

**Babeş-Bolyai University**  
**Faculty of Chemistry and Chemical Engineering**

**SYNTHESIS OF SOME CROWN ETHERS WITH  
AROMATIC PENDANT ARMS AND OF SOME  
METAL ORGANIC FRAMEWORKS**

**Summary of Phd Thesis**

**Maria COROŞ**

**Scientific Advisor:**  
**Prof. Dr. Mircea VLASSA**

**Cluj-Napoca**

**2010**

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**Cluj-Napoca**

**2010**

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Keywords: perazacrown ethers, macropolycyclic compounds, metal organic frameworks.

## ***INTRODUCTION***

The first chapter contains synthesis of polyamines; many amines are now commercially available; the available compounds include tri and tetra amines with a mix of ethylene, trimethylene and tetramethylene units between the nitrogen atoms. Of particular interest are tetraamines where the two internal amines are tertiary and the terminal amines are secondary. These compounds can be used in the ring closure reaction to form the perazacrown ethers.

Peraza-crown ethers form the most numerous group of polidentated macrocycles and, therefore, the most studied. The interest given to them has its explication in their numerous applications due to their unique and selective property to form complexes with cations, anions and organic molecules. Their complexes are used in the most different fields of human activity: treatment of poluted waters<sup>1</sup>, as well as artificial enzymes<sup>2</sup> or agents of contrast in NMR imaging,<sup>3</sup> in the treatment of cancer or SIDA,<sup>4</sup> to mobilize stem cells<sup>5</sup> or as catalysts<sup>6</sup> etc. They are also blocks of construction in the synthesis of natural products with potential pharmaceutical actions.<sup>7,8</sup>

The first two parts include a study of literature with regard to the methods of synthesis used to obtain polyamines, as well as methods of functionalization of crown ethers. The third part presents the original contributions brought in the studies carried out on some polyamines with the purpose of using them in the construction of some supramolecular structures. The researches followed several directions: the preparation of new polyamines, the methods of synthesis for these polyamines which were used to obtain the appropriate peraza crown ethers, the synthesis of cyclen and methods of monofunctionalization of cyclen and of cyclam.

The second chapter treats an interesting field, which is developing at an extraordinary pace, the study of metal–organic frameworks (MOFs). This class of compound includes coordination polymers comprising metal ions bridged by organic ligands.

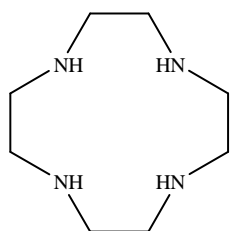
The chemistry of metal–organic frameworks (MOFs) is in continuous development, with an exponential growth in the number of research papers and reviews appearing in the chemical literature.<sup>9</sup>

These materials are compounds that contain both inorganic and organic moieties as parts of a network with infinite bonding connectivity in at least one dimension. This definition excludes systems in which the organic part is merely a guest inside an inorganic porosity like the zeolites. The hybrid frameworks are divided into two categories: 1) The coordination polymers or Metal Organic Frameworks which are defined as extended arrays composed of isolated metal atoms or clusters that are linked by polyfunctional organic ligands and 2) the extended inorganic hybrids which often contain infinite metal-oxygen-metal arrays as part of their structure.

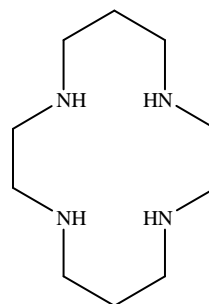
In the literature part are presented the methods of synthesis for metal organic frameworks and their utilization. The original contribution part presents the synthesis and analysis of some crystalline, microporous compounds from the family of metal organic structures. The characterization of the products was made through spectroscopy IR, X-ray diffractometry in powder, thermogravimetric analysis, adsorption/desorption of nitrogen at 77K.

## ***1.1. SYNTHESIS OF POLYAMINES***

In this paper are presented the synthesis and characterization of some new polyamines which were used to obtain the appropriate peraza crown ethers. Cyclen (1, 4, 7, 10-tetraazacyclododecan) and cyclam (1, 4, 8, 11-tetraazacyclotetradecan) are amongst the perazacrown ethers which are most used in the preparation of many important molecules with practical applications as contrast agents in NMR imagistic or as sensors for fluorescent samples and for heavy metals<sup>12, 13</sup> (cyclen) or in medicine<sup>14</sup> (cyclam).



Cyclen



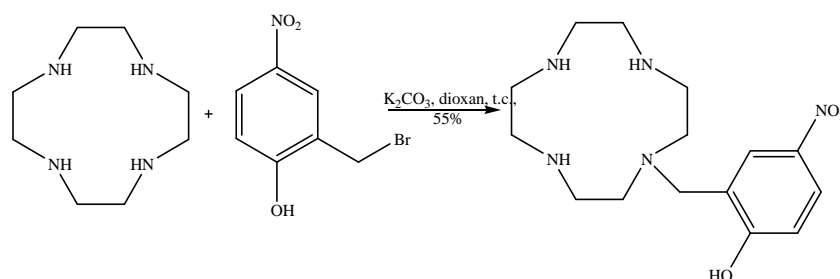
cyclam

## ***1.2. SYNTHESIS OF FUNCTIONALIZED CROWN ETHERS***

Mainly, there are three general methodologies for the synthesis of *N*-functionalized crown ethers: synthesis from acyclic precursors, alkylation of cyclen, and treatment of cyclen with acylation and sulfonylation reagents, or combinations thereof.

The synthesis of cyclens from acyclic precursors is the oldest methodology and often requires manipulation of protective groups in order to obtain the desired product. Taking into account that cyclen is now commercially available, contemporary syntheses of *N*-functionalized cyclens are commonly achieved by its direct *N*-functionalization by using a wide variety of alkylating, acylating and sulfonylating agents.

The *N*-monosubstituted benzyl cyclen can be obtained (55% yield, after chromatographic separation) upon stirring (at room temperature) the mixture of cyclen (1), 2-hydroxy-5-nitrobenzyl bromide and K<sub>2</sub>CO<sub>3</sub> in dioxane:<sup>43</sup>



### 1.3. ORIGINAL CONTRIBUTIONS

This chapter presents the original contributions brought in the studies carried out on some polyamines with the purpose of using them in the construction of some supramolecular structures. The researches followed several directions:

- the preparation of new polyamines, the methods of synthesis for these polyamines which were used to obtain the appropriate peraza crown ethers,
- the synthesis of cyclen and
- methods of monofunctionalization of cyclen and of cyclam.



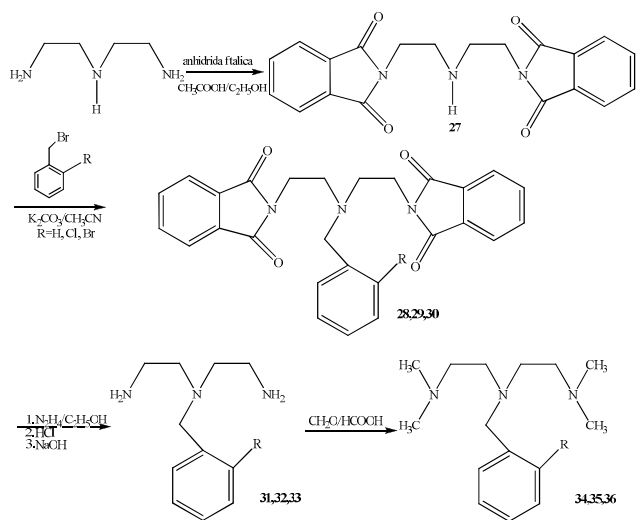
### *1.3.1. Synthesis of permethylated diethylenetriamines*

The method used for synthesizing polyamines consists in the protection of the primary amino groups, functionalization of the secondary amine, then deprotection.

