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Synthetic and Crystallographic Studies on Pyridinophanes

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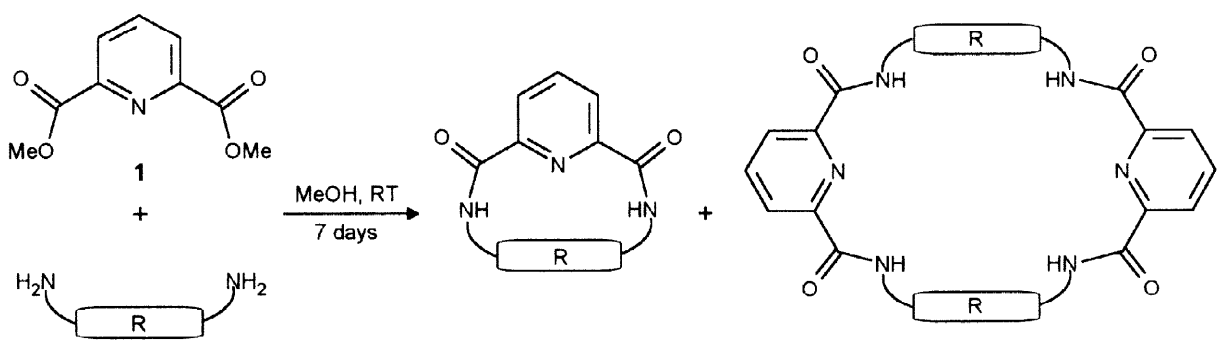
Abstract: Eight macrocyclic bisamides and tetramides have been synthesized by reaction of dimethyl pyridine-2,6-dicarboxylate **1** with α,ω-diaminoethers in methanol as a solvent. Relationship between structure of an amine used and a ratio of bisamide to tetramide has been investigated. The X-ray structure of macrocyclic amides **8**, **9**, **14** and linear amide **16** are reported. They show intramolecular hydrogen bond patterns within macrocyclic cavities involving $N_{Py}\cdots NH_{amide}$, and in the cases of **9**, **14** and **16**, neutral molecules of water. Stability constants of selected ligands were measured using voltammetry.

There is a continuing interest in the synthesis of macrocyclic polylactams.[1,2] The polyamide macrocycles have complexation properties that are complementary to all-oxygen crowns, which strongly complex alkali metal ions, and all-nitrogen cyclams, which strongly complex heavy metal cations. The macrocyclic amides act also as hydrogen-bond donors and hydrogen-bond acceptors and can complex neutral molecules of biological interest.[3-5] The most popular method for the preparation of macrocyclic amides consists in reacting a diacid dichloride with a diamine.[2,6] At the beginning of the nineties we found[7-9] that α,ω-diamino aliphatic ethers reacted under ambient conditions with dimethyl α,ω-dicarboxylates, to afford the macrocyclic diamides (which can be readily transformed into the corresponding diamines using for example $BH_3\times Me_2S$). The optimum reaction conditions proposed by us are as follows: methanol, room temperature, 7 days, concentration ~0.1 M. These conditions or similar ones were used recently for preparing several types of macrocyclic amides.[10-13]

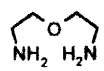
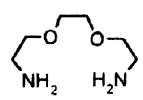
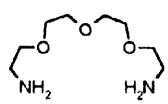
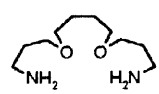
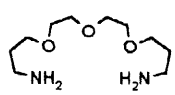
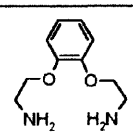


Scheme 1

PII: S0040-4020(98)00385-8

On the other hand, introduction of the pyridine unit into a macrocyclic framework is of particular interest. Pyridinophanes and related compounds possessing 2,6-disubstituted pyridine moiety are the subject of numerous studies[14,15] and display ion complexation[16-19] and chiral recognition.[20-22] A preparation of macrocyclic bisamides, from pyridine-2,6-dicarboxylic acid dimethyl ester **1** and aliphatic poliamines has been reported.[23,24] Following the procedure adapted previously, we decided to obtain macrocyclic polylactams from dimethyl pyridine-2,6-dicarboxylate **1** and α,ω-diaminoaliphatic ethers. Due to the fact that stability constants of synthetic macrocyclic amides are not often studied, we decided to measure the constants for selected ligands. In our investigations we used six various diamines differing in length of chain between nitrogen atoms (5-13 atoms), in number of oxygen atoms (1-3), and in rigidity. The aim of our research were to test dependency of a yield of both bisamides and tetramides as well as stability constants of their complexes upon these experimental variables (Scheme 1). Results of syntheses of macrocyclic bis- and tetramides are summarized in Table 1.

