

TRANSITION METAL COMPLEXES OF TOPOLOGICALLY CONSTRAINED
TETRAAZAMACROCYCLES

by

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ABSTRACT

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The coordination chemistry of tetracyclic and bicyclic ligands based on tetraazamacrocyclic-glyoxal condensation is presented. Novel transition metal complexes were synthesized of the rigid bidentate ligands produced from the above condensation. Pd²⁺, Cu⁺, and Cu⁺ coordination represent the first transition metal complexes of these folded, panel-like tetracyclic tetraamines, the glyoxal condensates of cyclam (1,4,8,11-tetraazacyclotetradecane), [13]aneN₄, (1,4,7,10-tetraazacyclotridecane), cyclen (1,4,7,10-tetraazacyclododecane) and *iso*-cyclam (1,4,7,11-tetraazacyclotetradecane). The synthesis, characterization, and X-ray crystal structures of these complexes are discussed. The ligands and complexes are proposed as useful molecules for supramolecular and biomimetic studies.

Further reaction of the above glyoxal condensates results in bicyclic, cross-bridged tetraazamacrocyclics. These macrobicycles' solution behavior has been examined by potentiometric titrations, confirming their proton sponge nature. Two ligands, the known cyclam derivative 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane and the novel ligand *racemic*-4,5,7,7,11,12,14,14-octamethyl 1,4,8,11-tetraazabicyclo[6.6.2]hexadecane, have also been characterized by X-Ray crystallographic studies of successive products through the course of their multi-step syntheses. With the ultimate goal of producing useful oxidation catalysts for aqueous applications, these coordination chemistry of these ligands was chosen for study because of their considerable topological and rigidity constraints. Their novel transition and other metal complexes, as well as analogues based on cyclen and

[13]aneN4, have been synthesized, overcoming their proton sponge nature by limiting the activity of protons in the reaction media. Full characterization of the ligand complexes with metal ions including Mn^{2+} , Mn^{3+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Co^{3+} , Ni^{2+} , Cu^+ , Cu^{2+} , and Zn^{2+} has been completed, including X-ray crystallography, electrochemistry, magnetic moments, molar conductances and electronic, nuclear magnetic resonance, and electronic spin resonance spectroscopies. Several of the complexes have exhibited unusually large kinetic stabilities in harsh aqueous media, with the manganese complex of the cyclam derived ligands of particular interest to industry.

DEDICATION

I dedicate this work to my wife, Becki Jo Hubin, who has sacrificed some of her dreams so that this dream of mine could come true, and to our son David, who makes it all worthwhile.

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TABLE OF CONTENTS

INTRODUCTION	1
Why Topologically Constrained Tetraazamacrocycles?.....	1
Factors for strong binding: Molecular Organization.....	1
Choosing Metal Ions and Ligands for Biomimicry.....	8
Who, When, and How Topologically Constrained Tetraazamacrocycles.....	11
Direct Organic Synthesis.....	13
Template Directed Synthesis.....	16
Protection/Deprotection Synthesis.....	19
Condensation Synthesis.....	25
Goals of this Research Project.....	30
RESULTS AND DISCUSSION	34
Ligand Synthesis and Structure.....	34
Complexes of Tetracyclic Ligands.....	49
Synthesis and Characterization of Pd ²⁺ Complexes.....	49
Synthesis and Characterization of Cd ²⁺ and Cu ²⁺ Complexes.....	53
Synthesis of Copper-Tetracycle Complexes.....	54
Crystal Structures.....	56
Electronic Structure.....	61
Solution Properties.....	63
Complexes of Cross-Bridged Tetraazamacrocycles.....	67
The Proton Sponge Problem.....	67
Synthesis and Characterization of Cd ²⁺ and Zn ²⁺ Complexes.....	71
Complex Synthesis and Structure.....	71
Electronic Structure.....	76
Kinetic Stability in Acidic Solution.....	78
Synthesis and Characterization of Iron and Manganese Complexes.....	83
Fe ²⁺ and Mn ²⁺ Complexes of Methyl Substituted Ligands.....	83
Complex Synthesis and Structure.....	83
Electronic Structure.....	87
Solution Properties.....	89
Fe ³⁺ and Mn ³⁺ Complexes of Methyl Substituted Ligands.....	95
Complex Synthesis and Structure.....	95
Electronic Structure.....	97
Solution Properties.....	100
Additional Mn(B14N4) ³⁺ Complexes.....	102
Complexes of Unsubstituted and Benzyl Substituted Ligands.....	112
Complex Synthesis.....	112
Crystal Structures.....	114

