

1. ABSTRACT

The subject of this PhD was macrocyclic compounds derived from *trans*-1,2-diaminocyclohexane and 2,6-diformylpyridine. As part of the conducted research, 12 new macrocycles were obtained, (including 3 macrocycles of very large size) and cryptands, for 8 of them crystal structures were determined. Moreover, 32 new complexes of this type of macrocycles with Cd(II), Zn(II), Cu(II), Ni(II), Pd(II), Co(II), Ag(I), Au(III), Fe(II), Na(I) and K(I) ions were obtained, and crystal structures were determined for 18 of these complexes. Previously known [2+2] **L1** and [4+4] **L5** macrocycles formed in the condensation of racemic *trans*-1,2-diaminocyclohexane and 2,6-diformylpyridine were used as substrates for further syntheses. A method has been developed for the purification of imine macrocycle **L5** contaminated with macrocycle **L1**, based on the use of selective complexation of macrocycle **L1** in the presence of lead nitrate(V). In this reaction, macrocycle **L2** is also recovered as the reduced form of macrocycle **L1**. The pure macrocyclic imine *meso*-**L5** was reduced to obtain the analogous macrocyclic amine *meso*-**L6**.

A method has been developed to obtain large macrocyclic amines by using unusual "stitching together" reaction of several units of the *meso*-[2+2] type macrocyclic imine **L1** templated by cadmium(II) ions. The products of this reaction are large even-numbered imine macrocycles [6+6], [8+8], etc. in the form of complexes with Cd²⁺ ions, which then subjected to reduction and demetallation lead to macrocyclic amines. A method has been developed for the separation of [6+6] **L8** and **L10** amine macrocycles in the form of mineral acid salts. A library of dynamic cadmium imine complexes derived from *rac-trans*-1,2-DACH and 2,6-DFP was studied. The conditions for obtaining products with kinetic and thermodynamic stability were determined.

Macrocyclic amine [2+2] **L2** was used in an *N,N*-alkylation reaction to obtain cryptand **M22** containing two additional pyridine fragments, capable of binding Na⁺ and K⁺ ions. A half-cryptand **M21** containing one additional pyridine fragment was also obtained by this type of reaction, which was then used to obtain transition metal complexes.

For all the obtained macrocycles: **L6**, **L8**, **L10**, **M21**, **M22**, full spectroscopic characterization was performed based on 2D NMR and ESI MS methods, as well as X-ray structural analysis of derivatives with mineral acids. For ligands **L6**, **L8**, **M21** and **M22**, a study of coordination ability was carried out for transition metals of the periodic table. For ligand **L6**, complexation was carried out using salts: CuSO₄, CoSO₄, NiSO₄, ZnSO₄, Ag₂SO₄, CuCl₂, ZnCl₂, PdCl₂, AuCl₃, K[AuCl₄] and Zn(NO₃)₂. The crystal structures of these complexes show a reach variety of complexation modes of **L6** resulting in interesting polynuclear complexes. For ligand **L8**, complexation was carried out using salts: CuSO₄, Cu(NO₃)₂, CuCl₂, and ZnCl₂ leading to hexanuclear complexes. For ligand **M21**, complexation was carried out using salts: CuSO₄, CoSO₄, NiSO₄, ZnSO₄, FeSO₄, CuCl₂,

CoCl₂, NiCl₂, ZnCl₂, Cu(NO₃)₂, Ni(NO₃)₂, and Zn(NO₃)₂ leading to mononuclear complexes of unique coordination sphere. Full spectroscopic analysis was carried out for all the complexed compounds obtained, and X-ray-structural measurements were performed for the resulting monocrystals.