Table 1. Product Distribution in the Reactions of Amines **2-7** with Dimethyl Pyridine-2,6-dicarboxylate **1**

Amine		Bisamide		Tetramide	
	**2**	____		20.8 %	**13**
	**3**	82.8 %	**8**	6.3 %	**14**
	**4**	42.1 %	**9**	____	
	**5**	45.2 %	**10**	16.1 %	**15**
	**6**	58.8 %	**11**	____	
	**7**	67.6 %	**12**	____	

During our investigations of the reaction of dicarboxylate **1** with diamines we found that:

1. Reactions with the 'short' diamine **2** led to the formation of tetramide only.
2. Reactions with diamines **3** and **5** afforded bisamides as well as tetramides.
3. Reactions with diamines **4**, **6** and **7** led to the formation of bisamides only.

It is not easy to explain all these results. The highest yield of bisamide (**8**, 82.8%) was achieved using diamine **3**, but in this reaction a formation of tetramide **14** was also observed. If we elongated the chain with the additional O-CH_2-CH_2- group, tetramide disappeared, but yield of bisamide **11** decreased too. A detailed consideration of the problem revealed possibility to explain these results, while keeping in mind three factors which overlap each other:

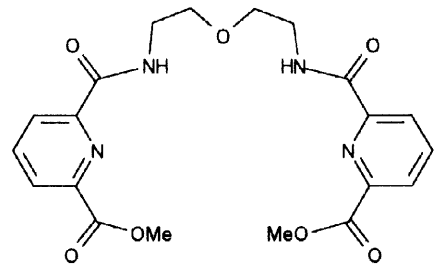
1 Conformational lability of diamines, which increases together with the length of chain.

2 Fitting of the preferred conformation of diamine into a distance between ester groups in molecule of completely rigid diester **1**.

3 Position of oxygen atoms in molecule of diamine, which influences hydrogen bonds, what in our opinion is crucial for the formation of the presented macrocycles.

We could conclude that diamine **2** is to short for formation of the respective bisamide with diester **1**. But this conclusion seems to be wrong, because Vögtle achieved the respective bisamide using a high dilution technique.[19] It is also possible to obtain a corresponding bisamide from 1,5-pentanediamine (simple analogue of **2**) using a high dilution technique.[25] Thus, the mechanisms of reactions determine differences in results between these two methods.

Differences in structure between diamines **3** and **7** seem to be unimportant. However, two rigid molecules (e.g. **7** and **1**) fit each other worsely than e.g. rigid **1** and relatively labile **3**. Therefore, yield of **12** is lower than that of **8**. Disturbance of the system of hydrogen bonds in diamine **5** as compared with similar amines **3** (the same number of oxygen atoms) and **4** (similar length of aliphatic chain) results in the formation of significant amount of tetramide **15.** It is noteworthy that in all cases we do not observed exclusive formation of macrocyclic products. Sometimes, we noticed also formation of non-polymeric products. We isolated and characterized one of them, namely, the bisamide diester **16**.



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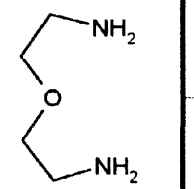
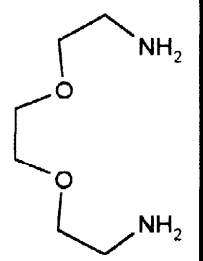
In the second part of our synthetic studies, we decided to test influence of high pressure conditions on the ratio of products in the reaction of dicarboxylate **1** with diamines. We selected diamines **2** and **3** as model components of this reaction. In the latter case we expected the formation of the respective bisamide. Results are collected in Table 2.