Electrochemistry.....	120
Synthesis and Characterization of Cobalt Complexes.....	123
Complex Synthesis and Structure.....	123
Electronic Structure.....	127
Solution Properties.....	132
Synthesis and Characterization of Nickel Complexes.....	137
Complex Synthesis and Structure.....	137
Electronic Structure.....	142
Solution Properties.....	145
Miscellaneous Observations.....	149
X-Ray Crystal Structure Determination of <i>trans</i> -Dioxocyclam (1,4,8,11-tetraazacyclotetradecane-5,12-dione) and its Ni ²⁺ Complex.....	149
Cu ⁺ and Cu ²⁺ Complexes of Bn ₂ B14N4.....	155
The Square Pyramidal Pd ²⁺ Complex of B14N4.....	157
A Cyclam-like Macrocycle Side-Bridged by a Propyl Chain.....	158
EXPERIMENTAL	161
Materials and Instrumentation.....	161
Crystallography.....	163
Titration.....	164
Decomposition of Cu(L) ²⁺	165
Decomposition of Zn(L) ²⁺	166
Decomposition of Mn(L) ²⁺	166
<u>Ligand and Ligand Precursor Syntheses:</u>	166
Q14N4 (<i>cis</i> -decahydro-3a,5a,8a,10a-tetraazapyrene), Q13N4 (<i>cis</i> -Decahydro-3a,5a,7a,9a-tetraazacyclopent[gh]phenalene), Q12N4 (<i>cis</i> -Decahydro-2a,4a,6a,8a-tetraazacyclopent[fg]acenaphthylene), <i>iso</i> -Q14N4 (<i>cis</i> -Decahydro-2a,4a,7a,10a-tetraazanaphth[2,1,8-c,d,e]azulene), <i>racemic</i> -Q14N4Me ₆ (<i>racemic</i> -1,1,3,6,6,8-Hexamethyl- <i>cis</i> -decahydro-3a,5a,8a,10a-tetraazapyrene), and <i>meso</i> -Q14N4Me ₆ (<i>meso</i> -1,1,3,6,6,8-Hexamethyl- <i>cis</i> -decahydro-3a,5a,8a,10a-tetraazapyrene).....	166
[H ₂ Q14N4] ₂ [Fe ₂ OCl ₆]Cl ₂ · CH ₃ CN, Bis-(3a,8a-dihydro- <i>cis</i> -decahydro-5a,10a-diaza-3a,8a-diazoniapyrene) Dichloride(μ-Oxo)bis[trichloroferrate(III)] 1-Acetonitrile.....	167
[MeQ14N4]I, 3a-Methyl- <i>cis</i> -decahydro-5a,8a,10a-triaza-3a-azoniapyrene Iodide.....	167
[Me ₂ Q14N4]I ₂ , 3a,8a-Dimethyl- <i>cis</i> -decahydro-5a,10a-diaza-3a,8a-diazoniapyrene Diiodide.....	168

Me ₂ B14N ₄ , 4,11-Dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane	168
[H ₂ (Me ₂ B14N ₄)](TFA) ₂ , 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane Bis(trifluoroacetate).	168
<i>racemic</i> -[HMeQ14N ₄ Me ₆] ₂ CH ₃ CN H ₂ O, <i>racemic</i> -1,1,3,3a,6,6,8-Heptamethyl- 5a-hydro- <i>cis</i> -decahydro-8a,10a-diaza-3a,5a-diazoniapyrene Diiodide 1-Acetonitrile 1- Hydrate).....	169
<i>racemic</i> -[Me ₂ Q14N ₄ Me ₆] ₂ , <i>racemic</i> -1,1,3,3a,6,6,8,8a-Octamethyl- <i>cis</i> -decahydro- 5a,10a-diaza-3a,8a-diazoniapyrene Diiodide.....	170
Me ₂ B14N ₄ Me ₆ , <i>racemic</i> -4,5,7,7,11,12,14,14-Octamethyl-1,4,8,11- tetraazabicyclo[6.6.2]hexadecane	171
[H ₂ (Me ₂ B14N ₄ Me ₆)](TFA) ₂ H ₂ O, <i>racemic</i> -4,5,7,7,11,12,14,14-octamethyl- 1,4,8,11- tetraazabicyclo[6.6.2]hexadecane Bis(trifluoroacetate) 1-Hydrate.....	171
Me ₂ B12N ₄ , 4,10-Dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane	172
[H ₃ (Me ₂ B12N ₄)]Cl ₃ 2H ₂ O, 4,10-dimethyl-1,4,7,10- tetraazabicyclo[5.5.2]tetradecane Tris(hydrochloride) 2-Hydrate	172
Me ₂ B13N ₄ , 4,10-dimethyl-1,4,7,10-tetraazabicyclo[6.5.2]pentadecane.....	172
[H ₃ (Me ₂ B13N ₄)]Cl ₃ H ₂ O, 4,10-dimethyl-1,4,7,10-tetraazabicyclo[6.5.2] pentadecane Tris(hydrochloride) 1-Hydrate	172
Bn ₂ B14N ₄ (4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane).....	173
H ₂ B14N ₄ (1,4,8,11-tetraazabicyclo[6.6.2]hexadecane).....	173
Bn ₂ B12N ₄ (4,10-dibenzyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane).....	173
H ₂ B12N ₄ (1,4,7,10-tetraazabicyclo[5.5.2]tetradecane).....	173
<i>trans</i> -14N ₄ O ₂ , 1,4,8,11-tetraazacyclotetradecane-5,12-dione	173

