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کزین برتر اندیشه برنگذرد

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ز نام و نشان و گمان برترست
نگارنده‌ی بر شده پیکر است

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که او برتر از نام و از جایگاه

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ز دانش دل پیر برنا بود

از این پرده برتر سخن‌گاه نیست
ز هستی مر اندیشه را راه نیست

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Bu-Ali Sina University
Faculty of Chemistry

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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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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 metal ions

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

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^3ligands, 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 stiochemiomeytic 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, ^{1}HNMR, ^{13}CNMR, DEPT, COSY, HMQC and microanalysis. The crystal structures of [Cd(NO$_3$) (L^7)(μ- NO$_3$) Cd(NO$_3$) (L^7)] 0.5Cd(NO$_3$)$_4$ (**1**) (Fig. 3.1) and [Cd L^7(NO$_3$)(CH$_3$OH)]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 [MnL^{10}(MeOH)](ClO$_4$)$_2$ (**1**), [MnL^{11}(MeOH)](ClO$_4$)$_2$ (**2**), [MnL^{12}(MeOH)](ClO$_4$)$_2$ (**3**), [CdL^{10}(H$_2$O)](NO$_3$)$_2$ (**4**) and [CdL^{11}(H$_2$O)](NO$_3$)$_2$ (**5**) from the metal ion templated cyclocondensation reactions of 2-[2-(2-formylphenoxy)etho-xy]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$_3$O$_2$ 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, ^{1}HNMR , ^{13}CNMR, 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 $[CuL^{14}](ClO_4)$ *(2) and* $[NiL^{15}](ClO_4)$ *(3) were determined by X-ray diffraction. The zinc complex,* $[ZnL^{14}](ClO_4)_2$ *(1), has been studied by IR,* ^{1}*HNMR ,* ^{13}*CNMR, DEPT, COSY , HMQC and microanalysis.*

Chapter 6: *Macroacyclic complexes.*

$[CdL^{17}(NO_3)_2]$, $[CdL^{18}(NO_3)_2]$, $[CdL^{19}(NO_3)_2]$, $[CoL^{17}(NO_3)_2]$, $[CoL^{18}(NO_3)_2]$, $[CoL^{19}(NO_3)_2]$, $[LaL^{20}]Cl_3$ *and* $[La_2L^{21}]Cl_2$ *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 methal ions. The Cd(II) and La(III) complexes have been studied with IR,* ^{1}*HNMR,* ^{13}*CNMR, DEPT, COSY, HMQC and microanalysis. The complex* $[CdL^{17}(NO_3)_2]$ *(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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