

*In The Name
of Allah*

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Bu-Ali Sina University

Faculty of Chemistry

THESIS

Submitted in Partial Fulfillment of the Requirements for the Degree
of Doctor of Philosophy (Ph.D.) in Inorganic Chemistry

Title:

**Synthesis and Characterization of Some Macrocyclic
and Macroacyclic Schiff-Base Complexes Containing
Pyridine and Piperazine Moieties
with a Number of Metals**

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*The aim of life is to live, and to live means to be aware- Joyously,
Serenely, Divinely,*

God grant me the:

Serenity to accept the things I can't change

Courage to change the things I can

And

Wisdom to know the difference

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In The Name of Allah

**Synthesis and Characterization of Some Macrocyclic and
Macrocyclic Schiff Base Complexes Containing Pyridine and
Piperazine Moities with a Number of Metals**

Thesis Submitted in Partial Fulfillment of the Requirements for the Degree
of Doctor of Philosophy (Ph.D.) in Inorganic Chemistry

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Abstract

In this project some polyamine ligands and their novel macrocyclic and macroacyclic Schiff-base complexes in the presence of appropriate metal ions were synthesized and characterized. After a brief introduction (**Chapter 1**) it continues in the following chapters:

Chapter 2: *describes the synthesis and characterization of some tetra-amine ligands containing piperazine moiety*

Two tetraamine ligands, N, N'-bis(2-aminoethyl)piperazine and a novel N,N'(2-aminoethyl)(3-aminopropyl)piperazine were prepared as tetrahydro bromide or tetrahydrochloride salts. Furthermore, the other tetraamine ligand containing piperazine moiety with two aromatic arms has also been prepared. The amines have been characterized by various methods including ^1H , ^{13}C , DEPT(135), COSY(H, H) and HMQC(H, C) NMR studies, microanalysis and FAB-MS spectrometry.

Chapter 3: *describes the synthesis and characterization of some macrocyclic Schiff-base complexes containing piperazine moiety*

In the presence of Cd(II), Mn(II) or Zn(II) metal ions, tetraazaamine ligands, N, N'-bis(3-aminopropyl)piperazine or N, N'(2-aminoethyl)(3-amino propyl)piperazine were condensed with 2,6-diacetylpyridine or 2,6-pyridine dicarbaldehyde. In these cases, cyclocondensation have readily occurred. X-ray crystal structures of the selected Cd(II), Mn(II) and Zn(II) macrocyclic

complexes were also reported. In all complexes, metal ions are bonded to five nitrogens of a macrocyclic ring in the equatorial positions and certain anions in the axial positions. The complexes have been characterized by various methods including IR, FAB-MS, microanalysis, conductivity measurements and for Cd(II) complexes, ^1H , ^{13}C , DEPT(135), COSY(H, H) and HMQC(H, C) NMR studies.

Chapter 4: *describes the synthesis and characterization of a reduced form of Mn(II) macrocyclic Schiff-base complex containing piperazine moiety by the insitu reduction using NaBH_4 and related complexes with Pb(II), Mn(II) and Ag(I)*

From the reaction of Pb(II), Mn(II) and Ag(I) metal ions and the above diamine macrocyclic ligand the corresponding complexes were produced and characterized with various spectroscopic methods. The crystal structure of Pb(II) macrocyclic complex has also been determined.

Chapter 5: *describes the synthesis and characterization of some Schiff-base ligands containing piperazine moiety and their related macrocyclic Schiff-base complexes*

These Schiff-base ligands were prepared from condensation of N, N'-bis(2-aminoethyl)piperazine or N, N'-bis(3-aminopropyl)piperazine and a number of various aldehydes such as: salicylaldehyde derivatives, pyridine-2-carbaldehyde, thiophene-2-carbaldehyde and 2-hydroxy-1-naphthaldehyde. These ligands were produced in two different methods in the presence or

absence of solvent (solvent-free). Microwave used in the solvent-free synthesis. The advantages of the latter method includes a simple reaction set-up, high product yields, short reaction times and no need of solvents. The products have been characterized by their melting point, elemental analysis, IR, EI-MS, ^1H and ^{13}C NMR spectra.

In the end of this chapter the synthesis of three macroacyclic Schiff-base complexes containing piperazine moiety have also reported and characterized with some spectroscopic methods and one of them with X-ray.

