂Cu: C, 54.80; H, 2.74; N, 17.90. Found : C, 54.25; H, 2.73; N, 17.71.

2.3.2 Syntheses of Homonuclear Copper(II) Dimer Complexes.

Preparation of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Dicyd})][\text{CF}_3\text{SO}_3]_2$

To a solution of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (1.15 g) and dicydH_2 (0.19 g) in 2-methoxyethanol was added, under an argon atmosphere, the ligand dien (0.23 g) and triethylamine (1 mL). The concentrated reaction solution was then filtered and the filtrate placed in a freezer (-16°C) overnight, precipitating the brown microcrystalline product. The crude product was recrystallized by slow evaporation of a solution of the complex in methanol.

Yield: 0.50 g (27%).

Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{N}_{10}\text{O}_6\text{F}_6\text{S}_2\text{Cu}_2$: H, 3.81; N, 17.77; Cu, 16.17. Found: C, 27.53;

H, 3.77; N, 17.74; Cu, 16.01 ± 0.22 .

Preparation of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$

The same procedure as above was followed with $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (1.04 g) and $\text{Me}_2\text{dicydH}_2$ (0.2 g). The Crude product was recrystallized in 2-methoxyethanol by slow evaporation. Yield: 0.52 g (29%).

Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{N}_{10}\text{O}_6\text{F}_6\text{S}_2\text{Cu}_2$: C, 29.45; H, 4.17; N, 17.17; Cu, 15.58.

Found: C, 29.38; H, 3.99; N, 16.80; Cu, 15.53 ± 0.11 .

Preparation of $\{[Cu(dien)]_2(\mu-Cl_2Dicyd)][CF_3SO_3]_2$

Under an argon atmosphere, $Cu(CF_3SO_3)_2$ (1.0g) and $[AsPh_4]_2[Cl_2dicyd]$ (1.06 g) were dissolved in acetone (400mL). The ligand dien (0.23 g) was then added. Almost immediately, the pale green product began to precipitate from solution. After 1 h, the product was filtered off, and recrystallized from methanol by slow evaporation.

Yield: 0.44 g (24%).

Anal. Calcd for $C_{18}H_{28}N_{10}O_6F_6S_2Cu_2$: C, 25.23; H, 3.25; N, 16.38; Cu, 14.84.

Found: C, 25.33; H, 3.33; N, 15.99; Cu, 14.66 ± 0.15

Preparation of $\{[Cu(bpii)]_2(\mu-Cl_2dicyd)\}$

Degassed 1-methyl-2-pyrrolidinone (100 mL) was transferred under argon to a reaction flask containing $Cu(bpii)CF_3SO_3$ (0.62 g) and $Cl_2dicydH_2$ (0.14 g). Triethylamine (0.73 g) was then added and the solution allowed to stir for 4 h. The now green solution was filtered and the product forced out of filtrate by the addition of water (150 mL). The resultant green precipitate was collected by filtration and washed with copious quantities of water, acetone and finally ether. The crude product was recrystallized twice from hot 1,2-dichlorobenzene and dried in vacuo at $110^\circ C$.

Yield: 0.26 g (45%). Anal. Calcd for $C_{44}H_{26}N_{11}C_{12}Cu_2$:

C, 55.70; H, 2.76; N, 20.67; Cu, 13.38. Found: C, 55.06; H, 2.78; N, 20.29; Cu, 13.27 ± 0.10

Preparation of $\{[Cu(bpii)]_2(\mu-Me_2Dicyd)\} \cdot 1/6(1,2-dichlorobenzene)$

This complex was prepared in a similar manner to the Cl_2dicyd analogue except that $Cu(bpii)Br$ (1.0 g) was used instead of $Cu(bpii)CF_3SO_3$. Yield: 0.55 g(56%). Anal. Calcd for $C_{47}H_{32.6}N_{14}Cl_{0.3}Cu_2$: C, 60.56; H, 3.50; N, 21.03; Cl, 1.27, Cu, 13.62. Found: C, 59.19; H, 3.43; N, 21.04; Cl, 1.00; Cu, 13.55 ± 0.18 .

Preparation of $\{[Cu(bpii)]_2(\mu-Dicyd)\} \cdot 1/2(1,2-dichlorobenzene)$

This complex was prepared in a similar manner to Cl_2dicyd analogue. Yield: 0.41 g(42%). Anal. Calcd for $C_{45}H_{28.6}N_{14}Cl_{0.3}Cu_2$: C, 59.76; H, 3.17; N, 21.69; Cu, 14.05. Found: C, 58.50; H, 3.26; N, 21.95; Cu, 14.31 ± 0.12

2.4 Preparation of Heteronuclear Dimer complexes

The mixed metal complexes have been prepared from the mononuclear pentaammineruthenium(III) complexes of the type $[(\text{NH}_3)_5\text{RuL}]\text{X}_2$ where $\text{L} = \text{DicydH}^+$, $\text{Cl}_2\text{DicydH}^+$, $\text{Me}_2\text{DicydH}^+$; $\text{X} = \text{PF}_6^-$, ClO_4^- and the precursor complexes $\text{Cu}(\text{bpil})\text{X}$ ($\text{X} = \text{PF}_6^-$, ClO_4^-)

2.4.1 Preparation of Mononuclear Pentaammineruthenium(III) Complexes

The complexes have been prepared using a procedure adopted from Nacklicki et al. [76].

Preparation of $[(\text{NH}_3)_5\text{RuDicydH}][\text{PF}_6]_2$

$[(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$ (0.80 g, 1.6 mmol) was dissolved in 80 mL acetone. To this solution was added a solution of DicydH_2 (0.36 g, 2.3 mmol) in acetone (20 mL). The yellow solution turned green and finally blue-green. 30 drops of 0.1 M HClO_4 was then added to ensure the complex remained protonated. The reaction mixture was allowed to stir for 4 h and then filtered. To the filtrate was added a solution of 3.0 g tetrabutylammonium bromide in 20 mL acetone and immediate precipitation of the crude blue bromide salt occurred. This was then filtered through a fine glass frit and the collected product washed with 3×5 mL portions of cold acetone and dried in vacuo.

The crude bromide salt was purified by dissolving it a minimum amount of 1.0 M NaCl, filtering and loading the solution onto a column of CM-Sephadex C25 cation exchange resin. Elution with a 1.0 M NaCl solution separated out a yellow band which was most likely due to unreacted ligand, followed by the blue band containing the desired mononuclear species with a charge of +2. The mononuclear species was all collected and crushed out as the tetraphenylborate salt by adding 2.0 g of NaBPh₄. The dirty white solid was collected on a medium porosity glass frit, washed with copious amounts of cold water, and air dried. After drying the product was dissolved in acetone, gravity filtered and again precipitated out by adding 1.5 g of tetrabutylammonium bromide. The bromide salt was filtered out and washed severally with cold acetone and dried in vacuo. The now dry bromide salt was then dissolved in a minimum amount of water and precipitated as the hexafluorophosphate salt by adding excess NH₄PF₆. The fine precipitate was collected on a fine glass frit and washed with 1 mL of cold water, then ether and dried in vacuo.

Yield: 0.42g(38%)

Preparation of [(NH₃)₅RuMe₂DicydH][PF₆]₂

The same procedure used to prepare [(NH₃)₅RuDicydH](PF₆)₂ was followed using [(NH₃)₅(H₂O)](PF₆)₂ (0.80 g, 1.6 mmol) and Me₂DicydH₂ (0.38 g, 2.1 mmol). Yield: 0.41 g (36%).

Preparation of $[(\text{NH}_3)_5\text{RuCl}_2\text{DicydH}][\text{PF}_6]_2$

To $[(\text{NH}_3)_5\text{Ru}(\text{H}_2\text{O})][\text{PF}_6]_2$ (0.40 g, 0.8 mmol) in acetone (20 mL) was added a solution of $\text{Cl}_2\text{DicydH}_2$ (0.25 g, 1.1 mmol) in 200 mL acetone. 10 drops of 0.1 M HClO_4 was then added and the now blue solution stirred for 4 h. The blue solution was filtered and precipitated out as the bromide salt by adding 2.0 g of tetrabutylammonium bromide in 10 mL acetone. The precipitate was collected on a fine glass frit, washed with cold acetone and dried in vacuo. Yield 210 mg.

The crude bromide salt was purified by metathesis. The bromide salt was dissolved in water and again precipitated as the tetraphenylborate salt by adding 1.5 g NaBPh_4 . The product was filtered through a medium porosity glass frit, washed severally with copious amounts of cold water and dried in air. The resultant product was then dissolved in acetone (20 mL) and precipitated as the bromide salt with 2.0 g Bu_4NBr . The bromide salt, after washing with cold acetone and drying in vacuo was dissolved in water (10 mL) and obtained as a PF_6^- salt by adding NH_4PF_6 . Yield: 180 mg (32%).

2.4.2 Preparation of Heteronuclear Dimer Complexes

Preparation of $[(\text{NH}_3)_5\text{Ru}(\mu\text{-Dicyd})\text{Cu}(\text{bpil})][\text{PF}_6]_2 \cdot 2\text{H}_2\text{O}$

$\text{Cu}(\text{bpil})\text{PF}_6$ (0.20g, 0.4 mmol) was dissolved in 200 mL methanol and the solution degassed. Similarly, $[(\text{NH}_3)_5\text{RuDicydH}][\text{PF}_6]_2$ (0.27 g, 0.4 mmol) was dissolved in 200 mL

methanol and degassed. The two solutions were then mixed, and the green solution that resulted was stirred for 5 h under argon. The solution was then concentrated to 50 mL by rotary evaporation, filtered and the complex precipitated by adding ether (100 mL). The green crude product was recrystallized twice by ether diffusion to an acetone solution.

Yield: 0.15 g (38%). Anal Calcd for $C_{26}H_{35}N_{14}RuCuCl_2O_2F_{12}P_2$: C, 30.30; H, 3.39; N, 19.03.

Found: C, 29.71; H, 3.38; N, 19.12.

Preparation of $[(NH_3)_5 Ru(\mu-Cl_2 Dicyd) Cu(bpii)] [PF_6]_2 \cdot 3H_2O$

$Cu(bpii)PF_6$ (0.1 g, 0.2 mmol) was dissolved in 100 mL acetone and the solution degassed. To this solution was added a previously degassed solution of $[(NH_3)_5 RuCl_2 DicydH] [PF_6]_2$ (0.14 g, 0.2 mmol) in acetone (200 mL). The deep green solution was stirred for a further 4 h and the volume of the solution reduced to approximately 50 mL, filtered and finally the complex precipitated by adding ether (100 mL). The deep green crude solid was recrystallized twice from ether diffusion to an acetone solution of the complex.

Yield: 0.09 g (45%).

Anal. Calcd for $C_{26}H_{35}N_{14}RuCuCl_2O_3F_{12}P_2$: C, 27.92; H, 3.13;

N, 17.54. Found: C, 27.59; H, 3.13; N, 17.09

2.5 Physical Measurements

2.5.1 Infrared Spectra

Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer which was online to a Hewlett-Packard Colorpro Plotter. All samples were prepared as KBr (oven dried at 120 °C) disks. Reference spectra of air were run prior to all sample spectra.

2.5.2 Electronic Absorption Spectra

Electronic spectra were recorded on a Cary 5 UV-vis/NIR Spectrophotometer interfaced with a Raven 386/33 PC online to a HP laser IID printer. Solution samples were run using matching quartz cells and a background correction was performed prior to each run. Solid state spectra were performed on the same spectrophotometer. Samples were prepared as Nujol mulls and a Nujol background correction was carried out before each run.

2.5.3 Cyclic Voltammetry

The experimental setup used to perform the cyclic voltammetry experiments has already been described[77]. Cyclic voltammetry was recorded on a BAS cv-27

electrochemistry system online to a BAS x-y Recorder. The electrochemical cell consisted of a double-jacketed glass container with an inner volume of approximately 15 mL. Cell temperature was controlled by means of a Haake D8-G refrigerated bath and circulator (accuracy ± 0.02 °C). The cell was fitted with a Teflon plug through which holes had been drilled to permit insertion of electrodes and an argon gas inlet frit. Non-aqueous cyclic voltammetry was performed in 2-methoxyethanol (MET) and 1,2-dichloroethane (DCE) (0.1 M tetrabutylammonium hexafluorophosphate (TBAH) at 25 °C using a three electrode system consisting of a platinum-disk working (BAS 1.6 mm diameter) and a wire counter electrodes and a silver-wire quasi-reference electrode. The ferricenium/ferrocene couple ($E^\circ = 400$ mV vs NHE) was used as an internal calibrator[78].

2.5.4 Magnetic Susceptibility Measurements

Variable temperature magnetic susceptibility measurements were performed at the Institute for Materials Research at McMaster University, Hamilton, Ontario, by Prof. J.E. Greedan and Guo Liu using a Quantum Design Superconducting Quantum Interference Device (SQUID) susceptometer.

2.5.5 Electron Spin Resonance (ESR) Measurements

ESR measurements were performed at Memorial University, St. John's, Newfoundland using a Bruker ESP 300 X-band spectrometer at 295 and 77 K, respectively under the supervision of Prof. Laurence Thompson. Both solid state and solution ESR

measurements were obtained using quartz capillaries. Solution ESR measurements were obtained in degassed and undegassed *N,N'*-dimethylformamide (DMF), acetonitrile and dimethyl sulphoxide (DMSO).

2.5.6 NMR Spectroscopy

All ^1H NMR spectra were recorded on a Bruker AMX-200 or AMX-400 NMR spectrometer at ambient temperature. Normally, 5 mg samples were dissolved in 0.5 mL of *d*₄-methanol or *d*₁-chloroform and analyzed in a Norell XR-55 NMR tube. Chemical shifts were derived from internal TMS reference.

2.5.7 Spectroelectrochemistry

Spectroelectrochemistry was performed in a cell constructed from a quartz cuvette with a quartz fritted compartment separating the working and counter-electrode units. The counter electrode was a Pt-wire and the working electrode was a Pt-mesh cylinder mechanically supported by Pt strip and located just above the quartz cuvette. Stirring was accomplished by bubbling with argon. A silver wire was used as the reference electrode and was placed in the working electrode compartment isolated from the working electrode. The potential of the cell was controlled by using a BAS CV-27 apparatus.

2.5.8 Mass Spectrometry

FAB MS was performed at the Ottawa-Carleton Universities Centre for Mass Spectrometry

2.5.9 Elemental Analyses

Elemental analyses (C, H, N) of all samples were performed by Canadian Microanalytical Services Ltd. The % Cu was determined by atomic absorption spectroscopy with a Perkin-Elmer 600 spectrophotometer. Standard solutions of 2 ppm, 4 ppm, 6 ppm, 8 ppm, 10 ppm and 15 ppm were made from Analytical grade $\text{Cu}(\text{NO}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. The solid samples (weighed to four decimal places) were digested in hot 50 mL concentrated nitric acid and the nitric acid evaporated to dryness. The solid left behind was extracted with distilled deionized water, filtered and made up to volume in 100 mL volumetric flasks. After obtaining the calibration curve, absorbances of the sample solutions were determined. Three determinations were undertaken for each complex, from which the average % Cu and the standard deviation was calculated.

CHAPTER 3

PHYSICAL CHARACTERIZATION AND RESULTS

DISCUSSION

3.1 Mononuclear and Homonuclear Dimer Copper(II) Complexes

The elemental analyses of all the complexes are consistent with their proposed stoichiometry while evidence that Dicyd^{2-} is coordinated and bridges two Cu(II) ions can be found through an examination of the copper complexes' visible electronic absorption and IR spectroscopies, electrochemistry and magnetochemistry.

3.1.1 Infrared Spectroscopy

IR spectra of the precursor, mononuclear and dinuclear copper(II) complexes are shown in Figures 3.1 - 3.8. The mononuclear and dinuclear complexes all show the characteristic strong $\nu(\text{NCN})$ stretch. The IR spectra of the tetraphenylarsonium salts of the Dicyd^{2-} , $\text{Me}_2\text{Dicyd}^{2-}$, $\text{Cl}_2\text{Dicyd}^{2-}$ show a strong single band assigned to $\nu(\text{NCN})$ at 2089, 2093 and 2100 cm^{-1} respectively. Upon coordination to Cu(II) , $\nu(\text{NCN})$ shifts to higher energies in a manner which seems largely dependent on the charge of the complex. On the other hand, in the dinuclear Ru(III) complexes the $\nu(\text{NCN})$ shifts to lower energies[24]. The cyanamide stretching frequencies of these complexes are given in Table 3.1.

Table 3.1 Characteristic $\nu(\text{NCN})^a$ for the Free Ligands^b, Dinuclear Cu(II) and Ru(III)^c Complexes

Ligand(L)	$[(\text{AsPh}_4)_2\text{L}]$	$[\{\text{Cu}(\text{dien})\}_2\text{L}]^{2+}$	$[\{\text{Cu}(\text{bpil})\}_2\text{L}]$	$[\{\text{NH}_3\}_3\text{Ru}\}_2\text{L}]^{4+}$
Dicyd ²⁻	2089	2155	2110	2087
Me ₂ Dicyd ²⁻	2093	2157	2108	2088
Cl ₂ Dicyd ²⁻	2100	2169	2123	2098

Abbreviations:

^a In cm^{-1} , absorptions are strong unless stated. All spectra were obtained in KBr.