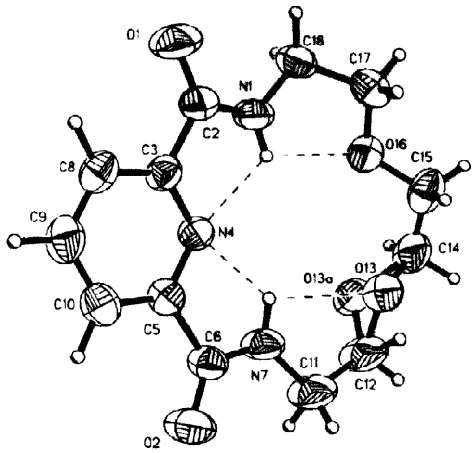
Table 2. Yields of Reactions of Amines 2 and 3 with Dimethyl Pyridine-2,6-dicarboxylate 1

	Pressure [bar]	Conversion [%]	Yield of bisamide [%]	Yield of tetramide [%]	Yield of bisamide diester [%]
	1	95.4	0	20.8	5.7
	12000	100	0	23.5	0
	1	96.9	82.8	6.3	—
	12000	100	79.7	2.7	—

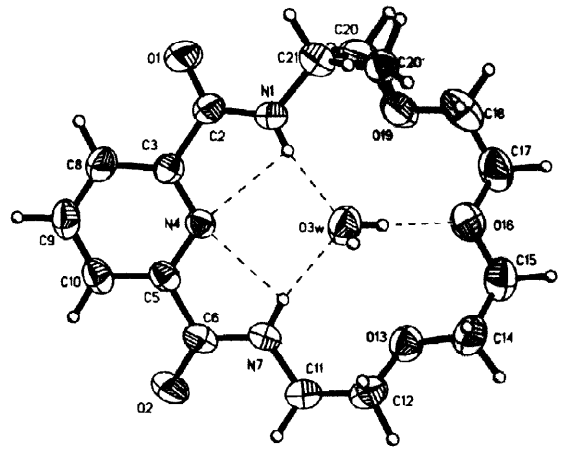
We can state that changing of conditions did not affect the results considerably. Conversion of diester **1** increased to 100 %. Bisamide diester **16** disappeared, but we did not observe respective bisamide. Total yield of **8** and **14** decreased imperceptibly. We observed more oligomeric linear products (using TLC) but we did not isolate them.

We are able to obtain compounds **8**, **9**, **14** and **16** as monocrystals suitable for X-ray analysis. Figure 1 shows conformations of compounds **8**, **9**, **14** and **16** along with numbering scheme adopted in structure determination. In the case of **14** and **16** only half of the molecule is symmetrically independent. In the molecule **14** the other half is related by the centre of symmetry and in **16** by two-fold axis. We found a positional disorder in molecules **8** and **9**. In the molecule **8** it involves the etheral oxygen atom O13. In **9** the carbon atom C20 is disordered. The population ratio is about 1 : 1 in both cases.

As it was recently[26,27] calculated using MM (force field CHARMM), presence of the pyridine nitrogen atom in such a position like in amide of pyridine-2,6-dicarboxylic acid, favours the flattened conformation with two intramolecular H-bonds of the $N_{Py}\cdots H\cdots N$ type. Our results agree with these calculations, i.e. we have also observed intramolecular H-bonds of such type. The amide groups are only slightly twisted with respect to the pyridine ring (torsion angles for **8**, **9**, **14** and **16** are summarized in Table 3). It is due to the stabilising effect of



8



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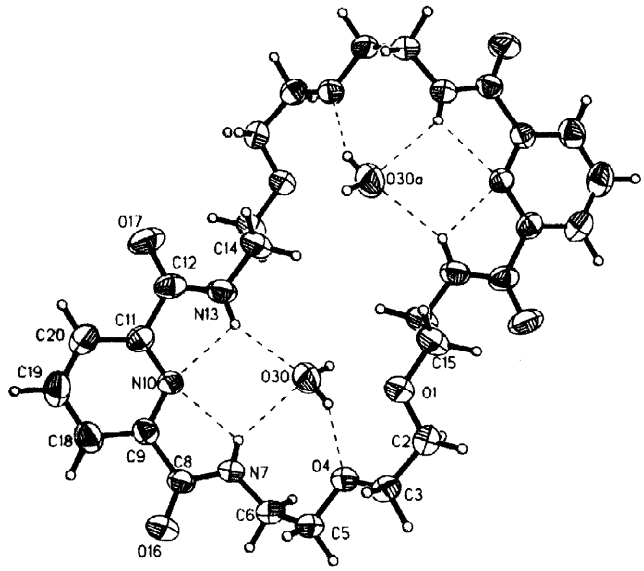