Chapter 6: *describes the computational study of ligands and related macrocyclic Schiff-base complexes containing piperazine moiety*

We were interested to know whether or not the structures of ligands L^2 and L^4 in the presence or absence of coordinating metal ions are different. Therefore, we have chosen *ab initio* molecular orbital calculations to assess the structural parameters of these complexes in gas phase. To do this we have undertaken a full geometry optimization at B3lyp/6-31G* and B3lyp/LANL2DZ for free ligands and related cadmium complexes, respectively. The result of optimized structure of uncoordinated free ligands showed that preparation of present macrocyclic ligands in the absence of metal ion was hardly possible. The result of single-point calculations on optimized structure of ligands and on the structure of ligand in their optimized Cd complexes showed that the rearrangement in structure of ligands, L^2 and L^4 from their free state to the corresponding structure in cadmium complexes needs energy about 8 and 15.4 kcal/mol, respectively.

Table of Contents

	page
Chapter 1: Introduction	
1-1 Schiff-bases	1
1-1-1 Synthesis of Schiff-base Complexes	2
1-1-2 Macrocyclic Schiff-base Complexes	3
1-2 Macrocyclic Ligand Complexes Containing Pyridine Moiety	4
1-3 Macrocyclic Compounds Containing Piperazine Moiety	25
References	29
Chapter 2: Experimental (Synthesis of Polyamine Ligands Containing Piperazine Moiety)	
2-1 Introduction	52
2-2 Tetraamine Ligands	53
2-3 Experimental Section	55
2-3-1 Synthesis of N-(p-tolylsulfonyl)-2-chloroethylamine; ClEtNHTs	55
2-3-2 Synthesis of N-(p-tolylsulfonyl)aziridine	55
2-3-3 Synthesis of linear tetraamines with Piperazine Moiety	56
2-3-3-1 Synthesis of N,N'-bis((p-tolylsulfonyl)amino)ethyl)piperazine	56
2-3-3-2 Synthesis of N,N'-bis(2-aminoethyl)piperazine.tetrahydrobromide	56
2-3-3-3 Synthesis of N,N'-bis(2-phthalimidoethyl)piperazine	57
2-3-3-4 Synthesis of N,N'-bis(2-aminoethyl)piperazine.tetrahydrochloride	58
2-3-3-5 Synthesis of N,N'(2-aminoethyl)(3-aminopropyl)piperazine	59
2-3-3-6 Synthesis of N,N'-bis(2-nitrophenyl)piperazine	60
2-3-3-7 Synthesis of N,N'-bis(2-aminophenyl)piperazine	61

2-4	Synthesis of 2,6-pyridinedicarbaldehyde	62
	References	63
Chapter 3: Macrocyclic Schiff-base Complexes Containing Piperazine Moiety		
3-1	Macrocyclic Compounds Containing Piperazine Moiety	67
3-2	Cd(II) macrocyclic Schiff-base complexes Containing Piperazine Moiety	69
3-3	Experimental Section	70
3-3-1	Complex Synthesis	70
3-4	Results and Discussion	73
3-4-1	Mass Spectrometry Results	74
3-4-2	Crystal Structure Determination	74
3-4-3	Description of the Crystal Structures	75
3-4-4	NMR Studies	81
3-5	Conclusion	85
3-6	Mn(II) Macrocyclic Schiff-base Complexes Containing Piperazine Moiety	85
3-7	Experimental Section	87
3-7-1	Complex Synthesis -General procedure	87
3-8	Results and Discussion	88
3-8-1	Mass Spectrometry Results	89
3-8-2	Magnetic Susceptibility Measurement	90
3-8-3	Crystal structure Determination	91
3-8-4	Description of the Crystal structures	92
3-9	Conclusion	96
3-10	Zn(II) Macrocyclic Schiff-base Complexes Containing Piperazine Moiety	96
3-11	Experimental Section	98

3-11-1	Complex Synthesis	98
3-11-2	Crystal Structure Determination	99
3-12	Results and Discussion	101
3-12-1	Mass Spectrometry Results	102
3-12-2	Crystal Structure Determination	102
3-12-3	Descriptions of the Crystal structure	103
3-13	Conclusion	105
	References	106

