

به نام خداوند جان و خرد	کزین برتر اندیشه برنگذرد
خداوند نام و خداوند جای	خداوند روزی ده رهنمای
خداوند کیوان و گردان سپهر	فروزنده ماه و ناهید و مهر
ز نام و نشان و گمان برترست	نگارنده‌ی بر شده پیکر است
به بینندگان آفریننده را	نبینی مرنجان دو بیننده را
نیابد بدو نیز اندیشه راه	که او برتر از نام و از جایگاه
سخن هر چه زین گوهران بگذرد	نیابد بدو راه جان و خرد
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ستودن نداند کس او را چو هست	میان بندگی را بیایدت بست
خرد را و جان را همی سنجد اوی	در اندیشه‌ی سخته کی گنجد اوی
بدین آلت رای و جان و زبان	ستود آفریننده را کی توان
به هستیش باید که خستو شوی	ز گفتار بی کار یکسو شوی
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از این پرده برتر سخن گاه نیست	ز هستی مر اندیشه را راه نیست



Bu-Ali Sina University
Faculty of Chemistry

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Doctor of Philosophy (Ph.D.) in INORGANIC CHEMISTRY**

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**Synthesis and characterization of macroacyclic
and macrocyclic complexes derived from various
mono- and di- aldehydes and some polyamines in
the presence of different metal ions**

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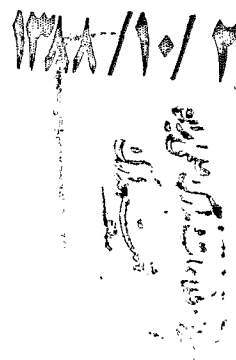
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Dedicated to:

My dear and honourable parents

*My dear and kind wife who accompanied
me all the time*

And

My dear and lovely daughter

Rozhan

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*Thanks for all the great times and helping me through. **I couldn't have done it without you.***



Bu-Ali Sina University

Faculty of Chemistry

In The Name of Allah

**Synthesis and characterization of macroacyclic and
macrocyclic complexes derived from various mono- and di-
aldehydes and some polyamines in the presence of different
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Abstract

Synthesis and characterization of macroacyclic and macrocyclic Complexes derived from various mono- and di- aldehydes and some polyamines in the presence of different metal Ions

By
Reza Azadbakht

In this project six new polyamine ligands and a number of novel complexes of corresponding macrocyclic and macro-acyclic Schiff-base ligands were synthesized and characterized.

Chapter 1: Introduction

Chapter 2: Polyamine ligands synthesis

Three new polyamine ligands of N1-(2-nitrobenzyl)-N1-(2-aminoethyl)ethane-1,2-diamine (L^1), N1-(2-nitrobenzyl)-N1-(2-aminoethyl)propane-1,3-diamine (L^2) and N1-(2-nitrobenzyl)-N1-(3-aminopropyl)propane-1,3-diamine (L^3) were synthesized and their complexes with cadmium (II) ion were prepared. Three new asymmetric tripodal tetraamine ligands, 2-((bis(2-aminoethyl)amino)methyl)benzenamine (L^4), 2-((2-amino-ethyl)(3-aminopropyl)amino)methyl)benzenamine (L^5) and 2-((bis(3-aminopropyl)amino-) methyl)benzenamine (L^6) were synthesized by reducing of the only nitro group of the relevant L^1 , L^2 and L^3 ligands, so that leading to asymmetrical tripodal ligands that contain one primary aromatic amine group and two primary aliphatic amine groups.

Chapter 3: Synthesis and characterization of N_3O_2 macrocyclic Schiff-base complexes with 2-nitrobenzyl side chain

The cyclocondensation of three polyamine ligands of L^1 or L^2 and/or L^3 with 2-[2-(2-formyl phenoxy)ethoxy]benzaldehyde in the presence of various

metal(II) ions were examined. These reactions only in the presence of a stoichiometric amount of cadmium(II) ion gave related cadmium(II) macrocyclic Schiff-base complexes. In the other cases no cyclic complexes have been obtained and metal(II) polyamines were the only products. The complexes have been studied with IR, ^1H NMR, ^{13}C NMR, DEPT, COSY, HMQC and microanalysis. The crystal structures of $[\text{Cd}(\text{NO}_3)(\text{L}^7)(\mu\text{-NO}_3)\text{Cd}(\text{NO}_3)(\text{L}^7)] 0.5\text{Cd}(\text{NO}_3)_4$ (1) (Fig. 3.1) and $[\text{CdL}^7(\text{NO}_3)(\text{CH}_3\text{OH})]\text{ClO}_4$ (2) have been also determined.