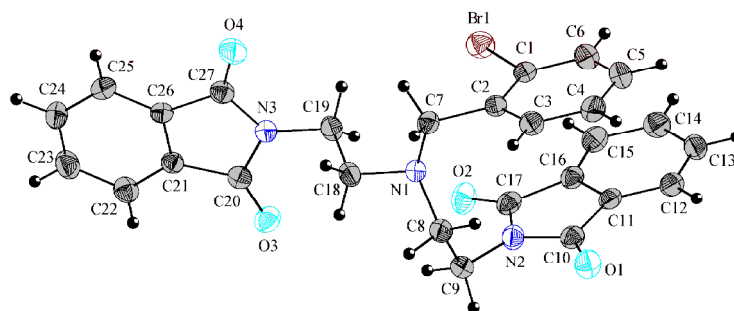
For obtaining N, N''-tetramethyl-N'-benzil diethylenetriamines, with chloride or bromide in the position *orto* of the benzenic nucleus, commercially available diethylenetriamine was used as raw material. The issues that intervene in the synthesis of the above mentioned compounds are due to the fact that the raw material contains primary amino functions and an internal tertiary amine. In this case the primary amino groups must be protected with phthalil groups, bisphthalimides being obtained.

The synthesis of the compounds **34**, **35**, **36** begins by protecting the primary amino groups through phthalilation, being used for that the phthalic anhydride in acetic acid. In order to precipitate the protected amine ethanol is added, after the acetic acid was removed through distillation.<sup>56</sup> The next stage involves the methylation or benzilation of the tertiary nitrogen atom. Methylation is made in formic acid with paraformaldehyde; after neutralization the desired compound is obtained as a white precipitate.<sup>57</sup> Benzilations take place in acetonitril, with potassium carbonate and benzyl bromide, bromo-benzyl bromide or chloro-benzyl bromide, as necessary. The mixture is refluxed for 48 hours then it is processed, benzilated compound powders<sup>58</sup> being obtained.

For deprotection a hidrazinolisis was made (in the case of benzilated polyamines) or acidolisis (for methylated amine) the result being free amines. In the end, the compounds were permethylated through reductive methylation, a mixture of paraformaldehyde and formic acid being used:<sup>57</sup>



Intermediate **30** was analyzed in detail.

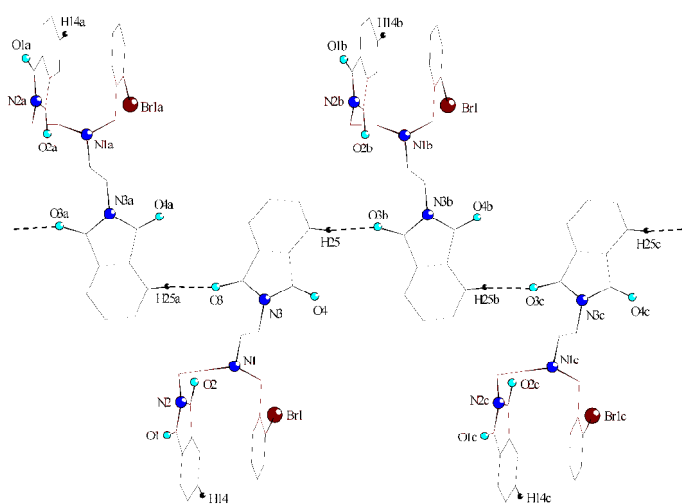


**Figure I.6.** ORTEP plot of [2-{1',2'-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>}<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (**30**)

The molecule of **30** (Fig. I.6) exhibits three basically planar fragments: two phthalimido-containing C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NC fragments and the CC<sub>6</sub>H<sub>4</sub>Br group. As a result, the NC<sub>3</sub> cores including the N(2) and N(3) atoms are planar, with different nitrogen-carbon distances, *i.e.* two shorter N-C(sp<sup>2</sup>) bonds (ca. 1.39 Å) from the aromatic phthalimido moiety and a longer N-C(sp<sup>3</sup>) bond (ca. 1.45 Å). The third NC<sub>3</sub> core around the N(1) of the pendant arm is, as expected, distorted *pseudo*-tetrahedral, with N-C(sp<sup>3</sup>) bond distances of about 1.46 Å. An interesting feature of the molecule of **30** is that one of the arms bearing a phthalimido group is twisted to bring the planar C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NC fragment almost parallel to the CC<sub>6</sub>H<sub>4</sub>Br fragment [C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>N(2)C/ CC<sub>6</sub>H<sub>4</sub>Br dihedral angle 3.6°], a behavior which might be due to some π-π interaction between the two

aromatic systems. The second arm is twisted in opposite direction with its  $C_6H_4(CO)_2NC$  fragment almost orthogonal to the previous two planar systems [ $C_6H_4(CO)_2N(3)C$  /  $C_6H_4(CO)_2N(2)C$  and  $C_6H_4(CO)_2N(3)C$  /  $CC_6H_4Br$  dihedral angles of  $88.1^\circ$  and  $84.8^\circ$ , respectively].<sup>60</sup>

A closer check of the crystal structure revealed that the molecules are associated into chain polymers (Fig. I.7) through intermolecular  $O(3)\cdots H(25a)$  ( $2.41 \text{ \AA}$ ) contacts shorter than the sum of van der Waals radii for the corresponding atoms [cf.  $\Sigma r_{vdW}(O,H)$  ca.  $2.60 \text{ \AA}$ ].<sup>61</sup>



**Figure I.7.** View of the chain polymer association in the crystal of **30** based on intermolecular  $O\cdots H$  contacts (only hydrogens involved in such contacts are shown) [symmetry equivalent atoms  $(x, 2.5 - y, 0.5 + z)$ ,  $(x, 2.5 - y, -0.5 + z)$ , and  $(x, y, -1 + z)$  are given by ‘a’, ‘b’ and ‘c’].

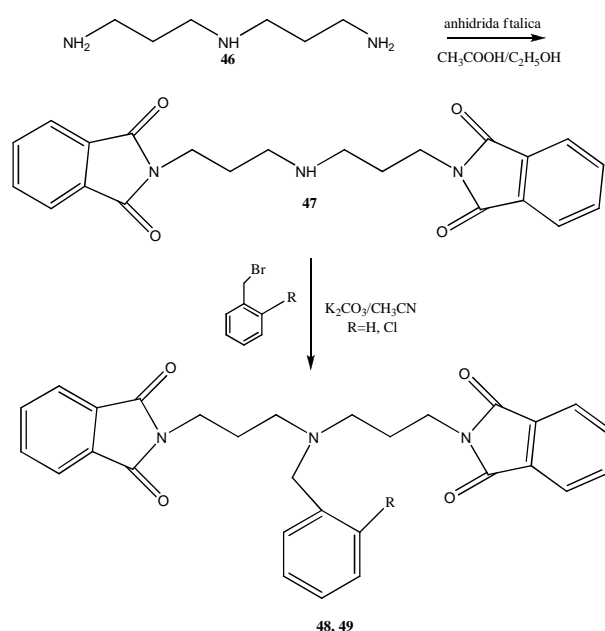
### ***I.3.2. Synthesis of polyamines subjected to a study of lipophilicity***

Lipophilicity is a property of a molecule which depends on and can be changed by modifications in its molecular structure.<sup>67</sup> Lipophilicity of some of the synthesized polyamines was determined by the use of reversed phase thin- layer

chromatography and was compared with the lipoficity values calculated by computational methods.

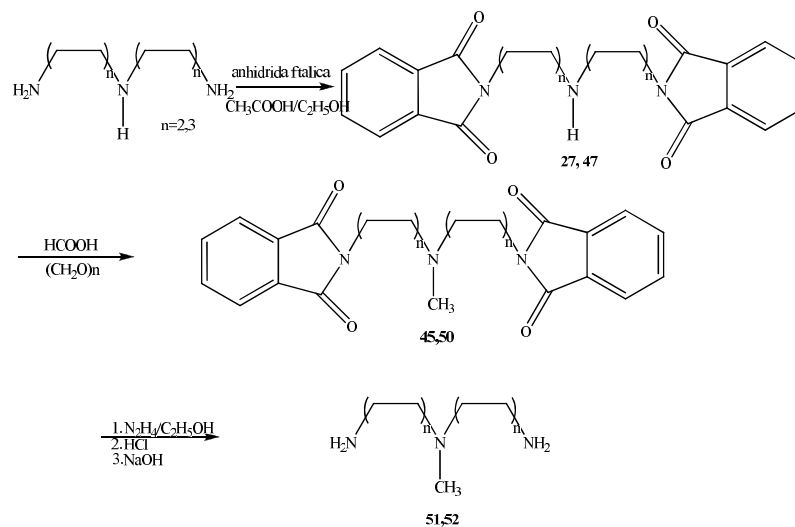
### *1.3.3. Synthesis of benzylated propilentriamines*

Polyamines having as raw material N-(3-aminopropil)-1,3-propane diamine (norspermidine-comercially available) were also synthesized:

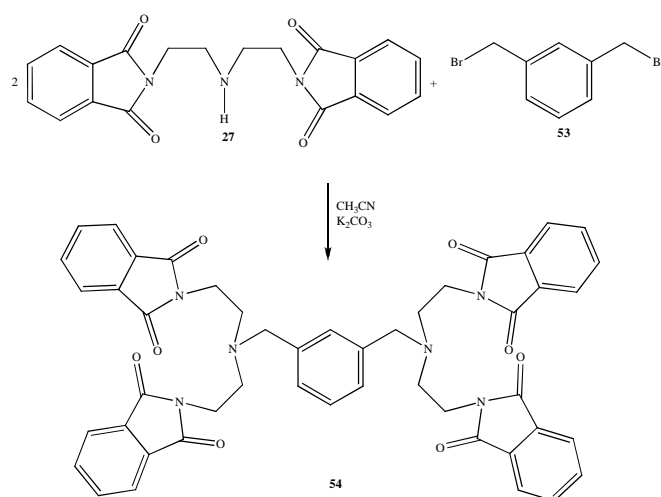


### *1.3.4. Synthesis of methylated and benzylated diethylenetriamine*

Phthalylated diethylenetriamine was also methylated, the compound being used to obtain the cyclen functionalized with methyl:



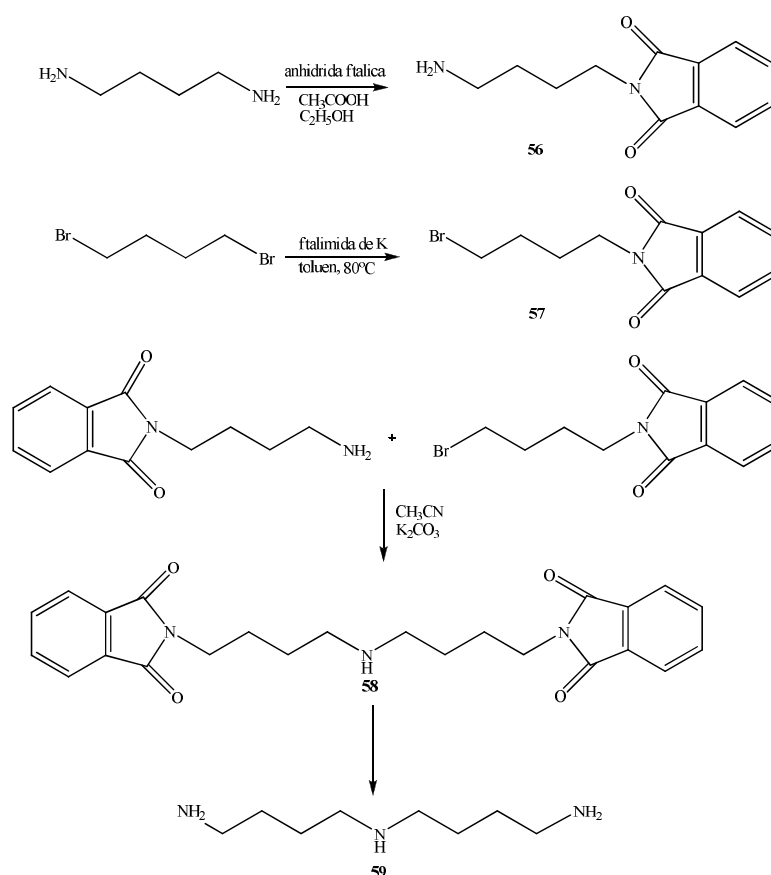
With the purpose of synthesizing a macrocycle with possible usages in medicine, we obtained the compound **54** starting from diethylenetriamine protected in reaction with  $\alpha, \alpha'$ -dibromo m-xilen:



It is to be used in a reaction of cyclization with tritosilated diethanolamine; after deprotection monofunctionalization with 4-bromobutylphthalimide will be tried.

### 1.3.5. Synthesis of spermidine

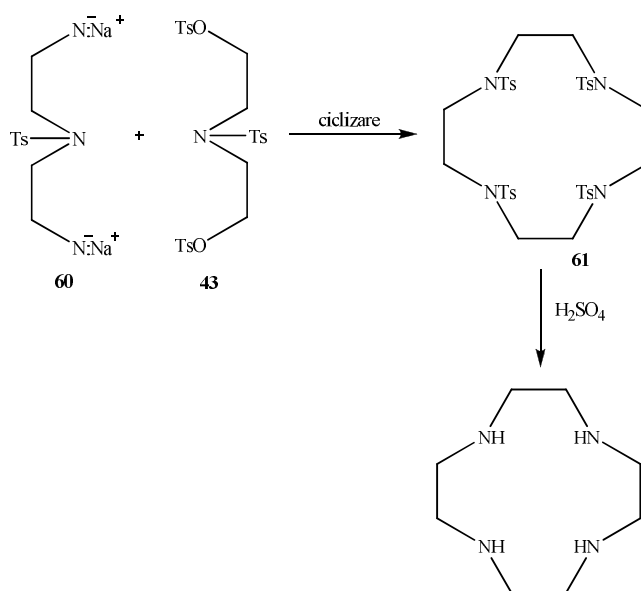
Tetraethyltriamine (spermidine) (**59**) was synthesized in  $\text{CH}_3\text{CN}$ , in the presence of  $\text{K}_2\text{CO}_3$ , through the reaction between 1,4-monophthalilated diaminobutane (**56**) and 1,4-monophthalilated dibrombutane (**57**).



### 1.3.6. Synthesis of cyclen

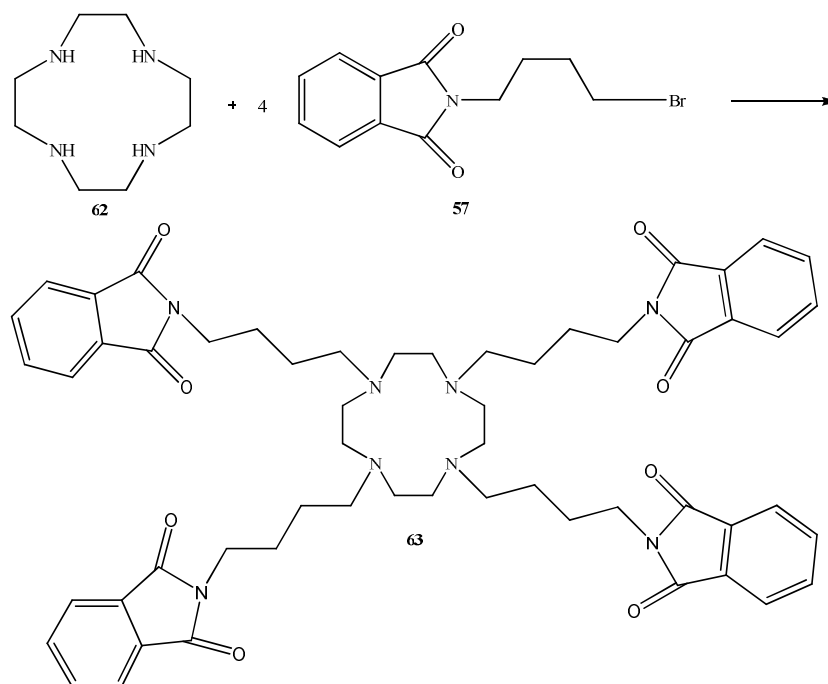
For the synthesis of tetratosilated cyclen (**61**), the salt of sodium of tritosilated diethylenetriamine was first prepared, which dissolved in DMF, to this solution was added a solution of tosilated diethanolamine (**43**). The mixture was maintained at  $100^\circ\text{C}$  for 2 hours. After cooling, water is added and the

tetratosilated cyclen precipitates. For detosilation, the tosilated cyclen was treated with  $\text{H}_2\text{SO}_4$ :