<i>meso</i> -5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazabicyclo[9.3.3]heptadecane.....	173
<u>Syntheses of Metal Complexes of Tetracyclic Ligands:</u>	174
Pd(Q14N4)Cl ₂ , Dichloro(<i>cis</i> -decahydro-3a,5a,8a,10a-tetraazapyrene) palladium(II).....	174
Pd(Q12N4)Cl ₂ , Dichloro(<i>cis</i> -decahydro-2a,4a,6a,8a- tetraazacyclopent[fg]acenaphthylene)palladium(II).....	175
Cu(L)Cl ₂ , L = Q14N4 = Dichloro(<i>cis</i> -decahydro-3a,5a,8a,10a- tetraazapyrene)copper(II), L = Q13N4 = Dichloro(<i>cis</i> -decahydro-3a,5a,7a,9a- tetraazacyclopent[gh]phenalene)copper(II), L = Q12N4 = Dichloro(<i>cis</i> -decahydro- 2a,4a,6a,8a-tetraazacyclopent[fg]acenaphthylene) copper(II), and L = <i>iso</i> -Q14N4 = Dichloro(<i>cis</i> -decahydro-2a,4a,7a,10a-tetraazanaphth[2,1,8-c,d,e]azulene) copper(II).....	175
[Cu(Q14N4) ₂]PF ₆ , Bis(<i>cis</i> -decahydro-3a,5a,8a,10a-tetraazapyrene)copper(I) Hexafluorophosphate.....	176
[(Q12N4)Cu(μ-OH) ₂ Cu(Q12N4)][PF ₆] ₂ · 1.5 H ₂ O, Bis-μ-hydroxobis(<i>cis</i> -decahydro- 2a,4a,6a,8a-tetraazacyclopent[fg]acenaphthylene)copper(II) Hexafluorophosphate 1.5-Hydrate	176
<u>Syntheses of Metal Complexes of Bicyclic Ligands:</u>	177
[Cu(Me ₂ B14N4)Cl]PF ₆ , Chloro(4,11-Dimethyl-1,4,8,11- tetraazabicyclo[6.6.2]hexadecane)copper(II) Hexafluorophosphate	177
[Cu(Me ₂ B14N4Me ₆)Cl]Cl · H ₂ O, Chloro(4,5,7,7,11,12,14,14-Octamethyl-1,4,8,11- tetraazabicyclo[6.6.2]hexadecane)copper(II) Chloride 1-Hydrate	178
[Cu(L)Cl]Cl · H ₂ O, L = Me ₂ B13N4 = Chloro(4,10-dimethyl-1,4,7,10- tetraazabicyclo[6.5.2]pentadecane)copper(II) chloride 1-Hydrate, L = Me ₂ B12N4 = Chloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)copper(II) Chloride 1-Hydrate	178
ZnLCl ₂ , L = Me ₂ B14N4 = Dichloro(4,11-dimethyl-1,4,8,11- tetraazabicyclo[6.6.2]hexadecane)zinc(II), L = Me ₂ B13N4 = Dichloro(4,10-dimethyl- 1,4,7,10-tetraazabicyclo[6.5.2]pentadecane)zinc(II) 1-Hydrate, L = Me ₂ B12N4 =	

Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane) zinc(II).....	179
Mn/Fe(Me ₂ B14B4/Me ₂ B12N4)Cl ₂ , M = Mn ²⁺ , L = Me ₂ B14N4 = Dichloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)manganese(II); M = Mn ²⁺ , L = Me ₂ B12N4 = Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane) manganese(II); M = Fe ²⁺ , L = Me ₂ B14N4 = Dichloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)iron(II); M = Fe ²⁺ , L = Me ₂ B12N4 = Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)iron(II).....	180
[Mn/Fe(Me ₂ B14N4/Me ₂ B12N4)Cl ₂]PF ₆ , M = Mn ³⁺ , L = Me ₂ B14N4 = Dichloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)manganese(III) Hexafluorophosphate; M = Mn ³⁺ , L = Me ₂ B12N4 = Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2] tetradecane)manganese(III) Hexafluorophosphate; M = Fe ³⁺ , L = Me ₂ B14N4 = Dichloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane) iron(III) Hexafluorophosphate 0.5-Hydrate; M = Fe ³⁺ , L = Me ₂ B12N4 = Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)iron(III) Hexafluorophosphate	181
[Mn(Me ₂ B14N4)(N ₃) ₂]PF ₆ , Bis(azido)(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)manganese(III) Hexafluorophosphate.....	182
[Mn(Me ₂ B14N4)(OH)(OAc)]PF ₆ NH ₄ OAc NaCl, Acetatohydroxo(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)manganese(III) Hexafluorophosphate 1-Ammonium Acetate 1-Sodium Chloride	183
[Mn(Me ₂ B14N4)(OMe) ₂]PF ₆ , Dimethoxy(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2] hexadecane)manganese(III) Hexafluorophosphate.....	184
Mn(Bn ₂ B14N4)(CF ₃ SO ₃) ₂ , Bis(trifluoromethanesulfonato)(4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)manganese(II).....	184
Mn/Fe(Bn ₂ B14N4/Bn ₂ B12N4)Cl ₂ , M = Mn ²⁺ , L = Bn ₂ B14N4 = Dichloro(4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)manganese(II); M = Mn ²⁺ , L = Bn ₂ B12N4 = Dichloro(4,10-dibenzyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane) manganese(II); M = Fe ²⁺ , L = Bn ₂ B14N4 = Dichloro(4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)iron(II); M = Fe ²⁺ , L = Bn ₂ B12N4 = Dichloro(4,10-dibenzyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)iron(II).....	185
M(H ₂ B14N4)Cl ₂ , M = Mn ²⁺ = Dichloro(1,4,8,11-tetraazabicyclo[6.6.2] hexadecane)manganese(II), M = Fe ²⁺ = Dichloro(1,4,8,11-tetraazabicyclo[6.6.2]	