**Chapter 4: Macrocylic Ligand and Related Complexes Containing
Piperazine Moiety**

4-1	Introduction	113
4-2	Experimental Section	119
4-2-1	Synthesis of the Macrocylic Ligand (L)	119
4-3	Complex Synthesis	120
4-4	Results and Discussion	121
4-4-1	Mass Spectrometry Result	122
4-4-2	NMR Studies	122
4-4-3	Description of the Crystal Structure	124
	References	127

**Chapter 5: Schiff-base Ligands and Related Macroacyclic Complexes
Containing Piperazine Moiety**

5-1	Introduction	130
5-2	Experimental Section	133
5-2-1	Ligand Synthesis-General procedure	133
5-3	Application of Microwave in Organic Synthesis	140
5-4	Experimental Section	141

5-4-1	Synthesis of Schiff-base Ligands-General procedure	141
5-5	Result and Discussion	142
5-5-1	Infrared Spectra	142
5-5-2	NMR Studies	142
5-5-3	Mass Spectrometry Result	144
5-6	Complex Synthesis -General procedure	144
5-7	Result and Discussion	146
5-7-1	Mass Spectrometry Result	147
5-7-2	NMR Studies	147
5-7-2	Description of the Crystal Structure	148
	References	152
Chapter 6: Computational Study of Macrocyclic Schiff-base Complexes		
Containing Piperazine Moiety		
6-1	Introduction	155
6-2	Basis Set	157
6-2-1	Minimal Basis Sets	158
6-2-2	Split Valance Basis Sets	158
6-2-3	Polarized Basis Sets	158
6-2-4	Basis Sets for Post-Third-Row Atoms	159
6-3	Computational Section	159
6-4	Ab Initio Study of Ligands, L ² and L ⁴ and Related Complexes	159
	References	166
	Appendix	167

List of Tables

Table 1-1	Macrocyclic ligands derived from 2,6-pyridinedicarbaldehyde and 2,6-diacetylpyridine	5
Table 1-2	Macrocyclic ligands and related complexes containing piperazine moiety	26
Table 3-1	Microanalysis results of Cd(II) complexes	73
Table 3-2	Selected IR (cm^{-1}) data of Cd(II) complexes	74
Table 3-3	Crystal data and structure refinement for $[\text{CdL}^2\text{Cl}](\text{ClO}_4)$ (CH_3OH) and $[\text{CdL}^4(\text{NO}_3)(\text{H}_2\text{O})]\text{ClO}_4$	76
Table 3-4	Selected bond lengths (\AA) and angles ($^\circ$) for $[\text{CdL}^2\text{Cl}]^+$ and $[\text{CdL}^4(\text{NO}_3)(\text{H}_2\text{O})]^+$	80
Table 3-5	^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral assignments for $[\text{CdL}^1]^{2+}$, $[\text{CdL}^2]^{2+}$, $[\text{CdL}^3]^{2+}$ and $[\text{CdL}^4]^{2+}$ recorded at 300 and 400 MHz in DMSO-d_6	83
Table 3-6	Microanalysis results of Mn(II) complexes	89
Table 3-7	Selected IR (cm^{-1}) data of Mn(II) complexes	89
Table 3-8	Crystal data and structure refinement for $[\text{MnL}^2\text{Cl}](\text{CH}_3\text{OH})\text{ClO}_4$ and $[\text{MnL}^4\text{Cl}]\text{PF}_6$	91
Table 3-9	Selected bond lengths (\AA) and bond angles ($^\circ$) for $[\text{MnL}^2\text{Cl}](\text{CH}_3\text{OH})^+$ and $[\text{MnL}^4\text{Cl}]^+$	95
Table 3-10	Crystal data and structure refinement for $[\text{ZnL}^2\text{Br}]\text{ClO}_4$	100
Table 3-11	Microanalysis results of Zn(II) complexes	101
Table 3-12	Selected IR (cm^{-1}) data of Zn(II) complexes	101
Table 3-13	Selected bond lengths (\AA) and angles ($^\circ$) for $[\text{ZnL}^2\text{Br}]\text{ClO}_4$	103