^b From Ref.69. ^c From Ref. 24,69. *dien* = Diethylenetriamine ; *bpil* = 1,3-bis(2-pyridylimino)isoindolinato

The shift in $\nu(\text{NCN})$ from the free ligand values is not only a property of dinuclear complexes, but has also been observed in mononuclear complexes, a few of which are shown in Table 3.2. Phenylcyanamide (pcyd) has two resonance forms and there are two filled orthogonal π_{nb} molecular orbitals in resonance form B (see Figure 1.3). The shift in $\nu(\text{NCN})$ in the mononuclear species as seen in Table 3.2 is similar to that observed in the dinuclear copper(II) complexes and largely depends on the polarization of electron density of the phenylcyanamide by the metal ions. Polarisation effects are dependent on the effective charge and size of the cationic species and this effect is reflected in the $\nu(\text{NCN})$ observed in these complexes.

Table 3.2. IR Data $\nu(\text{NCN})^a$ of Pcyd anion-metal complexes

Pcyd anion (L)	Tl(L)	$[(\text{trpy})\text{PdL}]^+$	$[(\text{bpil})\text{NiL}]^+$	$[(\text{bpy})_2\text{CuL}]^+$	$[(\text{NH}_3)_5\text{RuL}]^{2+}$
2-ClPcyd	2098 ^e	2142 ^b	2154 ^c	2108 ^d	2115 ^e
2,3-Cl ₂ Pcyd	2102 ^e	2178 ^b	2146 ^c	2154 ^d	2111 ^e
2,4,6-Cl ₃ Pcyd	2135 ^b	2184 ^b	-	-	-
2,4,5-Cl ₃ Pcyd	2085 ^e	-	2184 ^c	2155 ^d	2111 ^e
2,3,5,6-Cl ₄ Pcyd	2097 ^e	-	2196 ^c	2151 ^d	2137 ^e

Abbreviations:

^a In cm^{-1} , all absorptions are strong unless stated. All spectra were obtained in KBr. ^b from Ref. 65. ^c from Ref. 64.

^d from Ref. 23. ^e from Ref. 57. Tl = Thallium; trpy = 2,2',2''-terpyridine; bpy = 2,2'-bipyridine; bpil = 1,3-bis(2-pyridylimino)isoindolinato

Figure 3.1. Infrared Spectrum of $[\text{Cu}(\text{dien}) (2,3\text{-Cl}_2\text{Pcyd})][\text{NO}_3]$ (KBr)

Figure 3.2. Infrared Spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Dicyd})][\text{CF}_3\text{SO}_3]_2$ (KBr)

Figure 3.3. Infrared Spectrum of $[\{Cu(dien)\}_2(\mu-Me_2Dicyd)][CF_3SO_3]_2$ (KBr)

Figure 3.4. Infrared Spectrum of $[\{Cu(dien)\}_2(\mu-Cl_2Dicyd)][CF_3SO_3]_2$ (KBr)

The infrared spectra of the free dien ligand exhibit absorptions at 3360 and 3295 cm^{-1} assigned to primary and secondary amines, respectively. Upon coordination, these bands are shifted to lower wavenumbers by 80 and 74 cm^{-1} , respectively. These shifts are strong evidence that the ligand is coordinated in a tridentate mode [75]. The dien derivative complexes also exhibit an intense absorption at 1270 cm^{-1} , assigned to $\nu(\text{CF}_3\text{SO}_3^-)$. The presence of the counter anion absorption bands is indicative of charged species in sharp contrast to the bpil derivatives which show none. The IR spectra of the Cu(bpil) derivative complexes are shown in Figures 3.5 - 3.8. In these complexes, the pyridyl skeletal absorptions appear in the 1600-1400 cm^{-1} region. A notable feature of IR spectra of these complexes is the absence of the strong $\nu(\text{CF}_3\text{SO}_3^-)$ at 1270 cm^{-1} . The absence of this band in the IR spectra of Cu(bpil) species while it is present in that of the Cu(dien) derivatives and the Cu(bpil) CF_3SO_3 precursor complex is diagnostic of the neutrality of these complexes.

In addition, crystallographic and IR studies have shown that inequivalent cyanamide groups result in multiple $\nu(\text{NCN})$ bands [23,67]. The observation of only one sharp $\nu(\text{NCN})$ band in the IR spectra of all the dinuclear copper complexes leads to the conclusion that both cyanamide groups of a respective bridging ligand are in equivalent coordination environments.

Figure 3.5. Infrared Spectrum of [Cu(bpii) (2,3-Cl₂Pcyd)] (KBr)

Figure 3.6. Infrared Spectrum of [{Cu(bpii)}₂(μ-Dicyd)] (KBr)

Figure 3.7. Infrared Spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Me}_2\text{Dicyd})]$ (KBr)

Figure 3.8. Infrared Spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Cl}_2\text{Dicyd})]$ (KBr)

3.1.2 Electronic Absorption Spectroscopy

3.1.2.1 Diethylenetriaminecopper(II) Complexes

The UV-vis spectra of precursor complex, mononuclear complex and a representative one for dinuclear complexes in methanol are shown in Figures 3.9 - 3.11. The spectra of the mononuclear and dinuclear complexes show two major bands in the visible region, which is in contrast to the visible spectrum of $\text{Cu}(\text{dien})(\text{NO}_3)_2$ which has only one broad absorption at 615 nm in methanol. The higher energy band has been assigned to a $\sigma^* \leftarrow \pi$ LMCT transition of the Cu(II) - cyanamide chromophore while the lower energy band has the assignment metal centered d-d transition, in analogy to the similar visible spectra of $[\text{Cu}(2,2'\text{-bipyridine})_2(\text{phenylcyanamide})]^+$ complexes[23]. The solid state spectrum (Nujol mull) of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{dicyd})]^{2+}$ shown in Figure 3.11 has an absorption band at 479 nm. The occurrence of this band both in solution and in the solid state is strong evidence that complex integrity is maintained in solution. Similar spectra were obtained for the other complexes and the data obtained from solution spectra are put in Table 3.3.

Table 3.3 Visible Electronic Absorption Data^a for Diethylenetriaminecopper(II) complexes and [Cu(bpy)(2,3-Cl₂Pcyd)][PF₆]^d

COMPLEX	LMCT($\sigma^* \leftarrow \pi$)	d-d transitions
[Cu(dien)(NO ₃)][NO ₃]		615(2.15) ^b
[Cu(dien)(2,3-Cl ₂ pcyd)][NO ₃]	403(2.89) ^b	610(2.35) ^b
[Cu(dien) ₂ (μ -dicyd)][CF ₃ SO ₃] ₂	435(3.02) ^b	631(2.83) ^b
[Cu(dien) ₂ (μ -Me ₂ dicyd)][CF ₃ SO ₃] ₂	455(3.06) ^b	622(2.85) ^b
[Cu(dien) ₂ (μ -Cl ₂ dicyd)][CF ₃ SO ₃] ₂	452(3.03) ^b	637(2.75) ^b
[(bpy) ₂ Cu(2,3-Cl ₂ pcyd)][PF ₆] ^d	495(3.15) ^c	704(2.69) ^c

^a In nm (log ϵ in M⁻¹ cm⁻¹ in parentheses)

^b In Methanol

^c In Acetonitrile

^d From Ref. 23

Figure 3.9. UV-vis absorption spectrum of $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{Pcyd})][\text{NO}_3]$

Figure 3.10. UV-vis absorption spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$
 2.27×10^{-4} M in methanol

Fig 3.11. UV-vis solid state absorption spectrum of
 $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$ (Nujol mull)

3.1.2.2 1,3-bis(2'-pyridylimino)isoindolinatocopper(II) Complexes

The electronic absorption spectra of the complexes containing 1,3-bis(2'-pyridylimino)isoindinato (bpⁱⁱ) as the terminal ligand are shown in Figures 3.12 - 3.13. A representative spectrum for the dinuclear complexes is shown by Figure 3.13 and the electronic absorption data of these complexes are collected in Table 3.4. The electronic absorption spectrum is dominated by the $\pi^* \leftarrow \pi$ band of the bpⁱⁱ ligand. At 500 - 600 nm a weak LMCT transition arising from the Cu(II) - cyanamide chromophore is observed in the spectra of the dinuclear complexes. These LMCT transitions are also observed in the solid state spectra of the Cu(bpⁱⁱ) complexes as seen in the example spectrum shown in Figure 3.14.

In summary, as seen in Tables 3.3 and 3.4, the d-d band energies are higher for the Cu(dien) complexes compared to Cu(bpⁱⁱ) complexes which likely reflects a greater compression from tetrahedral towards a more planar geometry in the Cu(dien) complexes [79]. Predictably the energy of the d-d band shifts to lower energies as the π -donor properties of the Dicyd²⁻ bridging ligand increases [80]. The intensity of the ligand-to-metal transfer (LMCT) transitions is proportional to the square of the overlap integrals of the orbitals involved[79]. From the LMCT data given in Tables 3.3 and 3.4 one can conclude that the overlap of the Cu(II) σ^* orbitals and the bridging ligand orbitals is therefore, greater in the Cu(dien) derivatives than it is in the Cu(bpⁱⁱ) species. In addition, the complexes containing Me₂Dicyd²⁻ as the bridging ligand have intense LMCT transitions.

Table 3.4. Electronic Absorption Data^a for Cu(II) complexes containing bpII as terminal ligand

COMPLEX	$\pi^* \leftarrow \pi$	LMCT	d-d transitions
[Cu(bpII)CF ₃ SO ₃]	447(3.96), 421(4.04)	-	690(2.41)
[Cu(bpII)(2,3-Cl ₂ Pcyd)]	453(4.18), 422(4.28)	-	690(2.40)
[{Cu(bpII)} ₂ (μ -Dicyd)]	452(4.45), 421(4.49)	564(2.65)	690(2.48)
[{Cu(bpII)} ₂ (μ -Me ₂ Dicyd)]	451(4.88), 421(4.95)	575(2.99)	689(2.62)
[{Cu(bpII)} ₂ (μ -Cl ₂ Dicyd)]	453(4.47), 422(4.88)	580(2.78)	692(2.53)

^a In nm (Log ϵ in M⁻¹ cm⁻¹ in parentheses)

Figure 3.12. Electronic Absorption Spectrum of: (a). $[\text{Cu}(\text{bpil})(2,3\text{-Cl}_2\text{Pcyd})]$ 1.2×10^{-4} M in 1,2-dichloroethane. (b). Same solution but spectrum enlarged by a factor of 50.

Figure 3.13. Electronic Absorption Spectrum of: (a). $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Me}_2\text{Dicyd})]$
 1.43×10^{-4} M in 1,2-dichloroethane (b). Same solution but spectrum
 enlarged by a factor of 40.

Figure 3.14. UV-vis solid state spectrum of $[\{Cu(bpii)\}_2(\mu-Dicyd)]$ (Nujol mull)

3.1.3 Cyclic Voltammetry

3.1.3.1 Bridging ligands

The cyclic voltammetry of the three bridging ligands was performed in 2-methoxyethanol and in 1,2-dichloroethane, using a platinum working and counter electrode, a silver wire pseudo-reference electrode and the ferrocene/ferrocenium couple (0.400 V vs NHE) as an internal reference [78]. Two representative voltammograms are shown in Figures 3.15 - 3.16. As mentioned earlier in the introduction, all of the ligands showed two characteristic one-electron redox processes .

The free Dicyd^{2-} ligands are easily oxidized and show two redox couples whose potential depends largely on the nature of the substituents on the phenyl ring [69,80]. The Dicyd couples for the three derivatives show good reversibility in both 2-methoxyethanol and 1,2-dichloroethane, having equivalent anodic and cathodic currents and peak to peak separations of 60mV independent of scan rate (50 to 500 mV/s). On the other hand, the Dicyd^{2-} couples show evidence of irreversibility with peak to peak separations > 100 mV. The electrochemical data of the free Dicyd^{2-} ligands are given in Table 3.5.

Figure 3.15. Cyclic voltammogram of $[\text{AsPh}_4]_2[\text{Cl}_2\text{Dicyd}]$ in 2-methoxyethanol, 0.1 M TBAH, scan rate 0.1 Vs^{-1}

Figure 3.16. Cyclic Voltammogram of $[\text{AsPh}_4]_2[\text{Cl}_2\text{Dicyd}]$ in 1,2-dichloroethane, 0.1 M TBAH, scan rate 0.1 Vs^{-1}

3.1.3.2 Diethylenetriaminecopper(II) Complexes

The cyclic voltammograms of the mononuclear complex $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{Pcyd})][\text{NO}_3]$ and that of the dinuclear complex, $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$ are shown in Figures 3.17 - 3.18. The mononuclear complex shows an irreversible Cu(II/I) couple at -0.665 V vs NHE. In the dinuclear copper complexes, only the $\text{Dicyd}^{0/+}$ couple is well defined while the Dicyd^{-2-} and Cu(II/I) waves are so broadened that an exact determination of peak potential is difficult. The redox potentials are summarized in Table 3.5.

Figure 3.17. Cyclic voltammogram of $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{pcyd})][\text{NO}_3]$ in 2-methoxyethanol (0.1 M TBAH, scan rate 0.1 Vs^{-1})

2

PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

PRECISIONSM RESOLUTION TARGETS

Figure 3.18. Cyclic Voltammograms of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$ in 2-methoxyethanol (0.1 M TBAH, scan rate 0.1 Vs^{-1})

3.1.3.3 1,3-bis (2'pyridylimino)isoindolinatocopper(II) Complexes

Cyclic voltammetric studies of Cu(bpil) dinuclear complexes in 1,2-dichloroethane yielded well resolved cyclic voltammograms, in contrast to those of the Cu(dien) complexes (see Figure 3.18). The Cyclic voltammograms of the mononuclear complex [Cu(bpil)(2,3-Cl₂Pcyd)] and the dinuclear complex [{Cu(bpil)}₂(μ-Me₂Dicyd)] are shown in Figures 3.19 - 3.20. The Cyclic voltammogram of the mononuclear complex showed the Cu(II/I) cathodic wave at -0.90 V vs NHE (see Figure 3.19 and Table 3.5). A similar situation is observed in the cyclic voltammogram of the precursor complex, Cu(bpil)CF₃SO₃ in dichloroethane which showed only the Cu(II/I) cathodic wave at -0.82 V vs NHE.

The dinuclear Cu(bpil) complexes were the best behaved showing well defined ligand and copper waves (Figure 3,20). The Dicyd^{0/-} couple of these copper complexes showed little change in potential compared to the corresponding free ligand couple. However, the Dicyd⁻²⁻ couple was shifted anodically by approximately 300 mV (see table 3.5) and indicates the preference of Cu(II) ions for the dianion bridging ligand.

Figure 3.19. Cyclic voltammogram of $[\text{Cu}(\text{bpil})(2,3\text{-Cl}_2\text{Pcyd})]$ in 1,2-dichloroethane (0.1 M TBAH, 100 mV/s)

Figure 3.20. Cyclic Voltammogram of $\{[\text{Cu}(\text{bpil})]_2(\mu\text{-Me}_2\text{Dicyd})\}$ in 1,2-dichloroethane (0.1 M TBAH, 100 mVs⁻¹).

Table 3.5. Electrochemical Data^a of Free 1,4-Dicyanamidebenzene Dianion Derivatives and Copper(II) Complexes

Species	L ⁰⁺		L ⁻²⁻		Cu(II/I)	
	MET	DCE	MET	DCE	MET	DCE
Dicyd ²⁻	0.260	0.128	-0.147	-0.529		
Me ₂ Dicyd ²⁻	0.209	0.030	-0.285	-0.598		
Cl ₂ Dicyd ²⁻	0.505	0.365	0.045	-0.363		
[(L ₁ Cu) ₂ (μ-Dicyd)] ²⁺	0.255		id			
[(L ₁ Cu) ₂ (μ-Me ₂ Dicyd)] ²⁺	0.205		id			
[(L ₁ Cu) ₂ (μ-Cl ₂ Dicyd)] ²⁺	0.492		id			
[(L ₁ Cu)(2,3-Cl ₂ pcyd)]					-0.665 ⁱ	
[(L ₂ Cu) ₂ (μ-Dicyd)]		0.098		-0.227 ^P		-0.691 ⁱ
[(L ₂ Cu) ₂ (μ-Me ₂ dicyd)]		-0.008		-0.343 ^P		-0.693 ⁱ
[(L ₂ Cu) ₂ (μ-Cl ₂ dicyd)]		0.310		-0.066 ^P		-0.610 ⁱ
[(L ₂ Cu)(2,3-Cl ₂ pcyd)]						-0.931 ⁱ

^aAll potentials are in volts versus NHE. Cyclic voltammetry was performed in 2-methoxyethanol (MET) or in 1,2-dichloroethane (DCE) (0.1M TBAH, 100 mVs⁻¹) at T = 25°C. ⁱIrreversible cathodic wave only. ^P Partially reversible. ^{id} ill-defined irreversible reduction couple. L₁ = diethylenetriamine (dien); L₂ = 1,3-bis(2'-pyridylimino)isoindolinato(bpii')

3.1.4 Variable Temperature Magnetic Susceptibility

Magnetic susceptibility measurements of all of the complexes were made over the temperature range 5-300 K using a superconducting quantum interference device (SQUID) susceptometer. The measurements were made at McMaster University, Hamilton, by Professor John E. Greedan using 50-100 mg of the complex in pellet form. The fitted plots of molar magnetic susceptibility versus temperature are shown in Figures 3.21 - 3.25. The raw data were fitted to a modified Bleaney - Bowers expression for $S = 1/2$ spin-coupled dimers mentioned in the introduction (equation 1.10 and shown below).

$$\chi_m = (2Ng^2\beta^2/3kT)[1+(1/3)\exp(-2J/kT)]^{-1} + TIP$$

In this equation all the symbols have their usual meaning. *TIP* is a correction for any temperature independent or Van Vleck paramagnetism which is usually present in Cu(II) systems and *g* is the powder average *g* value. The appropriate fitting parameters have been placed in Table 3.6.