hexadecane)iron(II).....	186
M(H ₂ B12N ₄)Cl ₂ , M = Mn ²⁺ = Dichloro(1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)manganese(II), M = Fe ²⁺ = Dichloro(1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)iron(II).....	186
[Cl(H ₂ B14N ₄)Fe(μ-O)Fe(H ₂ B14N ₄)Cl]Cl ₂ · 2 H ₂ O, μ-oxobis(chloro(1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)iron(III)) Chloride 2-Hydrate.....	187
[Cl(H ₂ B12N ₄)Fe(μ-O)Fe(H ₂ B12N ₄)Cl][PF ₆] ₂ , μ-oxobis(chloro(1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)iron(III)) Hexafluorophosphate	187
CoLCl ₂ , L = Me ₂ B14N ₄ = Dichloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)cobalt(II), L = Me ₂ B13N ₄ = Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[6.5.2]pentadecane)cobalt(II), L = Me ₂ B12N ₄ = Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)cobalt(II).....	188
[Co(Me ₂ B14N ₄ Me ₆)Cl] ₂ [CoCl ₄], Bis(chloro(4,5,7,7,11,12,14,14-Octamethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)cobalt(II)) Tetrachlorocobaltate(II).....	189
[Co(Me ₂ B14N ₄ Me ₆)Cl]PF ₆ , Chloro(4,5,7,7,11,12,14,14-Octamethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)cobalt(II) Hexafluorophosphate	189
[CoLCl ₂]PF ₆ , L = Me ₂ B14N ₄ = Dichloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)cobalt(III) Hexafluorophosphate, L = Me ₂ B13N ₄ = Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[6.5.2]pentadecane)cobalt(III) Hexafluorophosphate, L = Me ₂ B12N ₄ = Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)cobalt(III) Hexafluorophosphate.....	190
[NiL(acac)][Ni(acac) ₃] · THF, L = Me ₂ B14N ₄ = Acetylacetonato(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)nickel(II) Tris(acetylacetonato)nickelate(II) 1-Tetrahydrofuran, L = Me ₂ B12N ₄ = Acetylacetonato(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)nickel(II) Tris(acetylacetonato)nickelate(II) 1-Tetrahydrofuran.....	191
NiLCl ₂ , L = Me ₂ B14N ₄ = Dichloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)nickel(II) 2-Hydrate, L = Me ₂ B13N ₄ = Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[6.5.2]pentadecane)nickel(II) 1-Hydrate, L = Me ₂ B12N ₄ = Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)nickel(II) 0.5-Hydrate	191

[Ni(Me ₂ B14N4Me ₆)Cl]PF ₆ , Chloro(4,5,7,7,11,12,14,14-Octamethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)nickel(II) Hexafluorophosphate	192
Ni(<i>trans</i> -14N4O ₂) H ₂ O, (1,4,8,11-tetraazacyclotetradecane-5,12-dione)nickel(II) 1-Hydrate	193
[Cu(Bn ₂ B14N4)]PF ₆ 0.5 CH ₃ CN, 4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecanecopper(I) Hexafluorophosphate 0.5-Acetonitrile.....	194
[Cu(Bn ₂ B14N4)(CH ₃ CN)][PF ₆] ₂ H ₂ O, Acetonitrile(4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)copper(II) Hexafluorophosphate 1-Hydrate.....	194
[Pd(Me ₂ B14N4)Cl]Cl 2H ₂ O, Chloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)palladium(II) Chloride 2-Hydrate	194
FOOTNOTES AND REFERENCES.....	196
APPENDIX.....	207
Data For X-Ray Crystal Structure Determinations.....	207
Experimental data for [H ₂ Q14N4] ₂ [Fe ₂ OCl ₆]Cl ₂	
M e C N	2 0 7
Experimental data for [MeQ14N4]I.....	210
Experimental data for [HMeQ14N4][ClO ₄] ₂	213
Experimental data for [Me ₂ Q14N4]I ₂	216
Experimental data for [HMeQ14N4Me ₆]I ₂	
M e C N	2 1 9
Experimental data for [Me ₂ Q14N4Me ₆]I ₂ 2H ₂ O.....	223
Experimental data for [H ₂ (Me ₂ B14N4Me ₆)Cl ₂ 2.5H ₂ O.....	227
Experimental data for <i>t r a n s</i> - 1 4 N 4 O ₂	
2 H ₂ O	2 3 3
Experimental data for H ₂ [<i>meso</i> -5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazabicyclo[9.9.3]heptadecane]ICl	
Et ₂ O.....	235
Experimental data for Pd(Q14N4)Cl ₂	240
Experimental data for Pd(Q12N4)Cl ₂	243
Experimental data for Cu(Q14N4)Cl ₂	246