Table 4-1	^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral assignments for L and $[\text{PbL}](\text{ClO}_4)_2$ recorded at 300 and 400 MHz in CDCl_3 and DMSO-d_6	123
Table 4-2	Crystal data and structure refinement for $[\text{PbLClO}_4](\text{ClO}_4)$	124
Table 4-3	Selected bond lengths and bond angles of $[\text{PbL}](\text{ClO}_4)_2$	126
Table 4-4	Hydrogen bond interaction for $[\text{PbL}](\text{ClO}_4)_2$	126
Table 5-1	Synthesis of $\text{L}^1\text{-L}^{10}$ in the presence or absence of solvent	143
Table 5-2	^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral assignments for $[\text{CdL}^{10}(\text{NO}_3)]\text{ClO}_4$ recorded at 400 in DMSO-d_6	147
Table 5-3	Crystal data and structure refinement for $[\text{CdL}^{10}\text{NO}_3]\text{ClO}_4$	149
Table 5-4	Selected bond lengths (\AA) and bond angles ($^\circ$) for $[\text{CdL}^{10}(\text{NO}_3)]^+$	151
Table 6-1	Selected bond lengths (\AA) and bond angles ($^\circ$) for $[\text{CdL}^2\text{Cl}]^+$ and $[\text{CdL}^4(\text{NO}_3)]^+$	164
Table 6-2	Single point energies of ligands L^2 and L^4 at B3LYP/6-311+G* level of theory	165

List of Figures

Fig. 3-1	Ligands under discussion in this section	72
Fig. 3-2	The molecular structure of the cation $[\text{CdL}^2(\text{Cl})]^+$	75
Fig. 3-3	The molecular structure of cation $[\text{CdL}^4(\text{NO}_3)(\text{H}_2\text{O})]^+$	77
Fig. 3-4	The π, π -interactions in $[\text{CdL}^2\text{Cl}](\text{CH}_3\text{OH})\text{ClO}_4$	78
Fig. 3-5	Hydrogen bonds interactions in $[\text{CdL}^4(\text{NO}_3)(\text{H}_2\text{O})]\text{ClO}_4$	79
Fig. 3-6	Schematic structures of the $[\text{CdL}^n]^{2+}$ cations showing the lettering scheme for NMR assignments	84
Fig. 3-7	Some Mn(II) macrocyclic complexes as mimics of superoxide dismutase ligands	86
Fig. 3-8	Crystal structure of the cation $[\text{MnL}^2\text{Cl}(\text{CH}_3\text{OH})]^+$	93
Fig. 3-9	Crystal structure of the cation $[\text{MnL}^4\text{Cl}]^+$	94
Fig. 3-10	Crystal structure of the cation $[\text{ZnL}^2\text{Br}]^+$	102
Fig. 3-11	π, π -Stacking interaction between the pyridine units of adjacent ligands.	104
Fig. 4-1	Schematic structures of the L showing the lettering scheme for NMR assignments	123
Fig. 4-2	Crystal structure of $[\text{PbL}](\text{ClO}_4)_2$	125
Fig. 5-1	A schematic representation of Schiff-base ligands	131
Fig. 5-2	Schematic structures of the $[\text{CdL}^n]^{2+}$ cations showing the lettering scheme for NMR assignments	148
Fig. 5-3	The crystal structure of cation $[\text{CdL}^{10}(\text{NO}_3)]^+$	148
Fig. 6-1	Energy diagram of the conformers of piperazine, calculated with a semiempirical method (PM3)	160
Fig. 6-2	Optimized molecular structure of free ligands, L^2 and L^4 and $[\text{CdL}^2\text{Cl}]^+$ and $[\text{CdL}^4(\text{NO}_3)]^+$	163