Table 3.6. Summary of Magnetic Susceptibility Data^a

COMPLEX ^b	$-2J$ (cm ⁻¹)	g_{av}	TIP (emu mol ⁻¹)
$[\{Cu(L_1)\}_2(\mu-Me_2Dicyd)]^{2+}$	21.26	2.06	8.81×10^{-4}
$[\{Cu(L_1)\}_2(\mu-Cl_2Dicyd)]^{2+}$	9.00	2.09	1.43×10^{-2}
$[\{Cu(L_2)\}_2(\mu-Dicyd)]$	< 7.00	-	1.95×10^{-4}
$[\{Cu(L_2)\}_2(\mu-Me_2Dicyd)]$	9.80	1.99	1.18×10^{-3}
$[\{Cu(L_2)\}_2(\mu-Cl_2Dicyd)]$	7.00	2.04	3.19×10^{-2}

Abbreviations:^a measured from 5 - 300 KL₁ = diethylenetriamine (dien)L₂ = 1,3-bis(2'-pyridylimino)isoindolinato (bpil)

Five of the six complexes show characteristic antiferromagnetic behavior. The curve shapes are similar to that shown in Figure.1.1(b)(iii). Only one complex, $[\{Cu(dien)\}_2(\mu-Dicyd)][CF_3SO_3]_2$ showed Curie - Weiss behavior in the temperature range covered. A possible explanation is that crystal packing forces may distort the Cu(II) coordination spheres sufficiently to decouple Cu(II) ions from superexchange via Dicyd²⁻. The observation of intramolecular antiferromagnetic exchange for these dinuclear Cu(II) complexes is extraordinary considering that it occurs at a separation between Cu(II) ions of

over 13 Å. This must be attributed to the special nature of the bridging ligand and this will be explored later in this Thesis.

The J values obtained for Ru(III) complexes containing similar bridging ligands as the Cu(II) complexes described in this thesis, range from -100 to ≥ 800 cm⁻¹ [24]. Such a magnitude of antiferromagnetic coupling has been attributed to a favorable superexchange pathway. In order to rationalize the results obtained for the Cu(II) systems a favorable superexchange pathway will be proposed in Chapter 5 after the results of the heteronuclear complexes have been discussed..

Figure 3.21. Experimental (*) and modelled (-) temperature dependences of the molar magnetic susceptibility of $[[\text{Cu}(\text{dien})]_2(\mu\text{-Me}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$

Figure 3.22. Experimental(o) and modelled(-) temperature dependences of the molar magnetic susceptibility of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$

Figure 3.23. Temperature dependences of the molar magnetic susceptibility of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Dicyd})]$

Figure 3.24. Experimental (o) and modelled (-) temperature dependences of the molar magnetic susceptibility of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Me}_2\text{Dicyd})]$

Figure 3.25. Experimental (*) and Modelled (-) temperature dependences of the molar magnetic susceptibility of $[\text{Cu}(\text{bpil})_2(\mu\text{-Cl}_2\text{Dicyd})]$

3.2 Heterodinuclear Complexes

3.2.1 Infrared Spectroscopy

The Infrared spectrum of one of the precursor complexes is shown by Figure 3.26. The characteristic feature of this spectrum is the presence of two cyanamide (NCN) stretching frequencies at 2100 and 2214 cm^{-1} which are assigned to $\nu(\text{NCN})$ and $\nu(\text{NCNH})$, respectively. On complexation the high energy band disappears while the low energy band remains which is indicative of deprotonation of the bridging ligand.

The IR spectra of the heterodinuclear complexes are shown in Figures 3.27 - 3.28. The complexes exhibit strong $\nu(\text{NCN})$ between 2100 - 2140 cm^{-1} and show evidence of splitting due to the different coordination environments experienced by the cyanamide group. For the complexes of the type $[(\text{bpil})\text{Cu}(\mu\text{-L})\text{Ru}(\text{NH}_3)_5]^{2+}$ where $\text{L} = \text{Dicyd}^{2-}$, $\text{Cl}_2\text{Dicyd}^{2-}$ the NH_3 stretches are seen in the range 3100 - 3350 cm^{-1} and these are also observed in the precursor complexes $[(\text{NH}_3)_5\text{RuLH}]^{2+}$ and are similar to the values reported by Nakamoto[81]. The IR spectra of the heterodinuclear complexes also show the strong characteristic bpil bands at 1450 - 1600 cm^{-1} described in section 3.1.1.

Figure 3.26. IR spectrum of $[(\text{NH}_3)_5\text{Ru}(\text{DicydH})][\text{PF}_6]_2$ (KBr)

Figure 3.27. IR Spectrum of $[(\text{bpii})\text{Cu}(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$ (KBr)

Figure 3.28. IR Spectrum of $[(bpii)Cu(\mu-Cl_2Dicyd)Ru(NH_3)_3][PF_6]_2$ (KBr)

3.2.2 Electronic Absorption Spectroscopy

The dinuclear mixed metal complexes are expected to exhibit spectra that has characteristic absorption bands of the respective chromophores that constitute the complex. In these complexes, the $\pi^* \leftarrow \pi$ transitions associated with the bpil terminal ligand and the bridging ligand are expected in the UV region while the LMCT transitions arising from the Cu-cyanamide and Ru-cyanamide chromophores should be major features in the Vis-NIR region. The UV-vis-NIR spectra of the precursor mononuclear complex and dinuclear complexes are shown in Figures 3.29 - 3.31 and indeed, the spectra of the dinuclear complexes exhibit absorption bands at approximately 700 - 1100 nm which are the LMCT transitions for the Ru-cyanamide chromophore and those at 300-500 nm are the charge transfer transitions for the bpil terminal and bridging ligand, respectively. The LMCT for the (bpil)Cu-cyanamide chromophore may either be obscured by the intense terminal ligand $\pi^* \leftarrow \pi$ transitions or the LMCT for the Ru-cyanamide chromophore. These intense $\pi^* \leftarrow \pi$ transitions for the bpil terminal ligand are also observed in the UV-vis spectra of dinuclear Cu(II) complexes discussed in section 3.1.2.2.

The individual band assignments for mononuclear pentaammineruthenium(III) phenylcyanamide complexes have appeared elsewhere[57,59]. For the Ru(III)-cyanamide chromophore the two ligand orbitals, upon mixing with the appropriate metal orbitals, give rise to two ligand to metal charge transfer (LMCT) transitions in the visible spectrum. The lower energy LMCT bands (710 - 1050 nm) have been assigned to an allowed $b_1^* \leftarrow b_1 (d\pi^* \leftarrow \pi_1)$

transition and the higher energy LMCT (350 - 465 nm) to a formally symmetry forbidden $b_1^* \leftarrow b_2 (d\pi^* \leftarrow \pi_2)$. These bands can be observed in Figure 3.29 which is the spectrum of $[(\text{NH}_3)_5\text{RuDicydH}][\text{PF}_6]_2$, a precursor complex used in the synthesis of one of the Ru(III)-Cu(II) complexes. In the mixed metal complexes of this study, the higher energy LMCT is obscured by the very intense ligand based $\pi^* \leftarrow \pi$ transitions of the terminal ligand bpil. A summary of the IR and electronic absorption data is given in Table 3.7. Thus, the presence of the absorption bands characteristic of the two different chromophores in the electronic absorption spectra and the characteristic bands in the IR of the mixed metal complexes is indicative of the dinuclear nature of these complexes.

Table 3.7 Infrared Data^a and Electronic Absorption Data^b of Mononuclear Precursor Complexes and [Ru(III) - Cu(II)] Complexes.

SPECIES	$\nu(\text{NCN})$	$\pi^* \leftarrow \pi^c$	LMCT
$[(\text{NH}_3)_3\text{RuDicydH}]^{2+}$	2108	-	875(4.08)
$[(\text{NH}_3)_3\text{RuCl}_2\text{DicydH}]^{2+}$	2127	-	748(3.83)
$[\text{Cu}(\text{bpil})(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_3]^{2+}$	2106	415(4.37)	1086(4.16)
$[\text{Cu}(\text{bpil})(\mu\text{-Cl}_2\text{Dicyd})\text{Ru}(\text{NH}_3)_3]^{2+}$	2119	416(4.21)	1022(3.89)

^a In cm^{-1}

^b In NM (Log ϵ in $\text{M}^{-1} \text{cm}^{-1}$ in parentheses) . ^c bpil ligand only

Figure 3.29. UV-vis spectrum of $[(\text{NH}_3)_5\text{RuDicydH}][\text{PF}_6]_2$ 1.50×10^{-4} M in acetonitrile

Figure 3.30. UV-vis-NIR spectrum of $[\text{Cu}(\text{bpii})(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$ 5.00×10^{-5} M in acetonitrile

Figure 3.31. UV-vis Spectrum of $[\text{Cu}(\text{bpil}) (\mu\text{-Cl}_2\text{Dicyd}) \text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$ 4.30×10^{-5} M
in acetonitrile

3.2.3 Cyclic Voltammetry

The cyclic voltammograms of the Ru(III)-Cu(II) complexes in acetonitrile are shown in Figures 3.32 - 3.33 and a summary of the redox potentials are put in Table 3.8. For these complex systems, four redox couples are expected: two ligand centered couples (A and B) and two metal centered couples (C and D). The cyclic voltammograms of $[\text{Cu}(\text{bpil})(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5]^{2+}$ (Figure 3.32) show two well defined ligand based couples and one ill-defined metal couple. The sharpness of peak E is clearly due to anodic stripping of the copper metal electrodeposited on the platinum electrode after traversing the peak D; the so-generated Cu^+ ion is further oxidized to Cu^{2+} at peak F. The peak G since it occurs at a more positive potential than the peak A is probably due to the oxidation of Ru(III) to Ru(IV). On the other hand, the cyclic voltammograms of $[\text{Cu}(\text{bpil})(\mu\text{-Cl}_2\text{Dicyd})\text{Ru}(\text{NH}_3)_5]^{2+}$ (Figure 3.3) are well defined showing the two characteristic ligand centered redox processes (A and B), and two metal centered waves (C and D) as expected for such a complex. The metal centered waves consist of a reversible one-electron redox process and an irreversible redox process. The reversible one-electron process is assigned to the $\text{Ru}^{3+/2+}$ couple while the irreversible cathodic wave to the $\text{Cu}^{2+/+}$ couple. These assignments are in agreement with previous cyclic voltammetric studies on mononuclear complexes of the type $[(\text{NH}_3)_5\text{RuL}]^{2+}$ ($\text{L} = \text{DicydH}^+$, $\text{Cl}_2\text{DicydH}^+$) [76] and also the mononuclear and dinuclear copper(II) complexes containing bpil as the co-ligand, discussed in section 3.1.3.3.

Analysis of the cyclic voltammetric response exhibited by the Ru(III)-Cu(II) peak system and the two ligand peak systems of $[\text{Cu}(\text{bpil}) (\mu\text{-Cl}_2\text{Dicyd}) \text{Ru}(\text{NH}_3)_5]^{2+}$ with scan rate (20 - 100 mV/s) shows that: (i) the i_{pa}/i_{pc} ratio is constantly equal to unity and (ii) the peak-to-peak separation is scan rate independent and equal to approximately 60 mV for both the Ru(III/II) peak system (C) and the most anodic ligand peak system (A). All these parameters are diagnostic for a simple one-electron redox process, reversible in character[82,83]. The data in Table 3.7 shows that in all the bridged complexes, the ligand waves are shifted to much more anodic potentials than the corresponding ligand waves which may certainly be due to the stabilization of ligand upon complexation.

Table 3.8 Redox potentials^a for the Free Dicyd²⁻ ligands, the mononuclear Ru(III) complexes, dinuclear Ru(III) complex, and the Ru(III)-Cu(II) complexes.

SPECIES ^b	L ^{0/+}	L ^{+2/+}	Ru ^{3+/2+}	Cu ^{2+/+}
Dicyd ²⁻	+0.210 ^d	-0.465 ^d	-	-
Cl ₂ Dicyd ²⁻	+0.465 ^d	-0.175 ^d	-	-
[(NH ₃) ₃ RuDicydH] ²⁺	-	-	-0.217 ^e	-
[{Ru(NH ₃) ₃ } ₂ (μ-Dicyd)] ⁴⁺	1.027 ^f	0.565 ^f	-0.134 ^f	-
[Cu(bpil)(μ-Dicyd)Ru(NH ₃) ₃] ²⁺	0.788	0.223	-0.310 ^e	-0.310 ^e
[Cu(bpil)(μ-Cl ₂ Dicyd)Ru(NH ₃) ₃] ²⁺	0.934	0.399	-0.206	-0.500 ^e

^a In acetonitrile, values are in volts vs NHE (Fc⁺/Fc = 0.400 V vs NHE, scan rate 0.1 Vs⁻¹). ^b Counterions have been left out for clarity. ^c Cathodic potentials only

^d From Ref. 69 ^e From Ref. 76

^f From Ref. 97

Figure 3.32. Cyclic voltammograms of $[\text{Cu}(\text{bpii})(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$ in acetonitrile (0.1M TBAH, at scan rate 100 mV s^{-1})

Figure 3.33. Cyclic voltammogram of $[\text{Cu}(\text{bpii})(\mu\text{-Cl}_2\text{Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$ in acetonitrile (0.1 M TBAH at scan rates 100 mV s^{-1})

3.2.4 Variable Temperature Magnetic Susceptibility

The variable temperature magnetic susceptibility measurements were performed in a similar way as for the homonuclear copper(II) complexes. The temperature dependence of the magnetic susceptibility of $[\{\text{Cu}(\text{bpil})(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5\}](\text{PF}_6)_2$ is shown in Figure 3.34 and follows the Curie-Weiss Law while the plot for the inverse of the molar magnetic susceptibility versus temperature is shown in Figure 3.35. Fitting the higher temperature data (80 - 300 K) to the Curie-Weiss Law (Equation 1.9), yields the following parameters: $C = 0.931$; $\Theta = -28.273$; $TIP = 3.45 \times 10^{-4} \text{ emu mol}^{-1}$. These values are consistent with normal $g \approx 2.00$ and as mentioned in section 1.2.2, a negative value of Θ is indicative of antiferromagnetic spin interactions [37]. Attempts have been made to estimate the antiferromagnetic coupling constant, J by least squares fitting of the magnetic data to the ferrimagnet dimer Equation 3.1[29]

$$\chi_m = \frac{N \mu_B^2}{2kT} \frac{[(g_1 + g_2)^2 + (g_1 - g_2)^2 / x] e^x - (g_1 - g_2)^2 / x}{1 + 3e^x} + TIP \quad (3.1)$$

where $x = 2J/kT$ and g_1 and g_2 are the g values for metal 1 and metal 2, respectively. All the other symbols have their usual meanings and have been defined in section 1.2.2. From this equation are derived the following parameters; $J/K = -3.583$, $g_1 = 0.254$, $g_2 = 2.050$ and

$TIP = 4.024 \times 10^{-3} \text{ emu mol}^{-1}$. However, the unrealistically small value for g_i puts doubt on the magnitude of J obtained. The importance of these results will be broached once again in Chapter 5.

Figure 3.34. Temperature dependences of the molar magnetic susceptibility of $[\text{Cu}(\text{bpii})(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_2$

Figure 3.35. Plot of $1/\chi_m$ versus temperature of $[\text{Cu}(\text{bpil})(\mu\text{-Dicyd})\text{Ru}(\text{NH}_3)_5](\text{PF}_6)_2$.

CHAPTER 4

ELECTRON SPIN RESONANCE SPECTROSCOPY OF COPPER(II) COMPLEXES

4.1. Background

For paramagnetic complexes, the electron spin-nuclear spin interactions provide a detailed probe of the electronic structure. In principle, a paramagnetic metal complex offers a choice of magnetic resonance techniques. Transitions involving a change in electron spin quantum number may be studied by ESR and attention is focussed on the metal ion and its immediate environs and the question is asked "how have the properties of the free ion been modified by interaction with the ligands ?[84,85].

The electron has associated with it a magnetic moment so it may be treated as a tiny bar magnet. Free electrons (in the absence of a crystal or magnetic field) are aligned at random but in the presence of an external magnetic field, the lower energy state occurs when electrons are lined up with magnetic field. A higher energy state occurs when the electrons line up in opposition to the magnetic field. The difference in energy between these two states is proportional to the applied field H_0 [84].

$$\Delta E = g\beta_e H_0 \quad (4.1)$$

The constant of proportionality g equals 2.0023 for a free electron and is called the spectroscopic splitting factor, or just the g factor. It is equivalent to the Lande g factor of atomic spectroscopy [84,85].