14

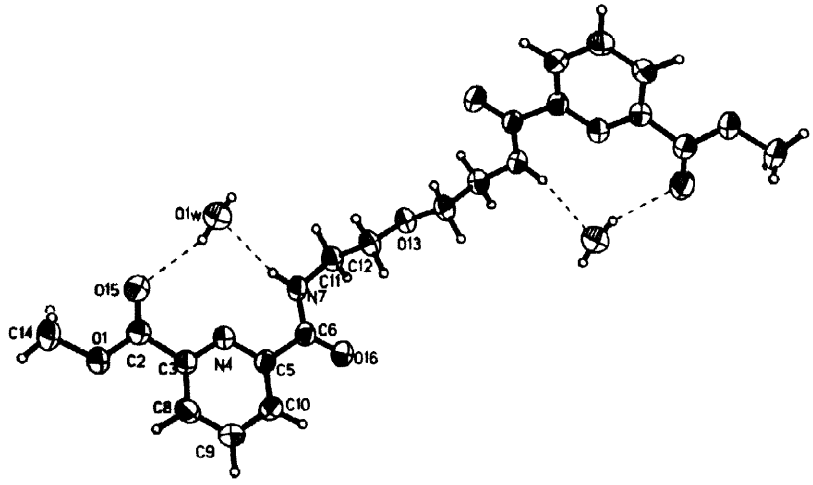

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Figure 1. Crystal Structures of Compounds **8**, **9**, **14** and **16**

hydrogen bonds between the amide and pyridine nitrogen atoms. In the analogous compounds, possessing an isophtalic part instead of pyridine, the above-mentioned torsion angles are much larger.[28]

Additionally, in the molecule **8** are present intramolecular hydrogen bonds involving amide N-H and etheral oxygen atoms. In the remaining cases, water molecules participate in formation of hydrogen bond pattern. Molecule **9** binds one molecule of water, while tetramide **14** and open-chain compound **16** bind two water molecules. It is noteworthy that water molecules are well defined in the cavity, i. e. hydrogen atoms are well localized. The water molecules, due to presence of amide hydrogen atoms and etheral oxygen atoms commit to two types of hydrogen bonds.

Table 3. Torsion Angles N_{Py}–C–C–N for **8**, **9**, **14** and **16**

Compound	Torsion Angle
8	-5.6 1.8
9	4.4 -4.2
14	-16.4 5.5
16	1.2

It is obvious that compound **16** should be precursor of **13**. We hoped that we would observe effects of preorganization of this molecule. Since the conformation in the solid state is extended, the only hint is possibility of binding of the ester group to the amide group *via* water molecule. We can carefully assume that similar interactions (but rather with methanol molecules instead of water ones) exist in the solution, on the stage directly preceding the ring closure. Although transfer of a solid state interaction into solution is difficult, some of strong interactions can manifest themselves in both phases.[29]

Complexing properties of macrocyclic bisamides, as we stated earlier, are not very often studied. In case of secondary macrocyclic amides stability constants are usually not measurable.[30-33] However for ternary amides in some cases relatively high stability constants were reported. [34-35] Therefore, we decided to carry out preliminary investigations of binding behavior of several representative macrocyclic bis- and tetramides, obtained during this study. We selected three bisamides (**8**, **10** and **11**) and three tetramides (**13**, **14** and **15**) as ligands and four typical cations (Na^+, K^+, Cd^{2+}, Pb^{2+}).

We started our voltammetry investigations using bisamides **8**, **10** and **11**. The stability constants of lead and cadmium were determined directly using DeFord-Hume method.[36] The potentials used for calculations were

taken as averages between the cathodic and the anodic voltammetric peak. Alternatively, the voltammograms were semi-differentiated[37] and average values of cathodic and anodic semiderivative peak used in calculations. The results obtained in these two manners were very close to each other and logβ values obtained in both ways were practically the same.