List of Spectra

Spec. No. 2-1	Positive Ion FAB-MS spectrum of N, N'-bis(2-phthalimidoethyl) piperazine	168
Spec. No. 2-2	¹ H NMR spectrum of N, N'-bis(2-phthalimidoethyl)piperazine recorded at 400 MHz in CDCl ₃	168
Spec. No. 2-3	¹³ C{H}NMR spectrum of N, N'-bis(2-phthalimidoethyl)piperazine recorded at 500 MHz in CDCl ₃	169
Spec. No. 2-4	¹³ C{H}NMR spectrum of N, N'-bis(2-aminoethyl)piperazine. tetrahydro chloride recorded at 90 MHz in CDCl ₃	169
Spec. No. 2-5	Positive Ion FAB-MS spectrum of N, N'(2-aminoethyl)(3-aminopropyl) piperazine	170
Spec. No. 2-6	¹ H NMR spectrum of N, N'(2-aminoethyl)(3-aminopropyl)piperazine recorded at 400 MHz in D ₂ O	170
Spec. No. 2-7	¹³ C{H}NMR spectrum of N, N'(2-aminoethyl)(3-aminopropyl) piperazine recorded at 400 MHz in D ₂ O	171
Spec. No. 2-8	¹³ C{H}NMR expand spectrum of N, N'(2-aminoethyl)(3-aminopropyl) piperazine recorded at 400 MHz in D ₂ O	171
Spec. No. 2-9	COSY(H,H) NMR spectrum of N, N'(2-aminoethyl)(3-aminopropyl) piperazine recorded at 400 MHz in D ₂ O	172
Spec. No. 2-10	HMQC(C,H) NMR spectrum of N, N'(2-aminoethyl)(3-aminopropyl) piperazine recorded at 400 MHz in D ₂ O	172
Spec. No. 2-11	¹ H NMR spectrum of N, N'-bis(2-nitrophenyl)piperazine recorded at 300 MHz in CDCl ₃	173
Spec. No. 2-12	¹³ C{H} NMR spectrum of N, N'-bis(2-nitrophenyl)piperazine recorded at 300 MHz in CDCl ₃	173
Spec. No. 2-13	Infrared spectrum of N, N'-bis(2-aminophenyl)piperazine recorded as liquid films between NaCl plates	174
Spec. No. 2-14	¹ H NMR spectrum of N, N'-bis(2-aminophenyl)piperazine recorded at 90 MHz in CDCl ₃	174
Spec. No. 2-15	¹³ C{H}NMR spectrum of N, N'-bis(2-aminobenzyl)piperazine recorded at 300 MHz in CDCl ₃	175
Spec. No. 3-1	Infrared spectrum of [CdL ¹ Cl]ClO ₄	175
Spec. No. 3-2	Infrared spectrum of [CdL ² Cl]ClO ₄	176
Spec. No. 3-3	Infrared spectrum of [CdL ³](ClO ₄) ₂	176
Spec. No. 3-4	Infrared spectrum of [CdL ⁴ (NO ₃)(H ₂ O)]ClO ₄	177

Spec. No. 3-5	Positive Ion FAB-MS spectrum of $[\text{CdL}^1\text{Cl}]\text{ClO}_4$	177
Spec. No. 3-6	Positive Ion FAB-MS spectrum of $[\text{CdL}^2\text{Cl}]\text{ClO}_4$	177
Spec. No. 3-7	Positive Ion FAB-MS spectrum of $[\text{CdL}^3](\text{ClO}_4)_2$	178
Spec. No. 3-8	Positive Ion FAB-MS spectrum of $[\text{CdL}^4(\text{NO}_3)(\text{H}_2\text{O})]\text{ClO}_4$	179
Spec. No. 3-9	^1H NMR spectrum of $[\text{CdL}^1]^{2+}$ recorded at 400 MHz in DMSO-d_6	179
Spec. No. 3-10	^1H NMR expand spectrum of $[\text{CdL}^1]^{2+}$ recorded at 400 MHz in DMSO-d_6	180
Spec. No. 3-11	^1H NMR spectrum of $[\text{CdL}^2]^{2+}$ recorded at 400 MHz in DMSO-d_6	180
Spec. No. 3-12	^1H NMR expand spectrum of $[\text{CdL}^2]^{2+}$ recorded at 400 MHz in DMSO-d_6	181
Spec. No. 3-13	^1H NMR spectrum of $[\text{CdL}^3]^{2+}$ recorded at 400 MHz in DMSO-d_6	181
Spec. No. 3-14	^1H NMR expand spectrum of $[\text{CdL}^3]^{2+}$ recorded at 400 MHz in DMSO-d_6	182
Spec. No. 3-5	^1H NMR spectrum of $[\text{CdL}^4]^{2+}$ recorded at 300 MHz in DMSO-d_6	182
Spec. No. 3-16	$^{13}\text{C}\{\text{H}\}$ NMR spectrum of $[\text{CdL}^1]^{2+}$ recorded at 400 MHz in DMSO-d_6	183
Spec. No. 3-17	$^{13}\text{C}\{\text{H}\}$ NMR spectrum of $[\text{CdL}^2]^{2+}$ recorded at 400 MHz in DMSO-d_6	183
Spec. No. 3-18	$^{13}\text{C}\{\text{H}\}$ NMR spectrum of $[\text{CdL}^3]^{2+}$ recorded at 400 MHz in DMSO-d_6	184
Spec. No. 3-19	$^{13}\text{C}\{\text{H}\}$ NMR spectrum of $[\text{CdL}^4]^{2+}$ recorded at 300 MHz in DMSO-d_6	184
Spec. No. 3-20	DEPT 135 spectrum of $[\text{CdL}^1]^{2+}$ recorded at 400 MHz in DMSO-d_6	185
Spec. No. 3-21	DEPT 135 spectrum of $[\text{CdL}^2]^{2+}$ recorded at 400 MHz in DMSO-d_6	185
Spec. No. 3-22	DEPT 135 spectrum of $[\text{CdL}^3]^{2+}$ recorded at 400 MHz in DMSO-d_6	186
Spec. No. 3-23	DEPT 135 spectrum of $[\text{CdL}^4]^{2+}$ recorded at 300 MHz in DMSO-d_6	186
Spec. No. 3-24	COSY(H, H) spectrum of $[\text{CdL}^1]^{2+}$ recorded at 400 MHz in DMSO-d_6	187