In quantum mechanical terms, the allowable electron spin states are quantized, and the component M_s of the electron spin vector in any direction can only take one set of discrete values which are $+S$ or $-S$, i.e. $M_s = +\frac{1}{2}$ and $-\frac{1}{2}$. Electrons in the lower state, $M_s = -\frac{1}{2}$ and for a given applied field H_o (gauss), the energy ΔE required for the transition will be

$$\Delta E = h\nu = g\beta_e H_o \quad (4.2)$$

where ν is the frequency of the applied radiation (cycles/sec or Hz). Since the energy gap is very small, the most convenient radiation frequencies occur when the magnetic field is about 3000 gauss and ν then lies in the microwave region of the electromagnetic spectrum (~ 9.0 GHz). The constant g varies from 2.0023 when the unpaired electron is no longer free, i.e. when it is in a molecule.

The ESR spectrometer, thus measures the energy required to reverse the spin of an electron in an external magnetic field. Experimentally, this is performed by placing the substance containing unpaired electrons in an absorption cell in the form of a resonance cavity[83,84,85]. The sample is adjusted within the cavity in such a way that the microwave magnetic field is at its maximum and the electric field is at its minimum. The cavity is placed between the poles of the magnet. The microwave energy is modulated and the absorption

measured by detector coils, amplified and ultimately displayed on a chart recorder as the first derivative of the absorption. Since it is easier to vary the magnetic field rather than the frequency, the resonance condition $h\nu = g\beta_e H_0$ is observed at constant frequency, and the magnetic field varied so that an absorption may be observed[86].

4.2. The g -values and Hyperfine Coupling Constant, A

Basically the interpretation of the ESR spectrum of an isolated transition metal ion yields values for two different kinds of parameter. The spectroscopic splitting constants (g values) describe the frequencies (or energies) required to bring about transitions between the different electron spin states. The hyperfine coupling constants (A) describes the electron spin - nuclear spin interactions which give rise to the hyperfine structure observed in the spectrum.. Both of these parameters may be anisotropic, i.e. their values may depend on the orientation of the molecule with respect to the applied magnetic field. In addition, ions containing more than one unpaired electron will exhibit zero-field splitting effects due to electron spin-electron spin interactions and to spin orbit coupling. These interactions are described by the zero-field splitting parameters D and E [85,86].

The hyperfine coupling constant between electron spins and nuclear spins arises from three sources[83,84,85,86]. The first of these is a direct dipolar interaction. The magnetic moment of the electron produces a field at the nucleus, the direction of which depends on the orientation of the electron spin i.e. it is anisotropic. Secondly, there are spin-polarization (exchange) effects and the third and final source of hyperfine coupling is the Fermi contact

interaction. This mechanism demands a finite probability of finding the odd electron at the metal nucleus, i.e. there must be spin density in a metal s -orbital. Since s -orbitals are involved, it is an isotropic interaction. The observed hyperfine coupling constant is given by

$$A_{obs} = A_{iso} + A_{aniso} \quad (4.3)$$

For powders and frozen solutions all orientations are possible, but the principal A -values will be associated with the corresponding g -value. Thus, for an axial system, the $g_{\parallel}$ line will appear to be split into $2I + 1$ components separated by $A_{\parallel}$ and the $g_{\perp}$ line will be similarly split with separation $A_{\perp}$. The full structure of the spectrum may not be resolved; sometimes all that can be seen is a broadening of the lines. For solutions, the anisotropic effects are averaged to zero by the rapid tumbling of the molecules, and only A_{iso} remains. It therefore follows that

$$A_{iso} = (A_{\parallel} + 2A_{\perp})/3 \quad (4.4)$$

4.3. Monomer Complexes of the Cu(II) ion

In an octahedral environment the cupric ion, which has nine d electrons, would possess a degenerate 2E_g electronic ground state. A geometric distortion which removes this degeneracy would produce a more stable electronic structure, in accordance with the Jahn-Teller theorem. Consequently 6-coordinate Cu(II) is normally found in a tetragonal environment with four strongly bound equatorial ligands and one or two weakly bound axial

ligands. Tetragonal coordination geometry induces a splitting in the d orbitals which is shown in Figure 4.1 [87],

Figure 4.1. Site geometries and d -orbital splittings for copper(II) in octahedral and tetragonal environments.

The dx^2-y^2 orbital has the greatest repulsion with the equatorial ligands. Therefore, it is the highest-energy metal-centered orbital, is half occupied, and characterizes the tetragonal Cu(II) ground state as $^2B_{1g}$.

Spin orbit coupling mixes the $^2B_{1g}$ with the $^2B_{2g}(d_{xy})$ and $^2E_g(d_{xz}, d_{yz})$ excited states. Application of a magnetic field to this mixed ground state now gives [87].

$$g_{\parallel} = g_z = 2.0023 + [-8\lambda / \{E(xy) - E(x^2-y^2)\}] \quad (4.5)$$

$$g_{\perp} = g_x = g_y = 2.0023 + [-2\lambda / \{E(xz, yz) - E(x^2-y^2)\}] \quad (4.6)$$

where 2.0023 is the g value of the free electron, λ is the one-electron spin-orbit coupling constant for copper (equal to 830 cm^{-1} in the free copper ion, but reduced by covalency in the metal complex), and the denominators in the second term of each equation are energy differences between the d orbitals indicated[87]. In a similar way a tetragonally flattened tetrahedral Cu(II) geometry has a $^2B_2(dx^2-y^2)$ ground state with

$$g_{\parallel} = 2.0023 - [(8k_{\parallel}\lambda) / \{E(xy) - E(x^2-y^2)\}] \quad (4.7)$$

$$\text{and } g_{\perp} = 2.0023 - [(2k_{\perp}\lambda) / \{E(xz, yz) - E(x^2-y^2)\}]$$

where k is the orbital reduction factor. As g_x must equal g_y by symmetry, the above description is for an axial g tensor[86,87]. Thus, the ESR spectra of 4-coordinate complexes like the monomer complexes of this study are best described by equation 4.7.

Frozen glasses of inorganic complexes yield EPR spectra (plotted as the first derivative) which are the sum of transitions of individual copper centers randomly oriented with respect to the magnetic field [87]. The perpendicular region is more intense due to the greater probability of perpendicular orientation. The net effect is an EPR signal with $g_{\parallel} > g_{\perp} > 2$. In axial systems the g factors are different depending on whether a dx^2-y^2 or a dz^2 ground state is present, that is $g_{\parallel} \gg g_{\perp} > 2.0$ and $g_{\perp} > g_{\parallel} > 2.0$, respectively [89].

The copper nucleus ($^{63}\text{Cu} = 69\%$, $^{65}\text{Cu} = 31\%$) with a nuclear spin $I = 3/2$ couples to the unpaired electron and produces a hyperfine splitting of the transition into $2I+1 = 4$ components. For copper(II) complexes involving large ligands and anions, the physical separation, between Cu(II) ions, may display evidence for copper nuclear hyperfine splitting, $2I+1$, for ^{63}Cu and ^{65}Cu , $I = 3/2$ e.g. in $[\text{Cu}(\text{phen})_3][\text{ClO}_4]_2$ [89]. The hyperfine splitting is quite evident in the $g_{\parallel}$ region, but is significantly smaller and often unresolved in the $g_{\perp}$ region. Both isotropic and anisotropic ligand field terms contribute to this hyperfine splitting. The former are Fermi contact in nature while the latter is a function of dipole-dipole interaction between the nuclear and electron spins[87].

4.3.1 Powder ESR data

Hathaway et al.[88] have given a detailed account of the ESR spectra of polycrystalline Cu(II) complexes. Typical polycrystalline ESR spectra line-shapes, with the approximate g -values indicated in terms of the corresponding magnetic field, have been compiled by Hathaway[88]. The spectra may be considered in three general classes: isotropic spectra, axial spectra, and rhombic spectra. The two types of axial spectra given in Hathaway's review article[88], may be used as a criteria for distinguishing a dx^2-y^2 and dz^2 ground state, respectively. It has been shown by Hathaway[88] and later by Wilett[99] that the g tensor reflects the local symmetry of the Cu(II) ion. For high symmetry (axial) species (D_{4h} --- compressed or elongated octahedron, square planar; D_{3h} --- trigonal bipyramid; D_{2d} --- distorted tetrahedra, C_{4v} --- square pyramid) the g tensor is axially symmetric. For the compressed octahedron and trigonal bipyramid the unpaired electron lies in the d_z^2 orbital while for the other axial cases, the unpaired electron lies in the dx^2-y^2 orbital.

4.4. Binuclear Copper(II) Complexes

Binuclear cupric sites would be expected to have magnetic ground state and optical spectral features significantly perturbed due to interaction between the d^9 metal ions. In the limit of strong interaction, direct overlap of the copper orbitals would lead to metal-metal bonding and a completely spin-paired diamagnetic ground state[86,87]. Optical transition with energies on the order of $20,000\text{ cm}^{-1}$ from the HOMO to low excited state orbital in metal-metal bonded complexes are allowed and can dominate the spectrum[87]. There are, however,

no clearly defined cases of metal-metal bonding in binuclear cupric complexes [86,88]. An indirect weaker interaction is found when bridging ligands form a superexchange pathway leading to a valence-bond type coupling of the unpaired copper spin states. When two $S = 1/2$ ions couple they form a non-degenerate spin singlet ($S = 0$; $M_s = 0$) and a three-fold degenerate spin triplet ($S = 1$; $M_s = -1, 0, 1$), the energy difference between these states ($-2J$) depends on the strength of this interaction. If the singlet is lowest in energy (antiferromagnetic coupling), a diamagnetic ground state results. Temperature dependence of these signals can, thus be used to determine J . Poor superexchange orbital overlap or the lack of bridging ligands can lead to the limit ($-2J \rightarrow 0$) of very weak interaction. Here, only the ESR spectrum is perturbed through dipolar coupling of the spins[87]. This interaction, which depends on the separation (R) of the cupric ions, produces a zero- field splitting of the spin triplet, indicated by broadening and eventual splitting of the $\Delta M_s = \pm 1$ transitions in the ESR spectrum as the Cu-Cu separation decreases. A $\Delta M_s = \pm 2$ transition at half field also becomes weakly allowed, reaching maximum intensity when $D \approx h\nu/2$ ($\sim 15 \text{ cm}^{-1}$ for X band corresponding to $R \approx 3 \text{ \AA}$) [87]. All these phenomena are illustrated in Figure 4.2 below:

Figure 4.2. Dipolar-induced zero field splitting (D) of the EPR signals of a dipolar coupled binuclear cupric spin triplet at three metal-metal separations (R) solid lines are $\Delta M_s = \pm 1$ transitions and broken lines are $\Delta M_s = \pm 2$ transitions.

4.5. ESR fine structure: The case of Exchange Coupled Systems

When there is interaction between an unpaired electron and a magnetic nucleus, hyperfine structure may be detected. Different spectra are obtained when an isolated pair of ions, each with $S = 1/2$ and $I = 3/2$ is allowed to interact under different conditions. A single ion would give a 4 line-spectrum with hyperfine splitting A . If another identical molecule is allowed to approach it so that there is appreciable dipolar interaction between electron spins, then either of the following cases may arise [84].

- (i) If the rate of exchange between the electrons is slow compared with the electron resonance frequency (10^{10} sec), then during resonance each electron experiences interaction with the other electron and its own magnetic nucleus or
- (ii) If the rate of exchange is fast compared to the resonance frequency, then during resonance each electron spends half of its time on each magnetic nucleus and hence interacts with two equivalent nuclei as well as with the other electron.

Slichter [90] has shown that since each electron spends only half as long on each nucleus as in the previous example a hyperfine splitting of $A/2$ is obtained. For a system with $I = 3/2$ and the two electrons are on ions in different environments, a 14-line spectrum would be expected. However, if the ions are in similar environments a 7-line spectrum is observed.

For a system in which pairs of copper(II) ions are interacting, Slichter [90] has shown that the esr spectrum can be described by the spin Hamiltonian

$$H = -2JS_1.S_2 + A(I_1.S_1 + I_2.S_2) + \beta_e(S_{1z} + S_{2z})H_o + \beta_n(I_{1z} + I_{2z})H_o \quad (4.8)$$

where I_1 and I_2 are the nuclear spins S_1 and S_2 are the electron spins, β_e and β_n are the electron and nuclear Bohr magnetons and A is the hyperfine coupling constant. The term $-2JS_1.S_2$ represents the electron exchange interaction between pairs of electrons. In its absence, the energy levels obtained are described by the quantum numbers M_1 and M_2 for the two nuclei and m_1 and m_2 for the electrons. When there is no interaction, the energy terms are given by

$$E = A(m_1M_1 + m_2M_2) + \beta_e(m_1 + m_2)H_o + \beta_n(M_1 + M_2) \quad (4.9)$$

The allowed transitions in which $\Delta m_1 = \pm 1$, $\Delta m_2 = 0$ or $\Delta m_1 = 0$, $\Delta m_2 = \pm 1$ give a set of lines at energies $\beta_e H_o + AM_1$, where $M_1 = I, I-1, \dots, -I$. There are then $2I+1$ lines of spacing A . For copper with $I = 3/2$, four lines are expected when there is no interaction for instance in mononuclear Cu(II) complexes.

When there is an electron exchange interaction and $J \gg A$, the electrons form a system described by quantum numbers S and L where $S = 1, 0$ and $L = S, S-1, \dots, -S$, but the nuclei are still described by M_1 and M_2 . The states $S = 0$ and 1 are the well-known singlet or triplet states. The diagonal terms become

$$E = \frac{1}{2}A(M_1L + M_2L) + \frac{1}{2}J[S(S+1)-3/2] + \beta_e LH_o + \beta_n H_o(M_1+M_2) \quad (4.10)$$

The allowed transitions with $\Delta S = 0$, $\Delta L = \pm 1$, will give $4I+1$ lines at $\beta_e H_o + \frac{1}{2}A(M_1+M_2)$. The spacing is $A/2$ rather than A . For Cu(II) with $I = 3/2$ seven lines are now expected at a spacing of $A/2$. Exchange coupled dinuclear systems with similar ions, normally exhibit seven well-resolved hyperfine lines with an average splitting of $A/2$ [90,91,92,93,94]. Thus, the magnitude of the hyperfine coupling constant, A is an important parameter to gauge exchange coupled binuclear systems from either non-coupled binuclear or mononuclear systems.

4.6. Determinations of the ESR Parameters g and A

The ESR experiment involves obtaining the ESR spectra at room temperature (295 K) in which case g_{iso} and A_{iso} respectively can be calculated, and at liquid nitrogen temperatures (77 K) in which case $g_{\perp}$, $g_{\parallel}$, $A_{\perp}$ and $A_{\parallel}$ can be estimated. The sweep-range is normally selected so as to cover the likely region of interest, and a marker with a known g -value is often used as the reference. Common reference materials are DPPH (diphenylpicrylhydrazyl radical, $g = 2.0036$) and pitch ($g = 2.0028$) [86]. The g -value is calculated from the recorded value of the magnetic field at the resonance position

$$g_{sample} H_{sample} = g_{ref} H_{ref} \quad (4.11)$$

For a system in which the ESR lines are split into $2I+1$ or $4I+1$ lines, the parameter A is obtained as the difference in the field at two different chosen line positions. In an axial system at 77 K

$$g_{\perp} \cdot H_{\perp} = g_{ref} \cdot H_{ref} \quad (4.12)$$

$$\text{and } g_{\parallel} \cdot H_{\parallel} = g_{ref} \cdot H_{ref}$$

The lines in the $g_{\perp}$ region are rarely well resolved and equation 4.4 and 4.13 are used to calculate $A_{\perp}$ and $g_{\perp}$, respectively

$$g_{\perp} = \frac{1}{2}(3g_{iso} - g_{\parallel}) \quad (4.13)$$

4.7. Results and Discussion

ESR spectra for the mononuclear and dinuclear copper(II) complexes have been obtained in the solid state and in solution at 295 and 77 K, respectively.

4.7.1. Polycrystalline Powdered X-band ESR Spectra of Copper(II) Complexes

The powdered X-band ESR spectra of the copper(II) complexes have been obtained at 295 K and 77 K and are shown in Figures 4.3 - 4.9. The X-band ESR spectra of the mononuclear complexes $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{pcyd})][\text{NO}_3]$ and $[\text{Cu}(\text{bpil})(2,3\text{-Cl}_2\text{pcyd})]$ (Figures

4.3 and 4.4) can be classified as of type 'f' and type 'a' respectively according to the classification proposed by Hathaway et al. [88]. Five of the dinuclear complexes have powder ESR spectra (Figures 4.5 - 4.9) typical of an axial g tensor ($g_{\parallel} > g_{\perp} > 2.0$) and conforms to type 'b' of the Hathaway classification[88]. Only, one complex $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Dicyd})][\text{CF}_3\text{SO}_3]_2$ did not give an ESR line signal at 295 K or at 77 K. The magnetic behavior described in Chapter 3 of the same complex follows Curie- Weiss Law. From the negative sign for the Weiss constant and the ESR behavior one can conclude that intermolecular interactions occur in this complex. A summary of the powdered X-band ESR spectral parameters are given in Table 4.1. Since $g_{\parallel} > g_{\perp} > 2.0$, the single electron is contained in a $d_{x^2-y^2}$ orbital[89].