Stability constants for complexes with sodium and potassium were determined indirectly in competition experiments. Alkali metal cation was added to the solution containing both Cd^{2+} (or Pb^{2+}) ions and the ligand, and the changes in the potential of Cd^{2+} or Pb^{2+} ions reduction caused by decomplexation were measured. The calculated stability constants (logβ) are collected in Table 4.

Table 4. Stability constants (logβ) of complexes Cd^{2+}, Pb^{2+}, Na^{+}, K^{+} with bisamides **8**, **10** and **11**.

	Bisamide **8**	Bisamide **10**	Bisamide **11**
Cd^{2+}	*	1.9-2.0	2.6-2.7
Pb^{2+}	1.7	3.8	5
Na^{+}	*	2.4-2.5	2.8
K^{+}	*	*	2.4

*not mesurable

All reported results were obtained for 1:1 complexes. Calculations carried out under the assumption of other possible stoichiometries leaded to negative values of the higher-order stability constants. To check whether the protonation of the ligands can produce OH^{-} ions that are known to form complexes with lead, conductometric measurements of ligand solutions in acetonitrile were carried out. Values of conductivity, compared with conductivities of tetramethylammonium hydroxide solutions in the same solvent, allow to estimate that the degree of protonation is below 2%, thus the formation of hydroxide ions is negligible. Unfortunately, we were unable to measure stability constants for tetramides due to complex electrode processes caused by them.

Since the dipole moment of the N-R group is smaller than that of the -OR group, the substitution of oxygen atom by the N-R group leads to decrease of the electrostatic interaction between cation and ligand, what is more pronounced for hard cations. In our case three donor atoms are nitrogen ones, among them secondary amide nitrogen atoms can be excluded. In general stability constants of complexes of amides **8**, **10** and **11** are relatively high as compared with other synthetic macrocyclic amides.[32] We observed also that stability of complexes increases in order **8**<**10**<**11**, *i.e.* with size of the cavity and number of oxygen donor atoms.

Further studies on synthesis, structure and properties of more elaborated diazacoronands are in progress.

EXPERIMENTAL

General methods

^{1}H NMR spectra were recorded with Varian Gemini (200 MHz) and/or Bruker AM500 (500 MHz) spectrometers in $CDCl_3$ or DMSO-d_6 using TMS as an internal standard. ^{13}C NMR spectra were recorded using also Varian Gemini (50 MHz) and/or Bruker AM500 (125 MHz) spectrometers. High-resolution mass spectrometry (HRMS) experiments were performed on an AMD-604 Intectra instrument. IR spectra were recorded using Perkin-Elmer 1640 FTIR spectrophotometer in KBr pellets. Column chromatography was carried out on silica gel (Kieselgel-60, 200-400 mesh). Melting points were taken on a Köfler type (Boetius) hot stage apparatus and are not corrected. α,ω-Diamines **2** and **4** were prepared according to the literature procedures.[38,39] The diamine **7** was also prepared according to the known procedure.[40]

General procedure for the synthesis of macrocyclic bisamides and tetramides

An equimolar 0.1 M methanolic solution (1.5 mmol) of α,ω-diamine and pyridine-2,6-dicarboxylic dimethyl ester **1** was left at ambient temperature over a period of 7 days. Then the solvent was evaporated and the residue was chromatographed on a silica gel column using 0.5-3 % mixtures of methanol in chloroform.

6,9-Dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(17),14(18),15-triene-2,13-dione (**8**, 82.8 %): m.p. 200-201°C (lit.[18] m.p. 200-201°C); IR ν_{max} (KBr)/cm^{-1}, 3386, 2871, 1680, 1535, 1443, 1102, 663; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.79 (bt, 2H), 8.21 (dd, 2H, J=7.5 Hz, J=0.5 Hz), 8.11-7.89 (m, 1H), 3.92-3.40 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.7, 148.3, 139.4, 123.8, 70.8, 68.7, 38.8; HRMS m/z calcd. for $C_{13}H_{17}N_3O_4$ $(M)^+$ 279.1219, found 279.1220; Anal. calcd. for $C_{13}H_{17}N_3O_4$: C, 55.91; H, 6.14; N, 15.05; found: C, 55.73; H, 6.03; N, 14.94.