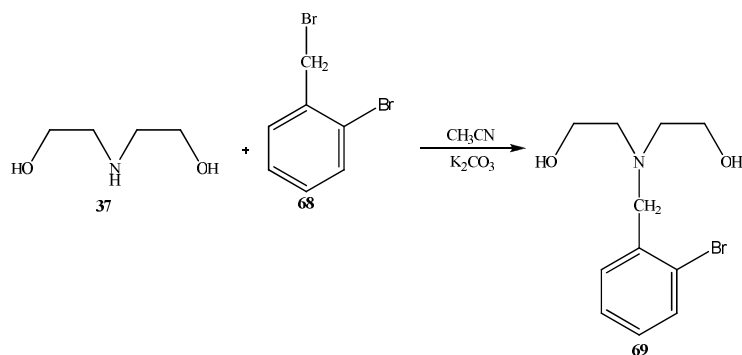
### *1.3.6.1. Synthesis of tetrafunctionalized cyclen*

Cyclen was functionalized by reaction with N-(4-bromobutyl)-phthalimide, obtained by monophtalilating 1,4-dibromobutane:

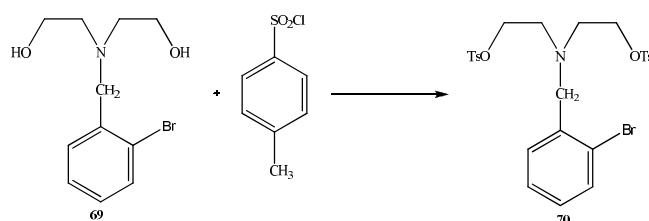


### ***1.3.6.2. Synthesis of monofunctionalized cyclen from acyclic precursors***

To obtain the monofunctionalized cyclen it went on from the diethanolamine which was benzylated, then tosylated, following next the stage of cyclization with the salt of sodium of the tritosylated diethylenetriamine:







The structural analysis of these compounds was carried out using the X-ray diffraction (for one of the compounds), the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra at room temperature, COSY and HMQC spectra.

### *II.1. Synthesis of MOFs*

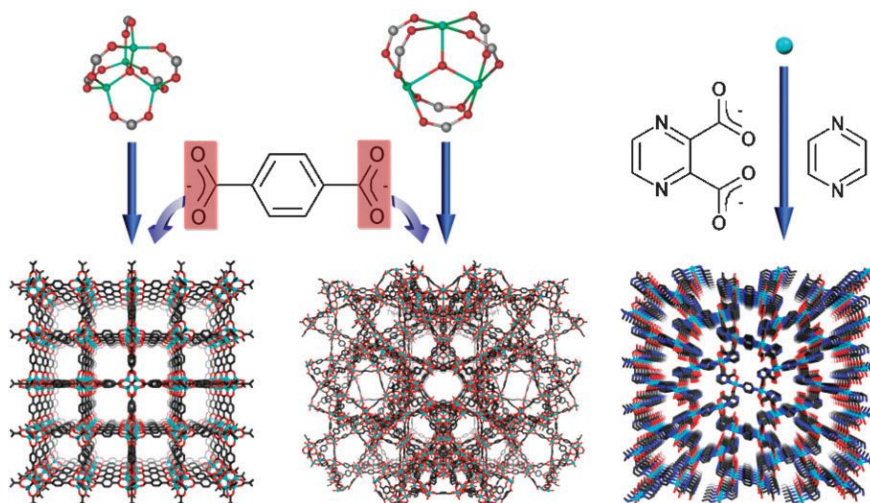
Porous materials encompass a wide range of adsorbents.<sup>85,86-94</sup> Some of them, such as zeolites, are structurally uniform with well-defined pore sizes and shapes, whereas others are less structurally-defined containing pores with a wide variety of sizes. Historically, the porous materials are defined depending on their property of adsorption.<sup>95</sup>

In the past decade, a new class of synthetic porous materials, metal–organic frameworks (MOFs),<sup>96-98</sup> also called porous coordination polymers (PCPs),<sup>99</sup> porous coordination networks (PCNs),<sup>100</sup> or other names,<sup>101</sup> has been developed into one of the most prolific areas of research in chemistry and of materials.

While the initial focus in the field of MOFs was the synthesis and structural characterization, an increasing number of MOFs are now being explored for their interesting properties, including optic,<sup>102,103-107,108-114</sup> magnetic and electronic properties,<sup>115-119</sup> as well as their various potential applications such as catalysis,<sup>120-124</sup> ion exchange,<sup>101,107,125-127</sup> gas storage,<sup>128-134</sup> separation of mixtures of gas or liquids,<sup>135-138</sup> sensing,<sup>139-142</sup> polymerization,<sup>143-145</sup> and drug delivery.<sup>146-148</sup> MOFs are ideal adsorbents for gas storage and gas separation due to their large surface areas, adjustable pore sizes. Selective gas adsorption and their separation represent

one of the most active areas of research in the study of MOFs. <sup>149</sup> Currently, the investigation of MOFs as adsorbents in gas separation is in its early stage.

The figure below presents three examples for the construction of MOFs: <sup>150-152</sup>



## ***II.2. ORIGINAL CONTRIBUTIONS***

The purpose of this paper is the synthesis and analysis of some crystalline, microporous compounds from the family of metal-organic structures. The characterization of the products was made through IR spectroscopy, X-ray diffractometry in powder, thermogravimetric analysis, adsorption/desorption of nitrogen at 77K.

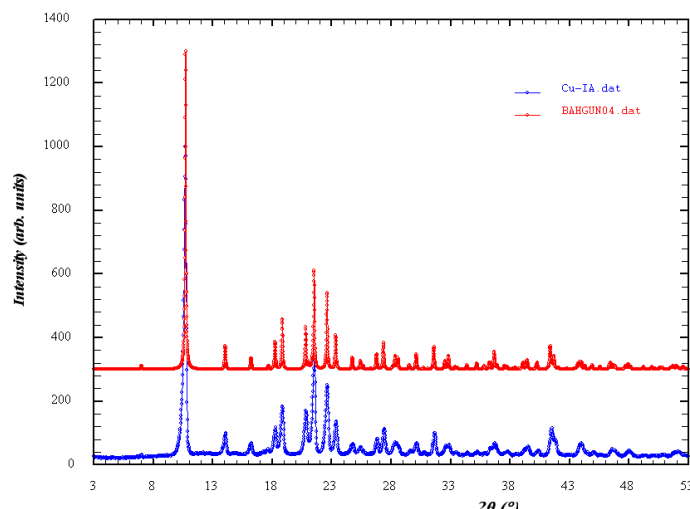
### *II.2.1. Synthesis Cu(INA)<sub>2</sub>*

We obtained Cu(INA)<sub>2</sub> by two different methods: in solid state and solvothermic in the attempt to increase the specific surface of the compound and, implicitly, its capacity to stock hydrogen.

#### *Synthesis Cu(INA)<sub>2</sub> in solid state*

We belabored Cu(OAc)<sub>2</sub> · H<sub>2</sub>O with izonicotinic acid (INA), for 30 minutes. During the belaboring, acetic acid was disengaged and the changing of the colour from green to blue was noticed. The belabored mixture was left under argon for 72 hours. It was degassed at 125°C, under vacuum. DMF was added over the solid mixture. After purification, the compound was analized. A compound of dark blue colour, **74a**, was obtained. At measuring the specific surface the sample was first degassed at 180°C.<sup>172</sup>

In literature, there are presented seven crystalline structures for Cu(INA)<sub>2</sub> registered in CCD, presented as: BAHGUN, BAHGUN 1, BAHGUN 2, BAHGUN 3, BAHGUN 4, UFUMUD and UFUMUD 1. The X-rays diffractogram in powder of compound **74a** was compared with the seven diffractogrames simulated from the dates of monocrystal existing in Cambridge Crystallographic Database, the perfect superposition being over codified diffractogram BAHGUN 4, being confirmed, in this way, the obtaining of the desired structure.

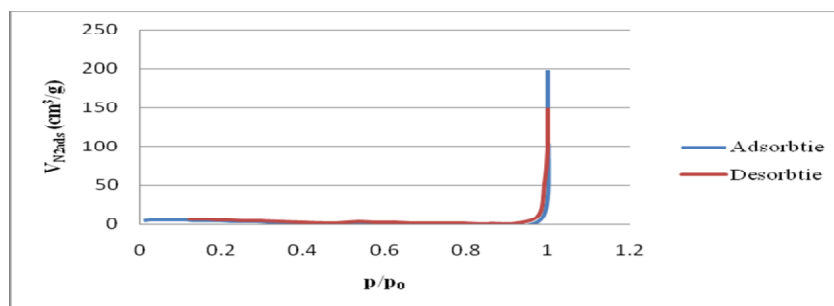


**Figure II.8.** Diffractogram XRD in powder of **74a** (blue) and diffractogram  $\text{Cu(INA)}_2$  simulated from cristalographic data (red)

### **II.2.1.2. Solvothermic synthesis of $\text{Cu(INA)}_2$**

$\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$  is dissolved in ethanol and izonicotinic acid in DMF. The obtained solutions are mixed and put in a steamer. The steamer is sealed and put in the oven, set to warm up at  $110^\circ\text{C}$ . This temperature is maintained for 24 h. After cooling at room temperature, the product is separated through draught and is purified by maintaining it under DMF, which is changed 6 times at a day interval. Activation is made by changing the solvent from pores with  $\text{CH}_2\text{Cl}_2$ , in the same manner as in the case of purification, and by thermic degassing under dynamic vacuum. A blue solid crystalline product, **74b**, is obtained.