Figure 4.3. X-band ESR spectrum for $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{Pcyd})][\text{NO}_3]$ (solid state) at 295 K (9.76 GHz)

Figure 4.4. X-band ESR spectrum for $[\text{Cu}(\text{bpii})(2,3\text{-Cl}_2\text{Pcyd})]$ (solid state) at 295 K (9.76 GHz)

Figure 4.5. X-band ESR spectrum of $[\{Cu(dien)\}_2(\mu-Me_2Dicyd)][CF_3SO_3]_2$
(solid state) at 77 K (9.76 GHz)

Figure 4.6. X-band ESR spectrum of $[\{Cu(dien)\}_2(\mu-Cl_2Dicyd)][CF_3SO_3]_2$
(Solid state) at 77 K (9.76 GHz)

Figure 4.7. X-band ESR spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Dicyd})]$ (solid state) at 77 K (9.76 GHz)

Figure 4.8. X-band ESR spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Me}_2\text{Dicyd})]$ (solid state) at 77 K (9.76 GHz)

Figure 4.9. X-band ESR spectrum of $[\{\text{Cu}(\text{bpil})\}_2(\mu\text{-Cl}_2\text{Dicyd})]$ (solid state at 77 K (9.76 GHz)).

4.7.2. Solution X-band ESR Spectra of Copper(II) Complexes

The X-band ESR spectra of the copper(II) complexes have been obtained in solution at room temperature and as frozen glasses (77 K). The ESR spectra for the mononuclear complex, $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{pcyd})]^+$ in DMF at 295 K and 77 K, respectively are shown in Figures 4.10(a) and 4.10(b). Figures 4.11 - 4.12 show the spectra of the same complex in DMSO and CH_3CN , respectively. All these spectra show four resonance lines expected for a non-coupled Cu(II) species ($I = 3/2$). The hyperfine coupling constants A_{iso} for these complexes are collected in Table 4.1. The mononuclear complex, $\text{Cu}(\text{bpil})(2,3\text{-Cl}_2\text{pcyd})$ gave an isotropic spectrum in DMF at 295 and 77 K respectively (Figure 4.13). The ESR spectra of the dinuclear complexes in DMF, acetonitrile and DMSO are shown in Figures 4.14 - 4.23. The dinuclear complexes gave ESR spectra with a different line pattern from that of the mononuclear copper(II) complexes when the solvent used was either DMF or DMSO. The ESR spectra of the dinuclear complexes in acetonitrile was however, similar to that obtained for the mononuclear complexes.

For a system of interacting copper(II) pairs ($I = 3/2$), Slichter[90] has shown theoretically that $4I + 1$ lines are expected for an exchange coupled system (see Section 4.5 for details). In this way, seven copper hyperfine lines with $A/2$ are expected for an exchange coupled Cu(II) dimer. Various examples which exhibit seven hyperfine lines are found in literature[90,94,96,97]. However, most of these examples are mixed-valence species where the odd electron interacts with both copper centers ($I = 3/2$). In these complexes as in the Cu(dien) complexes of this study the hyperfine splittings are approximately one-half that of the

mononuclear complexes. In addition the internally consistent hyperfine splittings imply the presence of only a single ESR active species[90]. In the dinuclear complex $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$, reported in this thesis, five resonance lines are clearly observed with the other two lost because of the poor resolution and the estimated average copper hyperfine splitting $A_{\text{iso}} = 41.7 \times 10^{-4} \text{ cm}^{-1}$ is approximately one-half that of the monomer complex, $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{pcyd})][\text{NO}_3]$ (Figure 4.11) for which $A_{\text{iso}} = 80.6 \times 10^{-4} \text{ cm}^{-1}$ as expected for an exchange coupled system [90,94,96,97]. The ESR parameters for Cu(II) complexes are all given in Table 4.1.

Figure 4.10. X-Band ESR Spectrum of [Cu(dien)(2,3-Cl₂pcyd)] [NO₃] in DMF at
(a) 295 K (9.76 GHz) and (b) 77 K (9.48 GHz)

Figure 4.11. X-band ESR spectrum of $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{pcyd})][\text{NO}_3]$ in DMSO at 295 K (9.76 GHz)

Figure 4.12. X-band ESR Spectrum of $[\text{Cu}(\text{dien})(2,3\text{-Cl}_2\text{pcyd})][\text{NO}_3]$ in Acetonitrile at 295 K (9.76 GHz).

Figure 4.13. X-band ESR Spectrum of $[\text{Cu}(\text{bpii})(2,3\text{-Cl}_2\text{pcyd})]$ in DMF at 295 K
(9.76 GHz)

Table 4.1 ESR Data^a of the Cu(II) Monomer and Dimer Complexes

COMPLEX	DMF/Powder ^a	$g_{\parallel}$	$g_{\perp}$	g_{iso}	$A_{iso} \times 10^{-4} \text{ cm}^{-1}$
[Cu(dien)(2,3-Cl ₂ Pcyd)] ⁺	DMF			2.13	80.6
	powder			2.07	
[Cu(bpii)(2,3-Cl ₂ Pcyd)]	DMF	2.10	2.07		50.8
	powder				
[{Cu(dien)} ₂ (μ-Dicyd)] ²⁺	DMF			2.07	55.2
	powder	2.23	2.07		
[{Cu(dien)} ₂ (μ-Me ₂ Dicyd)] ²⁺	DMF			2.07	41.7
	powder	2.23	2.07		
[{Cu(dien)} ₂ (μ-Cl ₂ Dicyd)] ²⁺	DMF			2.08	41.7
	powder	2.24	2.07		
[{Cu(bpii)} ₂ (μ-Dicyd)]	DMF	2.23	2.09		
	powder				
[{Cu(bpii)} ₂ (μ-Me ₂ Dicyd)]	DMF				
	powder	2.21	2.08		
[{Cu(bpii)} ₂ (μ-Cl ₂ Dicyd)]	DMF	2.20	2.07		
	powder				

In the presence of oxygen, these complexes decomposed in DMF solutions forming radical anion Dicyd[•] and gave monomer spectra (Figure 4.24). The complex, $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})]^{2+}$ showed the greatest resistance to oxidation, but even under rigorously oxygen free conditions, a weak radical anion Dicyd[•] absorption can still be seen in Fig. 4.20(a) in approximately the same position as DPPH. This decomposition can be an explanation for the somewhat large A_{iso} obtained for the complexes $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Dicyd})]^{2+}$ and $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})]$ (see Table 4.1). At 77 K [Figures 4.14(b), 4.17(b) and 4.20(b)], the copper hyperfine is lost and only a single broad resonance is observed. Only a radical Dicyd[•] resonance was observed for the Cu(bpii) derivatives (Figure 4.23).

Solution ESR spectra were obtained in other solvents such as dimethyl sulfoxide, acetonitrile and methanol/ethanol. Dimethyl sulfoxide gave the same results as DMF solutions as seen in the ESR spectrum shown in Figures 4.15, 4.18 and, 4.21. In other solvents, acetonitrile and methanol/ethanol solutions gave spectra that were characteristic of monomer Cu(II) complexes. An example spectrum is shown in Figure 4.16. Complex decomposition could explain the monomer Cu(II) ESR spectra but the visible electronic spectroscopy and cyclic voltammetry in 2-methoxyethanol is consistent with an intact Cu(II) dimer. Solvent perturbations might be decoupling Cu(II) ions in much the same manner as the one observed for Ru(III) ions in $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-Me}_2\text{Dicyd})]^{4+}$ [98].

Figure 4.14. X-band ESR spectra of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Dicyd})]^{2+}$ in DMF at (a) 295 K
(b) 77 K

Figure 4.15. X-band ESR Spectrum of $[\{Cu(dien)\}_2(\mu-Dicyd)]^{2+}$ in DMSO at 295 K

Figure 4.16. X-band ESR Spectrum of $[\{Cu(dien)\}_2(\mu-Dicyd)]^{2+}$ in Acetonitrile at 295 K

Figure 4.17. X-band ESR spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})]^{2+}$ in DMF at
(a) 295 K and (b) 77 K

Figure 4.18. X-band ESR Spectrum of $[\{Cu(dien)\}_2(\mu-Me_2Dicyd)]^{2+}$ in DMSO at 295 K

Figure 4.19. X-band ESR Spectrum of $[\{Cu(dien)\}_2(\mu-Me_2Dicyd)]^{2+}$ in Acetonitrile at 295 K

Figure 4.20. X-band ESR Spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Cl}_2\text{Dicyd})]^{2+}$ in DMF at (a) 295 K and (b) 77 K.

Figure 4.21. X-band ESR Spectrum of $[\{Cu(dien)\}_2(\mu-Cl_2Dicyd)]^{2+}$ in DMSO at 295 K

Figure 4.22. X-band ESR Spectrum of $[\{Cu(dien)\}_2(\mu-Cl_2Dicyd)]^{2+}$ in Acetonitrile at 77 K.

Figure 4.23. X-band ESR Spectrum of $[\{\text{Cu}(\text{bpii})_2(\mu\text{-Me}_2\text{Dicyd})\}^{2+}]$ in DMF at 295 K

Figure 4.24. X-band ESR Spectrum of $[\{\text{Cu}(\text{dien})_2(\mu\text{-Me}_2\text{Dicyd})\}^{2+}]$ in undegassed DMF at 295 K

CHAPTER 5

MAGNETIC EXCHANGE COUPLING: Coupling Mechanism and the Effects of Energy and Symmetry.

5.1. Background

The theoretical basis of magnetic exchange interaction, superexchange and superexchange mechanism have been discussed in detail in Chapter 1 and only the relevant concepts will be reiterated here to put what follows in some context. In bridged dinuclear systems, metal-metal coupling is mediated by the full set of bonding and antibonding orbitals of the bridging ligand[24]. Each ligand orbital contributes to the overall interaction between metal magnetic orbitals by an amount which is governed by the magnitude of its' orbital overlap with the coupled metal orbitals. In this regard, the relative symmetry and energy between orbitals play an important role. The relative energies of metal and bridging ligand orbitals can be obtained from electronic absorption spectroscopy if the dominant pathway for metal-metal coupling involves the same orbitals as those resulting in ligand-to-metal charge-transfer transitions (LMCT)[24].

In keeping with the orbital overlap requirements, the magnetic data for Cu(II) complexes of this study are rationalized by proposing a favorable superexchange pathway via the bridging ligand π orbitals. This is simply achieved by taking into consideration only

the highest occupied (HOMO) and the second highest occupied (SHOMO) molecular orbitals of the bridging ligand.

5.2. Homonuclear Cu(II) Dimer Complexes

The magnetic susceptibility results summarized in Table 3.6 establish weak antiferromagnetic exchange interactions for five of the six binuclear copper(II) complexes bridged by 1,4-dicyanamidobenzene dianion ligands. In these complexes the magnitude of antiferromagnetic exchange is in the range $6.0 \leq |2J| \leq 21.2 \text{ cm}^{-1}$ which is far weaker than that observed for the Ru(III) analogues where $100 \leq |2J| \leq 800 \text{ cm}^{-1}$.

In an antiferromagnetically coupled copper(II) binuclear complex, the ground electronic state is a singlet ($S = 0$) with triplet ($S = 1$) excited state at an energy of $-2J$. Thus, the exchange parameter J is just a parameter to gauge the energy separation between these two electronic states. According to the orbital model for the superexchange interactions developed by Hoffmann et al. [27], the singlet-triplet splitting $E_S - E_T$, for the interaction of two $S = 1/2$ ions can be expressed by the combination of a ferromagnetic term, denoted as J_F and an antiferromagnetic term, J_{AF} (Equation 1.16 and 5.1)

$$E_S - E_T = 2J_{AF} + 2J_F = -2J = 2K_{ab} - (2H_{ab}^2)/(J_{aa} - J_{ab}) \text{ in cm}^{-1} \quad (5.1)$$

where the ferromagnetic term K_{ab} is the energy required to pair electron spins, H_{ab} is the electron exchange integral and the difference between coulomb repulsion integrals J_{aa} and

J_{ab} represents the energy required to place both spins on the same atom. According to *ab initio* calculations of exchange coupled Cu(II) dimers, second order antiferromagnetic contributions are important[80]. However, these second order contributions become less important with increasing separation between metal ions as does the ferromagnetic term in equation 5.1. In the copper systems of this study the Cu(II) ions are separated by approximately 13 Å and the ferromagnetic term may very well be cancelled out by these antiferromagnetic contributions[81] and equation 5.1 can be simplified to equation 5.2.

$$-2J \approx (2H_{ab}^2)/(J_{aa} - J_{ab}) \quad (5.2)$$

The magnitude of the magnetic exchange parameter, $-2J$ of the Cu(II) dimers of this study, differ significantly from that obtained for the Ru(III) analogues [26]. There is considerable attenuation of antiferromagnetic superexchange for the Cu(II) dimers relative to their pentaammineruthenium(III) analogues, $[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-Dicyd})^{4+}$ [24]. The origin of this difference can be understood qualitatively by considering equations 5.1 and 5.2. As explained above, the ferromagnetic term K_{ab} is dominated by the antiferromagnetic term, and will probably not differ significantly between Ru(III) and Cu(II) dimers. The difference in energy between coulomb repulsion integrals J_{aa} and J_{ab} can be estimated from the difference in Ru(III/II) or Cu(II/I) photoelectron spectroscopy orbital binding energies. In this way, $J_{aa} - J_{ab}$ was estimated to be 2.6 eV for the dinuclear Ru(III) complexes [24] and 1.7 eV for the dinuclear Cu(II) complexes. It therefore, seems clear

that the major contributor to the relative difference between Ru(III) and Cu(II) antiferromagnetic exchange is the magnitude of the electron exchange integral H_{ab} . The magnitude of H_{ab} is governed by the interaction of the metal magnetic orbitals with the superexchange pathway provided by the bridging ligand. It is the electronic structure, i.e. orbital compositions and energies of the extended bridging unit as it interfaces with the metal magnetic orbitals that determine the magnitude of the resonance energy H_{ab} .

Extended Huckel calculations of all the Dicyd²⁻ ligands have already been performed assuming co-planarity of the cyanamide groups with the phenyl ring [24,69]. The frontier orbitals of the Dicyd²⁻ are illustrated by Figure 5.1, and show that both HOMO and SHOMO are of π symmetry and span the entire molecule.

Figure 5.1. Frontier orbitals of Dicyd²⁺ from EHMO calculations (From Ref. 24 with permission).

In bridged dinuclear systems, metal-metal coupling is mediated by a full set of bonding and antibonding orbitals of the bridging ligand. As shown in Figure 5.1, both the HOMO and SHOMO are continuous π MO's that span the entire bridging ligand and provide an energetically favorable pathway for superexchange. Long range antiferromagnetic exchange at a separation of 13.2 Å between Ru(III) ions was observed for dinuclear pentaammineruthenium(III) complexes containing 1,4-dicyanamidober.zene dianion (Dicyd^{2-}) and derivatives as the bridging units [26]. The magnetic exchange constant $-J$ ranged from 61.9 to $\geq 400 \text{ cm}^{-1}$. The magnitude of J at this separation is due to a continuous and energetically favorable superexchange pathway involving the Ru(III) $d\pi$ -orbitals and the π -HOMO or SHOMO of the bridging Dicyd^{2-} ligand. This interaction of the bridging ligands HOMO and SHOMO with the exchange coupled Ru(III) πd -orbitals are shown in Figure 5.2

Figure 5.2. Interaction of Ru(III) πd -orbitals and the bridging ligands HOMO and SHOMO (from Ref. 24 with permission).

Both the symmetry and energy of the magnetic orbitals have changed when one compares Cu(II) to Ru(III) dinuclear complexes. To understand the influence of symmetry, it is first necessary to identify the magnetic orbitals. The energy of the ligand field band observed for each of the complexes (Tables 3.3 and 3.4) is consistent with a tetragonally distorted coordination sphere with the Cu(II) dien complexes having the greatest distortion towards planarity. It is therefore not surprising that ESR studies of the Cu(II) complexes, show g values (Table 4.1) that indicate their magnetic orbitals are dx^2-y^2 . Various crystal structures of Cu(II) phenylcyanamide complexes have shown that the Cu(II)-NCN bond is bent with the bond angle varying from $141.4(7)$ to $165.3(9)^\circ$ [23,60,61]. The fact that this bond is bent is important because it allows for mixing of Cu(II) dx^2-y^2 with the π SHOMO of the Dicyd²⁻. Evidence for the electronic interaction is seen by the presence of a LMCT band in both the solution and solid state absorption spectra of Cu(II) complexes. However, the oscillator strengths of these LMCT transitions (Tables 3.3 and 3.4) are considerably smaller than those of their Ru(III) analogues [24] and is an indication of smaller overlap between donor and acceptor orbitals [35]. Thus, the effect of symmetry attenuated antiferromagnetic exchange is expected to be offset somewhat because of the overall low symmetry of the complexes.