	Experimental data for Cu(Q13N4)Cl ₂	251
	Experimental data for Cu(Q12N4)Cl ₂	254
	Experimental data for Cu(<i>iso</i> -Q14N4)Cl ₂	256
	Experimental data for [Cu(Q14N4) ₂]PF ₆	259
	Experimental data for [(Q12N4)Cu(μ-OH)Cu(Q12N4)][PF ₆] ₂	2
M e C N	[C u (M e ₂ B 1 4 N 4) C l] C l	2 6 3
2 H ₂ O	[C u (M e ₂ B 1 4 N 4 M e ₆) C l] C l	2 6 7
H ₂ O		2 7 0
	Experimental data for [Cu(Me ₂ B12N4)(MeCN) ₂][PF ₆] ₂	274
	Experimental data for [Cu(Bn ₂ B14N4)]PF ₆	0.5
M e C N		2 8 0
	Experimental data for [Cu(Bn ₂ B14N4)(MeCN)][PF ₆] ₂	0.25
H ₂ O		2 8 4
	Experimental data for Zn(Me ₂ B12N4)Cl ₂	290
	Experimental data for Fe(Me ₂ B14N4)Cl ₂	295
	Experimental data for Fe(Me ₂ B12N4)Cl ₂	299
	Experimental data for Mn(Me ₂ B12N4)Cl ₂	304
	Experimental data for Mn(Me ₂ B14N4)Cl ₂	309
	Experimental data for [Mn(Me ₂ B14N4)Cl ₂]PF ₆	313
	Experimental data for [Mn(Me ₂ B12N4)Cl ₂]PF ₆	317
	Experimental data for [Mn(Me ₂ B14N4)(N ₃) ₂]PF ₆	320
	Experimental data for [Mn(Me ₂ B14N4)(OH)(OAc)]PF ₆	324
	Experimental data for [Mn(Me ₂ B14N4)(OMe) ₂]PF ₆	329
	Experimental data for Mn(Bn ₂ B14N4)(CF ₃ SO ₃) ₂	332
	Experimental data for Mn(Bn ₂ B12N4)Cl ₂	336
	Experimental data for Fe(Bn ₂ B12N4)Cl ₂	339
	Experimental data for [Cl(H ₂ B14N4)Fe(μ-O)Fe(H ₂ B14N4)Cl]Cl ₂	
3 H ₂ O	[Cl(H ₂ B12N4)Fe(μ-O)Fe(H ₂ B12N4)Cl]Cl ₂	3 4 1
2 H ₂ O		3 4 8
	Experimental data for Co(Me ₂ B14N4)Cl ₂	353
	Experimental data for Co(Me ₂ B12N4)Cl ₂	356
	Experimental data for [Co(Me ₂ B14N4Me ₆)Cl][CoCl ₄] DMF	0.25
H ₂ O		3 6 1
	Experimental data for [Co(Me ₂ B12N4)Cl ₂]PF ₆	370
	Experimental data for [Ni(Me ₂ B14N4)(acac)][Ni(acac) ₃]	
T H F		3 7 3
	Experimental data for [Ni(Me ₂ B12N4)(acac)][Ni(acac) ₃]	
T H F		3 8 0

	Experimental data for $[\text{Ni}(\text{Me}_2\text{B14N4})(\text{OH}_2)_2]\text{Cl}_2$	386
	Experimental data for $[\text{Pd}(\text{Me}_2\text{B14N4})\text{Cl}]\text{Cl}$	
2 H ₂ O	390
	Experimental data for $\text{Ni}(\text{trans-14N4O}_2) \cdot 2\text{H}_2\text{O}$	393

LIST OF TABLES

Table 1.	Selected bond lengths and angles for Pd(Q14N4)Cl ₂ and Pd(Q12N4)Cl ₂	52
Table 2.	Selected bond lengths and angles for Cu(Q14N4) ₂ ⁺ , Cu(Q14N4)Cl ₂ , Cu(Q13N4)Cl ₂ , Cu(Q12N4)Cl ₂ , <i>iso</i> -Cu(Q14N4)Cl ₂ , and [(Q12N4)Cu(μ-OH) ₂ Cu(Q12N4)] ²⁺	55
Table 3.	Electronic spectra of Cu ²⁺ tetracycle monomer complexes in MeCN.....	62
Table 4.	Molar Conductance of Cu ²⁺ tetracycle monomer complexes.....	63
Table 5.	Electrochemistry of Cu ²⁺ tetracycle monomer complexes.....	65
Table 6.	Selected bond lengths and angles for Cu(Me ₂ B14N4)Cl ⁺ and Cu(Me ₂ B14N4Me ₆)Cl ⁺	72
Table 7.	Selected bond lengths and angles for Cu(Me ₂ B12N4)(MeCN) ₂ ²⁺ and Zn(Me ₂ B12N4)Cl ₂	74
Table 8.	Molar Conductance of copper(II) complexes.....	75
Table 9.	Selected bond lengths and angles for Mn(Me ₂ B14N)Cl ₂ , Fe(Me ₂ B14N)Cl ₂ , Mn(Me ₂ B12N)Cl ₂ , and Fe(Me ₂ B12N)Cl ₂	85
Table 10.	Magnetic data for Mn(Me ₂ B14N)Cl ₂ , Fe(Me ₂ B14N)Cl ₂ , Mn(Me ₂ B12N)Cl ₂ , and Fe(Me ₂ B12N)Cl ₂	88
Table 11.	Molar conductance of Mn(Me ₂ B14N)Cl ₂ , Fe(Me ₂ B14N)Cl ₂ , Mn(Me ₂ B12N)Cl ₂ , and Fe(Me ₂ B12N)Cl ₂	93
Table 12.	Electrochemistry of Mn(Me ₂ B14N)Cl ₂ , Fe(Me ₂ B14N)Cl ₂ , Mn(Me ₂ B12N)Cl ₂ , and Fe(Me ₂ B12N)Cl ₂	94
Table 13.	Selected bond lengths and angles for [Mn(Me ₂ B12N)Cl ₂]PF ₆ and [Mn(Me ₂ B14N)Cl ₂]PF ₆	97
Table 14.	Electronic spectra of Fe ³⁺ and Mn ³⁺ cross-bridged ligand dichloride complexes in MeCN.....	99
Table 15.	Molar conductance of Fe ³⁺ and Mn ³⁺ cross-bridged ligand dichloride complexes.....	101
Table 16.	Selected bond lengths and angle for Mn(Me ₂ B14N)(N ₃) ₂ ⁺ , Mn(Me ₂ B14N)(OH)(OAc) ⁺ , and Mn(Me ₂ B14N)(OMe) ₂ ⁺	107
Table 17.	Electronic spectra of Mn(Me ₂ B14N4) ³⁺ complexes in MeCN.....	109
Table 18.	Electrochemistry of M ³⁺ complexes in MeCN.....	110
Table 19.	Selected bond lengths and angles for benzyl-substituted cross-bridged ligand complexes.....	115
Table 20.	Selected bond lengths and angles for unsubstituted cross-bridged ligand complexes.....	118
Table 21.	Electrochemistry of unsubstituted and benzyl-substituted cross-bridged ligand complexes.....	120
Table 22.	Selected bond lengths and angles for cobalt complexes.....	125
Table 23.	Electronic Spectra of Co ³⁺ complexes in MeCN.....	130