The porosity of compound **74b** was studied by means of the same method as for compound **74a**, by volumetric method. The isotherms of adsorption/desorption are type I (Langmuir), so it is a microporous compound (*Figure II.13.*). From the dates of fisorption there were obtained values of  $120 \text{ m}^2/\text{g}$  for  $S_{\text{BET}}$  and  $0.1 \text{ cm}^3/\text{g}$  for the specific volume of the pores.



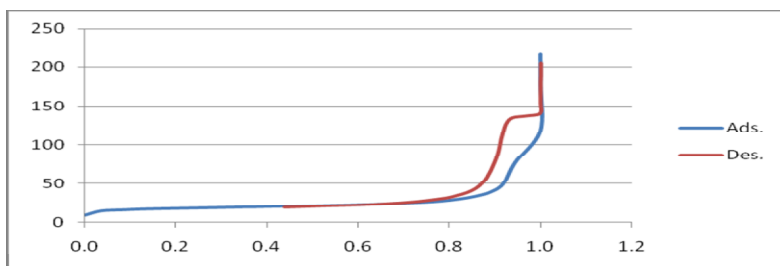
**Figure II.13.** Isothermes of adsorption/desorption of nitrogen in compound **74b**, at 77K

### **II.2.2. Synthesis $\text{Cu}_2(\text{BDC})_2$**

We synthesized  $\text{Cu}_2(\text{BDC})_2$  through a new method, in solid state, compound **75a**. For this, acetate of monohydrate Cu was belabored for 30 minutes with terephthalic acid 98%. A light blue solid resulted. For the purification/activation of the compound: DMF was added and was stirred for 24 hours. It was filtered, methylene chloride was added and was left over night. The solvent was decanted, and the solid was degassed 4 hours at 120°C. The characterization of the product was made by IR spectroscopy, thermogravimetric analysis, adsorption/desorption of nitrogen at 77K.

Given the small specific surface obtained by this method, we synthesized  $\text{Cu}_2(\text{BDC})_2$  by other methods as well. Acetate of Cu and terephthalic acid were dissolved in DMF and were put in a steamer. A blue gel was formed. The steamer was sealed and put in an oven at 100°C. Analysis proved that the same  $\text{Cu}_2(\text{BDC})_2$  was obtained. The porosity of the compound **75b** was studied, the dates obtained being compared to those of the compound **75a**.

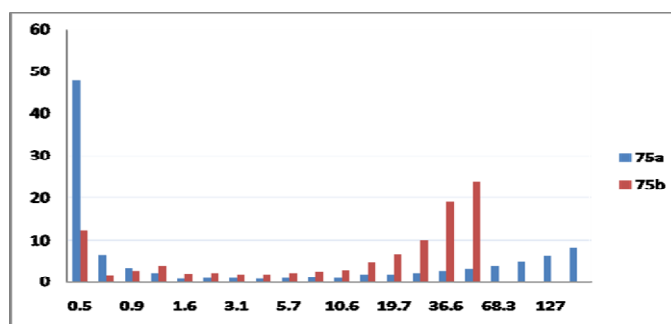
From the dates of fisisorption there were obtained values of 66  $\text{m}^2/\text{g}$  for  $S_{\text{BET}}$  and 0.11  $\text{cm}^3/\text{g}$  for the specific volume of the pores. Isotherms are of Langmuir type, confirming the permanent microporosity of the sample:



**Figure II.17.** Isotherms of adsorption/desorption of nitrogen in compound **75b**, at 77K

The isotherm present hysteresis of type H2, so the structure of the pores is complex and tends to consist of interconnected networks of pores with different sizes and shapes.<sup>190</sup> This type of hysteresis loop is related with the capillary condensation in mezopores.

From the graphic of distribution of the pores comes out that **75a** has its pores distributed as follows: micropores 59.57%, mezopores 14.08% and macropores 26.35%, and in **75b** distribution is: micropores 20.4%, mezopores 55.77% and macropores 23.83%.

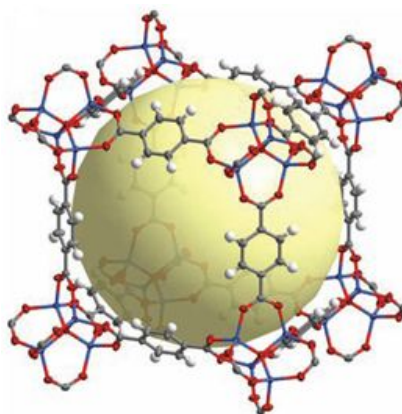


**Figure II.18.** Distribution of pores in **75a** (blue) and **75b** (red)

### ***II.2.3. Synthesis MOF-5***

MOF-5 is the most investigated metal-organic structure due to its large specific surface and to cheap raw material<sup>150,191,192,193,194</sup>.

In *figure II.20*. MOF-5 structure is presented in the form of ZnO<sub>4</sub> tetrahedrons connected by phenylene dicarboxylic units to form a cubical network with small pores (of 8 Å) and a big pore, spherical (with diameter of 12 (15) Å), submitted in the cube. The diameter of the big pore is determined by the distance between the van der Waals surfaces of the atoms.<sup>196</sup>



***Figure II.20.*** Structure MOF-5 (C-black, H-white, O-red, Zn-blue)

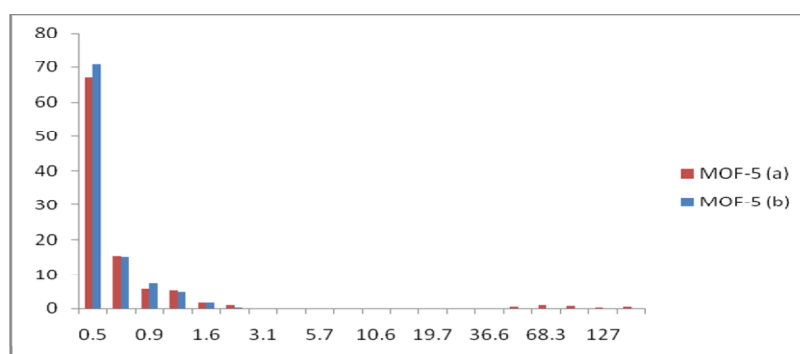
We synthesized MOF-5 by two different methods with the purpose of obtaining a compound with the biggest possible specific surface. The IR analysis for the two synthesized compounds confirm the obtaining of MOF-5, the dates obtained corresponding to those in literature.<sup>192</sup>

For the obtaining of MOF-5(a) we dissolved Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and terephthalic acid 98% in DMF and H<sub>2</sub>O, the mixture being warmed at 100°C for 22 hours, without magnetic stirring. White crystals were obtained. After cooling, the solvent

was decanted, introduced under Ar. The efficiency of the synthesis was of 92%. We also synthesized MOF-5(b), solvothermic, in teflon steamer at 100°C, for 24 hours, the efficiency being of 52%.

The purification of the two compounds was made by washing them with absolute DMF, leaving the solid, each time, in DMF, for 8 hours. DMF was decanted and the solid was washed with absolute CH<sub>2</sub>Cl<sub>2</sub>, leaving the solid, each time, in CH<sub>2</sub>Cl<sub>2</sub>, for 8 hours. After the last wash, CH<sub>2</sub>Cl<sub>2</sub> was syphoned and the pores were evacuated under dynamic vacuum.

The distribution of the pores for the two samples is reproduced in *figure II.22*. MOF-5 (a) and MOF-5 (b) have 82.34, respectively 85.58 % of the pores in the field of micropores (diameter smaller than 2nm) situations confirmed also by the type of the isotherms (*figure II.21*). The smaller the dimensions of the pores the bigger the energy of adsorption, as the vicinity of the walls intensifies the interactions adsorbate-adsorbent, decreasing also the relative pressure at which their filling happens.