6,9,12-Trioxa-3,15,21-triazabicyclo[15.3.1]heneicosa-1(20),17(21),18-triene-2,16-dione (**9**, 42.1 %): m.p. 128-130°C (lit.[18] 127-129°C); IR ν_{max} (CCl_4)/cm^{-1} 3522, 3424, 3350, 2916, 2876, 1679, 1540, 1127; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.11 (t, 3H, J=5.5 Hz), 8.33 (d, 2H, J=8.0 Hz), 8.02 (m, 1H), 3.90-3.49 (m, 16 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 148.7, 138.7, 124.7, 71.2, 70.3, 70.1, 38.9; HRMS m/z calcd. for $C_{15}H_{21}N_3O_5$ $(M)^+$ 323.1481, found 323.1480.

7,12-Dioxa-3,16,22-triazabicyclo[16.3.1]docosa-1(21),18(22),19-triene-2,17-dione (**10**, 45.2 %): m.p. 153-154°C; IR ν_{max} (KBr)/cm^{-1} 3373, 3252, 2868, 1675, 1652, 1529, 1122; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, 2H, J=7.5 Hz), 8.15 (bt, 2H), 8.02 (t, 1H, J=8.0 Hz), 3.72-3.51 (m, 12H), 2.05-1.92 (m, 4H), 1.77-1.68 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 149.1, 138.6, 125.0, 70.8, 69.0, 38.2, 28.3, 26.2; HRMS m/z calcd.

for $C_{17}H_{25}N_3O_4$ $(M)^+$ 335.1845, found 335.1847; Anal. calcd. for $C_{17}H_{25}N_3O_4$: C, 60.86; H, 7.52; N, 12.53; found: C, 60.89; H, 7.70; N, 12.47.

7,10,13-Trioxa-3,17,23-triazabicyclo[17.3.1]tricosa-1(22),19(23),20-triene-2,18-dione (**11**, 58.8 %): m.p. 95-97°C; IR ν_{max} (KBr)/cm^{-1} 3367, 2951, 2891, 1671, 1528, 1443, 1123; ^1H NMR (500 MHz, $CDCl_3$) δ 8.58 (bt, 2H), 8.36 (d, 2H, J=7.8 Hz), 8.00 (t, 1H, J=7.7 Hz), 3.8-3.6 (m, 16H), 1.91 (dd, 4H, J=5.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 149.2, 138.5, 124.7, 69.3, 68.5, 67.8, 37.1; HRMS m/z calcd. for $C_{17}H_{25}N_3O_5$ $(M)^+$ 351.1794, found 351.1792; Anal. calcd. for $C_{17}H_{25}N_3O_5$: C, 58.11; H, 7.17; N, 11.96; found: C, 57.93; H, 7.37; N, 11.92.

6,13-Dioxa-3,16,22-triazabicyclo[16.3.1.$0^{7,12}$]docosa-1(21),7,9,11,18(22),19-hexaene-2,17-dione (**12**, 67.6%): m.p. 242-244°C; IR ν_{max} (KBr)/cm^{-1} 3387, 2919, 1700, 1678, 1540, 1516, 1258, 1121; ^1H NMR (200 MHz, $CDCl_3$) δ 9.21 (bt, 2H), 8.31-8.01 (m, 3H), 6.98 (s, 4H), 4.25 (t, 4H, J=5.3 Hz), 4.01-3.89 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.1, 147.7, 147.4, 139.7, 123.5, 121.4, 112.6, 66.8, 37.2; HRMS m/z calcd. for $C_{17}H_{17}N_3O_4$ $(M)^+$ 327.1219, found 327.1218; Anal. calcd. for $C_{17}H_{17}N_3O_4$: C, 62.38; H, 5.23; N, 12.84; found: C, 62.37; H, 5.23; N, 12.86.