Table 24.	Molar Conductance of Co ²⁺ complexes.....	132
Table 25.	Electrochemistry of Co ²⁺ complexes in MeCN.....	134
Table 26.	Selected bond lengths and angles for Ni ²⁺ cross-bridged ligand complexes.....	140
Table 27.	Comparison of bond angles of cross-bridged ligand complexes with respect to metal ion.....	141
Table 28.	Electronic spectra of Ni ²⁺ complexes in MeCN.....	143
Table 29.	Molar Conductance of Ni ²⁺ cross-bridged ligand complexes.....	145
Table 30.	Electrochemistry of Ni ²⁺ cross-bridged ligand complexes in MeCN.....	146
Table 31.	Selected bond lengths and angles for copper-Bn ₂ B14N4 complexes.....	156
Table 32.	Selected bond lengths and angles for Pd(MB14N4)Cl ⁺	158

LIST OF FIGURES

Figure 1.	Entropy in the chelate effect.....	4
Figure 2.	Effective concentration in the chelate effect.....	4
Figure 3.	First donor dissociation in chelate vs. macrocycle.....	5
Figure 4.	Rigid non-macrocycle ligands.....	7
Figure 5.	Ethylene cross-bridged tetraazamacrocycles.....	9
Figure 6.	Metal coordination: clathrochelate vs. cross-bridged tetraazamacrocycle.....	10
Figure 7.	Classical bridged ligands.....	12
Figure 8.	The first “structurally reinforced” tetraazamacrocycles.....	13
Figure 9.	Large structurally reinforced macrocycles.....	14
Figure 10.	Substituted structurally reinforced tetraazamacrocycles.....	15
Figure 11.	Aromatic, doubly cross-bridged macrocycles.....	16
Figure 12.	Template closure of a side-bridged macrocycle.....	16
Figure 13.	Cu ²⁺ templated closure of a sulfur-containing macrobicycle.....	17
Figure 14.	1,4-diazacycloheptane containing macrobicycles.....	18
Figure 15.	Synthesis of spherical cryptands.....	19
Figure 16.	Cylindrical macrotricycles and quaternized spherical cryptands.....	20
Figure 17.	Cross-bridged cyclen macrobicycles.....	21
Figure 18.	Copper coordination of a pentadentate cross-bridged cyclen.....	22
Figure 19.	Cross-bridging <i>trans</i> -dioxocyclam.....	22
Figure 20.	Collinson’s pyridine-donor macrobicycle.....	23
Figure 21.	A large aromatic cross-bridged azamacrocycle.....	23
Figure 22.	Springborg’s propylene cross-bridged cyclens.....	24
Figure 23.	Springborg’s propylene cross-bridged [16]aneN4's.....	24
Figure 24.	Formaldehyde condensates with a) ammonia and b) macrocycles.....	25
Figure 25.	Tetracyclic cyclam-glyoxal condensate.....	26
Figure 26.	Synthesis of ethylene cross-bridged cyclams.....	26
Figure 27.	Tetracycle from successive aldehyde condensation with a diamine.....	27
Figure 28.	Tetraaminal from a triamine and glyoxal.....	27
Figure 29.	Tetraamine-diketone condensation leads to cyclam.....	28
Figure 30.	Cyclen synthesis from tetraamine-dmfdma condensation.....	28
Figure 31.	Solvent dependent cyclam-dmfdma condensations.....	29
Figure 32.	Tetracycles from 2,2'-biimidazole bridging.....	29
Figure 33.	General synthesis of ethylene cross-bridged tetraazamacrocycles.....	34
Figure 34.	Lone pair location in folded <i>cis</i> -tetracycles.....	34
Figure 35.	All ligands (with abbreviated names) used for metal ion coordination in this work.....	36
Figure 36.	Kinetic and thermodynamic arguments for <i>cis</i> -fused tetracycles.....	37
Figure 37.	Proposed tetracycle enantiomer interconversion.....	38