**Figure.II.22.** Distribution of the pores in MOF-5 (a) (red) and MOF-5 (b) (blue)

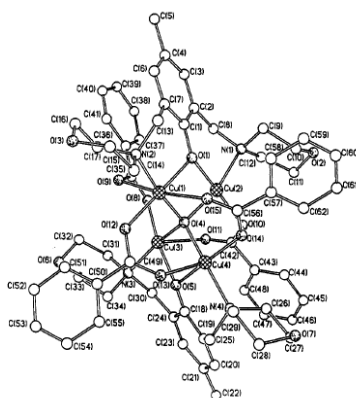
In conclusion, two samples of MOF-5 were synthesized, but their specific surfaces are not larger than those reported in literature; MOF-5 having one of the



largest specific surfaces:  $S_{\text{BET}}$  of 3800 m<sup>2</sup>/g and  $S_{\text{Lang}}$  of 4400 m<sup>2</sup>/g, the measured volume of the pores being of 1.55 cm<sup>3</sup>/g.<sup>191</sup>

#### ***II.2.4. Synthesis of compounds of the type $\text{Cu}_4\text{O}(\text{acid})_2(\text{ligand})_2$***

Bertrand and Bock<sup>197</sup> characterized the first complex with tetranuclear copper, with the formula  $[\text{Cu}_4\text{OX}_{10-n}\text{L}_n]_{n-4}$  where X represents a halogen ion and L is a ligand. Numerous compounds of this type were synthesized ever since, with the formula  $\text{Cu}_4\text{OX}_6\text{L}_4$ , X= Br, Cl. All these compounds have identical basic structure: four atoms of copper disposed in the corners of a tetrahedron around the central atom of oxygen and the atoms of halogen on the edge of the tetrahedron. The first complex of this type in which the halogen ions were replaced with benzoate groups is presented in *figure II.24*.



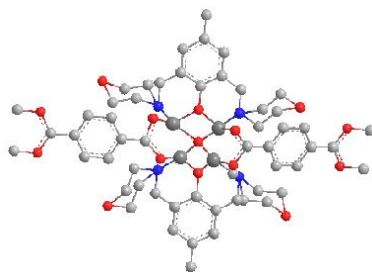
***Figure II.24.*** The first structure of type  $\text{Cu}_4\text{O}(\text{OBz})_4(\text{bmmk})_2$

With the help of 2,6-bis-(morpholinomethyl)-4-methylphenol we succeeded in synthesizing new polymers of type  $\text{M}_4\text{O}(\text{acid})_2$  ( $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_3$ )<sub>2</sub>, given that, by replacing the benzoic acid from the complex in *figure II.24* with a dicarboxylic acid, metal-organic structures might be obtained.

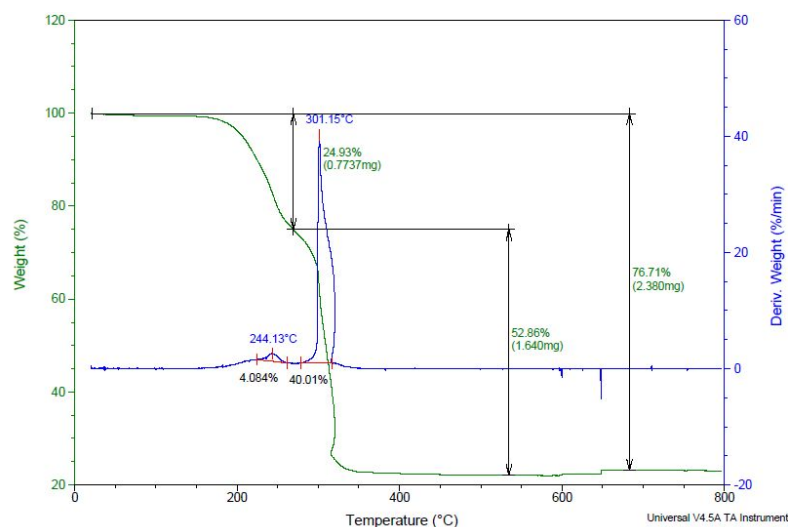
#### *II.2.4.1. Synthesis $\text{Cu}_4\text{O}(\text{BDC})_2(\text{bmmk})_2$*

For the obtaining of  $\text{Cu}_4\text{O}(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_3)_2$  (**76**), a solution of Hbmmk in methanol was added to a solution of copper perchlorate in methanol, by adding the Hbmmk solution the blue solution of copper perchlorate became green. To this mixture was added, under stirring, a solution of terephthalic acid in DMF. The solution was stirred for an hour at room temperature, a blue precipitate being obtained. After purification and desolvation a blue product was obtained, insoluble in organic solvents, which was analysed later on. The replacement of copper perchlorate with copper nitrate and that of methanol with ethanol did not major influenced the forming of the compound, the only difference being a slight increase of the efficiency when ethanol was used as a solvent.

A hypothetical structure of compound **76** is represented in the figure from below (C-gray, N-blue, O-red, hydrogen atoms were excluded for clarity):



The thermogravimetric analysis was made in air, with a heating of  $5^\circ\text{C}/\text{min}$ . The DSC-TGA curves prove that the product is thermally stable up to  $300^\circ\text{C}$ .



**Figure II.26.** TGA curve for compound **76**

From the thermogravimetric analysis can be determined if the expected formula of the compound is the correct one. The expected formula for compound **76** is:  $\text{Cu}_4\text{O}(\text{C}_8\text{H}_4\text{O}_4)_2 (\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_3)_2$ , the molecular mass being 1212. From the thermogram it is observed that the decomposition of the compound starts at 200°C. From the thermogravimetric curve comes out that the product no longer contains solvent. The first loss of weight (24.93%) could be due to the loss of acid, then of the fragment of bmmk (52.86%), the remaining waste being copper oxide (22.21%).

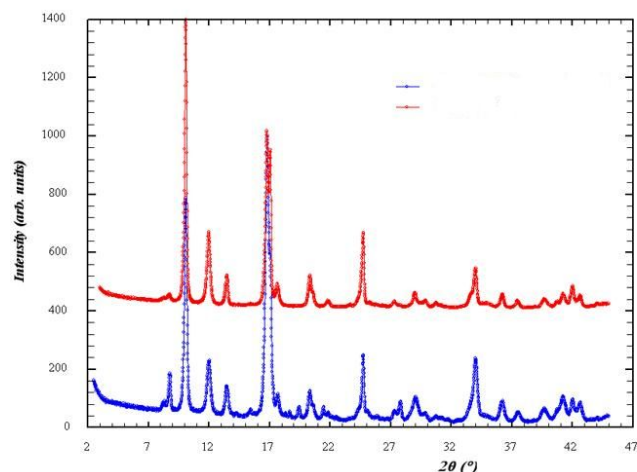
In *tabel II.1.* are the calculated values and the experimental ones:

**Tabel. II.1.**

	<b>BDC (%)</b>	<b>Bmmk (%)</b>	<b>Copper oxide (%)</b>
experimental	24.93	52.86	22.21
calculated	27.06	50.49	22.44

The close values between experimental and theoretical prove that the expected formula is correct. The analyses of X-rays is to be carried out for the exact confirmation of the structure.

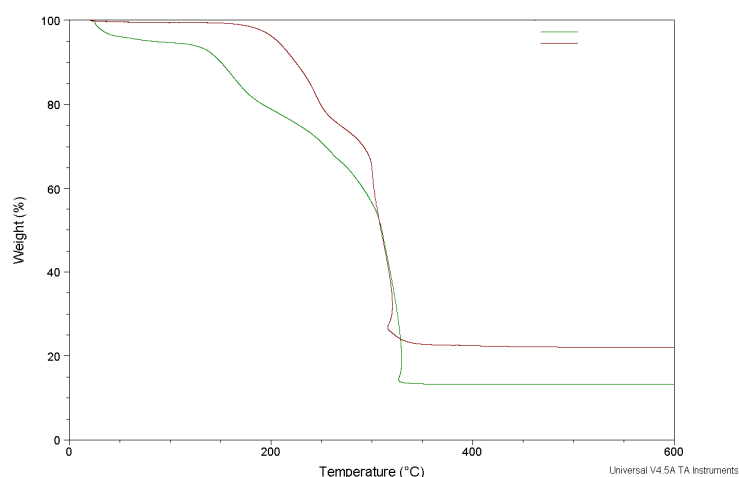
The comparison of X-rays diffractograms in powder of the compound **76**, synthesized with copper perchlorate, with the ones of the compound **77**, synthesized with copper nitrate, proves that the replacement of the perchlorate with nitrate did not influenced the crystallinity of the final compound.