As mentioned *vide supra*, extended Huckel calculations of all the Dicyd²⁻ ligands have already been performed assuming co-planarity of the cyanamide groups with the phenyl ring [24]. The calculations showed in each case that both π symmetry HOMO and SHOMO span the entire length of the molecule. Crystallographic studies [67] have clearly

demonstrated the preference for planar geometry of the Dicyd^{2-} ligands except under conditions of extreme steric strain [69]. A crystal structure of one of the dinuclear copper complexes is not available at this time. Nevertheless, the crystal structure of $[(\text{bpil})\text{Ni}(\text{2-Clpcyd})]$, where 2-Clpcyd is 2-chlorophenylcyanamide, shows that the nickel ion is in a tetragonally distorted tetrahedral coordination sphere, the Ni-NCN bond is bent and the plane of the phenyl cyanamide ligand is at approximately right angles to the best plane of the tridentate ligand bpil [64]. Bearing this geometry in mind, the proposed superexchange pathway for the Cu(II) dien complexes involving the Cu(II) $d_{x^2-y^2}$ orbitals and the π SHOMO of the Dicyd^{2-} bridging ligand is shown below.

Figure 5.3. Interaction of Cu(II) σ^* d -orbitals and the bridging ligands π SHOMO

A superexchange pathway involving the higher energy π -HOMO of Dicyd²⁻ cannot be excluded however the geometry of the nickel complex would seem to suggest a greater degree of overlap between SHOMO and dx^2-y^2 orbitals. The lack of crystal structure information relevant to the dinuclear Cu(II) complexes precludes assignment of a preferred π HOMO or SHOMO superexchange pathway for these complexes.

The energy separation (ΔE) between Cu(II) magnetic orbitals and the π SHOMO (shown above) will also influence the extent of antiferromagnetic superexchange. A measure of this difference in energy is given by equation 1.12 and shown below

$$\Delta E = E_{op} - \lambda$$

where E_{op} is the energy of the LMCT band maximum and λ is a correction to compensate for the change in inner and outer coordination sphere configurations resulting from a transition into an excited vibrational level. An estimate of $\lambda = 1.24$ eV was derived from the LMCT band energy observed for $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{L}(\text{ClO}_4)$, where L is a macrocyclic ligand in acetone solution [100]. Thus, for the complex $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Me}_2\text{Dicyd})][\text{CF}_3\text{SO}_3]_2$, ΔE was calculated to be 1.48 eV. This is considerably greater than the value of 0.48 eV calculated for the Ru(III) analogue $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-Me}_2\text{Dicyd})]^{4+}$ and may well be the dominant factor in explaining the attenuation of antiferromagnetic superexchange. Thus, both energy and symmetry mismatch contribute to the overall attenuation of

antiferromagnetic superexchange coupling in the Cu(II) complexes than in the Ru(III) analogues.

5.3. Heteronuclear Dimer Complexes

In comparison to dinuclear Cu(II) and Ru(III) complexes, the mixed metal systems follow Curie - Weiss Law. This is indeed contrary to expectations since one might have expected to observe antiferromagnetic exchange, with a magnitude of J somewhere between that observed for the Ru(III) complexes and the Cu(II) complexes, or perhaps ferromagnetic exchange because the magnetic orbitals are orthogonal. The observation of only Curie - Weiss behavior for the heteronuclear complexes implies that a continuous interaction between metal magnetic orbitals of the same symmetry is essential if the Dicyd²⁻ bridging ligand is to mediate exchange interactions.

5.4. Failure of the Coffmann and Buettner Limit Function

Coffmann and Buettner have proposed a limit function for long range ferromagnetic and antiferromagnetic exchange in exchange coupled dimers[5]. As shown by Figure 1.3, they entered available data on a plot of Log J vs. the distance, R in Å between paramagnetic centers. A straight line was then drawn such that all known systems fell to the left of this line. From this straight line, they proposed the limit function for long range antiferromagnetic exchange in exchange coupled dimers (equation 1.19 and below)

$$|2J_{lim}| = 1.35 \times 10^7 \exp(-1.80R) \text{ in cm}^{-1}$$

where J is the magnetic exchange coupling constant and R is the distance between metal ions (Å). From this equation the magnitude of $-2J$ at 13.2 Å would be $6.50 \times 10^{-4} \text{ cm}^{-1}$. The magnetic susceptibility data for dinuclear copper(II) complexes given in Table 3.6 show that $6.0 \leq |2J| \leq 21.2 \text{ cm}^{-1}$ and is in total disagreement with the magnitude of $-2J$ predicted by the Coffmann-Buettner relationship. Thus, the limit function proposed by Coffmann and Buettner[5] is inadequate in predicting the magnitude of coupling in the copper(II) systems of this study and in the Ru(III) analogues.

As presented earlier in Section 1.4, the failure of the Coffmann and Buettner relationship to predict the magnitude of the antiferromagnetic coupling constant in the Ru(III) complexes incorporating the 1,4-dicyanamidobenzene dianion bridging ligands arises because of the fundamental difference in the nature and properties of the electron exchange pathway in the complexes used to derive the limit function relationship. The data used to derive the above equation largely came from magnetic measurements of dinuclear Cu(II) complexes containing insulating σ -networks. For the Ru(III) complexes, electron exchange occurs via Ru(III) πd -orbitals and the π symmetry HOMO of the bridging Dicyd²⁻ ligand. The energy gap between these orbitals is relatively small (0.48 eV) and the bridging ligand can be classified as a semi-conducting medium.

The failure of the Coffmann and Buettner relationship to predict the magnitude of the antiferromagnetic exchange coupling in the dinuclear copper complexes may be

attributed to a stronger coupling via a high energy π pathway. In section 1.4 of Chapter 1, the distance dependence of superexchange has been reviewed and a number of examples of dinuclear copper complexes given in Table 1.1. In approximate agreement with equation 1.19, a study of distance dependence of the magnetic coupling between two Cu(II) complexes bridged by 4,4'-bipyridine, (metal ions separated by 11.1 Å), found $2J = -0.9 \text{ cm}^{-1}$ [101]. The authors pointed out that at this magnitude of coupling it would be difficult to distinguish between intermolecular and intramolecular mechanisms. In contrast, a later study found moderately strong intramolecular antiferromagnetic coupling ($2J = -140 \text{ cm}^{-1}$) between Cu(II) ions separated by 11.25 Å in $[\text{X}_2\text{Cu}_2(\text{OH})_2(\mu\text{-terephthalato})][\text{ClO}_4]_2$ where X = 1,4,7-trimethyl-1,4,7-triazacyclononane [102]. The difference in magnetic coupling between these two results is clearly dependent on the nature of the interaction of the magnetic orbitals with the bridging ligand. These results and the ones reported in this thesis support the possibility of long range antiferromagnetic coupling occurring between magnetic orbitals bridged by an extended π HOMO system. It seems likely that the low lying SHOMO of Dicyd²⁺ in the dinuclear Copper(II) complexes provides a pathway for magnetic exchange interaction.

CHAPTER 6

MODELING OF THE Cu(DCNQI)₂ MOLECULAR METALS

6.1. Introduction

In Section 1.1 of Chapter 1, it was mentioned that the study of magnetic exchange interactions could have practical applications. Important among these applications are the synthesis of novel solid state materials with suitable magnetic or electronic properties. The charge transfer (CT) salts display these novel magnetic and optical properties and have been the subject of interest for the last two decades. Perhaps the breakthrough in this field of molecular materials was the synthesis of the Cu(DCNQI)₂ molecular metals by Hünig and co-workers [18].

Conducting DCNQI radical anion salts have been characterized with π -donors (e.g. TTF), organic cations (e.g. tetramethylammonium) and metal cations [17,18,19,103]. The last class of compounds is the most interesting, especially those containing 2,5-disubstituted DCNQI acceptors. Very high conductivities are achieved with a variety of metal monocations in salts of general formula $M'(2,5\text{-Me}_2\text{DCNQI})_2$ ($M = \text{Cu, Ag, Tl, Ni, Na, K, Rb}$) [17,18,19,103]. The X-ray crystal structure of Cu(2,5-Me₂DCNQI)₂ reveals that each metal atom is tetrahedrally coordinated to four DCNQI ligands by strong Cu-N interactions and the acceptor forms one-dimensional columns with an intrastack distance

of 3.2 Å [18]. The conductivity of the salt $\text{Cu}(\text{2,5-Me}_2\text{DCNQi})_2$ increases as the temperature is lowered and indeed at 3.5 K, $\sigma = 5 \times 10^5 \text{ S cm}^{-1}$. The copper atoms are present in mixed valence state, viz. $\text{Cu}^{1.3+}$, which arises from admixture of the 3d orbitals on copper with the $p\pi$ conduction band of the Me_2DCNQi ligands [18,19]. In a recent publication, Hünig et.al [104] presented a new approach to understand the unique properties of the $\text{Cu}(\text{2,5-Me}_2\text{DCNQi})_2$ salts. This new approach is the "two conductors in one" concept, which is a unique combination of a common one-dimensional (anisotropic) conduction path along segregated stacks and a two-dimensional (isotropic) conduction path within a network of delocalized mixed-valent metal ions bridged by organic spacers allowing electron transfer [104].

Copper 1+/2+ mixed valency is a common feature in copper chemistry [105]. Robin and Day[112] have classified mixed valence compounds into three types: Class I, completely valence trapped (no coupling between metal ions); Class II, valence trapped (weak coupling between metal ions); and Class III, delocalized valency (strong coupling between metal ions). Though most mixed-valent copper compounds belong to class I or II (e.g. $\text{Cu}^{\text{I}}_2\text{Cu}^{\text{II}}$ (2,5-dithiahexane)₆(ClO₄)₄ [106]) or $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}$ (4-methylthiazole)₄Cl₃[107], a few class III compounds are also known (e.g. KCu_4S_3 [108]). The characteristics of class III are also met by the $\text{Cu}(\text{Me}_2\text{DCNQi})_2$ salts; that is, we have an infinite three-dimensional lattice of indistinguishable mixed-valent ions (formally $\text{Cu}^{\delta+}$, $1 < \delta \leq 1.33$) bridged by the DCNQi molecules.

The maintenance of class III behaviour, that is delocalization or rapid exchange of oxidation states, demands that there should be optimum interaction, both in terms of relative energy and in terms of geometrical overlap of Cu 3*d* orbitals and the ligand LUMO band, and thus, the coordination geometry around the copper ion is very important. Kobayashi et.al [109,110] has shown that if the splitting of the Cu 3*d* orbitals is rather small (low tetragonal compression) ie contribution of d_{xy} , d_{xz} and d_{yz} orbitals to the $p\pi$ - d interaction, the system stays metallic down to the lowest temperature [109,110]. However, if the splitting is large (high tetragonal compression), the $p\pi$ - d interaction is mainly determined by the d_{xy} orbital and the ligand LUMO band, and the system undergoes a metal-insulator phase transition [110,111].

As mentioned above, the Cu(2,5-Me₂DCNQI)₂ salts are a Robin-Day class III network of delocalized mixed-valent metal ions bridged by organic spacers allowing electron transfer. The three different classes of mixed valent compounds described above can be distinguished by studying intervalence transitions and ΔE of the couples ($M^{(n+1)+}/M^{n+}$) e.g. Cu(II/I)[36]. For class I, a mixed valence absorption has never been observed, so there is no evidence as to where in the electronic absorption spectrum it might be found. In contrast, the class II mixed valence systems are characterized by an absorption band in the visible region of the spectrum which is absent in the spectra of the constituent ions taken separately. Class III mixed valence species show an absorption in the NIR region[112].

In order to investigate the practical applicability of the dinuclear copper(II) complexes containing the 1,4-dicyanamidobenzene dianion bridging ligands as model compounds of the $\text{Cu}(\text{DCNQI})_2$ molecular metals, it was necessary to generate mixed valence complexes via oxidation or reduction of the dinuclear copper(II) complexes. The species that can be generated by oxidation of these complexes are given in scheme 6.1

L = Diethylenetriamine (dien) or
1,3-bis(2'-pyridylimino)isoindolinato (bpil)

scheme 6.1

Spectro-electrochemical studies of the dinuclear copper(II) complexes were undertaken using an optically transparent thin layer electrode cell (OTTLE) [113] and a specially designed spectroelectrochemical cell [114]. Numerous experiments were carried out and as seen in Figure 6.1, the radical anion ($\text{Dicyd}^{\cdot-}$) peaks were the major features of the electronic absorption spectrums' visible region and no intervalence transitions (IT) were observed in the NIR region. The species generated in the spectroelectrochemical studies was possibly of type I shown in scheme 6.1 and indicates localization of the single electron on the bridging ligand. It seems likely that the nature of the spectator ligands about copper stabilise the Cu(II) oxidation state and form a potential barrier to electron delocalization.

The primary goal of the spectroelectrochemical experiments was to generate a mixed valence species of type II, i.e. $\text{LCu}^{\text{II}}\text{-DCNQI-Cu}^{\text{I}}\text{L}$ (where L = dien or bpil) from the dinuclear copper(II) complexes reported in this thesis or in other words form mixed valence systems that could be classified as of class III according to the Robin and Day criteria. However, this was not possible because the spectator ligands (dien and bpil) formed a potential barrier to electron delocalization and thus, could not allow the formation of species II (see scheme 6.1). This species is essential for the hole transfer mechanism of conductivity in the $\text{Cu}(\text{DCNQI})_2$ to occur [18,19,20,103]. As a result of the failure to generate the above mentioned mixed valence species, it was imperative that a new system be developed.

Figure 6.1. Absorption Spectrum of $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-Dicyd})]^{2+}$ in methanol before and after oxidation

In this quest, a new tridentate ligand had to be designed and synthesized to replace diethylenetriamine (dien) and 1,3-bis(2'-pyridylimino)-isoindolinato(bpii). This ligand must ensure that the coordination geometry around the copper ion is tetrahedral and must have incorporated into it donor or acceptor groups that can participate in $d\pi-p\pi$ back bonding. The nitrile group is particularly suited to this task since nitriles are generally considered to be relatively moderate σ -donors and π -acceptors toward transition metals[115], and it can also mimic the NCN group of the $\text{Cu}(\text{DCNQI})_2$ molecular metals since, in these species the copper(II) metal ion is bound end-on to the nitrile of the DCNQI moiety.

The chemistry of metal-nitrile complexes is very extensive[116]. That organonitriles are of interest as ligands is not surprising in view of facts that the RCN: group is isoelectronic with molecular nitrogen and that organonitrile complexes can serve as convenient precursors for a wide variety of coordination compounds[116]. Organonitriles have two potential coordination sites, namely the nitrile-nitrogen lone pair (end-on), and the carbon-nitrogen triple bond (side-on). The majority of the nitrile complexes involve end-on where the $\text{R}-\text{CN} \rightarrow \text{M}$ is linear, but side-on interactions have been confirmed for a few complexes[117]. Cu(I) like other metals in low oxidation state form a wide range of organonitrile complexes. The stability of these complexes arises from the $d\pi-p\pi$ backbonding that takes place in these species as shown in scheme 6.2 below.

scheme 6.2

6.2 Design of a Tridentate Ligand

The successful synthesis of stable Cu(I) organonitrile complexes indicates that the incorporation of the -CN group in the ligands to be designed and synthesized would help in the stabilization of Cu(I) species. Apart from having the nitrile (-CN) donor-acceptor groups, the tridentate ligand had to have the right carbon framework in order to ensure that the coordination geometry around the copper ion was tetrahedral. In addition the $\text{-C-CN} \rightarrow \text{M}$ bond had to be linear. The number of methyl groups in the carbon framework, that would have the coordination geometry of copper metal ion as tetrahedral and at the same time ensure that the $\text{-C-CN} \rightarrow \text{M}$ bond was linear, was estimated using

both the Alchemy III molecular modelling software[118] and the ball and stick method[119]. In this way the appropriate number of methyl groups required were found to be four for each π -acceptor group as shown in Figure 6.2 below.