6,20-Dioxa-3,9,17,23,29,30-hexaazatricyclo[23.3.1.$1^{11,15}$]triaconta-1(28),11,13,15(30),25(29),26-hexaene-2,10,16,24-tetraone (**13**, 20.8 %): m.p. 335-340°C (lit[18] m.p. 338-340°C); IR ν_{max} (KBr)/cm^{-1} 3540, 3487, 3361, 2869, 1684, 1535, 1122; ^1H NMR (500 MHz, $CDCl_3$) δ 9.38 (t, 4H, J=5.7 Hz), 8.13-8.04 (m, 6H), 3.80-3.42 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 148.4, 139.2, 124.0, 69.0, 40.0; HRMS m/z calcd. for $C_{22}H_{26}N_6O_6$ $(M)^+$ 470.1914, found 470.1912.

6,9,23,26-Tetraoxa-3,12,20,29,35,36-hexaazatricyclo[29.3.1.$1^{14,18}$]hexatriaconta-1(34),14,16,-18(36),31(35),32-hexaene-2,13,19,30-tetraone (**14**, 6.3 %): m.p. 246-248°C; IR ν_{max} (KBr)/cm^{-1} 3470, 3321, 2932, 2888, 1676, 1540, 1065, 1030; ^1H NMR (500 MHz, $CDCl_3$) δ 9.35 (t, 4H, J=6.0 Hz), 8.19-8.11 (m, 6H), 3.60-3.45 (m, 24 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 148.6, 139.4, 124.2, 69.5, 69.1, 39.1; HRMS m/z calcd. for $C_{26}H_{34}N_6O_8$ $(M)^+$ 558.2438, found 558.2435; Anal. calcd. for $C_{26}H_{34}N_6O_8 \times 2H_2O$: C, 52.52; H, 6.44; N, 14.13; found: C, 52.31; H, 6.56; N, 13.97.

7,12,28,33-Tetraoxa-3,16,24,37,43,44-hexaazatricyclo[37.3.1.$1^{18,22}$]tetratetraconta-1(42),18,20,22,39(43),40 - hexaene-2,17,23,38-tetraone (**15**, 16.1 %): m.p. 244-246°C; IR ν_{max} (KBr)/cm^{-1} 3320, 2942, 2863, 1682, 1650, 1530, 1120; ^1H NMR (500 MHz, $CDCl_3$) δ 8.97 (t, 4H, J=5.5 Hz), 8.35 (d, 4H, J=8.0 Hz), 8.00 (t, 2H, J=8.0 Hz), 3.63-3.30 (m, 24H), 1.92-1.78 (m, 8H), 1.57-1.49 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0,

149.0, 138.9, 124.5, 70.7, 69.4, 38.3, 29.0, 26.6; HRMS m/z calcd. for $C_{34}H_{50}N_6O_8$ $(M)^+$ 670.3690, found 670.3689; Anal. calcd. for $C_{34}H_{50}N_6O_8$: C, 60.86; H, 7.52; N, 12.53; found: C, 60.56; H, 7.79; N, 12.23.

Methyl 6-{[2-(2-{[6-(methoxycarbonyl)-2-pyridyl]carboxamido}ethyl]carbamoyl}-2-pyridine carboxylate (**16**, 5.7 %): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.59 (bt, 2H), 8.36 (dd, 2H, J=1.3 Hz, J=7.7 Hz), 8.20 (dd, 2H, J=1.2 Hz, J=7.7 Hz), 7.99 (t, 2H, J=7.8 Hz), 3.98 (s, 6H), 3.82-3.60 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.0, 163.8, 150.3, 146.5, 138.5, 127.2, 125.5, 69.7, 53.0, 39.6; HRMS m/z calcd. for $C_{20}H_{22}N_4O_7$ $(M)^+$ 430.1488, found 430.1487.

General procedure for the synthesis of macrocyclic bisamides and tetramides under high pressure conditions

An equimolar solution of the dimethyl α,ω-dicarboxylate (0.5 mmol) and the appropriate α,ω-diamine (0.5 mmol) in 5 mL of methanol was filled into a Teflon ampoule, placed in a high-pressure vessel filled with ligroine as a transmission medium and compressed (12 kbar) at room temperature for 48 h. After decompression, the reaction mixture was transferred quantitatively to a round-bottomed flask and the solvent was evaporated. The residue was chromatographed on a silica gel column using 0.5-3 % mixtures of methanol in chloroform.