Spec. No. 3-25	COSY(H, H) spectrum of $[\text{CdL}^2]^{2+}$ recorded at 400 MHz in DMSO- d_6	187
Spec. No. 3-26	COSY(H, H) spectrum of $[\text{CdL}^3]^{2+}$ recorded at 400 MHz in DMSO- d_6	188
Spec. No. 3-27	COSY(H, H) spectrum of $[\text{CdL}^4]^{2+}$ recorded at 300 MHz in DMSO- d_6	188
Spec. No. 3-28	HMQC(C, H) spectrum of $[\text{CdL}^1]^{2+}$ recorded at 400 MHz in DMSO- d_6	189
Spec. No. 3-29	HMQC(C, H) spectrum of $[\text{CdL}^2]^{2+}$ recorded at 400 MHz in DMSO- d_6	189
Spec. No. 3-30	HMQC(C, H) spectrum of $[\text{CdL}^3]^{2+}$ recorded at 400 MHz in DMSO- d_6	190
Spec. No. 3-31	HMQC(C, H) spectrum of $[\text{CdL}^4]^{2+}$ recorded at 300 MHz in DMSO- d_6	190
Spec. No. 3-32	Infrared spectrum of $[\text{MnL}^1\text{Cl}]\text{ClO}_4$	191
Spec. No. 3-33	Infrared spectrum of $[\text{MnL}^2\text{Cl}]\text{ClO}_4$	191
Spec. No. 3-34	Infrared spectrum of $[\text{MnL}^3](\text{ClO}_4)_2$	192
Spec. No. 3-35	Infrared spectrum of $[\text{MnL}^4\text{Cl}]\text{ClO}_4$	192
Spec. No. 3-36	Positive Ion FAB-MS spectrum of $[\text{MnL}^1\text{Cl}]\text{ClO}_4$	193
Spec. No. 3-37	Positive Ion FAB-MS spectrum of $[\text{MnL}^2\text{Cl}]\text{ClO}_4$	193
Spec. No. 3-38	Positive Ion FAB-MS spectrum of $[\text{MnL}^3\text{Cl}]\text{ClO}_4$	194
Spec. No. 3-39	Positive Ion FAB-MS spectrum of $[\text{MnL}^4\text{Cl}]\text{ClO}_4$	194
Spec. No. 3-40	Infrared spectrum of $[\text{ZnL}^2\text{Br}]\text{ClO}_4$	195
Spec. No. 3-41	Infrared spectrum of $[\text{ZnL}^4](\text{ClO}_4)_2$	195
Spec. No. 3-42	Positive Ion FAB-MS spectrum of $[\text{ZnL}^2\text{Br}]\text{ClO}_4$	196
Spec. No. 3-43	Positive Ion FAB-MS spectrum of $[\text{ZnL}^4](\text{ClO}_4)_2$	196
Spec. No. 4-1	Positive Ion FAB-MS spectrum of L	197