**Figure II.27.** Diffractogram XRD in powder of the compound **76** (blue) and the diffractogram of the compound **77** (red)

The compound  $\text{Cu}_4\text{O}(\text{C}_8\text{H}_4\text{O}_4)_2 (\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_3)_2$  was synthesized solvothermally as well:  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was dissolved in ethanol, Hbmmk in ethanol and terephthalic acid in DMF. The hbmkk solution was dripped over the nitrate one, the result being a solution of green color which is mixed with the solution of acid and the obtained mixture is put in a steamer. The steamer is sealed and put in an oven, set to warm up at  $70^\circ\text{C}$ . It is maintained at this temperature for 6 h. After cooling at room temperature, the product is separated by draught and is purified by maintaining it under DMF, which is changed 6 times at a day interval.

The activation is made by changing the solvent from pores with  $\text{CH}_2\text{Cl}_2$ , in the same manner as in the case of purification, and by thermal degassing under dynamic vacuum (4 h at  $50^\circ\text{C}$  and  $100^\circ\text{C}$ , respectively). A blue solid crystalline, **78**, is obtained.



**Figure.II.28.** The comparison of the thermogrames of compounds **78** (green) and **76** (brown)

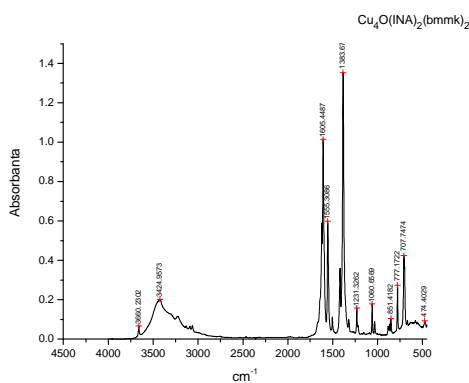
The resemblance of the thermogravimetric curves confirm the fact that product **78** has its structure identical with the one of compound **76**. The obtained compounds will be furthered analized to establish their specific surfaces and their capacity to adsorb hydrogen.

#### **II.2.4.2. Synthesis $\text{Cu}_4\text{O}(\text{INA})_2(\text{bmmk})_2$**

The changing of the terephthalic acid with other mono, di- or tricarboxylic acids led to the obtaining of some structures similar to the one described previously, new complexes of type  $\text{Cu}_4\text{O}$ .

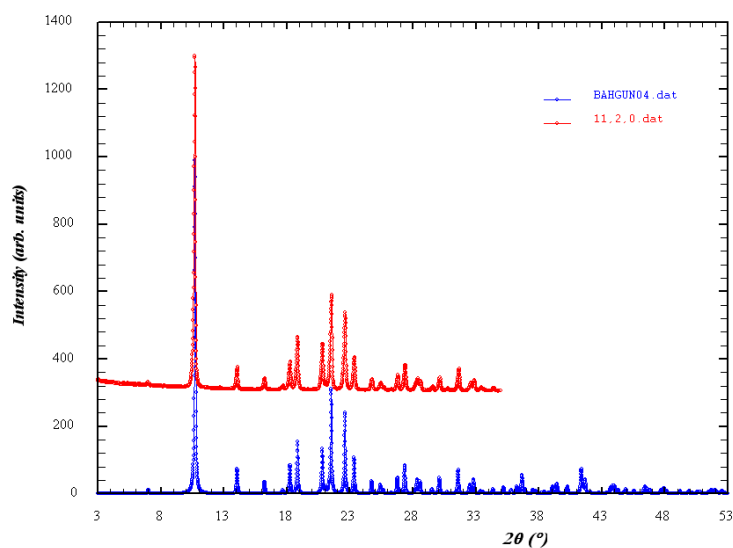
## IR Spectroscopy

IR spectra for **79** is dominated by the very intense bands of the symmetrical and asymmetrical vibrations of the carboxilate  $\nu_{\text{sym}}(\text{CO})(1383 \text{ cm}^{-1})$ ,  $\nu_{\text{as}}(\text{CO})(1605 \text{ cm}^{-1})$  and the large band  $\nu(\text{OH}) (3424 \text{ cm}^{-1})$ ; in the spectra are not given the characteristic signals of the binding Cu-O  $\nu_{\text{Cu-O}}(\text{Cu}_4\text{O})$ .



**Figure II.29.** IR Spectra of the compound **79**

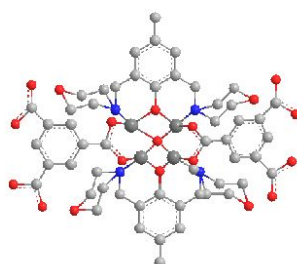
X-ray diffraction in powder confirms the fact that the obtained product is in fact  $\text{Cu}(\text{INA})_2$ , obtained through the reaction between the copper nitrate and izonicotinic acid, being noticed a perfect superposition of the diffractograms of the two compounds.



**Figure II.31.** Comparison of X-rays diffractogram in powder of compound **79** (red) with the simulated diffractogram from the crystalline dates for  $\text{Cu}(\text{INA})_2$  (blue)

#### **II.2.4.3. Synthesis $\text{Cu}_4\text{O}(\text{BTC})_2$ (*bmmk*)<sub>2</sub>**

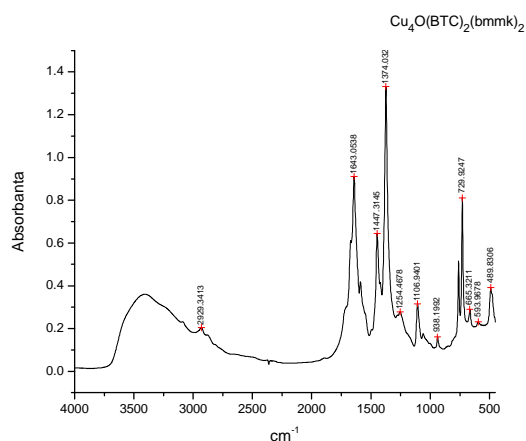
By replacing the terephthalic acid with trimesic acid a crystalline compound of green color was obtained, having the following structure:



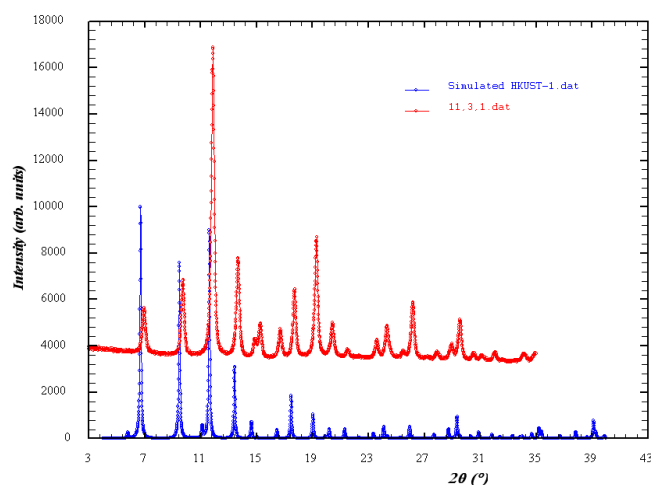
#### *IR Spectroscopy*

IR spectra for  $\text{Cu}_4\text{O}(\text{C}_9\text{H}_3\text{O}_6)_2(\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_3)_2$  (**80**) is dominated by the very intense bands of the symmetrical and asymmetrical vibrations of the carboxylate

$\nu_{\text{sym}}(\text{CO})(1374 \text{ cm}^{-1})$ ,  $\nu_{\text{as}}(\text{CO})(1643 \text{ cm}^{-1})$  and the large band  $\nu(\text{OH}) (3419 \text{ cm}^{-1})$ ; in the spectra the characteristic signals of the binding C-H  $\nu_{\text{C-H}}(729 \text{ cm}^{-1})$  and of the binding C-N  $\nu_{\text{C-N}}(1254 \text{ cm}^{-1})$  are also found, the binding Cu-O  $\nu_{\text{Cu-O}}(\text{Cu}_4\text{O}) (593 \text{ cm}^{-1})$  is present but has a very weak intensity, additional analysis being necessary to elucidate the structure of the obtained compound.