(a)

(b)

Figure 6.2. Alchemy III 3D molecular modeling of $N[(CH_2)_4CN]_3Cu$ (a) without the atom labels and the Hydrogens are shown (b) with the atom labels and the Hydrogens are omitted for clarity

6.3 Synthesis of the Tridentate Ligand, $N[(CH_2)_4CN]_3$

The synthesis of the tertiary amine was achieved via the steps shown in scheme

6.3.

scheme 6.3

Synthesis of Primary Amine Salt, $\text{ClH}_3\text{N}[(\text{CH}_2)_4\text{CN}]$ (1)

40 mL of liquid ammonia was obtained from anhydrous gaseous ammonia by condensation using a methanol/dry ice slush bath. To this liquid was added 4 g of 5-chlorovaleronitrile and the reaction flask stoppered and put inside a steel container. This was then put in a bomb apparatus and the steel container firmly secured. The mixture was then heated at 40°C for 3 h. After 3 hours the heating was stopped and the reaction mixture left to cool under a pressure of ammonia for 18 h. The ammonia pressure was then slowly released and the reaction flask removed from the steel container. All the ammonia was evaporated by placing the glass tube in a beaker of warm water. After all the ammonia was evaporated, the unreacted 5-chlorovaleronitrile was extracted with ether, leaving behind a white solid which is made up of NH_4Cl and the desired product. The white solid was extracted with 2 x 30 mL acetonitrile, filtered and concentrated to 20 mL by rotary evaporation. The desired product was precipitated out by adding 40 mL of ether followed by cooling to -16°C for 12 h. The crude product was recrystallized by slow ether diffusion to an acetonitrile solution of the amine salt. Yield: 2.77 g (60%) IR. $\nu(\text{CN})$ 2245cm^{-1} Anal. Calcd. for $\text{C}_5\text{H}_{11}\text{N}_2\text{Cl}$: C, 44.61; H, 8.24; N, 20.82 Found: C, 44.24; H, 7.89; N, 20.40; ^1H NMR (CD_3OD , 200 MHz) δ 1.72-1.79(m,4H), 2.52-2.58 (t,2H); 3.09 (t,2H). FAB MS calcd. for $\text{C}_5\text{H}_{11}\text{N}_2\text{Cl}^+$ $m/e = 134.5$ found 134.5

Preparation of Primary Amine, $\text{H}_2\text{N}(\text{CH}_2)_4\text{CN}$ (**2**)

2.72 g of $\text{ClH}_3\text{N}(\text{CH}_2)_4\text{CN}$ was dissolved in 20 mL water and 1.50 g of potassium hydroxide pellets was then added and the mixture stirred for 2 h. The organic layer was extracted with 3 x 100 mL portions of chloroform. The three chloroform extracts were then combined and the solvent evaporated to dryness by rotary evaporation, leaving behind a pale yellow oil. The oil was then dissolved in ether dried over Na_2SO_4 , filtered and evaporated to dryness by rotary evaporation leaving behind a pale yellow oil. Yield. 1.45g (73%) IR. ν (CN) 2245 cm^{-1} (strong). ^1H NMR (CDCl_3 , 200 MHz) δ 1.72 - 1.80 (m, 4H), 2.52-2.56 (t, 2H), 2.65-2.90 (t, 2H).

Preparation of Secondary Amine Salt, $\text{ClH}_2\text{N}[(\text{CH}_2)_4\text{CN}]_2$ (**3**)

1.45 g of the free primary amine, $\text{H}_2\text{N}(\text{CH}_2)_4\text{CN}$ was dissolved in 20 mL DMF and 2.20 g of 5-chlorovaleronitrile added. The mixture was stirred in an oil bath at 60-70°C under a nitrogen gas atmosphere for 48 h. The DMF was then vacuum distilled off and the orange oily residue extracted first with 20 mL ether and then with 20 mL acetonitrile. The ether extract contained both unreacted primary amine and the alkylating agent. The acetonitrile extract contained the desired product. The secondary amine salt was obtained by precipitating with ether and cooling to -16 °C in a freezer. The crude product was recrystallized by a slow ether diffusion to an acetonitrile solution of the amine salt. Yield 2.05 (64%) Mpt (197-198 °C), IR ν (CN) 2245 cm^{-1}
 Anal. Calcd. for $\text{C}_{10}\text{H}_{18}\text{N}_3\text{Cl}$: C, 55.67; H, 8.41; N, 19.48

Found: C, 55.75; H, 8.30; N, 19.50; ^1H NMR (CD_3OD , 400MHz) δ 1.73-1.86(m,8H), 2.53-2.56 (t,4H); 3.04-3.08 (t,4H). FAB MS m/e calcd. for $\text{C}_{10}\text{H}_{18}\text{N}_3^+$ = 180 found 180.2

Preparation of Secondary Amine, $\text{H}_2\text{N}[(\text{CH}_2)_4\text{CN}]_2$ (**4**)

The free secondary amine base was obtained from 2.05 g of secondary amine salt, $\text{ClH}_2\text{N}[(\text{CH}_2)_4\text{CN}]_2$ and 1.00 g of potassium hydroxide using the same procedure as for **2**. Yield: 1.58 g (69%) IR ν (CN) 2246 cm^{-1} (strong), ^1H NMR (200 MHz, CDCl_3), δ 1.71 - 1.78 (m, 8H), 2.52-2.60 (t, 4H), 3.10-3.22 (t, 4H)

Preparation of Tertiary Amine Salt, $\text{ClHN}[(\text{CH}_2)_4\text{CN}]_3$ (**6**)

To 1.58 g of the secondary amine base, $\text{H}_2\text{N}[(\text{CH}_2)_4\text{CN}]_2$ in 20mL DMF was added 1.50 g of 5-bromovaleronitrile and 2.00 g of 1,2,2',6,6'-pentamethylpiperidine (proton scavenger). The reaction mixture was stirred with heating at 50-60 °C in an oil bath under a nitrogen gas atmosphere for 48 h. The solvent was vacuum distilled off, leaving behind an orange oil. The oil was extracted with 20 mL ether to yield (**5**) and the purification was achieved by converting the crude tertiary amine to its hydrochloride salt by bubbling HCl gas through the solution for 2 min, upon which the solution turned milky white. On cooling to -16°C in a freezer for 48 h white needles formed.

Yield 1.02 g (38.61%), IR. ν (CN) 2244 cm^{-1}

Anal. Calcd. for $\text{C}_{15}\text{H}_{25}\text{N}_4\text{Cl}$: C, 60.69; H, 8.49; N, 18.88;

Found: C, 60.45; H, 8.35; N, 18.71.

^1H NMR (CD_3OD , 400MHz) δ 1.71-1.9 (m,12H), 2.54-2.61 (t,6H); 3.14-3.32 (t,6H).

FAB MS Calcd. for $C_{15}H_{25}N_4^+$ $m/e = 261.0$ found 261.2

Preparation of Tertiary Amine, $N[(CH_2)_4CN]_3$ (**5**)

The free tertiary amine base, $N[(CH_2)_4CN]_3$ (**5**) was obtained from the tertiary amine salt in the same way as that for the secondary amine base (**4**) or primary amine (**2**). The overall yield from 5-chlorovaleronitrile is approximately 21%. Yield 0.62 (68%). IR $\nu(CN)$ 2245 cm^{-1} , 1H NMR (200 MHz, $CDCl_3$) δ 1.70-1.89 (m, 12H), 2.35-2.49 (t, 6H), 2.62-2.78 (t, 6H).

The IR, 1H NMR and FAB MS spectra of 5-chlorovaleronitrile, the tertiary amine salt (**6**) and the free tertiary amine (**5**) are given in figures 6.3-6.8. All the other spectra for the intermediates 2-4 are given in the appendix.

6.4. Synthesis of metal complexes

With the successful synthesis of the tridentate ligand, the next step was to synthesize metal complexes. Due to time limitation this work could not be continued. However, preliminary studies seem to be promising as the tridentate ligand reacts with $(CH_3CN)_4CuPF_6$ in acetonitrile to form a yellow complex. The characterization of this precursor complex and the synthesis of dinuclear complexes will be the focus of future investigation.

Figure 6.3. (a) IR spectrum(neat) and (b) ^1H NMR (CDCl_3 , 200 MHz) of $\text{Cl}(\text{CH}_2)_4\text{CN}$

Figure 6.4. IR spectrum of ClHN[(CH₂)₄CN]₃ (KBr)

Figure 6.5. IR spectrum of N[(CH₂)₄CN]₃ (Neat)

Figure 6.6. 200 MHz ^1H NMR spectrum of $\text{CIHN}[(\text{CH}_2)_4\text{CN}]_3$ in CD_3OD

Figure 6.7. 200 MHz ^1H NMR of $\text{N}[(\text{CH}_2)_4\text{CN}]_3$ in CDCl_3

Figure 6.8. FAB MS spectrum of $\text{CIHN}[(\text{CH}_2)_4\text{CN}]_3$

CHAPTER 7

CONCLUSIONS AND FUTURE STUDIES

The past two decades have witnessed unabated interest in the synthesis and characterization of organic charge-transfer (CT) salts that display unusual solid-state properties. The motivation behind research on these exotic materials has been the fact that there are potentially many far-reaching technological applications within the arena of molecular electronic devices. The development of a new family of acceptors, the N,N'-Dicyanoquinonediimine (DCNQI) acceptors by Hünig and co-workers[18,19,103] has opened up new avenues in the development of novel electronic materials.

The primary goal of the present study was to explore the effect of metal magnetic orbitals on the magnitude of antiferromagnetic superexchange and in addition, investigate the practical application of the dinuclear systems as models of the $\text{Cu}(\text{2,5-Me}_2\text{DCNQI})_2$ molecular metals.

This thesis has achieved the aims that were outlined in section 1.6. It has dealt with the synthesis and characterization of mononuclear copper complexes, homonuclear dimer copper(II) complexes and heteronuclear dimer ruthenium(III)-copper(II) complexes incorporating the doubly reduced forms of the N,N'-dicyanoquinonediimine (DCNQI) acceptor compounds as the bridging ligands. Variable temperature magnetic susceptibility data of the homonuclear dimer copper(II) complexes was consistent with weak antiferromagnetic behavior as opposed to the Ru(III) analogues which exhibited moderate

to strong antiferromagnetic behavior. The weak antiferromagnetic behavior observed in the copper(II) complexes is attributed to both an energy and symmetry mismatch between the Cu(II) σ^* magnetic orbitals and the π -HOMO orbitals of the bridging ligand. The importance of symmetry is exemplified further by the heteronuclear Ru(III)-Cu(II) complexes which exhibit no antiferromagnetic coupling, but instead follow the Curie-Weiss Law.

Unfortunately, the "tuning" of the bridging ligand does not seem to have had a major impact on the magnetic coupling. However, the complexes incorporating $\text{Me}_2\text{Dicyd}^{2-}$ as the bridging ligand appear to have the largest antiferromagnetic coupling constant J ($2J$ is -21.2 cm^{-1} for Cu(II)). Ru(III) dimers show the same dependence ($2J \geq -800 \text{ cm}^{-1}$) [24] and this is probably due to the small energy difference (ΔE) between metal magnetic orbitals and the π_{nb} molecular orbitals of $\text{Me}_2\text{Dicyd}^{2-}$.

Although the observed magnetic behavior in the Cu(II) complexes is relatively far weaker than that observed for the Ru(III) analogues it nonetheless is still higher than that predicted by the Coffmann and Buettner relationship [5]. The Coffmann and Buettner limit function, outlined in the introduction, predicts an upper limit for J_{ex} , the magnetic coupling constant, at long intermetallic distances. The failure of the Coffmann and Buettner limit function to predict the magnetic coupling in the dinuclear copper(II) complexes implies that the distance between two or more metal centers is not the only limiting factor, but that the nature of the bridging ligand orbitals plays an important role as well. The long

range antiferromagnetic exchange observed in the Cu(II) systems of this thesis must therefore, be attributed to some degree of overlap between the Cu(II) magnetic orbitals and the ligand π_{nb} -orbitals. This $p\pi \rightarrow dx^2-y^2$ mixing in these complexes is important as this is one of the requirements necessary for the mixed valent state to be achieved in the Cu(DCNQI)₂ molecular metals.

The practical application of the Cu(II) systems reported in this thesis as models of the Cu(DCNQI)₂ has been investigated. As discussed in Chapter 6, the Cu(DCNQI)₂ molecular metals consist of a Robin and Day class III network of delocalized mixed valent metal ions bridged by DCNQI allowing electron transfer. The absorption spectra obtained from spectrochemical studies of the dinuclear Cu(II) complexes of this study exhibit no intervalence transitions. However, only intense radical anion peaks are observed and this is indicative of the formation of [LCu^{II}-Dicyd⁻-Cu^{II}L] instead of the required mixed valence species [LCu^{II}-DCNQI-Cu^IL] (where L = dien or bpil). This phenomena is attributed to the nature of the spectator ligands which seems to enhance the stability of Cu(II) and thus form a potential barrier to electron delocalization. It is a well established fact that the reduction of Cu(II) to Cu(I) is accompanied by stereodynamic strain [120], as Cu(II) prefer a tetragonal coordination environment while Cu(I) prefers a tetrahedral coordination sphere and the spectator ligand should also be able to confer stability to both copper species as they are formed during electrolysis. In order to synthesize better models of the Cu(DCNQI)₂ molecular metals, a spectator ligand that could ensure the stability of Cu(I)

PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

PRECISIONSM RESOLUTION TARGETS

and thus, reduce the potential barrier to electron delocalization is a necessary requirement for the successful modeling of the $\text{Cu}(\text{DCNQI})_2$ molecular metals. In Chapter 6 of this thesis, the successful design and synthesis of a new tridentate ligand which will be used in the synthesis of new copper complexes is reported. The use of this ligand in the synthesis of new complexes, thus, form the basis of future studies.

From the electronic absorption and magnetic data of the dinuclear copper(II) complexes, it is evident that a superexchange pathway is available for magnetic exchange interactions between the Cu(II) ions. This superexchange pathway is far from being optimal as there seems to be an energy and symmetry mismatch between the Cu(II) σ^* magnetic orbitals and the bridging ligands π_{nb} HOMO. As a consequence of this observation, future studies will investigate the dependence of superexchange via Dicyd²⁻ bridging ligands on the energy gap between metal magnetic orbitals and superexchange pathway. The stabilization of metal magnetic orbitals relative to the superexchange pathway may ultimately create a condition in which the bridging ligand functions as a conductive medium. The energy of the metal magnetic orbitals can be probed by changing the nature of the spectator ligands. As a continuation of the present work, future studies will involve the synthesis of dinuclear copper complexes incorporating the tridentate ligand described in Chapter 6. This ligand, it is hoped will stabilize both Cu(II) and Cu(I) in a tetrahedral coordination sphere and allow for the synthesis of better models of $\text{Cu}(\text{DCNQI})_2$ molecular metals.

APPENDIX

A.1. IR Spectrum of $\text{ClH}_3\text{N}(\text{CH}_2)_4\text{CN}$ (KBr)

A.2. IR Spectrum of $\text{H}_2\text{N}(\text{CH}_2)_4\text{CN}$ (neat on NaCl plates)

A.3. IR Spectrum of $\text{ClH}_2\text{N}[(\text{CH}_2)_4\text{CN}]_2$ (Kbr)

A.4. IR Spectrum of $\text{HN}[(\text{CH}_2)_4\text{CN}]_2$ (neat)

A.5. 200 MHz ^1H NMR Spectrum of $\text{ClH}_3\text{N}(\text{CH}_2)_4\text{CN}$ in d_4 -methanol

A.6. 400 MHz ^1H NMR Spectrum of $\text{ClH}_2\text{N}[(\text{CH}_2)_4\text{CN}]_2$ in d_4 -methanol

702644 Scan 4 RF=0.45 100%
LRP +FAB cell 11

A.7. FAB MS Spectrum of $\text{ClH}_3\text{N}(\text{CH}_2)_4\text{CN}$

Si0264 Scan 4 RT=0:46 100%=237180 mv 28 Oct 93 8:34
LRP +FAB 259

A.8. FAB MS Spectrum of $\text{ClH}_2\text{N}[(\text{CH}_2)_4\text{CN}]_2$

A.9. Letter of Permission to Adapt Figures

Copyright Administrator
 Publications Division
 American Chemical Society
 115 16th Street, N. W.
 Washington, DC 20036
 USA.

Dear Sir or Madame

I am preparing a Ph D Thesis to be submitted to Carleton University, Ottawa entitled:
Long Range Antiferromagnetic Exchange in Dinuclear Copper(II) Complexes. In order to
 qualify some arguments in this Thesis, I will require the use of some figures which are already
 in some Publications.

I should appreciate permission to reproduce or adapt the figures which appear in the
 following publications:

1. R. E. Coffmann and G. R. Buettner, *J. Phys. Chem.*, 1979, 83, 2387 - 2392.

Figure 1

2. M. A. S. Aquino, F. L. Lee, E. J. Gabe, C. Bensimon, J. E. Greedan and R. J. Crutchley, *J. Am. Chem. Soc.*, 1992, 114, 5130 - 5140. Figure 6 and diagrams on page 5138 and 5139.