X-ray structure investigations

Crystal data for all structures were measured on MACH3 κ-diffractometer using CuK_α radiation and ω-2θ scan mode. All structures were solved by using direct methods (SHELXS program) and refined using SHELX93 program. Hydrogen atoms were treated in a mixed way. Those of N-H, were found from Fourier differentional map. Crystal data: **Compound 8**: $C_{13}H_{17}N_3O_4$, orthorombic, space group Pbca, a=9.5604(2)Å, b=16.6999(6)Å, c=16.8799(6)Å, Z=8, D_c=1.377 g.cm^{-3}, μ=0.865 mm^{-1}, independent reflections 1768, data/restr/param 1768/0/223, final R1=0.0482, wR2=0.1227 [I>2sigma(I)]. **Compound 9**: $C_{15}H_{21}N_3O_5$ x H_2O, orthorombic, space group $P2_12_12_1$, a=8.7424(3)Å, b=11.8372(8)Å, c=16.938(2)Å, Z=4, D_c=1.294 g.cm^{-3}, μ=0.846 mm^{-1}, independent reflections 2301 [R(int)=0.0653], data/restr/param 2298/0/239, final R1=0.0472, wR2=0.1198 [I>2sigma(I)], extinction coeff. 0.0035(7). **Compound 14**: $C_{26}H_{34}N_6O_8$ x $2H_2O$, monoclinic, space group $P2_1/c$, a=13.6917(6)Å, b=14.2503(6)Å, c=7.4212(4)Å, β=94.430(4)°, Z=2, D_c=1.368 g.cm^{-3}, μ=0.892 mm^{-1}, independent reflections 2470 [R(int)=0.0185], data/restr/param 2470/0/207, final R1=0.0412, wR2=0.1262 [I>2sigma(I)]. **Compound 16**: $C_{20}H_{24}N_4O_8$, a=24.808(5)Å, b=4.3030(10)Å, c=10.640(2)Å, β=108.43(3)°, monoclinic, space group C2, Z=2, D_c=1.382 g.cm^{-3}, μ=0.108 mm^{-1}, independent reflections 799 [R(int)= 0.0513], data/restr/param 799/1/167, final R1=0.0409, wR2=0.1128 [I>2sigma(I)], extinction coeff 0.022(5).

Voltammetric investigations

The voltammetric measurements were carried out at a hanging mercury drop electrode (SMDE1, Laboratorni Pristroje, Praha) using Autolab electrochemical instrument (Eco Chemie, Netherlands). As the reference electrode an Ag/AgCl electrode filled with 0.1M solution of tetraethylammonium chloride in methanol, connected to the cell with an electrolytic bridge containing 0.1M solution of tetrabutylammonium perchlorate in acetonitrile, was used. A piece of platinum foil served as counterelectrode. In all experiments 0.1M solution of tetrabutylammonium perchlorate (Fluka, electrochem. grade) in acetonitrile (Fluka) was used as suppporting electrolyte. All solutions were deaerated with argon before the measurement. The concentrations of cadmium and lead ions in the solution in the cell were typically at the level of 10^{-4} M, obtained by addition of small volume of concentrated stock solutions, $CdSO_4$ (BDH, England) and $Pb(ClO_4)_2$ (SERVA, Germany), respectively, directly to the cell. Concentrations of sodium and potassium ions was varied from approximately 10^{-4} to approx. 10^{-2} M by addition of concentrated $NaClO_4$ (Koch-Light, Great Britain) and KPF_6 (Fluka) solutions. For each metal cation series of measurements were made for various metal/ligand concentration ratios. For each metal/ligand ratio the voltammograms were measured at scan rates 0.05, 0.1, 0.2 and 0.4 V/s. Each voltammogram was measured twice and averaged. Conductometric measurements were carried out using CDM 210 conductometer (Radiometer, Denmark) equipped with XE 110 probe, in a continuously stirred solution from which CO_2 was removed by bubbling with argon. All measurements were carried out in temperature 20±1°C. Results obtained indirectly(Na^+, K^+) may be influenced by the variation in the ohmic drop in the solution which shifts the potential toward positive values and apparently increases β.

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