Figure 38.	Previously characterized <i>racemic</i> -Q14N4Me ₆ (a-b) and <i>meso</i> -Q14N4Me ₆ (c) conformations.....	39
Figure 39.	Molecular structures of a) H ₂ Q14N4 ²⁺ , b) MeQ14N4 ⁺ , c) HMeQ14N4 ⁺ , d) Me ₂ Q14N4 ²⁺ , and e) H ₂ (Me ₂ B14N4) ²⁺	41
Figure 40.	Molecular structures of a) <i>racemic</i> -Q14N4Me ₆ , b) HMeQ14N4Me ₆ ²⁺ , c) Me ₂ Q14N4Me ₆ ²⁺ , d) H ₂ (Me ₂ B14N4Me ₆) ²⁺	44
Figure 41.	Pd ²⁺ complexation with Q14N4.....	51
Figure 42.	Molecular structures of Pd(Q14N4)Cl ₂ and Pd(Q12N4)Cl ₂	51
Figure 43.	A pentacyclic hexaamine related to the tetracycles.....	52
Figure 44.	Molecular structure of Cu(Q14N4) ⁺	54
Figure 45.	Molecular structures of a) Cu(Q14N4)Cl ₂ , b) Cu(Q13N4)Cl ₂ , c) Cu(Q12N4)Cl ₂ , d) Cu(<i>iso</i> -Q14N4)Cl ₂ , and e) [(Q12N4)Cu(μ -OH) ₂ Cu(Q12N4)] ²⁺	57
Figure 46.	Electronic spectrum of 0.1 mM Cu(Q13N4)Cl ₂ in MeCN.....	61
Figure 47.	77 K EPR spectra of a) Cu(<i>o</i> -Q14N4)Cl ₂ and b) Cu(Q14N4)Cl ₂	63
Figure 48.	Cyclic voltammograms of a) Cu(Q12N4)Cl ₂ and b) Cu(<i>iso</i> -Q14N4)Cl ₂ in MeCN.....	64
Figure 49.	Titration curves for a) Me ₂ B14N4, b) Me ₂ B13N4, c) Me ₂ B12N4, and d) Me ₂ B14N4Me ₆	68
Figure 50.	Molecular structures of a) H ₂ (Me ₂ B14N4Me ₆) ²⁺ and b) H ₃ (Me ₂ B12N4) ³⁺	69
Figure 51.	Molecular structures of a) Cu(Me ₂ B14N4)Cl ⁺ and b) Cu(Me ₂ B14N4Me ₆)Cl ⁺	72
Figure 52.	Molecular structures of a) Cu(Me ₂ B12N4)(MeCN) ₂ ²⁺ and b) Zn(Me ₂ B12N4)Cl ₂	73
Figure 53.	Cyclic voltammograms of a) Cu(Me ₂ B14N4Me ₆)Cl ⁺ , b) Cu(Me ₂ B12N4) ²⁺ , c) Cu(Me ₂ B13N4)Cl ⁺ and d) Cu(Me ₂ B14N4)Cl ⁺	76
Figure 54.	Electronic spectra of a) Cu(Me ₂ B14N4)Cl ⁺ and b) Cu(Me ₂ B14N4Me ₆)Cl ⁺ in MeCN.....	77
Figure 55.	77 K EPR spectra of a) Cu(Me ₂ B14N4Me ₆)Cl ⁺ and b) Cu(Me ₂ B14N4)Cl ⁺	78
Figure 56.	The electronic spectrum of 0.1 mM Cu(Me ₂ B14N4) ²⁺ (a) in 1 M HCO ₄ and (b) its change (at 300nm) over 1000 h at 40 °C.....	79
Figure 57.	¹³ C NMR spectrum of Zn(Me ₂ B14N4) ²⁺ in 1 M DCl at 298 K.....	80
Figure 58.	Springborg's (a) and Bencini's (b) cross-bridged ligands.....	82
Figure 59.	Molecular structures of a) Mn(Me ₂ B14N4)Cl ₂ and b) Fe(Me ₂ B12N4)Cl ₂	84
Figure 60.	Molecular structures of a) Fe(Me ₂ B14N4)Cl ₂ and b) Mn(Me ₂ B12N4)Cl ₂ beside Newman projections that demonstrate the "gauche" vs. "eclipsed" conformations of the methyl groups.....	87