Chapter 4: macrocyclic Schiff-base complexes with 2-aminobenzyl pendant arm

[1+1] Macrocyclic Schiff-base complexes containing 1, 2-diphenoxyethane head units and 2-aminobenzyl pendant arm, were synthesized as $[\text{MnL}^{10}(\text{MeOH})](\text{ClO}_4)_2$ (1), $[\text{MnL}^{11}(\text{MeOH})](\text{ClO}_4)_2$ (2), $[\text{MnL}^{12}(\text{MeOH})](\text{ClO}_4)_2$ (3), $[\text{CdL}^{10}(\text{H}_2\text{O})](\text{NO}_3)_2$ (4) and $[\text{CdL}^{11}(\text{H}_2\text{O})](\text{NO}_3)_2$ (5) from the metal ion templated cyclocondensation reactions of 2-[2-(2-formylphenoxy)ethoxy]benzaldehyde with (L^4), (L^5) or (L^6) tripodal tetraamine ligands. The crystal structure determination of (1) and (5) showed that the complex cations that had formed consisted of a pentagonal bipyramidally coordinated Mn(II) and Cd(II) ions, centrally located in a N_3O_2 macrocycle, with one 2-aminobenzyl pendant arm and a solvent molecule in axial positions. The cadmium complexes (4 and 5) have been studied by IR, ^1H NMR, ^{13}C NMR, DEPT, COSY, HMQC and microanalysis.

Chapter 5: Macrocyclic ligand complexes containing pyridine moiety

Cyclocondensation of the asymmetric tripodal tetraamine ligand, 2-((bis(3-aminopropyl)amino)-methyl)benzenamine (L^6), in the presence of Ni(II), Cu(II) and Zn(II) ions, with 2,6-diacetylpyridine (DAP) were investigated. In the presence of Ni(II) ion, only a mono Schiff-base

macroacyclic complex was obtained but in the presence of Zn(II) and Cu(II) ions novel [14]-membered macrocyclic diimine Schiff-base complexes were the final products. Surprisingly, in both cases (Zn(II) and Cu(II)) metal ions 2-aminobenzyl unit is a part of macrocycle. The crystal structures of $[\text{CuL}^{14}](\text{ClO}_4)$ (2) and $[\text{NiL}^{15}](\text{ClO}_4)$ (3) were determined by X-ray diffraction. The zinc complex, $[\text{ZnL}^{14}](\text{ClO}_4)_2$ (1), has been studied by IR, $^1\text{HNMR}$, $^{13}\text{CNMR}$, DEPT, COSY, HMQC and microanalysis.

Chapter 6: Macroacyclic complexes.

$[\text{CdL}^{17}(\text{NO}_3)_2]$, $[\text{CdL}^{18}(\text{NO}_3)_2]$, $[\text{CdL}^{19}(\text{NO}_3)_2]$, $[\text{CoL}^{17}(\text{NO}_3)_2]$, $[\text{CoL}^{18}(\text{NO}_3)_2]$, $[\text{CoL}^{19}(\text{NO}_3)_2]$, $[\text{LaL}^{20}]\text{Cl}_3$ and $[\text{La}_2\text{L}^{21}]\text{Cl}_2$ macroacyclic Schiff-base complexes were prepared by template condensation of 2-pyridinecarboxaldehyde, salicylaldehyde or 3-methoxysalicylaldehyde with L^1 or L and/or L^3 in the presence of corresponding metal ions. The Cd(II) and La(III) complexes have been studied with IR, $^1\text{HNMR}$, $^{13}\text{CNMR}$, DEPT, COSY, HMQC and microanalysis. The complex $[\text{CdL}^{17}(\text{NO}_3)_2]$ (1) has been characterized through X-ray crystallography. In the complex 1 the Cd is in a six-coordinate environment comprised of the ligand N_4 -donor set and two oxygen atoms of two nitrate groups. In the case of reaction of 2-pyridinecarboxaldehyde and L_B (2.6.11.2) and Mn^{2+} one dication (9) compound was also synthesized and crystal structure of 9 has been determined with X-ray crystallography.

Chapter 7: Computational studies

As the crystal structure of some complexes could not be properly refined, we chose *ab initio* molecular orbital calculations to assess the structural parameters of these complexes in gas phase. We undertook a full geometry optimization at the LanL2MB, HF/3-21G* and 6-31G* levels of theory, by using LanL2DZ basis set for some of metal ions. We also undertook the same level of *ab initio* calculations for complexes that we refine the crystal

structures to observe the comparability of the predicted gas phase structural parameters with that determined in the solid state.

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