For your convenience, a copy of this letter may serve as a release form; the duplicate copy is
 for your files. Permission is being requested of the author and of the publisher separately

Sincerely

Linus Cherulyot

PhD candidate,

Chemistry Department

Carleton University,

Ottawa, Canada K1S 5B6

REFERENCES

1. Willet, R. D.; Gatteschi, D.; Kahn, O. (Eds); *Magneto-Structural Correlations in Exchange Coupled Systems*, Reidel, Dordrecht, Holland, **1985**.
2. Marcus, R. A.; Sutin, N., *Biochim. Biophys. Acta.* **1995**, 811,265
3. Hendrickson, D. N. in *Magneto-Structural Correlations in Exchange Coupled Systems*, Willet, R. D.; Gatteschi, D.; Kahn, O. (Eds), Reidel, Dordrecht, Holland, **1985**, 523.
4. Kahn, O. *Angew. Chem. Int. Ed. Engl.* **1985**, 24, 834.
5. Coffmann, R. E.; Buettner, G. R. *J. Phys. Chem.* **1979**, 83,2387.
6. Moss, T. H.; Petering, D. and Palmer, G. *J. Biol. Chem.* **1969**, 244,2275.
7. Palmer, G.; Babcock, G. T.; Vickery; L. E. *Proc. Natl. Acad. Sci. USA* **1976**, 73, 2206
8. Dunham, W. R.; Palmer, G.; Sands, R. H., and Bearden, A. J. *Biochim. Biophys. Acta.*, **1971**, 253, 373
9. Moss, T. H.; Moles, K. C.; York, J. L. *Biochemistry*, **1971**, 10, 840
10. Dooley, O. M.; Scott, R. A.; Ellinghaus, J.; Solomon, E. I. *Proc. Natl. Acad. Sci. USA*, **1978**, 75, 3019
11. Himmelwright, R. S.; Eickmann, N. C.; LuBien, E. D. and Solomon, E. J. *J. Am. Chem. Soc.* **1980**, 102, 5378
12. Petersson, L.; Angstrom, J.; and Ehrenberg , A., *Biochim. Biophys. Acta.* **1978**, 526,

13. Moss, T. H., and Vanngard, T. *Biochim. Biophys. Acta.* **1974**, 371, 39
14. Ferraro, J. R.; Williams, J. M. *Introduction to Synthetic Electrical Conductors*, Academic, New York, **1987**.
15. Kahn, O.; Pei Yu; Verdaguer, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, 110, 782.
16. Kahn, O.; Kollmar, C. *J. Am. Chem. Soc.* **1991**, 113, 7987
17. (a) Wudl, F.; Smith, G. M.; Hutriagel, E. G. *J. Chem. Soc., Chem. Commun.* **1970**, 1453
(b) Ferraris, J.; Cowan, D. O.; Walatka, V. V.; Perstein, J. H. *J. Am. Chem. Soc.* **1973**, 95, 948 .
18. Aümüller, A.; Erk, -P.; Klebe, G.; Hünig, S.; Von Schutz, J.U.; Werner, H. -P., *Angew Chem. Int. Ed. Engl.* **1986**, 25, 740
19. Schmeisser, D.; Graf, K.; Gopel, W.; Von Schutz, J.U.; Erk, -P.; Hünig, S., *Chem. Phys. Lett.* **1988**, 148, 423.
20. (a) Erk, P.; Hünig, S.; Von Schutz, J. U.; Werner, H. -P.; Wolf, H.C. *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 267
(b) Mori, T.; Bandow, S.; Inokuchi, H.; Kobayashi, A.; Kato, R.; Kobayashi, H.; *Physics Rev. B.* **1988**, 38, 5913
(c) Mori, T.; Bandow, S.; Inokuchi, H.; Kobayashi, H. *Solid State Commun.* **1988**, 67, 565

- (d) Werner, H. -P.; Von Schutz, J. U.; Wold, H. C.; Kremer, R.; Gehrke, M.,
Aümüller, A.; Erk, P.; Hunig, S. *Solid State Commun.* **1988**, 65, 809
21. Mori, T.; Imaeda, K.; Kato, R.; Kobayashi, A.; Kobayashi, H.; Inokuchi, H. *J. Phys. Soc. Jpn.* **1987**, 56, 3429
22. Tomic, S.; Jerome, D.; Aümüller, A.; Erk, -P.; Hünig, S.; Von. Schutz, J.U.
Europhys. Lett. **1988**, 5, 553.
23. Crutchley, R. J.; Hynes, R.; Gabe, E. J. *Inorg. Chem.* **1990**, 29, 4921
24. Aquino, M. A. S.; Crutchley, R. J.; Lee, F. L.; Gabe, E. J.; Greedan, J. E. *J. Am. Chem. Soc.* **1992**, 114, 5130
25. Aquino, M. A. S.; Crutchley, R. J.; Bostock, A. E. *Inorg. Chem.* **1990**, 29, 3642
26. Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Greedan, J. E.; and Crutchley, R. J.,
Inorg. Chem. **1991**, 30, 3234
27. Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, 97, 4884
28. Curie, P. *Ann. Chim. Phys.*, **1895**, 5, 289
29. O'Connor, C. J.; *Prog. Inorg. Chem.* **1982**, 29, 212
30. Bleaney, B. and Bowers, K. D., *Proc. R. Soc. London, Sc. A.* **1952**, 214, 451
31. Earnshaw, A., *Introduction to Magnetochemistry*, Academic. New York, **1968**
32. Sutin, N.; Brunshwig, B. S. in *Electron Transfer in Biology and the Solid State*,
Advanced Chem Series 226 , Johnson, M. K. et al.(Eds), American Chemical Society,
Washington D. C, **1989**, 65
33. Crutchley, R. J.; McCaw, K.; Lee, F. L.; Gabe, E. J., *Inorg. Chem.* **1990**, 29, 2576

34. Saleh, A. A.; Crutchley, R. J. *Inorg. Chem.* **1990**, 29, 2132
35. Crutchley, R. J.; Saleh, A. A.; MCaw, K.; Aquino, M.A.S. *Mol. Cryst. Liq. Cryst.* **1991**, 194, 93
36. Crutchley, R. J., *Advances in Inorg. Chem.*, **1994**, 41, 273 and references there in.
37. Felthouse, T. R.; Laskowski, E. J. and Hendrickson, D. N. *Inorg Chem.* **1977**, 16, 1077
38. Pierpont, C. G.; Francesconi, L. C.; and Hendrickson, D. N., *Inorg. Chem.* **1977**, 16, 2367
39. Anderson, P. W. *Phys. Rev.* **1959**, 115, 2
40. Hatfield, W. E. in *Magneto-Structural Correlations in Exchange Coupled Systems*. Willet, R. D. et al. (Eds), Reidel D. Publishing Co., **1985**, 555
41. Kahn, O., in *Magneto-Structural Correlations in Exchange Coupled Systems*, Willet, R. D. et.al. (eds), Reidel, **1985**, 37
42. Kahn, O. *Inorg. Chim. Acta.* **1982**, 62, 3
43. Kahn, O., in *Magneto-Structural Correlations in Exchange Coupled System*, Willet, R. D. et. al. (eds), Reidel, **1985**, 57
44. Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J. and Hatfield, W. E., *Inorg. Chem.* **1976**, 15, 2107
45. Roundhill, S.G. N.; Roundhill, D. M.; Bloomquist, D. R.; Landee, C., Willet, R. D.; Dooley, D. M.; and Gray, H. B. *Inorg. Chem.* **1979**, 18, 831

46. Esters, W. E.; Hatfield, W. E.; Von Ooijen, J. A. C. and Reedijk, J., *J. Chem. Soc. Dalton Trans.* **1980**, 2121
47. Hatfield, W. E.; Weller, R. R., and Hall, J. W. *Inorg. Chem.* **1980**, 19, 3825
48. Felthouse, T. R.; Laskowski, E. J. and Hendrickson, D. N., *Inorg. Chem.* **1977**, 16, 1077
49. Yoshino, A. and Nowacki, W. Z. *Kristallogr.* **1974**, 139, 337
50. Felthouse, T. R.; Hendrickson, D. N. *Inorg. Chem.* **1978**, 17, 444
51. Felthouse, T. R.; Hendrickson, D. N., *Inorg. Chem.* **1978**, 17, 2636
52. Solans, X., Aguito, M., Gleizes, A.; Faus, J.; Julve, M.; Verdaguer, M. *Inorg. Chem.* **1990**, 291, 775
53. Castro, I.; Sletten, J.; Faus, J.; Julve, M.; Journaux, Y.; Lloret, F.; Alvarez, S., *Inorg. Chem.* **1992**, 31, 1889
54. Oberhausen, K. J.; Richardson, J. F.; Buchanan, R. M.; McCusker, J. K.; Hendrickson, D. N.; Marc Latour, J. *Inorg. Chem.* **1991**, 30, 1357
55. Francesconi, L. C.; Corbin, D. R.; Clauss, A. W.; Hendrickson, D. N.; Stucky, G.D. *Inorg. Chem.* **1981**, 20, 2059
56. Chaudhuri, P., Oder, K., Wiegardt, K., Gehring, S., Haase, W., Nuber, B., Weiss, J., *J. Am. Chem. Soc.* **1988**, 110, 3657
57. Crutchley, R. J. and Naklicki, M. L., *Inorg. Chem.* **1989**, 28, 1955
58. Hollebone, B. R.; Nyholm, R.S.; *J. Chem. Soc. A.* **1971**, 332
59. Naklicki, M. L.; Crutchley, R. J., *Inorg. Chem.* **1989**, 28, 4226

60. Brader, M.L.; Ainscough, E. W.; Baker, E. N.; Brodie, A. M.; Ingham, S. L., *J. Chem. Soc. Dalton Trans.* **1990**, 2785.
61. Ainscough, E. W.; Baker, E. N.; Brader, M. L.; Brodie, A.M.; Ingham, S.L.; Waters, J .M.; Hanna, J. V.; and Healy, P. C., *J. Chem. Soc. Dalton. Trans.* **1991**, 1243
62. Golub, M. M.; Kohler, H.; Skopenko, V. V.; (Eds), *Chemistry of Pseudo-Halides*, Elsevier, New York, **1986**
63. Vrieze, K. and Van Koten, G., in *Comprehensive Coordination Chemistry*, Wilkison, G., Gillard, R. D., and McCleverty, J.A. (Eds), Pergamon, Oxford ,**1987**, vol 2, 225
64. Letcher, R. J.; Zhang, W.; Bensimon, C.; Crutchley, R. J. *Inorg. Chim. Acta.* **1993**, 210, 183
65. Zhang, W.; Bensimon, C.; Crutchley, R. J. *Inorg. Chem.* **1993**, 32, 5808
66. Rezvani, A. R.; Crutchley, R. J. *Inorg. Chem.*, **1994**, 33,170
67. Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Bensimon, C.; Crutchley, R. J. *Acta. Crystallogr. C.* **1993**, 49, 1543
68. Rezvani, A. R.; Crutchley, R. J. *Unpublished results*
69. Aquino, M. A. S., *PhD. Dissertation*, Carleton University, **1991**
70. Clarke, R. E., *Master's Thesis*, University of California at Santa Barbara, **1978**
71. Sullivan, B. P.; Baumann, J. A.; Meyer, T. J.; Salmon, D. J.; Lehmann, H.; Ludi, A.. *J. Am. Chem. Soc.* **1977**, 99, 7368
72. Siegl, W. O. *J. Heterocyclic Chem.* **1981**, 18, 1613

73. Letcher, R. J. *M.Sc. Thesis*, Carleton University, Ottawa, **1991**
74. Zhang, W. *M.Sc. Thesis*, Carleton University, Ottawa, **1993**
75. Krestl, A. M.; Manoussakis, G.; Bolos, C.; St. Nikolov, G., *Inorg. Chimica. Acta.* **1990**, 175, 255
76. Naklicki, M.; Crutchley, R. J. *Unpublished results*
77. McDonald, D. R.; Crutchley, R. J. *Inorg. Chem.* **1994**, 33, 1899
78. Gagne, R. R.; Marill, W. A.; Marks, D. N.; Siegl, W. O.; *Inorg Chem.* **1981**, 20, 3260
78. Gagne, R. R.; Koval, C. A.; Lisensky, G. C., *Inorg. Chem.* **1980**, 19, 2855
79. Lever, A. B. P., *Inorganic Electronic Spectroscopy*, 2nd Ed.; Elsevier Publishing Co.; Amsterdam, **1985**, P569
80. Aümüller, A.; Hünig, S., *Justus Liebigs Ann. Chem.* **1986**, 142, and 165
81. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds (4th Ed)*, Wiley and Sons, New York, **1986**, Pgs 191, 253
82. Cinquantini, A.; Opromolla, G.; Zanello, P.; *J. Chem. Soc. Dalton Trans.* **1991**, 3161
83. Lintvedt, R. L., in *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*, Karlin, K. D.; Zubieta, J. (Eds), Adenine Press, **1982**, 129
84. Goodman, B. A.; Raynor, J. B.; *Adv. Inorg. Chem and Radiochem.* **1970**, 13, 135
85. Eaton, D. R.; Zaw, K. *Coord. Chem. Rev.* **1971**, 7, 197
86. Parish, R.V. *NMR, NQR, EPR. and Mossbauer Spectroscopy in Inorganic Chemistry.*, Ellis Horwood, London **1990**, 168-193

87. Solomon, E. I.; Penfield, K.W. and Wilcox, D. W., *Structure and Bonding* , 1983, 53, 1
88. Hathaway, B. J. and Billing, D.E., *Coord. Chem. Rev.* 1970, 5, 143
89. Hathaway, B. J. in *Comprehensive Coordination Chemistry*, Wilkinson, G., Girard, R. D.; Mcleverty, J. A. (Eds), Pergamon Press, London, 1987, vol 5, P 656-675
90. Slichter, C. P., *Phys. Rev.* 1955, 99, 479
91. Gagne, R. R.; Koval, C. A.; Smith, T. J. *J. Am. Chem. Soc.* 1977, 99, 8367
92. Hendrickson, D. N.; Long, R. C.; Hwang, Y. J.; Chang, H. -R, in *Copper Coordination Chemistry: Biochemical and Inorganic perspectives*, Karlin, K.D. and Zubieta, J. (Eds), Adenine Press, New York, 1985, P 222
93. Hall, G. R.; Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* 1975, 14, 1956
94. Santokh, S. T.; Thompson, L. K; Bridson, J. N., and Dewan, J. C., *Inorg. Chem.* 1994, 33, 54
95. Carlin, R. L., *Magnetochemistry*, Springer-Verlag, Berlin, 1986
96. Bencini, A.; Gatteschi, D., *EPR of Exchange Coupled Systems*, Springer-Verlag, Berlin, 1990
97. Mandal, S. K.; Thompson, L. K.; Newlands, M. J.; Gabe, E. J., *Inorg. Chem.* 1990, 29, 3556
98. Naklicki, M. L.; Crutchley, R. J. *J. Am. Chem. Soc.* 1994, 116, 6045
99. Willett, R. W. in *Magneto-structural Correlations in Exchange Coupled Systems*, R. D. Willett et. al. (Eds), D. Reidel Publishing Company, 1985, 389.

100. Gagne, R. R.; Koval, C. A.; Smith, T. J.; Cimolino, M. C. *J. Am. Chem. Soc.* **1979**, 101, 4571
101. Julve, M.; Verdaguer, M.; Faus, J.; Tinti, F.; Moratal, J.; Monge, A.; Gutiérrez- Puebla, E. *Inorg. Chem.* **1987**, 26, 3520.
102. Chaudhuri, P.; Oder, K.; Wieghardt, K.; Gehring, S.; Haase, W.; Nuber, B.; Weiss, J. *J. Am. Chem. Soc.* **1988**, 110, 3657.
103. Hünig, S.; Erk, -P. *Adv. Mater.* **1991**, 3, 225
104. Hünig, S; et. al. *J. Am. Chem. Soc.* **1993**, 115, 7696
105. Hathaway, B. J. in *Comprehensive Coordination Chemistry*, Wilkinson, G., Gillard, R. D.; Mcleverty, J. A. (Eds.); Pergamon Press., New York, **1987**, vol 5, P533
106. Olmstead, M. M.; Musker, W. K.; Kessler, R. M., *Inorg. Chem.*, **1981**, 20, 151.
107. Marsh, W. E.; Hatfield, W. E.; Hodgson, D. J.; *Inorg. Chem.*, **1983**, 22, 2899.
108. Brown, D. B.; Zubieta, J. A.; Vella, P. A.; Wroblewski, J. T.; Watt, T.; Hatfield, W. E.; Day, P. *Inorg. Chem.* **1980**, 19, 1945
109. Kobayashi, A.; Kato, R.; Kobayashi, H.; Mori, T.; Inokuchi, H., *Solid State Commun.* **1987**, 64, 64.
110. Kobayashi, A.; Mori, T.; Kobayashi, H.; *Synth. Met.* **1988**, 27, B275
111. Kato, R.; Kobayashi, H.; and Kobayashi, A. *J. Am. Chem. Soc.* **1989**, 111, 5224.
112. Robin, M. B.; Day, P. *Adv. Inorg. Radiochem.* **1967**, 10, 247
113. Nevin, W. A.; Lever, A. B. P. *Analytical Chemistry* **1988**, 60, 727

114. Brewer, K. J.; Calvin, M.; Lumpkin, R. S.; Otvos, J. W., and Spreer, L. O.,
Inorg. Chem. **1989**, 28, 4446
115. Walton, R. A., *Q. Rev. Chem. Soc.* **1965**, 19, 126
116. Storhoff, B. N.; B.N., Lewis(Jr.); H. C., *Coord. Chem. Rev.* **1977**, 23, 1
117. Sutton, J. E. ; Zink, J. I. *Inorg. Chem.* **1976**, 15, 675
118. Alchemy III 3D *Molecular Modeling Software*, Tripos Associates Inc. equipped with
Alchemy Minizer
119. Orbit *Molecular Building System*, Aldrich Chem. Co. Ltd.
120. Rorabacher, D. R.; Martin, M. J.; Koenigbauer, M. J.; Malik, K.; Schroeder, R.
R.; Endicott, J. F.; Ochrymowycz, L. A.; in *Copper Coordination Chemistry:
Biochemical and Inorganic Perspectives*; Karlin and Zubieta (Eds), Adenine Press,
New York, **1982**, 167

END

2 6 - 0 5 - 9 5

FIN