Figure 61.	Magnetic data for a) $\text{Mn}(\text{Me}_2\text{B14N4})\text{Cl}_2$ and b) $\text{Fe}(\text{Me}_2\text{B12N4})\text{Cl}_2$	88
Figure 62.	Electronic spectra of a) $\text{Mn}(\text{Me}_2\text{B14N4})\text{Cl}_2$ and b) $\text{Fe}(\text{Me}_2\text{B14N4})\text{Cl}_2$ 0.1M in MeCN.....	89
Figure 63.	77 K EPR spectra of a) $\text{Mn}(\text{Me}_2\text{B12N4})\text{Cl}_2$ and b) $\text{Mn}(\text{Me}_2\text{B12N4})\text{Cl}_2$	89
Figure 64.	Kinetic data for ligand dissociation of $\text{Mn}(\text{Me}_2\text{B14N4})\text{Cl}_2$ 0.1 M in 1 M DCl at 298 K. (For the linear regression, $\bar{R} = 0.972$).....	90
Figure 65.	Titration curve for $\text{Mn}(\text{Me}_2\text{B14N4})\text{Cl}_2$	91
Figure 66.	Cyclic voltammograms of a) $\text{Fe}(\text{Me}_2\text{B12N4})\text{Cl}_2$, b) $\text{Fe}(\text{Me}_2\text{B14N4})\text{Cl}_2$, c) $\text{Mn}(\text{Me}_2\text{B12N4})\text{Cl}_2$, and d) $\text{Mn}(\text{Me}_2\text{B14N4})\text{Cl}_2$	94
Figure 67.	Molecular structures of a) $\text{Mn}(\text{Me}_2\text{B14N4})\text{Cl}_2^+$ and b) $\text{Mn}(\text{Me}_2\text{B12N4})\text{Cl}_2^+$	96
Figure 68.	Electronic spectra of a) $[\text{Mn}(\text{Me}_2\text{B14N4})\text{Cl}_2]\text{PF}_6$ and b) $[\text{Fe}(\text{Me}_2\text{B14N4})\text{Cl}_2]\text{PF}_6$ in MeCN.....	98
Figure 69.	77 K EPR spectra of a) $[\text{Fe}(\text{Me}_2\text{B12N4})\text{Cl}_2]\text{PF}_6$ and b) $[\text{Fe}(\text{Me}_2\text{B14N4})\text{Cl}_2]\text{PF}_6$	99
Figure 70.	Titration curve for $[\text{Mn}(\text{Me}_2\text{B14N4})\text{Cl}_2]\text{PF}_6$	100
Figure 71.	Synthesis of additional $\text{Mn}(\text{Me}_2\text{B14N4})^{3+}$ complexes.....	103
Figure 72.	Molecular structures of a) $\text{Mn}(\text{Me}_2\text{B14N4})(\text{N}_3)_2^+$, b) $\text{Mn}(\text{Me}_2\text{B14N4})(\text{OH})(\text{OAc})^+$, and c) $\text{Mn}(\text{Me}_2\text{B14N4})(\text{OMe})_2^+$	106
Figure 73.	Electronic spectra of a) $\text{Mn}(\text{Me}_2\text{B14N4})(\text{N}_3)_2^+$, b) $\text{Mn}(\text{Me}_2\text{B14N4})(\text{OH})(\text{OAc})^+$, and c) $\text{Mn}(\text{Me}_2\text{B14N4})(\text{OMe})_2^+$	108
Figure 74.	Cyclic voltammograms of a) $\text{Mn}(\text{Me}_2\text{B14N4})(\text{OMe})_2^+$, b) $\text{Mn}(\text{Me}_2\text{B14N4})(\text{OH})(\text{OAc})^+$, c) $\text{Mn}(\text{Me}_2\text{B14N4})(\text{N}_3)_2^+$ and d) $\text{Mn}(\text{Me}_2\text{B14N4})\text{Cl}_2^+$	109
Figure 75.	77 K EPR spectrum of air oxidized $\text{Mn}(\text{Me}_2\text{B12N4})\text{Cl}_2$	114
Figure 76.	Molecular structures of a) $\text{Mn}(\text{Bn}_2\text{B14N4})(\text{CF}_3\text{SO}_3)_2$ and b) $\text{Mn}(\text{Bn}_2\text{B12N4})\text{Cl}_2$	114
Figure 77.	Crystal packing diagram for $\text{Fe}(\text{B}_2\text{B12N4})\text{Cl}_2$	117
Figure 78.	Molecular structures of a) $[\text{Cl}(\text{H}_2\text{B14N4})\text{Fe}(\mu\text{-O})\text{Fe}(\text{H}_2\text{B14N4})\text{Cl}]^{2+}$ and b) $[\text{Cl}(\text{H}_2\text{B12N4})\text{Fe}(\mu\text{-O})\text{Fe}(\text{H}_2\text{B12N4})\text{Cl}]^{2+}$	117
Figure 79.	Molecular structures of a) $\text{Co}(\text{Me}_2\text{B14N4})\text{Cl}_2$, b) $\text{Co}(\text{Me}_2\text{B12N4})\text{Cl}_2$ c) $\text{Co}(\text{Me}_2\text{B14N4Me}_6)\text{Cl}^+$, and d) $\text{Co}(\text{Me}_2\text{B12N4})\text{Cl}_2^+$	124
Figure 80.	Electronic spectra of a) $\text{Co}(\text{Me}_2\text{B13N4})\text{Cl}_2$, b) $[\text{Co}(\text{Me}_2\text{B14N4Me}_6)\text{Cl}]\text{PF}_6$ 0.01 M in MeCN.....	128
Figure 81.	Electronic spectrum of 0.001 M $[\text{Co}(\text{Me}_2\text{B12N4})\text{Cl}_2]\text{PF}_6$ in MeCN.....	129
Figure 82.	Cyclic voltammograms of a) $\text{Co}(\text{Me}_2\text{B14N4Me}_6)\text{Cl}^+$ (PF_6^- electrolyte) and b) $\text{Co}(\text{Me}_2\text{B13N4})\text{Cl}_2$ (Cl^- electrolyte) in MeCN.....	133
Figure 83.	Ni^{2+} complex synthesis.....	137
Figure 84.	Molecular structures of a) $\text{Ni}(\text{Me}_2\text{B14N4})(\text{acac})^+$, b)	

	Ni(Me ₂ B12N4)(acac) ⁺ , and c) Ni(Me ₂ B14N4)(OH ₂) ₂ ²⁺	139
Figure 85.	Electronic spectra of a) Ni(Me ₂ B13N4)Cl ₂ and b) Ni(Me ₂ B14N4Me ₆)Cl ⁺ 0.01M in MeCN.....	143
Figure 86.	Cyclic voltammograms of a) Ni(Me ₂ B14N4Me ₆)Cl ⁺ and b) Ni(Me ₂ B12N4)Cl ₂ in MeCN.....	146
Figure 87.	Synthesis of <i>trans</i> -14N4O ₂ (a) and b) structures of related ligands.....	150
Figure 88.	Highly substituted <i>trans</i> -dioxocyclams known to complex Ni.....	150
Figure 89.	Molecular structures of a) <i>trans</i> -14N4O ₂ and b) Ni(<i>trans</i> -14N4O ₂ H ₂) along with its crystal packing diagram (c).....	151
Figure 90.	Electronic spectrum of 0.01 M Ni(<i>trans</i> -14N4O ₂ H ₂) in water.....	153
Figure 91.	Cyclic voltammogram of Ni(<i>trans</i> -14N4O ₂ H ₂) in water.....	154
Figure 92.	Molecular structure of a) Cu(Bn ₂ B14N4) ⁺ and b) Cu(Bn ₂ B14N4)(MeCN) ²⁺	155
Figure 93.	Molecular structure of Pd(Me ₂ B14N4)Cl ⁺	157
Figure 94.	Molecular structure of H ₂ (<i>meso</i> -5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazabicyclo[9.9.3]heptadecane) ²⁺	159