**Figure II.32.** IR spectra for compound **80**



**Figure II.34.** Comparison of X-rays diffractogram in powder of the compound **80** (red) with the simulated diffractogram from the crystalline dates for HKUST-1 (blue)



The X-rays diffractogram in powder of the obtained compound was compared with the one of the compound HKUST-1 (abbreviation for **H**ong **K**ong **U**niversity of **S**cience and **T**echnology- Structure 1), which is obtained from the reaction between copper nitrate and trimesic acid. A certain resemblance of the spectra may be noticed, but for the exact elucidation of the structure the analysis of X-rays on crystal will be carried out.

#### *II.2.5. Other compounds of the type $M_4O(acid)_2(bmmk)_2$*

We also synthesized other compounds of type  $M_4O(acid)_2(bmmk)_2$ , replacing Cu with other metals: Ni, Co, Zn. The compounds were analyzed only with the aid of IR spectroscopy, additional analysis being further carried out for their complete characterization.

### *IV. CONCLUSIONS*

I. The theoretical part of the first chapter contains the description of the synthesis of some polyamines and of some crown ethers derived from them. Polyamines are omnipresent and essential elements in the prokaryote and eukaryote cells. Simple polyamines, as spermidine and spermine, may cause condensations and aggregations of the DNA. Due to this fact, polyamines have potential to be used as antitumor medicines as well as in the chemotherapy of tropical diseases; the disadvantages associated with the usage of some simple polyamines for transport through biological membranes and the diverse toxic secondary effects prevents these compounds to be used in medicine. Perazacrown ethers coming from condensing the polyamines, as for instance cyclen and cyclam, are used in

synthetizing some important molecules with practical applications as agents of contrast in NMR imagistic or sensors for fluorescent samples and for heavy metals (cyclen) or in medicine (cyclam).

In this paper was presented the synthesis and characterization of some new polyamines with the purpose of using them for the obtaining of the corresponding perazacrown ethers. There were synthetized:

1. five new intermediate compounds, the polyamines benzilated with chlorine and bromine in the *orto* position of the benzenic nucleus, **29**, **30**, **32**, **33**, **49**.

The structural analysis of the compounds **29**, **32**, **33**, and **49** was carried out using the specters  $^1\text{H}$  and  $^{13}\text{C}$  NMR at room temperature. Compound **30** was identified on the basis of the specters  $^1\text{H}$  and  $^{13}\text{C}$  NMR, as well as of the bidimensional specters COSY and HMQC. The monocrystals of intermediate **30** were obtained from acetonitril and the molecular structure was established through difraction of X-rays. The crystal contains discrete monomers, without unusual intermolecular distances shorter than the sum of van der Waals radii between the heavy atoms. An interesting characteristic of the molecule of compound **30** is that one of the arms that bears a phtalimido group is twisted so as to bring the planar fragment  $\text{C}_6\text{H}_4(\text{CO})_2\text{NC}$  almost parallel with the fragment  $\text{CC}_6\text{H}_4\text{Br}$  [ $\text{C}_6\text{H}_4(\text{CO})_2\text{N}(2)\text{C} / \text{CC}_6\text{H}_4\text{Br}$  dihedral angle  $3.6^\circ$ ], a behaviour which might be due to some  $\pi$ - $\pi$  interactions between the two aromatic systems. The second arm is twisted in opposite direction to its  $\text{C}_6\text{H}_4(\text{CO})_2\text{NC}$  fragment almost orthogonal to the two previous planar systems [ $\text{C}_6\text{H}_4(\text{CO})_2\text{N}(3)\text{C} / \text{C}_6\text{H}_4(\text{CO})_2\text{N}(2)\text{C}$  and  $\text{C}_6\text{H}_4(\text{CO})_2\text{N}(3)\text{C} / \text{CC}_6\text{H}_4\text{Br}$  dihedre angles of  $88.1^\circ$  and  $84.8^\circ$ , respectively];

2. three permethylated new polyamines, **34**, **35**, **36**, analized with the help of NMR spectroscopy.

In the case of the compound **34**  $^1\text{H-NMR}$  spectra indicates, as expected, two triplets for the methylenic protons, while for the compounds **35** and **36** the two triplets modify in two doublets of doublets, due to the vicinal constant of coupling as a result of the modification of the  $\Phi$  dihedre angle of H-C-C-H, induced by the presence of the atom of halogen in the *orto* position of the benzenic ring;

3. one new intermediate compound, polyamine **54**. Compound **54** constitutes a precursor in the synthesis of a macrocycle which will be synthetized in the next experiments through reactions of cyclization and monofunctionalization.

4. one new tetrafunctionalized perazacrown ether, **63**;

The macrocycle is to be complexed with Zn(II), Cu(II), Ni(III) and Co(II), the complexes of cyclen being highly used in medical applications;

5. two new polyamines, Br-benzilated, **69** and **70**, analized with the aid of NMR spectroscopy

II. In the theoretical part of the second chapter are presented the methods of synthesis for the metal-organic structures, as well as their usages. The metal organic structures have some interesting properties, including optical, magnetical and electronic ones, as well as diverse potential applications, such as: in catalysis, as ion exchangers, in gas storage, separation of mixtures of gas or liquids, as sensors, in polymerization, or as carriers of medicines. The metal organic structures are ideal adsorbants for the storage and separation of gases due to their large specific surfaces and to the adjustable dimensions of the pores. The selective adsorption of gases and their separation represents one of the most active areas of research in the study of MOFs.

In this paper was followed the synthesis and analysis of some crystalline microporous compounds from the family of metal-organic structures. The characterization of the products was made by IR spectroscopy, X-rays

diffractometry in powder, thermogravimetric analysis, adsorption/desorption of nitrogen at 77K. There were synthesized:

1. five known microporous crystalline compounds **74b**, **75a**, **75b**, **75c**, **75d**, through new methods of synthesis, in the attempt to increase the specific surfaces of these compounds so as to be as efficient as possible in stocking hydrogen;

The compound **74b** was obtained solvothermally, the IR spectre confirming the obtaining of the desired compound. The porosity of the compound **74b** was studied by volumetric method; the isotherms of adsorption/desorption are of type I (Langmuir), so it is a microporous compound;

The compound **75a** was obtained for the first time through a synthesis in solid state; given the small specific surface ( $148 \text{ m}^2/\text{g}$ ) obtained with this method we synthesized  $\text{Cu}_2(\text{BDC})_2$  with other methods as well, obtaining thus the compounds **75b**– solvothermic, **75c**– in solution, at room temperature, **75d**- in solution at low temperature. The isotherm of absorption of compound **75b** presents hysteresis of type H2, so the structure of the pores is complex and tends to consist of interconnected networks of pores with different sizes and shapes. The hysteresis loop of this type is associated with the capillary condensation in mezopores, fact confirmed also by the graphic of distribution of the pores (55.77% mezopores).

2. two samples of **MOF-5**, the most investigated metal-organic structure given its large specific surface and the cheap raw materials, taking a try, in this case too, to increase the specific surface of the obtained compounds. By methods of synthesis tried out, 22 hours at  $100^\circ\text{C}$ , without stirring and solvothermic, two samples of MOF-5 were obtained, their specific surfaces not being larger than the ones reported in literature, MOF-5 having one of the largest specific

surfaces:  $S_{\text{BET}}$  of 3800  $\text{m}^2/\text{g}$  and  $S_{\text{Lang}}$  of 4400  $\text{m}^2/\text{g}$ , the measured volume of the pores being of 1.55  $\text{cm}^3/\text{g}$ .<sup>191</sup>

3. one new compound, **76**, which will be further analyzed, given the fact that for the structures of this type,  $\text{M}_4\text{O}(\text{acid})_2$  ( $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_3$ )<sub>2</sub>, some unusual magnetic properties were reported in literature; the compound was synthesized by means of two different methods: in solution (**76**) and solvothermally (**78**), following next the establishment of their specific surfaces and their capacity to adsorb hydrogen. Another six compounds of this type are being analyzed in order to establish exactly the obtained structures and their properties.

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